Between each stage the gas passed through steel traps and water cooled intercoolers.

The characteristics of this compressor are given below:

Stage	I	II	III	IV
Suction Pressure in atm.	1.0	3.0	9.0	15.0
Discharge " " "	3.0	9.0	15.0	60.0
Stroke in mm	150	150	150	150
Diam of cylinder in mm	190	190	105	66

The gas leaving the fourth stage at 60 atm was then liquefied by cooling with refrigeration. The liquefied HCl was then packed into steel cylinders. No large use for liquefied HCl had developed and the output was supplied mostly for laboratory use.

f. Iron and Nickel Carbonyl

The large iron and nickel carbonyl plant at Oppau was inspected in company with Drs. Wietzel and Timm, together with the technical man in charge of this operation whose name was not obtained. This operation was based upon the availability at Oppau of large quantities of quite pure CO produced from water gas for their alcohol syntheses.

Before the war, nickel matte, containing about 50% Ni, was purchased from the Mond Nickel Co. and was shipped from Canada. The Nickel Co. retained title to everything in the matte but the nickel content; i.e., copper, gold, silver and platinum, and after the extraction of the nickel the remainder had to be shipped back to them. Dr. Timm stated that this arrangement was a matter of foreign exchange and keeping marks in Germany. During the war nickel matte was obtained from Petsamo.

The matte was charged into steel pressure vessels approximately 18 inches I.D. by 25 ft. high. There were 32 of these reactors connected up in 8 series of four reactors each. Carbon monoxide gas under 200 atm pressure was passed through the nickel matte in series through four reactors. The temperature in each reactor was maintained at about 200°C. Not all of the CO was used up and it was therefore recycled. The nickel carbonyl which formed distilled out of the reactors and was condensed and collected in receivers all under the same pressure as the reactors, i.e., 200 atm. After venting the receivers down to atmospheric pressure, the condensed crude carbonyl was then allowed to run into storage tanks which were kept submerged under water because of the poisonous nature of the product. The other unreacted metals in the matte remained behind in the reactors and were unloaded when the reaction between the CO and nickel was complete.

The crude product was then distilled under atmospheric pressure to separate the iron carbonyl, formed by the iron present in the matte, from the nickel carbonyl. The re-distilled relatively pure nickel carbonyl was then decomposed to CO and nickel powder by heating in retorts to 200°C. The CO was recycled, and after recompression was fed back to the reactors. The nickel powder, containing about 0.1% carbon and of 300 mesh fineness was packed out of the bottom of the decomposing retorts into steel drums for shipment.

The capacity of the nickel carbonyl plant at Oppau was stated to be 5000 tons a year. The resulting pure nickel was used by Krupp and other steel companies.

Powder iron was produced in the same manner as the nickel powder. The reaction between iron and CO was said to be a little more touchy and harder to control than the CO-nickel matte reaction. Sponge iron was imported from Sweden as raw material. During the past few years the plant was operated largely on nickel rather than iron. Iron carbonyl was previously used as a gasoline anti-knock additive (motal) but this use was discontinued many years ago.

The carbonyl plant was not damaged very much by bombing.

3. MONOMERS AND POLYMERS

a. Introduction

Ludwigshafen, along with many other of the I.G. plants, has expanded its developments of polymer products greatly in recent years. For example, the total number of I.G. chemists engaged in research in the division on resins, synthetic rubber, lacquers and solvents doubled from 1939 to 1944 when a total of 500 men was employed. Ludwigshafen's activities covered practically all the important polymers with the exception of Höchst's polyvinyl acetate and Leverkusen's new polyisocyanate products at Ludwigshafen. Details are omitted in the case of Buna rubber since this important item has been covered previously by a special rubber group.

b. Phenol-Formaldehyde Resins (Luphens)

I.G. did not produce phenol formaldehyde molding powder. Ludwigshafen's activities were confined to the production of phenol formaldehyde resin for the manufacture of lacquers and acid resisting paints. Some phenol-cresol formaldehyde resins were made also for the same end use.

Para tertiary butyl phenol was produced by combining isobutylene with phenol in the presence of aluminum chloride catalyst under slight pressure. The butyl phenol was used largely for the manufacture of Koresin, although some was sold for the preparation of special lacquers. Amyl phenols were not produced.

c. Urea-Formaldehyde Resins - Pollopas, etc.

(1) Pollopas was a urea formaldehyde molding powder. It was not sold as such but was shipped to Troisdorf where the product had previously been manufactured ; it was not determined whether Troisdorf also continued to fabricate the resin.

Substitution of thiourea for part of the formaldehyde improved the water resistance of the product.

(2) Plastopal was a urea formaldehyde condensation product prepared in organic solvents, preferably butanol or isobutanol. The material was used for paints and lacquers to give a hard flexible film of good heat resistance. The product was modified in a number of ways. For example, Plastopal AT-0 contained in addition a condensation product of adipic acid with trimethylol propane. Substitution of succinic acid and of pentaerythritol, hexanetriol or hexanediol did not improve the product.

A similar product, Melopas, was made by substituting melamine, obtained from Mainkur, for the urea. Substitution of melamine reduced the brittleness of the film.

Considerable work was done on the substitution of other aldehydes but no marked advantages were found. Furfuraldehyde was tested extensively and found to give a superior product but its price, five to ten times as much as formaldehyde, mitigated against its use.

Ludwigshafen produced about 250 tons of Plastopals per month.

(3) Kaurit KF was a water soluble urea formaldehyde condensation product for textile applications. The material was a white powder readily soluble in water. Application to textiles, artificial silk or rayon, followed by after-condensation resulted in an improvement of the tear resistance, particularly in the moist state, and in improved shrink and crease resistance properties.

Applications were made in the following manner: A water solution of 120 to 150 grams of Kaurit KF plus 1 gm of ammonia and 5 gm of ammonium nitrate per liter was prepared. The textile was passed through this solution, excess liquor drained off and the cloth heated first to 80-100°C for predrying and finally, for 5 to 10 minutes, at 120-130°C in order to complete the condensation of the resin.

(4) Kauritleim was a 65% solution of urea formaldehyde in water prepared with an alkaline catalyst. This product was used for the glueing of plywood, using either the hot or the cold process. In the cold process the resin solution was mixed first with 10% of the cold hardening catalyst. The prepared wood pieces were then

coated with the mixture and glued together by the application of pressure for 4 to 6 hours at room temperature. In the hot process the resin solution was mixed with 10% of hot hardening catalyst and the mixture applied to the wood parts as before. The bonding occurred during hot pressing at 90-100°C. Condensation was completed at this temperature in a 10 to 15 minute cycle.

The cold hardening catalyst consisted of:

Ammonium chloride	15 parts
Water	85 "

The hot hardening catalyst contained:

Ammonium chloride	15 parts
Ammon. hydroxide-25%	20 "
Urea	30 "
Water	31 "
Tylose	1 "

Mixtures of Kaurit plus catalyst were stable for only 24 hours.

(5) Iporka was a foam-like insulating material containing small microscopic individual cells filled with air. The finished product had a density of only 15 kg per cubic meter (water equals 1000) making it one of the lightest insulating materials known. The product was a heat and sound insulator, non-inflammable, and insect and mold resistant.

300 gm of Iporka foam mixture containing:

Phosphoric acid - 65%	612 parts
Resorcinol	111 "
Nekal (diisopropyl naphthalene sulfonic acid)	720 "
Water	1550 "

were mixed with 2000 gm water in a vessel of 300 liters capacity. The mixture was stirred violently until the full volume of foam had been built up. Ten liters of Iporka solution and 3 liters of water were then added. After mixing a few minutes the mass was filled into forms and allowed to stand for four hours after which time it was self supporting. The block was stored overnight at room temperature, dried to constant weight at 40°C and finally condensed at 60°C.

The Iporka solution was prepared from:

Formaldehyde - 30%	1600 gm
Urea	525 "
Alcohol-hexanetriol	38 "

This mixture was heated to boiling for a few minutes, 50 gms additional urea were added and the mixture heated at the boiling point and at pH 5 for a period of two hours.

(6) Iporit, a somewhat similar material but having no resin binder, is described here as a matter of additional interest. Water glass (Na_2SiO_3), Nekal solution, cement and sand were mixed in a kneading type mixer to form a foamy mass. The mixture was poured into forms, allowed to set and then to air dry.

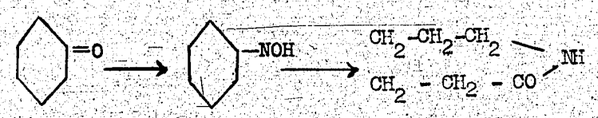
The bulk of the above data were given by Dr. Kollek, head of the Coloristic Department.

d. Dibasic Acids - Diamides (Igamid)

This development parallels the similar development in the U.S.A.

Igamide A was a condensation product of equal mols of adipic acid and hexamethylene-diamine.

Igamide B was a condensation product of epsilon amino caprolactam only. The lactam was prepared from phenol via cyclohexanone which was treated with hydroxylamine to form the oxime. The oxime was rearranged to the lactam in the presence of sulfuric acid.



This product was softer than Igamid A, had a lower melting point, and poorer electrical properties. It was suitable for injection molding.

Igamide 6A was a mixed condensate of 60 parts of Igamide A with 40 parts of Igamide B. It was used principally as a leather substitute.

Igamide 5A was a special water soluble product for the production of glues. It consisted of equal parts of Igamides A and B polymerized in a molten condition. It is essential that the 50/50 ratio be maintained in order to obtain water solubility.

Ludwigshafen's capacity for Igamids totaled 300 tons per month. They also produced hexamethylene diamine for the Desmophens (Igamide U) produced at Leverkusen. Since this development was quite new, production had attained a rate of only 20 tons per month. Ludwigshafen believes that Igamide U is better than A in that it has lower water solubility, better oxygen resistance and better electrical properties.

Details on the production of adipic acid and hexamethylene diamine were not obtained. Adipic acid was made from cyclohexanol using two different processes - the conventional nitric acid oxidation step, and catalytic oxidation with air (oxidation of cyclohexanol to cyclohexanone over a silver catalyst, then oxidation to adipic acid using manganese acetate catalyst.)

e. Polyethylene (Lupolen)

Two grades of polyethylene were produced at Ludwigshafen:

Lupolen N - a low molecular weight product, about 2000 to 3000 on the Staudinger scale, tested in a decalin solution, and

Lupolen H - a high molecular weight compound, about 20,000.

Both products were made by continuous high pressure polymerization of pure ethylene. Data were given by Dr. Hopff.

(1) Lupolen N

In preparing Lupolen N, ethylene was compressed to 200 atmospheres and pumped as a liquid into a pipe coil type polymerizer along with a solution of methanol containing about 0.6% benzoyl peroxide catalyst which was equivalent to ten percent catalyst based on the polymer formed. The reactor consisted of 40 meters of jacketed pipe 3 cm I.D. arranged in a number of sections so that independent temperature control could be obtained. The initial temperature, in the first steam heated section, was 110°C. The intermediate sections were water cooled in order to maintain the temperature at 100-120°C while the lower discharge end of the reactor was maintained at 150°C in order to keep the polymer sufficiently fluid. The reaction mixture leaving the coil contained about 79% methanol, 15% unreacted ethylene, 5% polymer and about 1% of by-products from the catalyst. It was discharged into a tower and maintained under slight pressure at 130°C to keep the methanol in the liquid state. The molten polymer, which is insoluble in methanol, collected in the bottom of the tower and was drawn off periodically to a cooling pan. The liquid methanol layer was expanded to atmospheric pressure, flash distilled to remove traces of polyethylene, benzoic acid etc. and then recycled to the system. The effluent ethylene gas was scrubbed with sodium hydroxide to remove formaldehyde and was then recycled to the compressors.

Conversion to polymer was about 20-25% per pass.

The polymer product drawn off was given a final treatment by blowing with a current of nitrogen for 15 minutes at 130°C in order to eliminate traces of contained benzoic acid. The resulting product having a melting point of 106°C and the consistency of paraffin oil when molten, solidified to a brownish hard wax which was blended with Oppanol B for preparation of cable dopes to yield a mixture containing only 10 to 25% of the pure Lupolen H. Some uses were found also in the preparation of polishes for furniture, floors, etc.

The yield on ethylene was better than 90%; in some trials when gas leakage was minimized a yield as high as 96% was obtained. Methanol losses were high, about 10% to 25% of the polymer formed.

Because of the corrosive nature of the by-products, the entire equipment was constructed of stainless steel.

A unit of the size described with a capacity of 10-15 tons of polymer per month was built at Zweckel from pilot plant data obtained in tests at Ludwigshafen.

(2) Lupolen H

The preparation of Lupolen H was carried out in a similar manner, but at much higher pressures and in absence of solvent.

Ethylene was compressed first to 300 atmospheres and then to 1500 atmospheres. Traces of oxygen were added as a catalyst using 0.05 to 0.10% based on the ethylene charged. Since the amount of oxygen was very important, a special control unit was designed. A portion of the feed mixture was withdrawn, mixed with a metered quantity of nitric oxide, NO, and then passed through a test cell located in a circuit containing a photoelectric cell. Oxygen reacted with the NO to produce brown nitric oxide the concentration of which was measured by the photo cell. Automatic control was arranged to hold the oxygen content at a predetermined level. It was stated that the unit was accurate to 0.001% oxygen in the feed gas.

The reactor proper consisted of a pipe coil 80 meters long by 16 mm ID (the discharge end was enlarged to 20 mm to permit ready discharge of the viscous polymer). At the entrance end of the coil the temperature was raised to 220 C. As soon as this temperature had been reached to initiate the reaction, cooling was applied to control the heat of reaction, maintain the temperature at 180-200°C in the bulk of the coil and finally deliver the discharged product at a temperature of about 130°C. The polymer syrup leaving the coil, at 130°C, passed through a manually operated control valve where the pressure was released and the product discharged to a receiver. Molten polymer collected in the receiver was withdrawn periodically and cast

in pans.

Conversion to polymer was only 10% per pass since a poor polymer of yellow color resulted if the reaction was carried too far. The ethylene leaving the receiver contained formaldehyde, formed almost quantitatively by the oxygen introduced as a catalyst. This gas was scrubbed with NaOH by passing in series through two towers, and was then returned to the compressors for recycling.

Typical feed gas contained:

Ethylene	96.8%
Ethane	1.8
Acetylene	0.1
Oxygen	0.3
Nitrogen	0.9

The oxygen concentration was lowered automatically by the reaction as described above. Recycling of the ethylene was continued until the ethylene concentration was reduced to 90% C_2H_4 at which time the gas was vented.

The product which was recovered as a pure white solid was used primarily for the production of materials for use in electrical insulation particularly for high frequency work. Military demands consumed the bulk of the production. For most uses the polymer was used as is. In special cases where a softer material was required about 10% Oppanol B was blended. This is the only known plasticizer which does not seriously reduce the good electrical properties of polyethylene.

The capacity of the plant described above was 2 to 5 tons per month. The Ludwigshafen plant was damaged badly and a new unit was recently erected in Gendorf. However, this had not yet come into production. Dr. Hopff made the following additional interesting remarks on polyethylene in general.

X-ray studies have shown that the polyethylene is a straight chain polymer. They have done no work on the preparation of short chain polymers of low chain length, say in the C_{20} range.

(3) Miscellaneous

A small amount of work was done on propylene polymers. Only oils or greases about the consistency of vaseline resulted. It was believed that these oils would have no advantages over the cable oils and lubricating oils now available.

Exploratory work had been carried out on a laboratory scale on the preparation of ethylene co-polymers. From these tests it could be generalized that ethylene was compatible and would co-polymerize with unsaturated hydrocarbons. Co-polymers with vinyl ethers, acrylates and methacrylates were not promising since these materials would co-polymerize at a faster rate than the ethylene resulting in a co-polymer of low ethylene content. Co-polymers with styrene, butadiene, maleic and fumaric acid esters were promising, that is, the rates of polymerization appeared to be equal. For example, a mixture of equal mols of styrene and ethylene would yield a product containing a ratio of 65 mols styrene to 35 of ethylene. Preliminary trials on equal molar ratios of monomers tested on a batch basis showed:

With styrene	-	more brittle product than ethy-
With fumaric ester	-	hard product lene alone
With maleic ester	-	tough product
With butadiene	-	rubbery product

Dr. Kopff indicated that under normal conditions additional work on co-polymers was planned since it was believed that polyethylene had considerable promise because of its potential low cost.

f. Styrene and Polystyrene

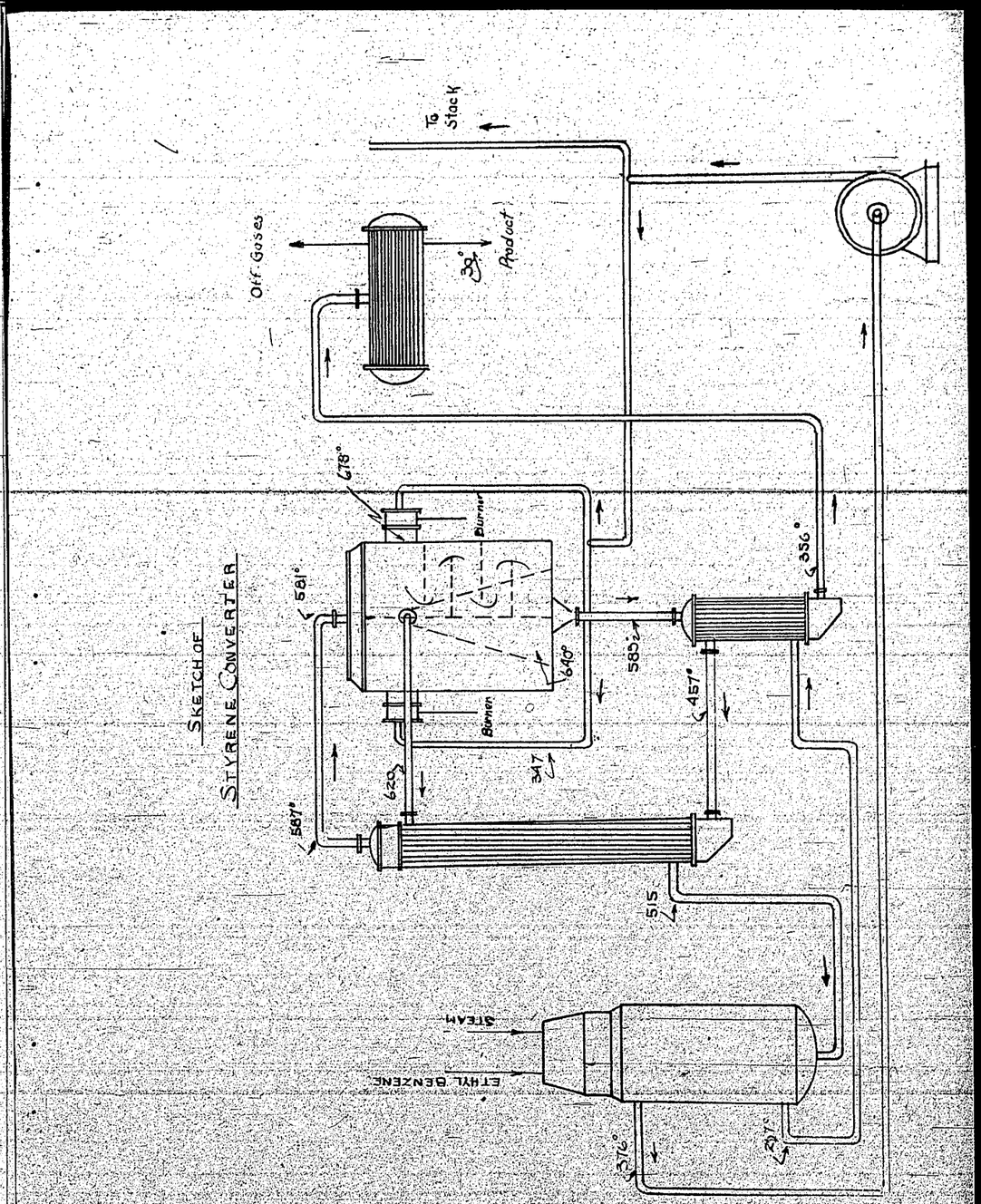
(1) Monomer Production

Styrene, in addition to being a key component of synthetic rubber, found considerable use as a polymer. Production of monomeric styrene was begun at Ludwigshafen in 1928, based on the development work of Mark and Wulff (now works manager at Schkopau).

Lugwigshafen's rated production capacity was:

In 1928	-	500 tons per year
1935	-	3000 tons per year
1943	-	14,000 tons per year

In addition, similar plants were built at Hüls and Schkopau. The Ludwigshafen styrene plant was very badly damaged and appears irreparable.



Briefly, the process consists in the manufacture of ethylene by catalytic dehydration of ethanol, reaction of ethylene with benzene in the presence of aluminum chloride to produce ethyl benzene, and the catalytic dehydrogenation of ethyl benzene to styrene. The ethylene generation and the alkylation steps have been covered fully by other groups and little material of interest can be added here. Therefore, special attention was given to the dehydrogenation and distillation operations.

(a) Dehydrogenation of Ethyl Benzene

The attached flow diagram shows the process in detail. A description of the process follows:

Ethyl benzene, about equal weights of fresh and recovered material, was mixed with about two times its weight of steam, passed to a vaporizer and then to a heat exchanger where the temperature was raised approximately to the reaction point. The mixture then passed down through a bed of catalyst contained in 220 mm diameter tubes which were heated externally by hot furnace gases in order to furnish the heat of reaction and maintain the vapors at about 600°C. The exit gases were cooled quickly by heat interchange and finally condensed to separate a product liquor containing about 40% styrene. Exit gases consisting principally of hydrogen were cooled first to 20°C, then to 0°C and finally scrubbed with ethyl benzene at 0°C before passing to storage for use as fuel. A discussion of salient features of the operation follows:

(b) Catalyst

The old type catalyst used prior to 1942 contained:

ZnO	-	50%
Al_2O_3	-	40
CaO	-	10
K	-	nil

Using this catalyst the off gas evolved amounted to 70 cubic meters per 100 kg of styrene produced, and its hydrogen content was low, roughly 70%. The operating life was about 6 months. The yield of styrene on ethyl benzene was fairly good, initially about 85%, but declined so rapidly that the average yield was not much better than 70%.

Two typical analyses of the new catalyst are given below together with the analysis of the catalyst used at Hüls (refer to CIOS report dated 14 May 1945).

	Lu-82	Lu 144	Hüls
ZnO	85.6%	82.0%	85.0%
Al_2O_3	3.3	8.0	5.0
CaO	5.1	5.0	5.0
MgO	-	5.0	-
K_2SO_4	3.0	3.0	2.0
K_2CrO_4	3.0	3.0	2.0

Operating data on these catalysts showed -

Operating life	-	One to two years
Off-gas - quantity-	-	40 cubic meters per 100 kg styrene
composition		CO_2 - 9.0% by vol.
		CO 0.5 " "
		H_2 88.6 " "
		CH_4 1.5 " "
		C_2H_4 0.4 " "

Liquid product -	Benzene -	0.4%
	Toluene -	0.8
	Ethyl benzene -	58.1
	Styrene -	40.0
	Tar -	0.7
		100.0

Yield of crude styrene - approx. 90%.

(c) Converter Details

The Ludwigshafen converters had a rated capacity of 100 tons of styrene per month each and contained 26 tubes, 220 mm ID by 3 meters long. These were arranged in a somewhat irregular pattern to permit proper passage of the heating gases which were circulated outside of the tubes. The alloy tubes were standard pipe gauge lined with copper-manganese alloy which was applied as a 3-4 mm sheet fitted inside the tube and welded to the tube sheet which likewise was clad with copper manganese alloy. The units showed some small cracks which, for example, would not be permissible if the equipment handled a corrosive liquid. Presumably, these cracks developed from heat stresses during operation.

Some of the original units were fitted with oval shaped tubes designed primarily for better distribution of the heating gas. This was later found to be unnecessary.

The catalyst volume was two cubic meters per converter. Other units within the I.G., at Hüls and at Schkopau, used smaller tubes - 92 tubes of 100 mm ID.

As indicated in the sketch, the furnace gases (fresh gas plus recycled gas) were fired at two sides of the converter which is divided into two separate heating chambers. The two streams of flue gas combined just before leaving the converter and passed to the heat exchanger to superheat the incoming ethyl benzene.

(d) Tube Material

The converter tubes proper were of CMT 5 steel -- this is understood to contain 9% chromium and 18% manganese although another reference states that sicromal steels (silica, chromium, aluminum type) were used. The lining alloy contained 97% copper with 3% manganese.

Laboratory tests using chromium steels showed a 3 to 4% lower yield and hence it was concluded that iron was the offending metal. However, additional laboratory tests made on two steel alloys, as shown below, gave no difference in yield as compared with copper-manganese:

	Test A	Test B
Manganese	6.5%	6.2%
Silicon	3.15	1.18
Chromium	8.8	3.1
Carbon	0.43	0.29
Iron	81.12	89.23

(e) Purity of Feed

Recovered ethyl benzene contained from 0.5 to 1.0% styrene. Hence the content of the feed including fresh ethyl benzene was about half of this quantity. No detailed plant data were available on the effect of operating with a higher styrene content in the feed. However, based on laboratory experience it was stated that a higher styrene content would result in a lower yield.

(f) Steam Ratio

The weight ratio of steam to ethylbenzene charged was originally fixed at two to one. This ratio was lowered gradually in plant operation until recently a ratio of 1.2 to one was used. One converter was operated as long as two months with a ratio of 0.8 lbs. steam per lb. of ethyl benzene with less than a 1% change in yield. However, it is known that the ratio cannot be lowered below 0.5 since carbon deposition on the catalyst results at this point. The minimum steam ratio may vary somewhat with slight variations in catalyst composition.

(g) Conversion

Detailed operating data on the relation between conversion and yield were not available. One test on a catalyst of the old type operated at 28% conversion and with a higher throughput (about 140% of normal) showed an improvement in yield of 5-6% over the previous standard. Probably the 90% yield cannot be improved appreciably by lowering the conversion below 40%.

(h) Tube Size

As stated previously, units at other I.G. Plants have 100 mm ID tubes. Operating under similar conditions it was indicated that an improvement of 1 to 2% in yield resulted under these conditions. Because of the relative increase in heating surface per pound of styrene produced, the temperature differential between the heating gas and the catalyst operating temperature was lowered by about 20°C when using smaller tubes. In contrast, it was thus possible to increase the heating temperature and obtain a greater throughput without raising the gas temperature about the safe limit of 650°C.

(i) Cracking Losses

It is known that temperature above 600°C promote thermal cracking. One plant experiment made in 1941 while using the old type catalyst showed a loss of 1.0% of the ethyl benzene through thermal cracking of the vapors prior to entering the converter. This was believed to be due in part to the fact that the Sicromal tube was not clad with copper manganese alloy.

(j) Throughput

The Ludwigshafen units, each designed for a rated capacity of 100 tons of styrene per month, have been operated at rates of 130 tons under the same conditions of conversion with no change in yield. From the data which were available it is believed that this study was not completed.

(k) Catalyst Life

The life of the new catalyst is one year or more. The attached table shows the change in operating temperature, yield, etc., for two different catalysts -- analyses of which were given previously -- when operating at 40% conversion.

Catalyst 144

Time on Stream-Months	Catalyst Temp. °C	Off Gas CM^3 per 100 kg styrene	Yield - percent theory
1	565	35	93.5
3	590	44	93
5	590	40	92
7	595	40	92
10	600	47	90.5
12	605	45	90
15	610	44	88
	Catalyst 82		
1-3	590	35-43	92-93
3-6	605	35-43	91-92
6-9	620	36	90-91

(1) Distillation

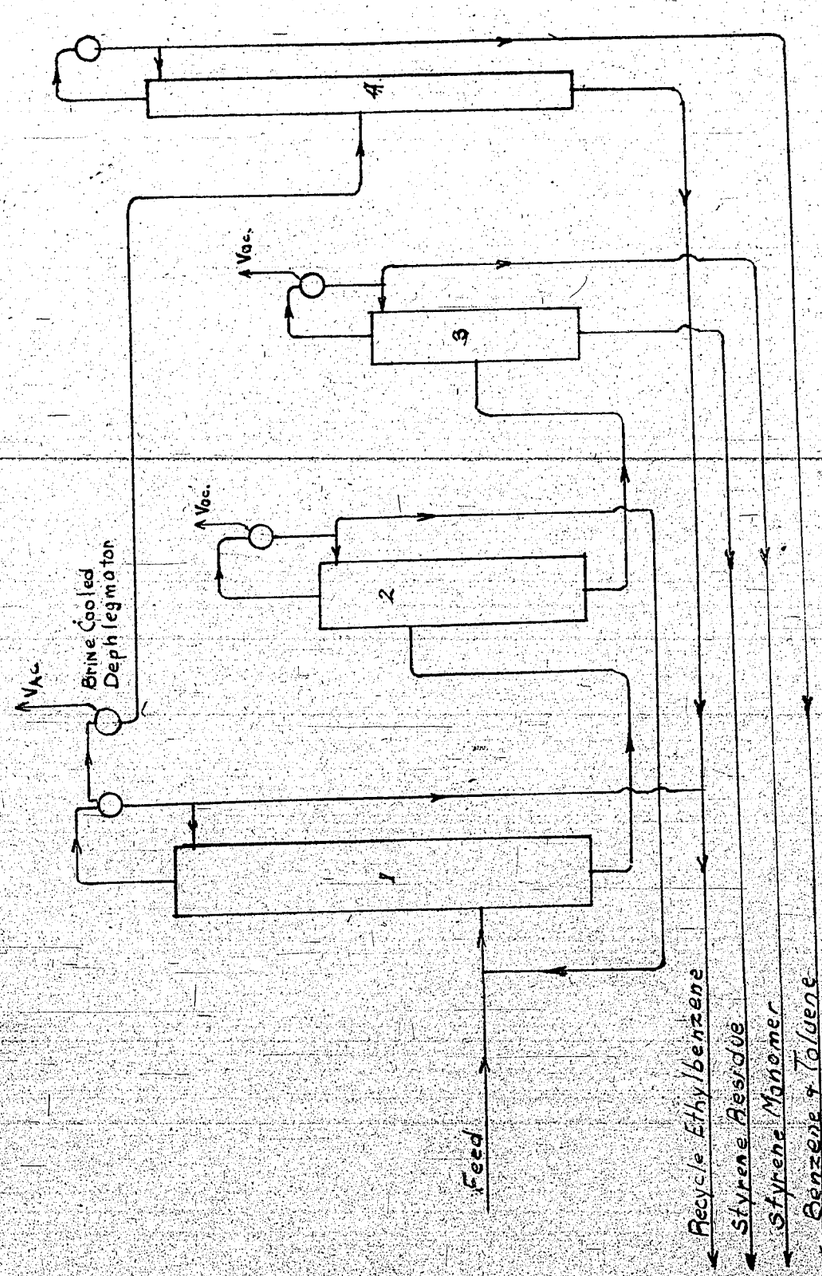
The distillation of the dehydrogenated liquor from the convertors for the recovery of styrene of 99.2% average purity minimum was carried out in a series of three stills as shown in the accompanying sketch.

The distilling columns appeared to be of conventional design with the exception that they were tin coated in order to minimize the polymerization of styrene. The 45 plate column illustrated was 78 inches in diameter, had a 14 inch tray spacing and contained 108 - 4 inch diameter bubble caps per tray. Measurements from a plant drawing indicated a static slot immersion of 10 mm.

Column No.	1	2	3	4
No. of plates	45	28	(10)	60
Plate spacing - cm	40	40	-	-
Column I.D. - m	2.0	2.0	1.0	Cal.0
Reflux ratio	4.5/1	10/1	0.75/1	10/1
Feed - % styrene	40	80	(102)	1
Overhead - % styrene	0.5-1.0	35-40	99.3	nil
Bottoms - % styrene	80	(102)	Ca50	1
Pressure - top, mm	30	30	30	760
Pressure - bottom, mm	210	120	75	900
Temperature - O.H. approx.	35	40	40	(100)
Temperature - bottom	92	85	80	150

Comments: - Column 3 is packed with Raschig rings.
Feed to column 4, dephlegmator condensate from column 1 contains about 10% benzene, 15% toluene and 75% ethyl benzene.
Feed rate to column 1 is 2700 liters per hour.

STYRENE DISTILLATION SYSTEM.



The yield of finished styrene from raw styrene in the charge was stated to be 99%. No ready means were available for checking this figure, which appears very good. However, the following yield data obtained from I.G. accounting records found in the Frankfort library confirms the good overall yield.

Yield Data - Hüls Styrene Plant

(Quantities in tons)

Period	3rd Qtr.1943	4th Qtr.1943	1st Qtr.1944
Ethyl benzene	5,750.3	4894.4	4478.9
Benzene - Toluene recov.	211.2	141.6	136.5
Styrene residues	80.6	69.5	62.7
Pure styrene	5,089.5	4314.5	3953.8
Yield - % theory	88.5	88.2	88.3

The styrene residues were mixed with high boiling residues from the ethyl benzene plant and used as plasticizers. In this case the styrene recovery was essentially 100%. Thus in the above data 60 to 80 tons of styrene equivalent would be added, thus increasing the yield by about 1.3%.

(2) Polymerization of Styrene

Styrene was polymerized by two methods, emulsion and mass. Emulsion products carried the E prefix in the symbol. Discussion on the principal products follows:

(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 molding purposes.

At one time, the product was prepared in a similar manner except that the emulsion was coagulated with formic acid, filtered, and the residue then drum dried. Products produced in this manner had a superior water resistance since the bulk of the emulsifier, etc., had been removed in the coagulating step.

Ludwigshafen's production capacity was 120 tons per month.

(b) Type EH contained 50% styrene, 25% acrylonitrile and 25% vinyl carbazole. It was prepared in a manner similar to EF except that only 20% of the batch was charged to the reactor and the balance of the charge added while boiling the mixture under reflux. Only 5 tons were prepared monthly. The material had a better impact test and heat resistance than polystyrene and was used as a substitute for type metal.

(c) Type EN, containing 70% styrene and 30% acrylonitrile, was used for injection molding. It was planned to replace EH with EN.

Production capacity was 10 tons per month.

(d) Type 3, a pure polystyrene having a K value of 70-73, was produced by polymerizing in mass, using a tower operated in a continuous manner. A stainless steel tower 80 cm in diameter by 6 meters high was divided into 6 sections each provided with jackets for heating with steam and with cooling coils. The monomer was pre-polymerized at 80°C to a 33% syrup in a stirred vessel. This syrup was then fed to the tower where the temperature was maintained at about 140°C in the top section, by application of heat, at 160°C in the center and about 180°C near the bottom outlet. The bottom of the tower ended in a screw type extrusion device which passed the product through two discharge slots 30 mm wide by 3 mm high to form bands which collected on a water cooled stainless steel belt. The cooled product was passed to a cutting knife to give about 1 inch pieces which later were ground to 1-3 mm size for the finished product.

Each unit had a capacity of one ton of polymer per day. The first units were installed in about 1930. Ludwigshafen operated a total of 14 such units.

(e) Type 4 product had a K value of 80-85. This material was produced on a special type vacuum drum drier. The polymer was prepared as a thick syrup containing about 35% polymer. This was fed between the rolls of a double drum drier operated under an absolute pressure of 15 mm mercury. The residual monomer was evaporated, condensed and recycled. The polymer residue scraped from the drum was collected in receivers and discharged batchwise.

Monthly production totaled about 20 tons.

(f) Miscellaneous - Small amounts of polystyrene polymerized in ethylbenzene solution, about 40% styrene, were made and sold for use as lacquers.

Some solid co-polymers of styrene (70%) and butyl acrylate (30%) were prepared but were not marketed extensively.

No commercial developments were found in the field of divinyl benzene or polychlorostyrenes.

"After-chlorinated" polystyrene had been produced at a rate of 1 to 2 tons per month. Polystyrene 3 dissolved to a 12% solution in carbon tetrachloride was chlorinated at 40 - 50°C to give a product containing 12.5% chlorine. The product was used as a substitute for chlorinated natural rubber in lacquer preparation. Production in recent years was negligible.

g. Butadiene and Synthetic Rubbers

Ludwigshafen prepared butandiene at a rate of roughly 1500 tons per month using the synthesis developed by Reppe; the reaction of formaldehyde with acetylene to form butindiol which was hydrogenated to butandiol and then dehydrated to butadiene.

Ludwigshafen also carried out the polymerization step for the production of finished Buna S-3 at a rated capacity of 2000 tons per month. Since both of these processes have been studied in detail by others, details of the operations will not be repeated here. However, in an attempt to determine whether any new rubber like materials were developed, a list of the known rubbers and their composition was requested from Dr. Bulow and Dr. Niemann. Following is a summary of these data:

Buna S-1 was a synthetic rubber containing 75% butadiene and 25% styrene.

Buna S-3 was similar to S-1 except for a change in the fatty acid and regulators used in the emulsion. This material is better in all respects and has a better workability than S-1 and could be used in the manufacture of tires without mixing with natural rubber.

Buna 32 was really a plasticizer instead of a rubber. This material was a low molecular weight butadiene polymer prepared by the sodium polymerization technique in the presence of a small amount (0.2%) of dioxan. All production was said to be at Schkopau.

Buna 85 was similar to Buna S-3. The 85 figure refers to the viscosity or K value on a Fikentscher scale. About 200 tons per month were produced at Schkopau. The product has good workability properties but poor strength.

Buna SR was a higher temperature polymer also containing 75% butadiene and 25% styrene. The product has a higher viscosity and was more workable than Buna S-3.

Buna SS was a product containing 40% styrene. It was thermoplastic and had good injection molding characteristics but poor low temperature resistance. Because of its higher styrene content, it was less elastic than regular Buna.

Buna SSGF was an odorless material of the same composition as SS. It was prepared by compounding of SS and was used for special items; e.g. for food wrappings, etc.

Buna SSE was similar to SS except that it was iron free. It was produced for pharmaceutical uses.

Buna N was the standard 25% acrylonitrile, 75% butadiene polymer. It possessed good oil resistance.

Buna K This item was listed in documents seen at the Frankfort Reichsbank document center. However, the Ludwigshafen technicians had no knowledge of it.

Buna M Experimental work was carried out on mixed polymers containing methacrylic esters and butadiene. These materials were not put into commerical production. These rubbers had good mastic properties. Chlorinated rubber was not produced at Ludwigshafen. Höchst was stated to be interested in this field.

Ludwigshafen made no rubber accelerators; most of this work was confined to Leverkusen. No information could be obtained relative to a statement noted in some I.G. reports that a non-sulfur organic material had been developed as a substitute for sulfur in the vulcanization of Buna.

Activities in the field of rubber antioxidants was confined to the manufacture of phenyl betanaphthylamine. Ludwigshafen produced 400 out of the total I.G. production of 500 tons per month. Koresin, a blending agent or tackifier for synthetic rubber, was prepared at a rate of about 100 tons per month. As has been reported previously in detail by another group, this material was made by vinylating para tertiary butyl phenol with acetylene in the presence of zinc naphthenate catalyst at about 200°C and 15 atmospheres.

h. Isobutylene (Oppanol)

The synthesis of isobutylene from isobutyl alcohol was not examined. Isobutylene was used in the synthesis of the following Oppanols:

Oppanol B was polyisobutylene co-polymerized with small amounts of diisobutylene. Products of molecular weights of

200,000, 150,000, 100,000 and 50,000 were prepared. The highest molecular weight product contained no diisobutylene; the addition of only 0.015% lowered the molecular weight to 150,000.

The polymerization was carried out in a rather novel manner. One part of isobutylene containing the required diisobutylene was mixed with an equal weight of ethylene cooled first by ammonia and then by refrigeration with ethylene to minus 80°C. This product was dropped to the entrance end of a continuous stainless steel belt conveyor about 18 inches wide by 30 feet long (60 feet total). Immediately thereafter a solution of one part of ethylene containing 0.003 parts of boron tri-fluoride catalyst was added at a point about one foot from the entering isobutylene. Polymerization was quite rapid so that by the time the belt, moving at a speed of about 200 feet per minute, reached the far end, the product had polymerized almost completely and the sticky polymer could be discharged from the end of the belt into a kneader (Baker Perkins type mixer). The belt was housed completely. The liquid ethylene, with the application of heat from radiation and polymerization, evaporated as the reaction proceeded and was collected, purified from aldehydes by passing over CaO and recycled to the process. Evaporation of ethylene held the reaction temperature at minus 80-100°C.

The B-P type mixing unit at the discharge end was steam heated to an operating temperature of 50-100°C so as to remove the last traces of ethylene and complete the polymerization. Finished plastic was extruded from the top of this mixer through a large opening.

The capacity of each unit was 5 tons per day; the limiting factor was the ethylene compressors rather than the polymerizer itself. Four units were installed to give a calculated capacity of 600 tons per month. It is understood, however, that operation was not entirely continuous since some stoppages for cleaning, etc. occurred.

Diisobutylene was the only co-polymerizing agent used. Isoprene or butadiene had not been tried, at least not beyond laboratory tests.

Oppanol C was not an isobutylene polymer as might be suspected from its designation, but a polymer of vinyl isobutyl ether. It is soluble in esters, ketones, and aromatic hydrocarbons but insoluble in gasoline and in alcohol. The material was used in adhesives, was permanently thermoplastic and had poor electrical properties.

Oppanol O was a mixture of 90% Oppanol B with 10% of polystyrene 3 usually prepared in sheet form.

Oppanol Oils - Grades B5, B3 and TZ 900 were oil soluble polymers used as viscosity improvers for lubricants. The viscosity of the several grades at 100°C was:

B5	-	50 Engler
B3	-	30 "
TZ 900	-	2-5 "

These polymers were produced in isobutane solution using boron trifluoride catalyst. The ratio of isobutylene to isobutane was varied - 1 to 3 for Grade B5; 1 to 2.5 for Grade B3 and 1 to 2 for Type TZ 900. The mixture of isobutylene and isobutane was charged to the top of a polymerizing tower together with a saturated solution of boron trifluoride in methanol. The mixture leaving this vessel was separated to remove the methanol layer and then passed to a Raschig ring filled tower where the isobutane was vaporized; collected, compressed and recycled to the process. The polymer residue was washed with water to remove methanol, etc. and then heated under vacuum to remove the traces of light end products. The raw product was mixed with Fullers earth, filtered and dried by passing a current of nitrogen through it.

i. Vinyl Chloride (Igelite)

Vinyl chloride monomer was not made at Ludwigshafen. Polymer was made from monomer shipped either from Schkopau or Rheinfelden.

A number of polymers and co-polymers were made. Detailed discussion on the various polymers and co-polymers based on vinyl chloride follows:

Igelite PCU, signifying polyvinyl chloride unchlorinated was the straight polymer. Production was at a rate of 200 tons per month. The method of production was as follows: The reactor tower consisted of an enamelled vessel, 10 meters high by 1.2 meters diameter, steam jacketed and fitted with a 40 r.p.m. stirrer of rectangular shape placed near the top of the reactor so that it was only half submerged. The tower was fed with a stream of water containing 5.5 to 6% of Emulgator MK -- a Mersolat product of low NaCl content prepared at Bitterfeld -- and 0.1 to 0.3% of potassium persulfate catalyst. Percentages were based on the monomers. The monomer was added as a second separate stream at a rate of 350 pounds per hour. The reaction was maintained at 30-50°C, under pressure to permit refluxing of any vinyl chloride. The product leaving the first tower was passed to a second similar tower, except that it contained no stirrer and was somewhat smaller, 0.5 meters diameter by 6 meters high. The mixture was maintained at 35-55°C to complete the reaction. The product from this tower containing about 5% free monomer was passed to storage. Ludwigshafen made no attempt to recover this monomer although it was claimed that Schopkau and Bitterfeld were making plans to do so.

The polymer emulsion, containing 40% polymer by weight, was fed directly to the top of the rolls of a double drum drier heated with steam at 160°C. The dried polymer melted to a thin sheet of paper thickness which was peeled off by a knife placed about 90 degrees before the feed. The polymer broke into small pieces as it fell from the knife and was later ground to a powder.

Plasticizers were added to the vinyl chloride by milling. This was done at the customers plant.

The only stabilizer used at Ludwigshafen was sodium carbonate. The amount used was 0.3% in the case of PCU and lower in other grades - for example, 0.1% in the MP grades. The stabilizer was added during the polymerization. Ludwigshafen admitted that this stabilizer was not satisfactory since it lowered the water resistance and produced turbidity. They felt, however, that it was the best material found to date. Dr. Kollek understood that phenyl indole was used as a stabilizer for vinyl chloride and had been in the develo - ment stage in Bitterfeld and Leverkusen. It had not yet attained commercial use.

Igelite PC was "after-chlorinated" polyvinyl chloride. Polyvinyl chloride PCU was dissolved and chlorinated so as to yield a product containing 60% Cl (56.8% Cl in PCU). This material was used chiefly in the production of fibres and was made at Bitterfeld and Rheinfelden.

Igelite MP referred to mixed polymers of vinyl chloride. The several types, their composition, uses and production are:

Type	Production Tons /Mo.	Composition and Use
MP A	100	80% vinyl chloride, 10% dimethyl maleate, 10% diethyl maleate or acrylate. Used as a glass substitute. Quite clear.
MP AK	50	80% vinyl chloride, 10% dimethyl maleate, 10% diisobutyl maleate. For electrical products.
MP K	50	84% vinyl chloride, 16% methyl acrylate. Used for cable preparation.
MP 400 (Vinoflex)	-	73% vinyl chloride, 25.5% vinyl isobutyl ether and 1.5% methyl acrylate.

The preparation of the MP polymers is essentially the same as that of the PCU with the exception that a 25% emulsion was prepared, and in order to obtain a clearer product the emulsion

was first coagulated with aluminum sulfate solution, filtered, washed with a large quantity of treated cold water (about 10 parts per one part of polymer) and dried either on a belt conveyor or in a discontinuous pan drier of stainless steel construction.

Type MP 400 was prepared by a batch process, since, because of the different rates of polymerization, it was necessary to adjust the monomer addition rates.

Several different molecular weights of PCU were prepared depending upon the intended use. Type G having a "K" value of 60 was used as a rubber substitute. Type F, with a "K" value of 75 was used for foils.

j. Acrylates - Accronals

Polymers of acrylic acid esters were termed Accronals. The products in commercial use were:

Accronal 1 - the methyl ester
2 - " ethyl "
4 - " butyl "

One series of polymers was prepared in organic solvents, preferably ethyl acetate. Accronal 1 was used in admixture with Buna for cable coverings where oil resistance was required. Accronal 2 was a good bonding agent for metals particularly magnesium and aluminum. It formed satisfactory paints and had good weather and light resistance. Accronal 4 was useful in the so-called Scotch tapes since it was permanently sticky. Another class of the Accronals was the water emulsion type, termed ID, etc. The chief general use for these materials was for the treatment of textiles.

Various special co-polymers of these esters have been made with styrene, vinyl isobutyl ether, vinyl acetate and vinyl benzoate.

Acrylic acid ester monomers were prepared from ethylene cyanhydrin purchased from Zweckel or Leverkusen where the product was prepared batchwise by the reaction of ethylene with aqueous HCN at 30°C in the presence of a catalyst - diethyl amine. The Reppe process using acetylene and methanol in the presence of nickel carbonyl, which furnished CO to the reaction, had been worked out in the laboratory and was considered promising. However, it had not yet been put into production.

To prepare the acrylic esters, the ethylene cyanhydrin was hydrolyzed with sulfuric acid and esterified with methanol or ethanol in one step. In the case of the butyl ester it was necessary to prepare acrylic acid and esterify it separately with butanol.

The polymerization in ethyl acetate was carried out in a 25 to 60% solution at 70 to 90°C using benzoyl peroxide catalyst and operating on an 8 to 12 hour cycle.

Emulsions were prepared in concentrations of 25 to 50% using 1 to 2% of Amfoseife 18 or Emulphor O as the emulsifying agent. Potassium persulfate catalyst, 0.05 to 0.10% was used at an operating temperature of 70-90°C with a cycle of 4 to 5 hours. In general, the technique for the acrylic esters was identical with that used for vinyl acetate. The nominal production at Ludwigshafen totaled 900 tons of the Accronal D type plus 200 tons of Accronal solution per month. The chief uses for these products were in the preparation of leather fiber binders, textile coatings and artificial leather.

The emulsions found their most important use in the treatment of textiles, in which case they appear also under the name of Appretans. Type A was a 25% emulsion of the methylester; Type B, the ethyl ester and Type G1, a 50% emulsion of equal parts of butyl acrylate and vinyl acetate. The Appretans were colorless dispersions which were completely miscible with water. These materials had the property of filling the fibres of the textile without affecting the hand. This results from the fact that on drying they form a permanently elastic film either when used alone or with other textile assistants as sizes, gelatin, etc. In application, the solution was diluted to a concentration of 25 to 50 grams per liter, applied to the cloth by dipping methods and then dried.

k. Vinyl Ethers (Igevin)

The vinyl alkyl ethers comprised a new series of compounds developed commercially by I.G. Work on these compounds was initiated in 1930, a pilot plant was constructed in 1934 and full scale production was begun in 1939. The products were made by the reaction of the particular alcohol with acetylene under pressure in the presence of potassium hydroxide catalyst. A long series of compounds has been prepared in the laboratory from alcohols, polyalcohols (glycols) and phenols. Only one acetylene group is introduced per hydroxyl group. Hence in the case of polyalcohols, either one or two hydroxyl groups can be reacted.

Total production capacity was about 400 tons per month. One third of this production was used for the preparation of co-polymers such as Igelite MP 400, the balance was polymerized for the preparation of:

Igevin M - polyvinyl methyl ether
" E - " ethyl "
" I - " isobutyl "

Grade E was used as a plasticizer for nitrocellulose, Grade I was used as a substitute for chewing gum, and as a grease or oil for leather. None of these products are suitable for molding powders since they form resins of low melting points, 50-75°C.

VINYL ETHERS

Summary of Operating Conditions

Name of Ether	Temp. °C	Pressure Atm. Ga.	Yield - % Theory Alcohol	Yield - % Theory C_2H_2	C_2H_2 in feed Approx. Vol. %	Approx. Annual Prod.-Tons
Methyl	160	20 - 22	90	90	55	200
Ethyl	155	18 - 20	92	92	60	1000
Isobutyl	150	4 - 5	95	92	90	2400
Butyl	150	4 - 5	92	90	90	50
Decahydronaphthol	170	0	85	88	90	20
Octadecyl	175	0	85	88	90	10
1,4- Butaniol divinyl	160	20	80	80	60	5
Diglycol divinyl	160	20	80	80	60	5

Production of Vinyl Ether - Dr. Christ supplied the data in the attached table which shows the several types of ethers prepared commercially and gives operating conditions and annual production as of 1944.

Production of the methyl vinyl ether, as an example, was carried out continuously in the following manner in equipment having a capacity of 300 tons per month. The equipment, of all steel construction, consisted of acetylene compressors, reactors for the preparation of the KOH-methanol solution; the reactor tower 700 mm diameter by 10 meters high, recycle compressors plus stills, etc. for the purification of the product.

Commercial anhydrous potassium hydroxide and pure methanol were boiled to remove traces of water and prepare a potassium methylate solution. This catalyst solution, together with fresh methanol, was pumped into the reactor as necessary to maintain the proper concentration, about 5% KOH, and to keep the reactor about 70% full. A mixture of acetylene (55%), with nitrogen, was compressed to the reaction pressure, 20 atmospheres, and bubbled through the solution maintained at 150-165°C. The gas leaving the top of the tower was cooled to recover the product as a solution of 60% vinyl ether in methanol. The off gas was recycled after adding the necessary fresh acetylene. A portion of the KOH alcohol solution was withdrawn from the bottom of the column from time to time, purified of salts, resins, oils etc. and recycled to the reaction. The crude vinyl ether was distilled to remove the dissolved acetylene, and to recover a 95% vinyl ether. The residual methanol was either recycled as such, or given an occasional clean up by a batch distillation. The vinyl ether was given a final treatment by washing with water and drying.

Other vinyl ethers were prepared in a similar manner. As the higher alcohols were used, the required pressure became lower.

The vinyl ethers were polymerized in mass by the block method using boron trifluoride catalyst in dioxan solution. Details of the process were not obtained. The block method refers to polymerization of the monomer as a mass of about 100 lbs total weight contained in a cylindrical container heated in an air or water bath.

1. Ethylene Imine

Ethylene imine, boiling point 60°C, is an interesting material for application particularly in the paper and textile fields. This product had been in production since 1938. Recent capacity was only 5 tons per month due in large part to lack of raw materials. The monomer was prepared by forming the HCl salt of monoethanol amine and reacting it with thionyl chloride:

$$\begin{array}{l} CH_2\text{-}CH_2\text{-}OH \\ | \\ NH_2\text{-}HCl \end{array} + SOCl_2 \longrightarrow \begin{array}{l} CH_2\text{-}CH_2\text{-}Cl \\ | \\ NH_2\text{-}HCl \end{array}$$

The product was then reacted with NaOH; on heating to 60°C the imine distills off:

$$\begin{array}{l} CH_2\text{-}CH_2\text{-}Cl \\ | \\ NH_2\text{-}HCl \end{array} + NaOH \longrightarrow \begin{array}{c} CH_2\text{-}CH_2 \\ \diagdown\ \diagup \\ N \\ H \end{array} + NaCl$$

Since acids catalyze the polymerization, the product was stored in carbon dioxide free atmosphere. Another method of synthesis, employed in the original research by Dr. Ulrich, was the reaction -

$$\begin{array}{l} CH_2\text{-}CH_2\text{.}OH \\ | \\ NH_2\text{-}HCl \end{array} + SO_3HCl \longrightarrow \begin{array}{l} CH_2\text{-}CH_2\text{-}OSO_3H \\ | \\ NH_2HCl \end{array}$$

On standing, the sulfate crystallizes out and can be isolated.

$$\begin{array}{l} NH_2\text{-}CH_2\text{-}CH_2 \\ | \quad\quad | \\ SO_3 \text{---} O \end{array}$$

On heating with ca. 40% caustic soda solution, the ethylene imine begins to distill at 60°C and can be recovered in about 80% yield. It was stated that sulfuric acid monohydrate may be used instead of chlorosulfonic acid. It is theorized that the imine on warming passes to its tautomeric form - vinyl amine $CH_2 = CH\text{-}NH_2$ which polymerizes quite readily. In application to paper for the production of high wet strength materials, the polymer was added in amounts of one to two percent based on the dry paper, adding it to the paper beater. The subsequent drying operations followed standard paper practice. The resulting paper had a high wet strength. A test sample examined after saturating it with water showed the same apparent strength as the original dry sheet. It was explained that in the preparation of the paper, the imine polymer solution penetrates the capillaries of the cellulose fibre, displacing the water therefrom. The viscous polymer cannot be removed by capillary action. Hence the paper does not lose its strength on washing in spite of the fact that the polymer per se is water soluble. No X-ray diffraction diagram studies have been made to demonstrate whether this theory is correct or whether, as is also plausible, the imine actually condenses with the hydroxyl groups of cellulose. The monomer imine, is quite poisonous. It combines with the albumins of the human organism, attacks the eyes, causes swelling and vomiting.

In addition to the principal use as a paper treating material, the polymer has been tried for the production of inner liners for shoes and in the preparation of a paper substitute for asbestos packing. Ethylene imine polymer can be prepared by heating in a stirred vessel in the presence of carbon dioxide at atmospheric pressure. The initial temperature of 60°C is gradually increased to 110°C at the end of the 24 hour cycle as the batch becomes more and more viscous. The mixture is then diluted with water to form an approximately 50% solution which is clear and light colored.

Ethylene imine monomer has been applied to fibres directly; i.e., to cotton and especially to rayon, to impart anti-swelling properties. Because of the slightly acid nature of the rayon fibres, the monomer polymerizes readily and forms the viscous polymer within the fibre capillaries thus rendering the fibre swell-proof. Since about 1936, Wolfen has marketed this material as Fibre XTH.

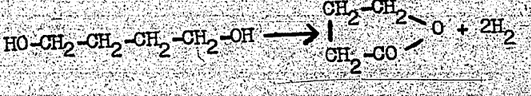
m. Vinyl Benzoate

Vinyl benzoate was a rather recent I.G. monomer product. It was used entirely in co-polymers, for example, with vinyl acetate. The total production to date was stated to have been about 15 tons.

Benzoic acid was charged continuously to a vaporizer held at about 200°C and a current of 99% acetylene gas then passed through the vaporizer to give a ratio of about 10 cbm of acetylene per kg of benzoic acid. The vapors were passed over the catalyst at 250-300°C and condensed to recover the crude vinyl benzoate. The excess acetylene was recycled. The catalyst used was a 10% mixture of about two parts of cadmium oxide and one part of aluminum oxide on activated charcoal. Its operating life was two to three weeks. The crude product containing from 1% to 10% benzoic acid when the catalyst became old was treated with sodium carbonate to remove the free acid and then purified by careful distillation at low vacuum.

n. Vinyl Pyrrolidon

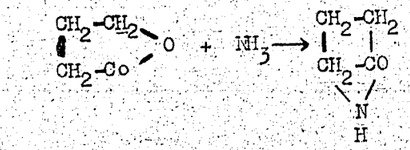
Vinyl pyrrolidon is a new polymerizable product from the I.G. developments in acetylene chemistry. It was introduced in 1942. The starting product was 1,4-butanediol, the intermediate in the synthesis of butadiene. This was dehydrogenated to gamma butyrolactone as follows:



Butandiol was vaporized at 200°C and passed together with a stream of hydrogen over a copper on silica catalyst maintained at 200-230°C. A feed rate of 20 gm of diol and 350 liters of hydrogen per

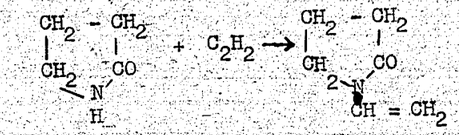
hour per liter of catalyst was used. The hydrogen split off in the reaction was scrubbed with water and the excess recycled as indicated. The crude butyrolactone containing small amounts of acetone, tetrahydrofuran, butyraldehyde and butanol was purified by distillation to yield the lactone boiling at 203°C at 760 mm.

The lactone was converted to pyrrolidone as follows: -



by heating in a stirred steel autoclave for 8 hours with anhydrous ammonia at 230°C under an initial pressure of 40 atmospheres which gradually decreased to 20-25 atmospheres. The product was purified by vacuum distillation.

The pyrrolidone was then vinylated under pressure -



50 kg of technical solid potassium hydroxide were added to 1,000 kg of pyrollidone and the mixture then heated under vacuum until about 15% of the pyrollidone had been distilled leaving an anhydrous solution in pyrollidone. About 200 kg of this was charged to a reactor, 200 mm diameter by 15 meter high, and heated to 150-160°C. Nitrogen was passed until a pressure of 20 atmospheres was attained and then acetylene was added until the content of the circulating gas stream reached 60% C_2H_2. The reaction was carried out thereafter in a continuous manner similar to that described for the manufacture of the vinyl ethers. The reaction product contained 50-60% vinyl pyrollidone and 20-30% unconverted pyrollidone. The product (boiling point 95°C at 14 mm) was recovered by vacuum distillation. The plant yield of vinyl compound was 70-80% on the pyrollidone charged.

The vinyl pyrollidone was polymerized in Gendorf, and detailed information was lacking at Ludwigshafen. In general, the polymerization was carried out by heating with a small amount of water and hydrogen peroxide catalyst to about 120°C initially and finally to 150°C to yield a stiff mass. The resulting polymer was water soluble. The product, after solvent purification to remove traces of monomer, was known as Kollidon or Periston and was used as a substitute for blood plasma; about one or two tons were said to have been employed in this manner.

o. Vinyl Carbazole

Vinyl carbazole monomer was produced by the action of acetylene on carbazole. The reaction was carried out with KOH catalyst under pressure similar to the preparation of the vinyl ethers. Vinyl carbazole was co-polymerized with styrene to produce -

Type M-150	Pure polyvinylcarbazole	Martens hardness	160
M-125	70% VC plus 30% styrene	"	130
M-100	ditto but lower mol. wt.	"	100

Some of the 150 grade was supplied for injection molding. For this purpose the molding powder was put through an extrusion press to orient the particles and add an asbestos like appearance. Polyvinyl carbazole was used to raise the softening point of the plastic. The product had about the same electrical properties as styrene and was somewhat less brittle.

p. Plasticizers

Ludwigshafen produced a number of plasticizers. Detailed data on these items were not obtained. However, as a matter of general information, the following table of plasticizer data obtained from an investigation at the Frankfurt Reichsbank files is attached. These data are understood to represent the total I.G. production for the year 1941.

I. G. PLASTICIZERS

TRADE NAME	COMPOSITION	REMARKS	ANNUAL PRODUCTION TONS - 1941
Palatinol A	Diethyl phthalate	----	5
" AH	Di-beta ethyl hexyl phthalate	Made in Lu	11
" BB	Dibenzyl phthalate	----	13
" C	Dibutyl phthalate	For lacquers and emulsions	150
" DP	Didodecyl phthalate	Used crude dodecanol	4
" F	Di C_5-C_{11} phthalate	Fatty acid alcohols - for plasticizing Igelit	18
" HS	Di C_{11}+ phthalate	Leuna 145-162°C cut available as by-product	200
" JC	Diisobutyl phthalate	For Röhm and Haas	3
" K	Glycol mono-butyl ether phthalate	----	25
" L	Di C_8 phthalate	Leuna alcohol 100-162° C cut	11
" M	Dimethyl phthalate	For cellulose acetate	30
" O	Dimethyl glycol ether phthalate	----	20
--	Diamyl phthalate	Supplied to Rumanian powder plant	30
--	Dicyclohexyl phthalate	For Kalle & Co. cellophane	2
--	Benzoic acid ester of diglycols	----	2
--	Glycerine + 6 mols ethylene oxide		5
No. 90	Tricresyl phosphate	Bitterfeld for PVC	180
--	Triphenyl phosphate	" " "	20
--	Trichloroethyl phosphate	--	12
Mesamoll	Phenyl ester of Mepasin sulfonic acid		100

q. "K" Value

The molecular weight of polymer was frequently determined as the K value. Details on the analytical method were not available at Ludwigshafen. However, the method has been described in detail in an article by Fikentscher, Cellulose-chem 13, 58 (1932).

r. Luvitherm

A mechanical method for the stretching of plastic sheets to orient the molecules and to give improved properties has been developed by I.G. The product, in the case of vinyl chloride, was known as Luvitherm.

Polyvinyl chloride (Igelite PCU) sheet made by this process as a 0.02 to 0.05 mm sheet had been developed as a wrapping material. It was claimed that bread which had been sealed in an envelope of Luvitherm and then sterilized (2 hours heating at 120°C) has been preserved for 6 months with little loss in freshness and a water loss of not more than 5% by weight. The Luvitherm was also used for the wrapping of cables.

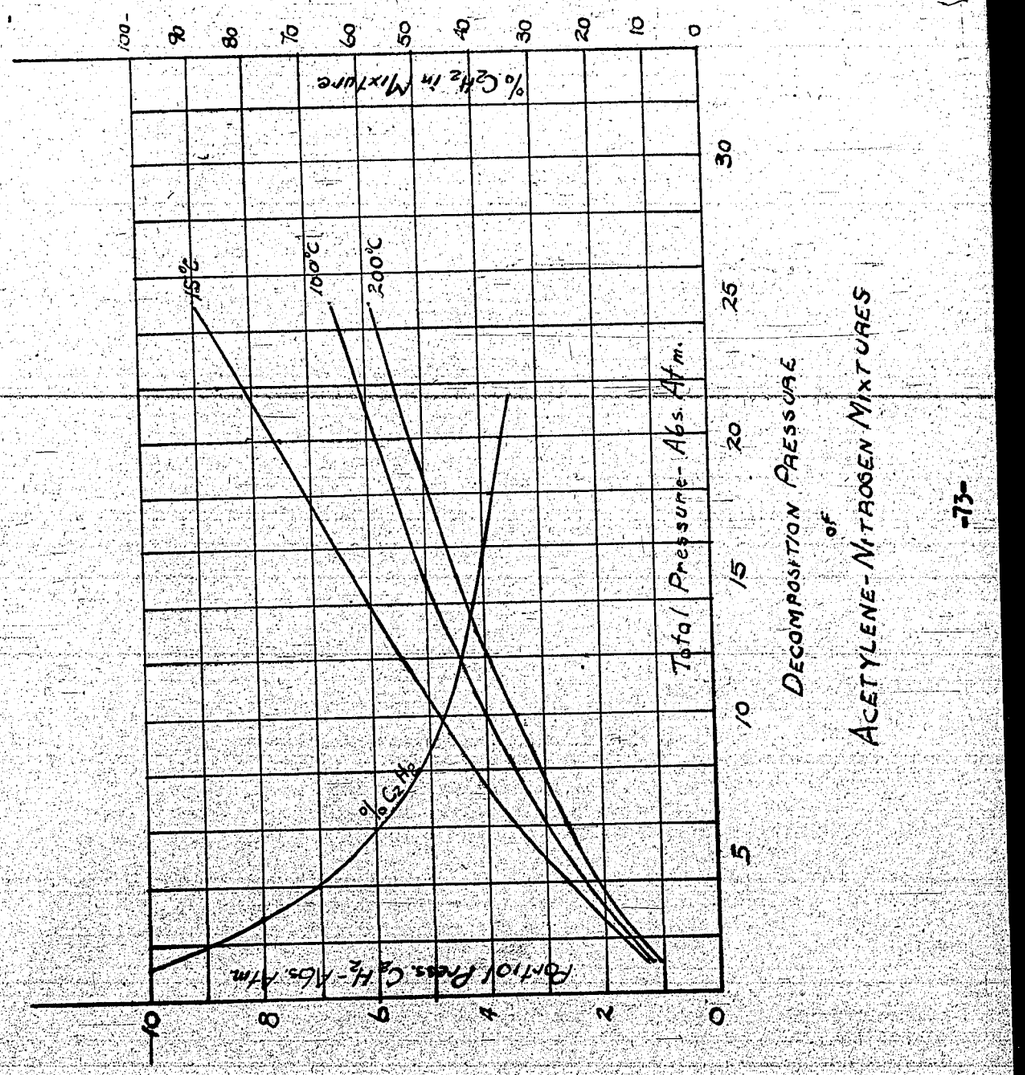
Igelite PC was ground to 300 mesh and milled with 1 to 2% I.G. wax at 160°C on a 4 high calender rubber mill to give a 0.040 mm sheet. The wax was added only to facilitate the milling. The sheet was then given the Luvitherm treatment which is a mechanical stretching in two directions. The sheet was drawn over a roll, heated to 200°C, at a rate of about 15 meters per minute and was picked up on a receiving roll running at a higher speed than the feed roll so as to give a 25% stretch to the sheet. At the same time a special mechanical device gripped the moving sheet on each side and exerted a tension so as to stretch the width by 10%. The resulting sheet showed a higher strength as a result of this orientation treatment, usually about double the original strength.

Luvitherm was made at Gendorf by the foregoing procedure. Dr. Otto Ambros stated that he thought that this was a very important development.

Igamid B sheet was said to be processed similarly at Wolfen.

s. Acetylene Compression and Handling

The key to the successful manufacturing process for vinyl ethers and other compounds such as butindiol, Koresin etc., is the safe compression of acetylene. It has long been known that acetylene is unstable when under pressure and decomposes with a considerable evolution of heat into carbon and hydrogen.



Decomposition Pressure of Acetylene-Nitrogen Mixtures

Experimental work at the Ludwigshafen laboratories in 1931 as well as tests at the Government Laboratories in Berlin in 1939 have determined the pressure at which acetylene decomposes when ignited with a spark. This pressure varies with the temperature as follows:

Temp. C.	Decomposition Press. (Atmospheres Gauge)
15	0.60
50	0.48
100	0.33
140	0.10

Saturation of the acetylene with water raises the decomposition pressure slightly to about 150% of that of dry acetylene.

These tests were made in small bombs. More recent data have shown that the decomposition pressure is lower for long lengths of pipe of large diameter.

The decomposition pressure of mixtures of nitrogen and acetylene are shown in the attached curve.

The following summarizes the practices used by Ludwigshafen in the safe handling of acetylene and acetylene mixtures at high pressures.—

All equipment, including such accessories as valves and piping, was designed for ten times the normal operating pressure when handling pure acetylene or for ten times the partial pressure of acetylene where mixtures with nitrogen were used.

Flame arrestors were installed after the compressors and in long lines where necessary. An ordinary check valve was installed following the compressor. This was followed by the flame arrestor which consisted of a 4 to 6" diameter pipe about 10' long filled with wire gauze or Raschig rings.

Copper and all copper alloys are avoided religiously. One explosion was experienced in an ethylene oxide plant where ethylene containing only traces of acetylene was contacted with copper equipment.

All pipe lines should be kept as short as possible. Where pipes of large diameter were used, as, for example, in the butadiene plant, they were filled with a number of small 1/4"pipes. The largest unfilled lines used were about 35 mm diameter. Lines as

large as 70 mm I.D. have been used. The free space in the equipment was maintained as small as possible. For example, a reactor 10 meters high had 3 meters freeboard. The largest vessels used were 800 mm diameter.

Compression of acetylene or acetylene mixtures was handled in regular type compressors with standard lubrication system and steel piston rings. A slow piston speed was used. For example, a 120 cbm compressor ran at 50-60 RPM. First stage compression was 4-5 atm; second stage, 10 atm, and third stage 30 atm. The largest compressor employed was 180 cbm capacity. The cylinders of the compressors were water cooled. One unit in the vinyl ether plant employed a water filled open trough surrounding the cylinders. A newer model had jacketed cylinders of the conventional type. The compressors had no after-coolers. Pure (99%) acetylene had been compressed to a maximum pressure of 30 atmospheres.

Ludwigshafen never experienced an explosion of consequence in their many high pressure acetylene operations. Several instances occurred in which decomposition actually took place but the speed of reaction was not sufficient to cause an explosion. It was observed, in these instances, that the recording pressure gauges showed pressures not more than three times the normal operating pressure instead of the factor of ten expected from calculations and allowed for in the design. After such explosions, the reactors and lines were filled with carbon decomposition products.

4. TANNING AGENTS (TANIGANS)

a. General

A number of synthetic tanning agents sold under the I.G. trade name of Tanigans were prepared at Ludwigshafen. These materials, principally built up from phenol formaldehyde condensation products, served as substitutes for such natural tanning agents as quebracho, as well as to augment natural tanning materials to yield improved leathers. Ludwigshafen's products appear to duplicate some of the materials produced by Höchst and by Leverkusen. The more important products of Ludwigshafen, together with tonnages produced in recent years, are listed below:

Year	1941	1942	1943	1944 *
Tanigan - Extra D	1845	1975	4060	2712
Tanning Agent QuE	-	212	787	1400
Tanigan Supra DLN	237	307	344	260
Tanigan FC	750	726	775	750
Tanigan FCBI	573	678	786	800

* Estimate based on figures for first 6 months.

b. Tanigan Extra D

3600 kg of phenol oil SR-1 were treated with 3800 kg of 98% sulfuric acid, the temperature was allowed to rise to 100°C and then was maintained at this point for 5 hours. The batch was cooled and 1170 kg water plus 960 kg urea were added. The above mixture was divided into two batches, each portion being treated separately as follows: 1800 kg of 30% formaldehyde were reacted, adding the first half during 24 hours and the second half during the next 12 hours and keeping the temperature at 30-35°C. The batch was diluted with 720 kg water containing 21 kg of oxalic acid and then neutralized with 25% ammonia water until a 10 gm test sample required 14 cc of normal NaOH to neutralize. Next, 760 kg of 25% ammonia were added, followed by 1080 kg of water and 1740 kg of phenol oil SR-1. Condensation of the phenol was accomplished by adding 1200 kg of 30% formaldehyde during an 8 hour period maintaining the temperature at 35°C. The batch was diluted with 1500 kg water, stirred 2 hours and neutralized with ammonia to pH 5, using about 800 kg of ammonia.

Finally about 530 kg of 85% formic acid were added so that the acidity of the batch showed 6.1-6.3 cc of N.NaOH per 10 gm sample, and the pH was approximately 3.

About 4.5 kg of leather perfume oil was added to finish the batch. The yield was 15,000 kg or 424% of the weight of the phenol oil.

Phenol oil SR-1 was a mixture of phenol, cresols and xylenols obtained in Leuna from the hydrogenation of brown coal. Tannigan Extra D was used in the tanning of uppers.

c. Tanigan Supra DLN

720 kg of dihydroxydiphenyl sulfone (moist 75-80% product) were charged to a cast iron vessel, and 1490 kg water, 230 kg of 30% HCHO and 330 kg of dry sodium sulfite were added. The mixture was heated to 150-155°C for 12 hours and then cooled to 100°C.

230 kg of 30% HCHO were added and the mixture heated 24 hours further at a temperature of 150-155°C. Reaction was continued until a test sample, diluted to 10% solution and treated with sulfuric acid equal to the Na_2SO_3 content, yielded a clear solution. 30 kg of carbon and 60 kg filter aid were added. The product was then filtered and washed with 500 kg water and the filtrate divided into three batches. Each portion was reacted with 280 kg of diphenyl acetone (reaction product of phenol, HCl and acetone) 260 kg of Na_2SO_3, 910 kg water and 250 kg 30% HCHO. The reaction was continued for 8 hours at 80-90°C and the batch then filtered. The mixture was next acidified with 465 kg of 98% sulfuric acid, 1500 kg of glycollic acid (37% purity) were added and the mixture heated at 95°C, concentrating somewhat until no SO_2 was evolved. The batch was finally cooled to 50°C and 30 kg Triton B added.

The product had a specific gravity of 1.21 to 1.22 at 20°C, a titre of 8 to 9 and a pH of 2.6 to 2.8. The actual tanning agent content was 22-23%.

The yield per 2160 kg of dihydroxydiphenylsulfone was 12,500 kg or 580% by weight.

This product was used for specialties, for example, for alligator skins.

d. Tanigan FC

This product was a mixture of 100 parts of Neutral Salt 2 powder, 39 parts of $NaHSO_4$ and 4.5 parts of oxalic acid crystals.

e. Tanigan FCBI

This product was a mixture of 100 parts of Neutral Salt 2 powder with 38 parts of $NaHSO_4$, 22 parts oxalic acid crystals, and 8.5 parts of potassium alum crystals.

Both of the above products stem from Neutral Salt 2 which was prepared in the following manner. Both products were used as auxiliaries with vegetable agents, particularly to assist in penetration.

f. Neutral Salt 2

2000 kg of naphthalene were melted, heated to 130°C and a total of 2000 kg of 98% sulfuric acid added during a one hour period. The temperature rose to 160-165°C and the batch was stirred at this temperature for 5 hours.

Next, 900 kg water were added and the batch cooled to 85°C, then 1065 kg of 30% HCHO were added slowly over a 20 hour period, following which the mixture was stirred for an additional two hours and then heated to 95-100°C and stirred until complete reaction of the HCHO resulted, as indicated by the absence of odor.

The mixture was neutralized with calcium carbonate and filtered to remove the calcium sulfate. The CaO required amounted to about 300-350 kg, which was added as a slurry with 4000 kg of water. The titre of the sample was 11.6 cc normal NaOH per 10 gm sample, specific gravity 1.137.

Two batches of filtrate, containing about 30% active material and known as Tanigan V were treated with 2800-3000 kg of NaOH. 600-800 kg of sodium carbonate were then added to remove the calcium. The solution was filtered and washed. Finally the solution was evaporated to a heavy solution in a two stage vacuum evaporator, and then drum dried to yield the finished Neutral Salt 2. 4000 kg of naphthalene

yielded 8000 kg of Neutral Salt 2.

g. Tanning Agent QuE

Details on the preparation of this product were not obtained. It was described as a condensation product of betanaphthol sulfonic acid with dihydroxydiphenyl sulfone and formaldehyde.

h. Ferrigan P

Ferrigan P, a solution of the ferrous salt of sulfophthalic acid, was used as an assistant in leather tanning. 2300 kg of phthalic anhydride were sulfonated with 3713 kg of 65% oleum. The mixture was diluted and reacted with about 1740 kg of iron borings at 65°C. A total of 555 kg of sodium chlorate was then added slowly at an operating temperature of 85°C in order to convert the iron to the ferric state. Next the batch was cooled to 40°C, neutralized with ammonia, adding about 2393 kg of 25% solution. The mixture was filtered to remove small amounts of insolubles and the solution then diluted to a concentration of 39% solids and sold as Ferrigan P.

5. ETHYLENE, ETHYLENE OXIDE AND GLYCOLS

a. General

Since ethylene was a very important basic raw material for I.G., Ludwigshafen carried out considerable research work on its production and purification. A brief summary of the work was obtained through discussions with Dr. Hauber.

Experimental work was carried out on the production of ethylene by the dehydration of ethanol and by the hydration of acetylene. Both of these processes were in commercial production and plant units have been described in connection with the rubber division reports.

Ludwigshafen's work on the production of ethylene from ethane and on the purification of ethylene by absorption in copper containing solutions is of additional interest and will be discussed below. Data refer to units of 3000 tons ethylene capacity per year. It is understood that such units were installed at Leuna.

b. Cracking of Ethane with Oxygen

Ethane was heated to 650°C, that is, just below the incipient cracking temperature, in pipe coil heaters operated at an inlet pressure of about 1 atm. A total of twelve 40 mm ID coils were used. Carbon deposition was minimized by operating with a high gas velocity, on the order of 100-150 meters per second. Oxygen was preheated to 550°C in a similar manner. The two gases were mixed in a very small mixing chamber, about one foot diameter by two feet long. The superheated ethane was injected at a velocity of 20 meters per second meeting the oxygen which was injected tangentially at a velocity of 100 meters per second. The gases reacted in a short throat section

and then passed to a tower, which was mounted on the burning chamber. This tower, 95 cm diameter by 2.5 meters high, was packed with 20 diameter refractory balls. The gas passing up through this packing at a superficial velocity of 1 to 2 meters per second and a temperature of 850°C was passed to a tower where it was quenched quickly by a stream of water. The cooled gases were collected, dried and then purified by low temperature distillation in a Linde designed system. It was stated that there was little or no formation of carbon or formaldehyde in this system. An approximate material balance over the burner is given in the following figures:

Feed Gases

(1) Ethane - 100 volumes

Ethane	-	92.2% by volume
Ethylene	-	2.2
Methane	-	1.6
Propane	-	1.1
Propylene	-	2.3
Nitrogen	-	0.6

(2) Oxygen - 27 volumes

Oxygen	-	98-99% by volume
Nitrogen	-	diff.

Product Gas - On a water free basis and not including small amounts of aromatic hydrocarbons removed (about 1% by volume)

Total volume - per feed above - 170 volumes

Hydrogen	-	26.3% by volume
Methane	-	7.6
Ethane	-	14.1
Ethylene	-	32.9
Propane	-	1.1
Propylene	-	0.5
Carbon monoxide	-	11.5
Carbon dioxide	-	0.7
Oxygen	-	0.6
Acetylene	-	0.5
Nitrogen	-	4.2

NOTE: The equipment was not tight. True nitrogen analysis should be obtained by calculation.

c. Thermal Cracking of Ethane

Extensive pilot scale experiments were made on the production of ethylene by the thermal cracking of ethane using externally heated pipe coils. A small unit was operated at Ludwigshafen in 1941-1942. This was later enlarged and in 1943 a large experimental unit of the same design was installed at Leuna.

The first pilot scale unit consisted of a steel preheater containing 6.2 m of 20 mm ID steel pipe arranged in a 0.3 m diameter coil. Connected to this preheater was the cracking coil proper, of FF 30 steel, a high chrome (25-30% Cr) nickel free (less than 0.2%) steel containing silicon. It was stated that the presence of silicon minimizes the cracking of hydrocarbons to carbon. The cracking coil consisted of 5 turns of 20 mm ID pipe arranged in a 0.75 m diameter coil to give a total length of 11.6 m. Gases leaving the coil were cooled immediately and then passed to the purification system.

The feed gas was a Saar gas ethane fraction of the following approximate composition -

Ethylene	-	1.8%
Propylene	-	0.5
Ethane	-	90.1
Methane	-	4.4
Hydrogen	-	3.2

This gas was purified by washing with NaOH-methanol mixture in order to remove the sulfur (present primarily as COS) in amounts equivalent to 200 mg S per cbm.

Ethane gas, charged at a rate of 30 cbm and a pressure of about 0.5 atm ga was preheated to 450°C and then passed to the cracking coil where it was heated to 800-880°C by hot flue gases which were passed concurrent to the feed. The exact temperature of the gas was not known. Temperature measurements on the tube wall showed 850-930°C. By means of tests when feeding nitrogen it was estimated that the tube wall temperatures were 50°C higher than the inner gas temperature. Under these conditions the exit gas volume was about 1.6 times that of the feed and contained about 33% ethylene by volume.

The cracked gas was hydrogenated at 180-230°C to remove traces of acetylene (about 0.3%), treated with carbon to remove traces of higher boiling hydrocarbons, and then treated with "copper" solution to absorb the olefins (refer to following section).

The weight yield of ethylene based on ethane feed was 76-85%. Based on converted ethane it was 79-88%.

The initial pilot test unit at Ludwigshafen contained a single coil and had a feed rate of 30 cbm per hour. A second unit was built later using two coils of equal diameter with a spacing of roughly 30 cm. A total flow of 60 cbm was split between the two coils, the lengths of which were adjusted so as to have the same heating surface. Following the completion of test data, a larger unit was installed at Leuna. This unit, with a 70 mm diameter coil had a feed rate of 600 cbm per hour. Sufficient data were obtained to indicate satisfactory performance and show a minimum tube operating life of one to one and one half years. Burning out of carbon deposits in the tube was stated to be unnecessary.

Plant units designed for Leuna were laid out for two concentric coils of 70 mm ID pipe about 4 meters long. The combined capacity was 1255 cbm of feed per hour. A total of 6 such units was planned with a rated capacity of 6500 cbm per hour, equivalent to about 75,000,000 pounds of ethylene per year. It was stated that 10 identical units were planned for Heydebreck, indicating more than 100,000,000 lbs ethylene per year.

d. Purification and Recovery of Ethylene

Ludwigshafen carried out experiments on the purification of ethylene gases in connection with their cracking experiments. Presumably most of the ethylene purification done to date has been by high pressure, low temperature fractionation using the Linde process. In 1942, Ludwigshafen studied the use of solvents for the removal of olefins, particularly ethylene, by absorption methods. Copper solutions were the most promising substances found and a program of work along this line was carried out. It was shown that the solubility of ethylene increased with increasing concentration of the copper salt to a maximum of about 20 gm Cu per 100 cc of solution. Some 30 different copper salts were tested. Since it was necessary to use ammoniacal copper salts, additional tests were made using various bases as substitutes for ammonia which would be too volatile for practical application. The final development led to the selection of a mixture of the following composition:

Copper (cuprous)	215 gm per liter
Copper (cupric)	15 gm per liter
Nitrate	330 gm per liter
Monoethanol amine	570 gm per liter
Ammonia	30 gm per liter
Water	220 gm per liter

Spec. gravity - 1.37
Crystallizing pt. - minus 30°C.

The use of ammoniacal copper solutions is not possible where carbon monoxide is present as for example in the case of a gas produced by the high temperature reaction of ethane with oxygen. It is suitable, however, for treating gases from the thermal dehydrogenation of ethane. The plants proposed for Leuna and Heydebreck presumably planned to employ this absorption method for the purification of ethylene. Following is an outline of the operations involved using this method.

Cracked gases containing about 35% ethylene were cooled to remove tars, etc., and then preheated to about 200°C prior to the acetylene hydrogenation step. This operation was carried out without the use of added hydrogen, under the following conditions:

Catalyst	-	95% Cr_2O_3 plus 5% Ni
Temperature	-	180 - 220°C
Throughput	-	100 gm (equals 145 cc) catalyst per 500-800 liters of cracked gas per hour.
Catalyst life	-	1 gm catalyst per 6-9 cbm of cracked gas.
Regeneration	-	Burn catalyst with air at 350 500°C then reduce with hydrogen at 320-340°C.

The product gas was passed over activated charcoal to remove traces of high boiling hydrocarbons compressed to about 15 atmospheres and then scrubbed with the copper solution to remove olefins. The olefin free gases were finally scrubbed with oil to recover ethane which was recycled to the process.

Ethylene was recovered from the absorbent copper solution by expanding the gas down from 15 atmospheres in several stages. The product gases released from the first expansion down to 3 atm plus those from the second stage, 1.4 atm., were combined and recycled to the absorption system. The resulting "fat" liquor was next expanded in three stages to 1.1, 0.35 and 0.1 atmospheres absolute. The resulting effluent gases containing about 96% ethylene were compressed to about 1 lb. ga, given a final wash with sulfuric acid, to remove traces of ammonia and with caustic to remove any acid mist.

The exact pressure and temperature conditions required in the recovery of ethylene from the "fat" liquor were not available. It is understood, however, that operating at sub-atmospheric pressure was necessary.

Ethylene Oxide and Ethylene Glycol

Ludwigshafen's operations in the field of ethylene oxide and ethylene glycol were discussed with Dr. Bülow, the division manager, and with Dr. Christ, the chemist in charge of operations.

e. Ethylene Oxide via Chlorhydrin

Ethylene, of about 96% purity, was prepared from ethanol by catalytic dehydration over lime. Yields were stated to be 92% of theory.

Ethylene oxide was prepared by the conventional chlorhydrin method. A stream of ethylene gas at about 1.5 atm. pressure was pumped continuously, by means of a steel rotary positive displacement blower, into the bottom of a 12 m high reactor tower of steel lined with rubber and brick. Metered quantities of chlorine and water were fed likewise to the bottom of the reactor so that a product containing about 5% HCl and 10% ethylene chlorhydrin overflowed from the reactor. The off-gases leaving the top of the reactor were vented in part; the balance was washed with water and recycled with the fresh ethylene stream. The reaction temperature was maintained at 60°C automatically.

The yield of crude chlorhydrin was 75-80% of theory on the ethylene; about 8-10% of the yield was formed as by-product dichlorethane. The product solution was collected in a wooden buffer storage tank. Lines were of steel or Haveg construction.

The ethylene chlorhydrin solution was then passed to a saponifier where it was mixed with the theoretical amount of calcium hydroxide as a 10% slurry and heated to 95°C by means of live steam. Ethylene oxide and unchanged dichlorethane distilled over. This mixture was purified first by continuous distillation at atmospheric pressure using a brine cooled condenser, at minus 10°C to minimize polymerization. The dichlorethane was recovered in a separate operation. The lime solution was wasted. The yield of oxide on chlorhydrin was 92-95% of theory, making an overall yield of 70-75%.

f. Ethylene Glycols

Ethylene oxide was mixed with five to six times its weight of water, heat exchanged with the final product solution and passed to a reaction tower where the temperature was maintained at 180-200°C for an average inventory time of one hour. The operating pressure of the tower was 200 lbs. gauge. The product delivered from the tower through the aforementioned heat exchanger was cooled to 80°C and passed to a multiple-effect evaporator which delivered a product containing 90-92% glycols with 10-8% water.

This mixture was purified by vacuum distillation in a series of steel columns. The first 28 plate column operating at 30 mm head pressure removed all the water as a water-glycol overhead. The second 30 plate column operating at 4 mm head pressure recovered pure ethylene glycol. The third column, similar to number two but operating at about 20°C higher temperature, recovered diethylene glycol. Residues from this column were distilled batchwise to recover triethylene glycol.

It was stated that under these conditions 100 kg of ethylene oxide yielded 115 kg of ethylene glycol and 12 kg of higher glycols, largely diethyleneglycol, to give an overall yield of 92%. Since conversion was said to be complete, this yield appears somewhat low.

In a later discussion it was stated that the ratios of products formed was 75 parts mono, 20 parts di and 5 parts triethylene glycol. By lowering the water-oxide ratio the formation of higher glycols is favored. In preparing diethylene glycol, a ratio of 80 parts di to 20 parts of triethylene glycol was produced.

Ludwigshafen produced a poly ethylene oxide sold under the name of Oxidewax. About 10-12 tons per month were made for use as a softening agent for Buna rubber, for a hand grease and for suppositories (Pastonal).

Ludwigshafen's rated monthly capacity was about 2000 tons of ethylene glycol, 200 tons diglycol and 50 tons triglycol.

g. Ethylene Oxide via Direct Oxidation

In recent years, Ludwigshafen worked extensively on a method for the direct oxidation of ethylene to ethylene oxide. Their work was confined to laboratory experiments and a series of tests on small multi-tube units. The Ludwigshafen pilot scale unit was destroyed by bombing. A rather large plant, still considered as an experimental unit however, was built in Zweckel but had not been completed at the time of the occupation. It was planned to produce ethylene oxide at Zweckel and ship it to Ludwigshafen, since Zweckel had a convenient source of ethane for ethylene.

The operating conditions for the unit projected for the oxidation step of the process are outlined below:

Catalyst	- pure silver on 5-7 mesh alundum
Pressure	- 0 to 1 atmospheres
Catalyst life	- expected one year minimum
Temperature	- 200 to 240°C
Contact time	- 5 to 7 seconds at 20°C 3 to 5 " at 200°C (both figures based on empty tube)
Throughput	- 300-400 kg ethylene oxide per day per cbm of bulk catalyst volume
Tube material	- Steel, galvanized
" diameter	- 25 mm
" length	- 3.2 m
" number	- 3300 per unit
Feed	- 4-5% ethylene by volume in air
Yield	- 50% based on ethylene charged
Off gas analysis	- Ethylene oxide - 2 to 2.2% Carbon dioxide - 4 to 6% Ethylene - 0.8 to 0.9%

It was indicated that 3-3.5% ethylene feed was planned originally but was later changed to 4-5%.

The problem of the recovery of ethylene oxide was studied at Ludwigshafen on the laboratory scale and in the pilot scale using an 800 liter carbon absorber. Based on laboratory data it was believed that adsorption on carbon was preferable to recovery by absorption in water followed by distillation. The full scale unit planned for the Zweckel plant was to consist of four absorbers each of 15 cbm carbon capacity. The cyclic operation was planned as follows:

The absorption cycle, operated at 20-30°C, was of about three hours duration, with a capacity of 20 kg of ethylene oxide per cubic meter of activated carbon; 300 kg ethylene oxide per cycle.

The desorption cycle was of 1 to 2 hours duration and comprised passing steam through the carbon at a uniform rate, using 600 kg of steam per cycle or 2 kg per kg of ethylene oxide. The vapors from this operation were to pass to a still where the oxide was to be recovered by fractionation at an overhead temperature of about minus 10°C.

Next, the carbon was to be dried in order that ethylene glycol would not be formed by hydrolysis during the absorption cycle. 9000 cbm of nitrogen gas which was dried and recirculated were required per cycle.

The final cycle comprised a cooling operation accomplished by passing dry nitrogen until the mass was cooled to room temperature. A total operating cycle of 8 hours was planned for the full scale unit. The life of the activated carbon was not determined but was believed to be well over one year.

6. MISCELLANEOUS ORGANIC CHEMICALS

a. Formaldehyde

Ludwigshafen manufactured large amounts of formaldehyde by the catalytic oxidation of methanol in the presence of a pure silver catalyst. Production was divided into two plants. The old plant, which was completely destroyed by bombing, consisted of a number of single units ranging in individual capacities from 5 to 10 tons per day with a total capacity of 300 tons of 30% formaldehyde per day. A new plant was constructed in 1942 principally to supply formaldehyde for the pentaerythritol and Buna programs. This plant contained single units of 100 ton per day capacity each. Four units were installed but the plant was planned for a maximum capacity of 800 tons per day.

The product contained:

Formaldehyde	30% by wt.
Methanol	0.5 to 1.5
Acidity (HCOOH)	0.03
Nickel	nil
Iron	0.0005

Briefly, the process comprised passing a mixture of 60% methanol plus 40% water over a pure silver catalyst maintained at 640°C. The product was cooled, condensed and collected as finished 30% formaldehyde solution. A detailed description of the process obtained through the plant manager, Dr. Koerding, follows:

The 30% product was used instead of the 37% solution common in the U.S.A. because such a product required little methanol stabilizer and eliminated the need for any concentrating operation. Furthermore, shipping was not an important cost item since most of the product was used at Ludwigshafen.

Synthetic methanol was metered to an evaporator where it was mixed with a stream of filtered distilled water (steam condensate). The mixture was maintained at about 60°C by means of a steam coil. A stream of filtered air delivered by a rotary blower at about 5 lbs gauge was bubbled into the base of the tower at a rate of 6000 cbm carrying the vapors in a weight ratio of 60 pounds methanol per 40 pounds of water. The vapors leaving the vaporizer were superheated to 100°C by passage through a steam heated exchanger and then delivered to the catalyst chamber.

The catalyst chamber, about 2 meters in diameter, contained 75 kg of pure silver catalyst, about 40 mesh size, carried as a 2 cm deep layer on a copper screen which in turn was supported on a perforated stainless steel plate. The rate of reaction was controlled by the temperature of the catalyst bed which was indicated by a thermocouple mounted in the center of the bed. This operating temperature was held at 640°C by simple control of the ratio of air feed.

The reaction product leaving the catalyst was passed quickly to a heat exchanger located immediately below the bed. In this manner, the vapors were cooled to 200°C, the heat being removed by the generation of steam at 15 lbs. gauge pressure in a quantity more than sufficient to vaporize the feed mixture. Vapors leaving the heat exchanger were passed to a vertical tubular cooler to condense the formaldehyde product and deliver an effluent at 30°C. The vent gases were subsequently scrubbed with water fed to the top of a 6 plate bubble cap column so as to remove all the formaldehyde and methanol before venting the vapors to the air. The products from the cooler and the scrubbing system were collected, combined and delivered to the finished product storage tank without further treatment.

The materials of construction were a combination of aluminum, stainless steel, V4A, and rubber lined. Aluminum was used for the vaporizer. Stainless steel was used for the superheater, catalyst chamber and heat exchanger. The final cooler and scrubbing tower were of aluminum or rubber lined construction. It was stated that stainless is the preferred material; aluminum was used since stainless was scarce. Aluminum is suitable for the liquid product or for handling formaldehyde or methanol vapors. However, aluminum is not suitable when in contact with mixtures of vapor and liquid as, for example, in the superheater following the vaporizer. Large, pure aluminum tanks, 10-12 feet in diameter by 30 feet long were used for formaldehyde storage.

The catalyst life was about 6 months. The silver metal was then removed, dissolved, and recovered as pure metal for reuse.

The yield on methanol used was 86 to 90 per cent of theory. For example:

Charge -	Methanol	100 kg
Product -	HCHO	80 "
	Methanol	5 "
	Gases	15 "
		89.7% of theory

The off gases contained:

H_2	12% by vol.
CO_2	3
CO	1
CH_4	0.7
O_2	trace
N_2	diff.-83.3%

It will be noted that the process therefore is, strictly speaking, not entirely one of oxidation but involves also a dehydrogenation of the methanol.

b. Phthalic Anhydride

Ludwigshafen produced phthalic anhydride by the catalytic oxidation of naphthalene. Four complete units, each with a rated capacity of 80 tons per month, were installed; the actual capacity approached 100 tons per month. Half of the converter units had been badly damaged by bombing. The balance of the units as well as the refining equipment was in good shape.

Air was delivered by positive pressure type rotary blowers of about 5000 cbm capacity operating at a discharge pressure of 200 mm Hg. The air was filtered through a plate type oil filter installed on the blower inlet. 6 blowers were installed for the four converter systems.

The air was passed first through a steel tubular heat exchanger counter-current to the converter exit gases. The preheated air, at a temperature of 160°C, entered the bottom of a so-called "step-type" evaporator into which molten naphthalene was fed at 90°C and at a rate of 120-130 kg per hour. Naphthalene flowing downward over a spiral annulus strip was completely vaporized except for tarry residues which collected at the bottom of the unit and were removed, at periods of about once per month. To permit continuous operation two vaporizers were installed per unit. The feed ratio was 36 gm of naphthalene per cbm of air. The naphthalene used had a freezing point of 78.8-79.5°C.

The naphthalene-air mixture at a temperature of about 150°C entered the converter and passed down through the catalyst. The converter was of steel construction similar to a heat exchanger but with a central core. Molten potassium nitrate was used as the heating medium surrounding the tubes. At the top of this central core was a vertical submerged axial flow pump of low head-large volume type which circulated the molten nitrate around the catalyst tubes and over a tubular air cooler, 40 cm diameter by 1.6 m high, located in the bottom of the central core. Since the reaction is quite exothermic, a considerable quantity of heat had to be removed. This was done by blowing atmospheric air through the tubes of the lower heat exchanger. The hot air was wasted. Each unit contained 3500 catalyst tubes, 25 mm ID by 3.0 m long. The catalyst was contained within the tubes as approximately 5 mm dia. x 5 mm high pellets. The temperature of the reaction was maintained at 350°C; in some cases as the catalyst became old this temperature was increased to as high as 400°C. The operating temperature recorded was measured at the exit of the converter. A total of 11 thermocouples were installed in various individual tubes located within cores so that the couple could be moved up and sown the catalyst tube for exploratory measurements. The location selected was that showing the maximum temperature. It was stated that the maximum variation between the temperature of any of the 11 thermocouples was 20°C.

The catalyst was 10% by weight on a silica carrier. One source said that it was pure vanadium pentoxide on silica. However, another reference indicates that the catalyst proper was 25% potassium sulfate plus 75% vanadium pentoxide on silica. Incidentally, catalyst preparations at Ludwigshafen were all made in a central plant and frequently the exact compositions were not known to the operating chemists.

The gases leaving the bottom of the converter passed through the preheater and were cooled to 160°C. Pressure drop through the catalyst was 150 mm. The converter exit pressure was maintained at substantially atmospheric pressure by an exhaust fan following the condensing system.

The crude phthalic acid was collected in an air cooled condensing system. The vapors passed first through a finned air-cooled tube and then into the first of a series of 15 coolers. These coolers were essentially sheet steel rectangular boxes about 20 feet long, 15 feet high and 2.5 feet wide. Gas passed into one end of the box, downward to the bottom around and under a central baffle and then upward, reversing the flow, to the exit. The solid phthalic anhydride collected in these units was removed by means of a screw conveyor located at the bottom of each unit and arranged to discharge the solids through a central bottom opening. The condensing units were piped so that any one could be cut out of the circuit for cleaning. This cleaning operation comprised a manual operation, rodding out the coolers through a number of 18 inch manholes. The first two condensers were water cooled; the balance simply air cooled. Phthalic acid discharged from the conveyor periodically was collected in barrels and delivered to the refining department.

The crude phthalic anhydride, containing quinones and other impurities was refined by treatment with sulfuric acid followed by vacuum distillation. A 17 ton batch of crude phthalic was mixed with 5-10 kg of concentrated sulfuric acid and heated at 200°C for 6-8 hours. The mixture was then neutralized with calcium carbonate and charged to a batch still of 5000 gallons capacity, heated by means of a heating coil welded to the outside of the still. Water heated to a temperature of ca. 300°C by means of a gas fired furnace was circulated through the coil by thermosyphon action. The still was fitted with a column containing 6 m of Raschig ring packing. The condenser was cooled with an ethylene glycol water mixture, the composition of which was adjusted so that the boiling point was one degree above the melting point of phthalic anhydride.

The charge of $CaCO_3$ neutralized phthalic anhydride was distilled at an overhead pressure of 30 mm Hg under slight reflux; the exact amount was not known. Distillation of several batches was continued until a total residue of about 4000 kg accumulated. These residues were then transferred to a second stirrer equipped still and heated to dryness. The overhead of phthalic anhydride was recycled to the crude phthalic storage. The powdery residue of dry calcium sulfate plus tar was discharged readily from the still and discarded. Operating pressure on this still was 100-200 mm.

The phthalic anhydride collected from the first refining still was stored as the liquid product, fed to a flaker and flaked to give the finished product.

The yield at the converter was stated to be 100 per cent by weight based on naphthalene charged. This is equivalent to 85% of theory. The yield of refined phthalic based on naphthalene charged was stated to be a minimum of 82% of theory.

Data obtained from the I.G. files at the Reichsbank, Frankfurt, showed the following yields during the first quarter of 1938.

Yield of crude phthalic anhydride -

Plant	kg of naphthalene required per 100.0 kg of crude phthalic
Ludwigshafen	102.8
Schkopau	105.2

Yield of refined phthalic anhydride -

Plant	kg of crude phthalic required per 100.0 kg of refined phthalic
Ludwigshafen	102.8
Schkopau	104.4

The overall figures are equivalent respectively to 81.9 and 78.8 percent of theory. Persumably the Schkopau units were similar to those at Ludwigshafen.

c. Benzoic Acid

Benzoic acid was prepared by the vapor phase catalytic decarboxylation of phthalic acid. A brief description of the process as given by Dr. Schnell follows:

Vapors leaving a phthalic anhydride converter unit as described previously were passed without further cooling or addition of other reactants directly over a decarboxylation catalyst consisting of zinc and aluminum oxides supported on a pumice carrier, about 4 mesh size. The exact composition of the catalyst was not known; it was said to contain about two parts of ZnO per one part of Al_2O_3, with a total concentration of about 10% catalyst, 90% pumice. The reaction temperature was maintained automatically at about 340°C since the reaction is slightly exothermic. Vapors leaving the converter were cooled and water scrubbed to collect the benzoic acid. The plant was arranged so that one 80 ton phthalic acid converter was connected to two benzoic acid converters in parallel each with a rated capacity of 30 tons of benzoic acid per month. The catalyst chamber was 2.5 meters diameter by 3.0 meters catalyst depth. The catalyst was supported on a grate so that its removal was facilitated, since the catalyst life was only about one month; 100 kg of benzoic acid were produced per 1L kg of the catalyst mass. The mass was not regenerated but was withdrawn from the bottom of the unit and discarded. In starting up the unit, air preheated electrically to about 350°C was passed through the phthalic and benzoic converters to attain the 350°C temperature before starting the naphthalene flow. The exact yield was not obtained; it was on the order of 90%.

The crude benzoic acid contained small amounts of phthalic acid and naphthaquinone. Crude acid was treated at 50°C with a solution of sodium bisulfite to dissolve the phthalic acid and react with the quinone. The operation was tested by preparing the sodium benzoate salt which should be completely soluble to a clear solution in 87% alcohol; turbidity indicates the presence of sodium phthalate.

A large portion of the product was shipped to Uerdingen for conversion to sodium benzoate. About 15 tons per month were purified to the medicinal grade by sublimation. This was accomplished by first dewatering the acid by melting and then subliming in air using a pan heated with steam at 20 atm. A current of air was led over a pan containing the acid and the sublimate was collected in a 5 m by 7 m by 4 m high, wood lined, brick chamber, the wooden walls being covered with textile to preserve the purity of the sublimate. The resulting product was collected as fine crystals which were not discolored on testing with concentrated sulfuric acid and gave a clear complete solution in dilute ammonia. The Ludwigshafen benzoic acid plant, with the exception of the sublimers, was destroyed by bombing.

d. Maleic Acid

Ludwigshafen produced maleic acid by the catalytic oxidation of crotonaldehyde -

$$4\ CH_2\text{-}CH = CH\text{-}CHO + 7O_2 \quad 4\ \begin{matrix} CH\text{-}COOH \\ \| \\ CH\text{-}COOH \end{matrix} + 2H_2O$$

Crotonaldehyde was used rather than benzene because of the non-availability of benzene in Germany. The crotonaldehyde was obtained from the I.G. Höchst plant by barge or tank car shipment. The new plant, built in 1939, was somewhat damaged (15%) by bombing.

Filtered air was delivered by a blower of 6000 cbm per hour capacity operating at a discharge pressure of about 75 mm Hg gauge. The air, after being preheated to about 150°C by the exit gases from the converter, entered the bottom of a step-type evaporator similar to that used in the phthalic anhydride process. Liquid crotonaldehyde was fed at a rate of 120 kg per hour. The air ratio was set at 20 gm crotonaldehyde per cbm of air.

The crotonaldehyde-air mixture entered the top of the converter and passed downward through the catalyst which was maintained at 350°C. The converter was a steel tank, approximately 3 m diameter by 2 m high. To remove the heat generated by the strongly exothermic reaction, a series of steel pipe cooling coils was imbedded in the catalyst mass. Nine separate flat coils of 25 mm pipe were arranged in nine horizontal planes spaced on 6 cm centers. The spiral coils were wound so as to leave an annular distance of 5 cm between adjacent pipes. Water was pumped through the coils at a temperature of 340°C and a pressure of 250 atm. using parallel flow so that the temperature at each individual coil could be controlled. Water circulation was maintained by a piston

type pump with a capacity of 10 cbm per hour. The pump was fitted with a special external valve box mounted some distance ahead of the cylinder of the pump. Between this valve box and the pump cylinder was a short section provided with a cooling jacket. In this manner the pump itself handled water at roughly 100°C imposing the by-draulic pressure on the external valve box which worked at the operating temperature, about 340°C. The circulating water was cooled by means of a cooling jacket. For starting up operations, the water was heated up to the operating temperature by a gas-fired furnace. Actually, two pumps, one for starting up and one for normal operation, were used. However, by adding interconnecting lines, the starting up pump also served as a spare.

The catalyst was a mixture of titanium dioxide, molybdenum oxide and vanadium pentoxide supported on 5-6 mm granules of punice,

Gases leaving the converter passed through the tubular steel heat exchanger to preheat the feed gases and were thus cooled to about 150°C. Additional cooling was accomplished by a water jacketed pipe section. The cooled gases were then passed to a quench tower of rubber lined steel construction, packed with stoneware rings. Water was fed at the top of the tower to yield a solution containing 30% maleic acid which was delivered to a storage tank. After treatment with decolorizing carbon the curde acid was fed to a batch type circulation evaporator and concentrated to 70% maleic acid content, Because of the corrosive nature of maleic acid solutions, the evaporator was constructed of rubber lined steel. Heating tubes were heavy copper, clad with pure silver, Concentration was carried out under vacuum at a temperature of 60-70°C. The 70% solution was cooled in a stirred vessel to 30°C in order to form crystals of maleic acid which were removed by centrifuging. The mother liquor was returned to the evaporator feed. The centrifuged dried product, produced in batches of 1.5 tons each and containing about 98% maleic acid plus 2% water was sold as such. Maleic anhydride was not produced.

The yield was 60 kg maleic acid per 100 kg crotonaldehyde. This is equivalent to 36% of theory.

The siggle converter unit at Ludwigshafen had a capacity of 50 tons per month.

e. Fatty Acids from Paraffins

The process for the manufacture of fatty acids consists in the catalytic oxidation of paraffins with air. A brief description of the process as outlined by the department manager, Dr. Kürfinger, follows:

The raw material was paraffin fractions from the Fischer-Tropsch synthesis. These were largely straight chain paraffins, which were preferable for the production of fatty acids. Paraffins in the range C_{15} to C_{35} were used, depending upon demands. However, the C_{20} to C_{30} range was preferred, since the lower chains showed a greater tendency to split into acids below C_{10}, which were of little value.

Potassium permanganate was used as a catalyst. Attempts to replace this material with other catalysts more readily available than manganese during war times were unsuccessful. The catalyst was prepared by dissolving $KMnO_4$ in water and then adding this solution to the molten paraffin at 130°C. The water flash evaporated leaving the $KMnO_4$ dispersed in the paraffin as a fine powder. The catalyst concentration varied from 0.08 to 0.15% based on the paraffin, and averaged 0.12%.

An 8 ton mixture of paraffins plus catalyst was charged to the batch reactor, an aluminum tower, 12 feet in diameter by 36 feet high, giving a liquor depth of about 24 feet and allowing a freeboard of 12 feet to take care of foaming. Air from a rotary compressor operating at 1.0 to 1.2 atmospheres was delivered to the reactor continuously at a uniform rate of 1500 cbm per hour entering the bottom of the tower through a sparger pipe. The reaction mixture was heated initially by means of an internal steam coil. Once the reaction began, it was necessary to apply cooling. This was done by allowing a spray of water to trickle down the outer wall of the reactor. The initial operating temperature was 130°C; thereafter it was maintained at 110-115°C. The operating cycle varied from 15 to 30 hours.

The off gas from the reactor contained 10 to 15% oxygen and carried practically all of the acids below C_5 plus a small amount of acids up to C_8. This gas was passed through a stainless steel tower, about 6 feet diameter by 25 feet high. The effluent solution contained about 10% formic acid, 10% acetic acid and 10% acids in the C_3 to C_8 range, largely the lower carbon acids. The product was collected and sold as such principally as a substitute for formic acid. The Ludwigshafen plant contained 8 reactors. Four reactors were grouped together with a single gas cooling and scrubbing system.

The oxidized mixture, containing about 30 to 35% fatty acids, was next treated with 35% sodium hydroxide and then heated to 150-170°C under pressure to assist separation. The upper paraffin layer was recycled to the oxidizers. The lower soap layer, containing some alcohols and ketones was heated continuously in a tube furnace to 200°C at 80-120 atmospheres and was then flashed at atmospheric pressure to yield steam plus volatiles and bottoms of molten soap which were discharged continuously into water to form a solution.

The C_6 to C_{15} alcohols and ketones which separated were either recycled or used for the preparation of detergents and plasticizers.

The soap solution was acidified with sulfuric acid, the fatty acids separated and purified by high vacuum distillation at 3 mm absolute pressure using high pressure steam as the heating medium. The fractions collected were:

Fraction	1	C_{10}
	2	$C_{10} - C_{16}$
	3	$C_{16} - C_{20}$
	4	$C_{18} - C_{24}$
	5	Residue

These fractions were sold as such or worked up for special purposes. In general, the lower acids were used for plasticizers and the main fraction (3) used for soap manufacture. The residues were used for the preparation of lacquers, vaseline like materials and foundry binders. As described in the report on Oppau and Ludwigshafen Wehrmacht items, these synthetic acids, after purification by hydrogenation, have been esterified to form suitable edible fats. Samples of such fats were shown. It is believed, however, that production of these materials at Ludwigshafen did not reach any sizeable amount.

The Ludwigshafen plant had a total capacity of 15 tons of fatty acids per day. The oxidizing section of the plant was about 10% damaged. The distillation section was about 50% destroyed.

7. INDEX

	Page No.
Chlorine Plant	23
Aluminum Chloride	32
Sodium Hydrosulfite	33
Calcium Carbide and Acetylene	34
HCl	37
Iron and Nickel Carbonyl	40
Phenol-Formaldehyde Resins (Luphen)	41
Urea-Formaldehyde Resins (Pollopas,etc).	42
Dibasic Acids - Diamides (Igamid)	44
Polyethylene (Lupolen)	45
Styrene and Polystyrene	48
Butadiene and Synthetic Rubbers	58
Isobutylene (Oppanol)	59
Vinyl Chloride (Igelite)	61
Acrylates (Acronal)	63
Vinyl Ethers (Igevin)	64
Ethylene Imine	66
Vinyl Benzoate	68
Vinyl Pyrrolidon	68
Vinyl Carbozole	70
Plasticizers	70
"K" Value	72
Luvitherm	72
Acetylene Compression and Handling	72
Cracking of Ethane with Oxygen	78
Thermal Cracking of Ethane	80
Purification and Recovery of Ethylene	81
Ethylene Oxide via Chlorohydrin	83
Ethylene Glycols	83
Ethylene Oxide via Direct Oxidation	84
Formaldehyde	85
Phthalic Anhydride	87
Benzoic Acid	90
Maleic Acid	91
Fatty Acids from Paraffins	92

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INTERROGATION OF GERMAN SCIENTIFIC PERSONNEL

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INTERROGATION OF GERMAN SCIENTIFIC PERSONNEL
I.G. FARBENINDUSTRIE A.G., LUDWIGSHAFEN
MARCH 25 - 31, 1945

Reported By
Mr. PAUL K. KUHNE, T.I.I.C.
10 APRIL 1945

Interrogators
Maj. E. TILLEY (Br.)
Capt. J.M. WHITTEN (U.S.)
Lt. J.H. MEHL (U.S.)

CIOS Target No. 30/4.03
Fuels and Lubricants

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

339

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TABLE OF CONTENTS

	SUBJECT	PAGE NO.
	GERMAN PERSONNEL INTERROGATED	
1.	Baumler, Rudolf	4
2.	Bossert, Karl	5
3.	Bulow, Wolfgon	5
4.	Daniel, Walter	6
5.	Eymann, Karl	6
6.	Futterer, Heinz	6
7.	Gloth, Hans W.	7
8.	Goggel, Karl	7
9.	Haarer, Erich	7 & 8
10.	Heinze, Fritz	9
11.	Johannsen, Adolf	9
12.	Keyssner, Ernst	10
13.	Klippel, Hermann	10
14.	Kollek, Leo	11
15.	Kosbahn, Tommy	11
16.	Krieger, Fritz	12
17.	Ludwig, Walter	12
18.	Niemann, Georg	13
19.	Penzig, Fritz	14 & 15
20.	Pflaumer, Karl	16
21.	Pfannmuller, Wilhelm	16
22.	Pfleiderer, Georg	17
23.	Raschig, Kurt	17
24.	Reicfs, Otto	18
25.	Santo, Camill	18
26.	Sebastian, Bernhardt	19
27.	Schnell, Berthold	20
28.	Spohn, Hans	21
29.	Weiss, Albrecht	21
30.	Wimmer, Karl	22
31.	Wittmann, Georg	22
32.	Wurster, Karl	23
33.	Zahn, Ludwig	32

MISCELLANEOUS PERSONNEL OF LESSER INTEREST.

1.	Lang, Georg	33
2.	Helwert, Fritz, Dr.	33
3.	Pfitzner, Helmut, Dr.	33
4.	Conrad, Johannes, Dr.	33
5.	Hopff, Heinrich, Dr.	33
6.	Hoffmann, Kurt	33
7.	Zenfel, Dr.	33

S E C R E T

Dr. RUDOLF BAUMLER.

Address: Ludwigshafen, Ostmark Str. 42.
Ground Floor.

Dr. Chem. Technische Hochschule, MUNICH, 1928.

Dual function: Betnibsfuhrer (Works Chief) of Eulysin Works., and in absence of Chief, acting head of the T.H. Section (Textil Hilfsmittel)

P.H.Salz - Ethylene Diamine Dinitrate, or a preliminary or primary product for explosives. Made in Bldg. L.U. 553, up to a year ago 75 tons a month, now less is made.

This product (P.H.Salz) is sold to 'Gesellschaft 2ur Verwertung chemischer Produkte', Wolfratshausen, nr MUNICH. It is used for explosives.

The primary product is not an explosive, because it has an approximate content of 6% water.

Betnibsführer Dr. Scholz can give all details.

No explosives made at Ludwigshafen (Same statement made by Dr. Wurster)

Ethyline Diamine Dinitrate - experiments on this carried on here until a few weeks ago. Baümler gave formula to specialists.

Baümler very co-operative and gave useful information, some of it he volunteered.

30 March 1945..

Dr. KARL BOSSERT.

Address: Hohingollern Str. 78 Ludwigshafen.

Dr. Phil (Chem) Munchen 1931. under Prof: Wieland.

Betriebsleiter in OPPAU of Methanol and Butyl Works.
O.P. 37 (in same building as Ammonia).
Production of Methanol and Butyl Alcohol, after long argument revealed that in O.P.85 in the Bunker, he had an iron chest in which he had production tables, analysis, flow sheets etc., etc. They proved of little value.

BOSSERT was not co-operative. He lied outrageously about his documents, and was altogether unpleasant.

Director Dr. Wolfgan Bülow.

With I.G. since 1924. Head of Plastics and Solvents Dept: Knows processes for Korosene and Ethylene Oxide Manufacture.
Very co-operative. Provided names of people who can help us further.

30 March 1945.

DR. WALTER DANIEL.

(Third interrogation - fuller notes taken by Lt. Comdr. MITCHELL, R.N.V.R. who had interrogated him previously.

DANIEL had helped on vital covers for U-Boats or Anti-Radar devices. He lied about documents and papers, denying that he had any hidden anywhere. After 40 minutes grilling, he admitted that he had concealed private papers in a Bunker in OPPAU and that some formulas and scientific documents could be there. Lt. Comdr. MITCHELL, went with him to the bunker, and found valuable data on opanol sheets for U-Boats and other secret products hidden under a pile of junk. Previously he had sworn that all his papers had been destroyed in air-raids or gone across the Rhine. Full scientific data brought to light in the interrogation is in Lt. Comdr. MITCHELL'S notes.
DANIEL stated that he made his last trip to Chemnitz 3 months ago, but could not remember the name of the firm.

DR. KARL EYMANN.

Ostmarkstrasse 34. 32 years with I.G.
Head of technical department dealing with policy matters, new construction and personal problems of technicians. Knows about Nitrate plants and oil plants in Japan. Obering Bachmeyer knows about liaison with Japan on Oil in 1944. He is in Heidelberg. Maybe Japanese plans in Bobenheim, in a Turnballe. Ing. Lampse is in charge says that machine shops from I.G. have been shipped elsewhere. Obering Schmidt at Ostmark Strasse 28, knows all the details.

CARL HEINZ FUTTERER.

Another assistant to Dr. Eymann. Familiar with drawings in Bau 10. Released because he is of minor importance.

DR. HANS W. GLOTH

Chief of High Pressure Plant for Gas Production at OPPAU. Has heard of 'SCHWALBE' Some generators and other parts of Oxygen plant sent there. Location is probably NIEDER-SACHSWERFEN, HARZ Mountains; other possible location, UNTERLOCKWITZ.
'LACK' is code name for proposed underground Nitrogen plant. Site not yet chosen. GLOTH is talkative, speaks English, and is ready to discuss all details.
Low pressure plant ready to operate again at 10% capacity. Some key parts hidden in OPPAU Bldg:299. and is bunker of Bldg:35.

Dr. KARL GOGGEL.

Chief of High Pressure Dept: OPPAU. Dr. Gloth has charge of first step of Ammonia production. Dr. Goggel second step. Goggel speaks fluent English.
Has under him OPPAU Buildings 1,4,5,6,15,37,38,65, 82,87,89,90,319,321,450,750 and 751.
Knows about 'LACK' code name for underground Nitrogen plant. Thinks possible location is BRIEG (GLEIWITZ) and also near KASSEL. Goggel was to send some part of OPPAU installation there. Thinks hydrogenation and possibly Methanol plants will be built underground. Goggel is ready to discuss all details.

DR. HAARER, Erich.

Address: Ludwigshafen, Ostmark Str 28.

Dr. Ing. Technische Hochschule, MUNICH, under Prof: Hans Fischer.

Acting Works Chief (Stellr Betriebsleiter) of Butyl distillation.

Young man, intelligent, co-operative, ready to reveal secrets. Volunteered much useful information. Gave details of specialists of 'Butyl distillation'. Specialists satisfied with process as described by him. Volunteered statement that he has in LU 590 complete design of HEYDEBRECK plant of I.G. He was responsible for designs and spent much time in HEYDEBRECK and helped to erect plant. None of Butyl distillation plant transferred elsewhere, because too large. Some of his plant, especially electrical instruments and Ringwagen (measuring instruments) stored for safety in Bunker 590. (Contd. Page 8)

Dr. HAARER, Erich. (Contd.)

First man to give information on TEL plant. Tetraethyl lead and other admixtures to aircraft gasoline added in Verbleingslager near OP 106. (He will show specialists the exact site and explain it on spot.) Dr. Rudolf AYER head of this plant escaped across Rhine with all assistants.

Iso octane made in small quantities in OP 559 & 560. None produced here for last 2 or 3 years. Since that time produced in LEUNA & HEYDEBRECK. Iso octance exactly same as Tanol (synonyms).

Does not know about synthetic lubricating oil or its manufacture here.

His building and office completely destroyed on 15 December 1944. All documents destroyed except a few less important files. What remains he has in LU 557. Haarer will show them to specialists and explain any details.

Dr. FRITZ HEINZE

Address: Ludwigshafen, Hanser Str. 36.

Dr. Phil (Chem) GREIFSWALD, 1918.

Group Chief (Gruffenfinhrer) of "Amytosaure" Works, Basic products works (Basenfabrik), Naphtol works, Amitophenol works.

Workers need no salve for protection of hands in manufacture of dinitrodiphenalamin. This is noxious only when dinitrochlorbenzol is added.

Monthly production here of dinitrodiphenalamin maximum 280, maximum annual production 2000 tons. No production since beginning 1943. Now made in WOLFEN.

HEINZE was very co-operative and was found truthful and helpful in every way by specialists.

Dr. ADOLF JOHANNSEN

Address: Hansa Strasse 1

With I.G. for 23 years. Assistant head of Inorganic Department under Pfanmuller, making sulfuric acid, chlorine and sulfur dioxide. Not a party member. No keys or documents in hiding places. Phosgene produced in BAU 150, until bombing put the plant out of operation in Sept. 1944. Not co-operative but has been warned.

Dr. ERNST KEYSSNER

Address: Hindenburg Strasse, 46.

With I.G. 16 years. Head of Kerosene Plant. Interviewed in presence of Dr. Hopkinson who took complete notes on the process for making Kerosene. Samples of catalysts and various materials are being obtained. Very co-operative.

Dr. HERMANN KLIPPEL

Address: Mutterstadt, Ockersheimer Str. 51

Dr. Phil (Chem.) HEIDELBERG, 1924

Section Chief (Betriebsfuhrer) of Nickelfactory OPPAU

Office Bldgs. OP 217
OP 46,286,287,482,310 and parts of others. Stores in Bldg. OP 706.

Most documents of Nickel Dept. removed to HEIDELBERG. 8/10 pounds of documents taken across Rhine by 4/5 secretaries on last day before fall of Ludwigshafen. The documents contained calculations, statistics, correspondence with Mond-Nickel Co., etc. Fraulein BAUM and Fraulein Erda GEBERBACH may not have reached east bank of Rhine and their parcels may still be in Ludwigshafen.

KLIPPEL has been very co-operative and specialists have found his information useful.

Dr. LEO KOLLEK

Address:- Ludwigshafen

Dr. of Chemistry, BRESLAU, 1927

Chief of KOLORISTISCHE ABTEILUNG
(Textile section, textile auxiliary products, fur dyes, papiertechnische abteilung, lackrohstoff abt., Kunststoffrohstoffe, Ledertechnische Abt., Lacktechnische Abt., technical advisor for sales department)

Scared but not necessarily truthful. Should be interrogated in detail on various sections in his department. If firmly handled will probably give all details.

Denies that documents and formula of his department are hidden in Ludwigshafen. Says some were buried, others removed to WEINHEIM (an der Bergstrasse), now in building of former firm of Freudenberg, Mullstrasse. WEINHEIM is now probably in our hands. It is approximately 20 Kilometeres N E COLOGNE.

Dr. Tommy Kosbahn

Address: Frankfurt am M.

Physicist. Assistant to Dr. Sachse. Quantitative spectrum analysis. Oxidation of methane with air or oxygen. Oxygen not used in the large units.

Direktor FRITZ KRIEGLER

Chief of Transport and Shipping Dept.
Also deals with purchasing and financial problems.

Volunteers any information in his possession.

Of interest for investigation of underground Buna plant or plants, code name ECKSTEIN. Stated that he did not know details of plant or exact location but that apparatus left I.G. Ludwigshafen from end Dec. 1944 to end Jan. 1945 by car for MANNHEIM, SCHWETZINGEN, HEIDELBERG then by train to LEOPOLDSHUTTE, HAINFELD or HEINAU near AMBERG (upper Palatinate), WEISSENSTADT in the FICHTELGEBIRGE, SCHWARZENFELS in the BAIRISCHERWALD, SCHKOPAU near MERSEBURG.

Details of shipments in Bldg. 389, second floor. SEBASTIAN of shipping department can furnish or reconstruct all shipments.

Dr. WALTER LUDWIG

Address: Schuckert Strasse 37.

Altersheim 10 years with I.G.

Assistant to Dr. Eymann in charge of Technical Department particularly on planning new production, etc.

Says Bachmeyer, in Heidelberg, know about some Japanese plans. Some plans are at Limburger Hof.

Says hydrogen peroxide is made at Heidebreck, I.G. Werk.

Ethyl quinone, catalyst for making hydrogen peroxide, made at Ludwigshafen. Code name is "RENAL".

Very co-operative.

Dr. GEORG NEUMANN

Chemist. (Dr. of Chemistry, Technische Hochscharle, MUNICH under Prof. FISCHER)

Chief of DYOL Dept.
(Bldgs. Nos. 432,436,453,137,128,134,165, 158,167,193 and 195)

Important man. Ready to reveal all secrets. Has revealed hiding place of barrel full of secret reports, formulae and other documents. Barrel buried in I.G. Farben plant only few days ago.

Documents, etc., partly in Bunker 99 in I.G. Works here, partly sent to Heidelberg and HEDDESBACH near HIRSCHHORN.

ECKSTEIN, code name for underground Buna works near SCHWANDORF. Details unknown. Plans for plant by Dr. AMBROS. Plans Section (Projektburo) was in Heidelberg but is now somewhere in Bavaria.

Secret REPPE Process in barrel secreted 5 meters of NORDOSTECKE 19, Bldg. 165. Diagrams, calculations, etc., are with Dr. SCHONEMANN, STARNBERG (Starnberger See)

Dr. FRITZ PENZIG

In charge of technical and mechanical testing laboratory.

Office: Oppau, and Ungstein, also a small one in Bad Durkbein.

Had been interrogated before and found acceptable. Complaints by specialists that he was withholding information. Re-interrogated by Major TILLEY in presence of five specialists and Lt. MEHL.

Results of re-interrogation

Had laboratory in OPPAU. Left because of bombs. New laboratory in UNGSTEIN, in fortified position in WEST WALL (Seigfried Line), rear area.

Discussion of Xylidin for aviation gasoline.

PENZIG had carried on experiments, had added xylidin to improve anti-knock qualities of aviation gasoline. Denied that he had papers anywhere showing results.

Admitted that laboratory, though important, was not registered at OPPAU or LUDWIGSHAFEN although administratively under them.

Denied that he had secreted secrets. When charged with burying them admitted that he had a quantity of records, results of experiments, buried in forest near UNGSTEIN. As he had lied and obstructed investigation he was placed under arrest.

On following day, 28 March 45, a large group of investigators went out to Ungstein, discovered two laboratories approximately 30 assistants and much material.
Contd. on page 15.

Dr. FRITZ PENZIG (Continued

Documents contained in 2 large boxes were unearthed in a forest near UNGSTEIN. They proved of great value, showing results of experiments on V1, V2 and Jet propelled A/C/ propellants. Documents may contain many other important experiments.

Third interrogation

Lied vigorously about his activities. Denied having any papers. Finally admitted that they were buried in a forest near UNGSTEIN. In his laboratory he carried out experiments on propellants for V1, V2 and jet-propelled A/C.

A very large box was found buried in the forest. The numerous papers should give interesting data on developments in propellants, possibly for a weapon subsequent to V1 and V2.

Dr. KARL PFLAUMER. Wöhlerstrasse 26.

Head of Dyes and Zwischen-produkte. With I.G. since 1920. Very systematic and methodical. His office contains file on dye formulae, left intact. Main products of war value were Ultra-violet and Infra-red paints, coloured smoked, tear gas and irritant gas. Chloraceto-phenol now made at E. de Heain at Selse, Hannover (?) Knows about the U-Boat paints and ferro compounds for jamming radar. Carbon black and iron carbonyl. Made ethyl quinone as catalyst to make hydrogen peroxide.
Nothing to do with Japan.
Very co-operative.

Dr. WILHELM PFANNMULLER.

Living in bunker. His assistant is Dr. Johannsen.
Organization is as follows:-

(a) Schwefelsaure, Nord. (Sulfuric Acid, North)
1. Dr. Wolf. 2. Dr. Danz.
(b) Schwefelsaure, Snd. (Sulfuric Acid, South)
1. Dr. Immel. 2. Dr. Spormann.
(c) Chlor-natronlauge, elektrolyse,
(Chlorine and sodium hydroxide) by electrolysis.
1. Dr. Hamberg. 2. Dr. Kunzel.
(d) Chlor-verflussigenge. (Chlorine liquefaction)
1. Dr. Ketschy.
(e) Alaun and Planherd (?)
1. Dr. Hülm, 2. Dr. Zimmeran, 3. Dr. Schulz.
(f) Chlorzinr (Zinc Chloride).
1. Dr. Hille. 2. Dr. Kälberer.
(g) Kontakt masse -5 oz. Buna,
Arriline, etc.
Catalyst for sulfuric Acid, synthetic rubber,
aniline etc.
1. Dr. Wimmerer. 2. Dr. Ludemann, 3. Dr. Leutert.
(h) Laboratory.
1. Dr. Wintersberger. 2. Dr. Janson.
3. Dr. Kudeba. 4. Mr. Banza (Spanish)
(i) Salzsoure. (Hydrochloric Acid)
1. Sdwabe.
(j) Sulphite.
1. Dr. Immel. 2. Dr. Sporman.
(k) Cyan-natrium. (Sodium Cynanide)
1. Dr. Lothar Zimmermann.
2. Herr Gobel. 3. Dr. Arendorf.

28 March 1945.

Dr. PFLEIDERER, Georg

Address: Ludwigshafen, KeKule Platz 8.

Dr. Phil. (Physics), BERLIN, 1909, under NERNST

Group Chief (Gruppenfuhrer) in Ammonink laboratorium, since 1934.

Bldg LU 949, also Central laboratory, Bldg. LU 51.

Previously: 'Elektrolyse von Wasser'
Corrosion of Metals, Elektrolytische
Gewinning von Chrom.

For 'Carbonyl Nickel' see Dr. DRAGESER, previously Leo FLECH

Claims not to know anything about 'Eisenpulver'

Motalin - composed of Benzin with a little 'Eisen Karbonyl'.

PFLEIDERER is a very stubborn man and refused all information but finally agreed to talk and tell the truth. He was the most difficult of all 16 people to break.

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28 March 1945.

Dr. KURT RASCHIG

Dr. Phil (chem.) HEIDELBERG 1924
Address: Mundenheimer Str. 80, Ludwigshafen.

With his brother owns Firma Dr. F. RASCHIG C.m.b.H.
(Tar products, artificial resins and a few chemical products.)

RASCHIG is specialist in Tar products.
Brother Klaus RASCHIG escaped across Rhine.
Father F. RASCHIG inventor of RASCHIG Ring.
Kurt RASCHIG inventor with the chemists in his firm of synthetic phenol process (Production of phenol from benzol)

In RASCHIG plant phenol is made from tar, not synthetically (Benzol-Clor benzol - Phenol).
'General Plastics' only connection in U.S.A. 'General Plastics' pay licence fee to RASCHIG.
Wehrmacht used no phenol for explosives, but toluol.
RASCHIG made no dinitro phenol, but dinitro cresol. Latter made from Orthocresol with sulphuric acid and saltpetre.

RASCHIG was co-operative and made no attempt to conceal secrets. He volunteered several important secrets not listed here.

Dr. Camill Santo

Assistant to Dr. Eymann in charge of all construction. Office in Engineering Building, Bau 10.

Claims no plans or blueprints were sent away, but many were burnt in air raid during January, 1945. Some of plans of a more secret nature on Buna factory may be in safe; however the safe has been forced open by troops. Santo had already been interrogated by a Major regarding air raid damage.

Otto Reicfs

Home address:- Hanserstrafe 6B

Chief of the Storage and Packing.

In charge of the sending away of everything ready for selling. Has been most helpful and tried hard to find all the addresses I wanted, but of course, it takes some time. Very truthful. Admits at once if papers have been purposely burned, but will try to give information that was on them and in one case I know he was right, and in another it was subsequently checked.

29/3/45.

SEBASTIAN, Bernhardt

Employee in Shipping Dept: I.G. Farben.
Address: Ludwigshafen, Baiernstrasse 73.

During February and March documents and machinery were sent daily from Ludwigshafen to various places in Germany.
On an average 3 lorries left Ludwigshafen daily with machinery.

Machinery was sent to the Saltmines at Heilbronn (for underground installations?) einheim, (Bergstrasse, BADEN (from Koloristische Abteilung) to Firma Freudenberg.

Chemical products went daily to the Palatinate, I.G. Farben stores, Heiligenstein near Speier.

Glass, etc. to stores at Bischheim near Kirchheim Bulanden.

Documents were sent from Building 1, Ludwigshafen by car to Heidelberg chiefly to (a) Karlstrasse 10, (b) Cafe Rosler, (c) Leopoldanlage der I.G.

Stupid unimportant official who was wanted only for specific shipping data.

Dr: BERTHOLD SCHNELL

Address: T-Force Jail, FRANKENTHAL

Dr. of Chemistry (Heidelberg and Marburg, 1924)

Chemist, Acting Chief of ZW Dept.
(ZW = Zwischenprodukte or Intermediate Products)
Chief of Dept., Dr. BAUMANN, now in DURCKHEIM.

Important man. Intelligent. Furnished all information readily and is ready to give all secret formulae, methods of production of all his sections. Refused to give location of Tetraethyl lead plants. Speaks a little English. Should not be released for detailed interrogation by specialists until his resistance is broken on location of secret plants in Germany.

His ZW Dept. turns out 200 products, such as Nitrobenzol, Aniline, Dimethylaniline, Phenyl Beta Naphtylamine (added to Buna), Beta Naphtol, Phtalic acid, Benzol Dicarbon acid, Formaldehyde, Chloroethane, Chlorbenzol, Cyclohexanol, Cyclohexanone, Adipic acid, Ethylorthotoluidin, etc.

XYLIDIN produced in small quantities for dyes before war in MULHOUSE (MUHLHAUSEN), ALSACE. End 43 or beginning 44 production started for aircraft engines. This xylidin was sent to Baiswische Motorwerke until loss of MULHOUSE. At first 50 tons produced each month in two MULHOUSE works, later 100 tons (50 tons in each).

Hans SPOHN (a) Mechanical Engineer (Höhere Technische Lehranstult MANNHEIM, 1931)
(b) Address: FRANKENTHAL, Nordring 14.
At present with his parents, FRANKENTHAL, FOLTZRING 79

(c) Mechanical engineer
of Betriebe IU 128, IU 158, IU 165
(Butindyol Works)

(d) Unimportant man. Eager to betray secrets. Information has proven to be accurate.

(e) Production of Dyol Section of I.G. Farben
(No details known)

(i) Acetylen
(ii) Butindyol (Dr. REPPE's procedure)
(iii) Butanedyol
(iv) Butadien
(v) Polymerisation to Buna S.

(f) Dyol Section destroyed 13 Sept. 1944. A few hundred tons produced in November and early Dec. 1944.
Plant completely destroyed, 5 Dec. 1944.

Dr. ALBRECHT WEISS

Head of Personnel Department
(a) Social
(b) Medical
(c) Economic
(d) Personnel Problems
(e) Casino (Directors Club)

He is not to be confused with Director Karl Weiss, who retired last year, after 40 years service with I.G., is now living in Weingarten/Würtemburg. Karl Weiss was in charge of the purchasing department and has been succeeded by Herr Krieger and Herr Schäfer, both available.

Albrecht Weiss is a willing talker but handles no technical problems.

Dr. KARL WILLER.

Address: Ludwigshafen, Shuckert Str. 37

Dr. Chem. Technische Hochschule. Stuttgart 1928.
Betriebsleiter (Works Chief) in the inorganic section under Direktor Dr. Pfannmuller.

WIMMER makes, in the Konfakfmassen fabrik,
Catalysts for (oxidation, Hydrogenation, DHD
(Absfalting von C.O. 2 Kohlensaure
(" " Wasser
(Kondensation

Wimmer does not specialise in, and knows little of use of catalysts or any methods of application. After considerable discussion, not at all friendly, Wimmer indicated that he had hidden all formulae, etc., for catalysts and accompanied specialists to cellar in Bldg. LU 492, where he had hidden all secret papers in a steel barrel.

Wimmer was unco-operative and tried his best to mislead us. He needs firm handling.

Dr. GEORG WITTMANN 35 years old.

Address: Ostmark Str 28, Ludwigshafen, Dr. Corr

Dr. Philos (Chem.) MUNCHEN 1936.
Inorganic Chemistry, under Prof. HONGSCHMIDT (Atomewichte)
In army Feb. - Sept. 1940, in A/KT unit - denies being party member.

Now head of small laboratory for inorganic analysis under Dr. FUNER. Testing laboratory for High Pressure Dept.

WITTMANN worked for Dr. ANDES, Dr. DONATH, Dr. PETERS, Dr. FUNE, Dr. SIMON. Most of these gentlemen departed hurriedly a few days after WITTMANN returned to LUDWIGSHAFEN.

WITTMANN had been bombed out approximately 2 months ago and moved to HEIDELBERG, leaving for Ludwigshafen every morning at 5:30. It is curious that he should have taken up residence in Ludwigshafen about the time that all his chiefs decided to leave for Heidelberg. Wittmann returned here on 14 March 1945.

Wittmann walked into an interrogation at I.G. with a large sandwich for Dr. Wurster for whom he was looking. He was severely reprimanded for his insolence. What is remarkable is that Whittmann should have known that Wurster was in the building and on what floor he would find him.

It is recommended that WITTMANN be further interrogated.

Dr. KARL WURSTER

Address: T-Force Jail, FRANKENTHAL

Dr. of Chemistry (Technische Hochschute, STUTTGART, 1923)
Managing Director, Ludwigshafen & OPPAU. Office on second floor, main office building I.G.

BETRIEBSFUHRER & Direktor, also Chief of "Anorganischer Betrieb".

First Interview March 26, 1945

Scared and ready to give full information. Intelligent. Precise. Despite protestations to contrary probably anxious to be on any subject which is difficult to check. Needs careful handling. Should not be told of charges of being a Nazi leader. Is trying to find out what we know about him. Knows of all major plans and methods, but few details. Speaks English.

Will furnish list of all key parts removed to places of safety, some on left bank of Rhine.

Will furnish list chiefs of sections.

Has heard of SCHWALBE, ECKSTEIN, etc., but disclaims knowledge of details.

Tetraethyl lead produced in Ethyl GBH, GAPEL near DOBERITZ. Another plant was planned in HEYDEBRECK, SILESIA now in Russian hands.

Technischer Betribsstoff fur Maschinen produced in OPPAU either in building 471, or in 472. Will indicate exact building on March 27, 1945.

Will indicate tomorrow where caches are for machinery and secret documents. States none in Ludwigshafen but many in unoccupied Germany (Heidelberg, SCHKOPAU, etc.)

Dr. KARL WURSTER (Continued).

Second Interview March 27 & 28, 1945.

1. Recent Career in I.G. FARBEN
Promoted Chief of Inorganic Section in 1931.
Promoted General Manager of LU & OP (Betriebsfuhrer) in 1 January, 1938.

2. Political Career
Party Member (Pf. or Parteigenosse) since 1938, admission to membership dated back to 1 May, 37. Given honorary rank of SCHARFUHRER (Approx. equivalent to sergeant) in NSKK (motorised or automobile section of Nazi machine). (NOTE It is unlikely that WURSTER should have held such a low rank in the Nazi Party.) President of Chamber of Commerce for the entire Palatinate (Vorsitzonder der Wirtschaftskammer fur die Pfalz).

3. WURSTER, MULLER-CUNRADI and AMBROS were equals in IG in every respect but one: administration which WURSTER directed in Ludwigshafen and OPPAU.

4. Plans and Code-Names.
Planning of big schemes done by LEUNA and Dr. PIER; BUTEFISCH for propellants, Dr. (chem.) SCHNEIDER for all other plans.

(i) LACK Plan. Substitute nitrogen plants, above and below ground.

(ii) SCHWALBEN. According to WURSTER they are small underground plants for propellants. One of them, for I.G. Farben, is probably in UNTERLOQUITZ (SAARFELD District, THURINGIA.) Personnel and machinery sent there by Dr. PIER. (NOTE. Dr. PIER & Dr. DONATH have given full details of this plant.)

(iii) BARBARA, ILSE and other girls' names. For smoke producing chemicals. One plant each in LUDWIGSHAFEN, LEVERKUSEN, HOCHST, LEUNA (small plant), MOOS BIERBAUM (AUSTRIA), WOLFEN (BITTERFELD), MAGDEBURG, VON HEYDEN Chemical Works in DRESDEN, RHEINFELDEN.

(iv) Code Names (not remembered by WURSTER, Oleum plants, e.g. Norddeutsche Affinerie in HAMBURG, or GIESCHE in MAGDEBURG.

(v) Jager of Jagerprogramm
Any chemicals or fuel needed for Jager (pursuit planes). Any chemical of I.G. FARBEN which may be used for pursuit planes is labelled "ESGEHORT" zum JAGERPROGRAMM". (It belongs to the pursuit planes programm.) (NOTE. WURSTER would not admit that "JAGER" means not merely pursuit planes but is a code name for all planes of the Luftwaffe. The files in which "Jagerprogramm" was found would indicate all chemicals belonging to or of use to the entire Luftwaffe.)

(vi) JAKOB
Wurster, like all other scientists, of I.G. FARBEN did not recognise this code name obtained at WESSELING.

5. I.G. PRODUCTS - Division (SPARTEN)

SPARTE I (LEUNA)	SPARTE II (FRANKFURT)	SPARTE III (WOLFEN FILM)
N	FARBEN	KUNSTSEIDE
	CHEMIKALIEN	ZELLWOLLE
TREIBSTOFF	METALLE	PHOTO
	PHARMA	
	BUNA	

Note: This division means that research and products are grouped in three "Sparten" and that each "Sparte" is administered from a a/m plant. Production may be carried on in any plant, however.

6. ORGANISATION OF LU & OP

LU

WURSTER

Anorganische Abt.
(Inorganic Section)

AMBROS

Zwischenprodukte
(Intermediate Products)
L.K. Ale
Diol
Farben (dyes)
Koloristische Abt.
Hauptlabor (main Laboratory)

LU-OP

SOZIAL

Techn. (Technical Section)
Einkauf (Purchasing Dept.)
Verkehr (Traffic & shipping)
Fabrikbuchhaltung (Accounting Dept.)
Sozial (Welfare etc.)

OP

MULLER-CUNRADI

Techn. Op.
Stickstoff
Landwirtschaft

LU (These two depts. for all of I.G., only geographically placed in LU, not administratively.)

V. KNIEREM

Rechtsabt (Legal Dept.)
Patent abt. (Patent Dept.)

7. NOTES ON ORGANIZATION OF IJ AND OP

WURSTER, head of entire IJ and OP plants, but only for administration. AMBROS, MULLER-CUNRADI and Von KNIEREM equal in rank to WURSTER and independent except for administration.

WURSTER, aside from chief of administration for IJA and OP also head of inorganic section and Welfare Dept, the latter apparently also including Nazi surveillance. Plant divided into three main sections: IJ, IJ-OP (area between IJ & OP) and OP. Legl and Patent Depts. transferred to HEIDELBERG 6-10 months ago. No CW or Explosives made in IJ or OP, but some intermediate products which are used in both.

The main lab. transferred to GENDORF, according to information obtained at HEIDELBERG, hence AMBROS' transfer to GENDORF fully explained.

8. IJ & OP DEPTS. AND NAMES OF HEADS.

X - Still in IJ
____(underlined) = Honorary rank of DIREKTOR

Admin., Inorganic Welfare -	WURSTER X
Textilhilfsmittel	ULRICH
Losungsmittel-Kunststoffe	BULOW X
Farben (Alizarin	PFLAUMER X
(Azo	Helwert X
(Trifarben	Teller
Diol (Buna)	NIEMANN X
Anorganika	PFANNMULLER X
Technische Abteilung	EYMANN X
Baufragen (Building)	Santo X
	Stechl X
Energie	Schafer X
Einkauf (Purchasing Dept)	KRIEGER X
Verkehr (Traffic, Shipping)	

9. Tech. Fuel (Technischer Betriebsstoff)

For engines (motors etc.) made in OP 471 or 472.

10. Key Parts of Various IJ & OP Buildings

Wurster can furnish list of addresses where they have been sent.

11. CSA (NEBELSAURE)

Wurster's special field. Can give all details. All CSA made at IJ was sent to WEHRMACHT who allocated it to its own services and to factories. Most CSA was used for smoke screens in armaments works.

12. Tetra-Ethyl Lead Plants

One in GAPEL near DOBERITZ (Ethyl G.m.b.H., GAPEL) Another planned, but probably not finished, in HEYDEBRECK, SILESIA.

(NOTE: SCHNELL, after one night in the "cooler", stated that one was in GAPEL, the other in FROASE (Central Germany). Neither worked satisfactorily because insufficient "Chlorethyl"(?) available. No. "Chlorethyl" made in IJ or OP for Tetraethyl lead. "Eisen Karbonyl" made in OPPAU as substitute for "Chlorethyl" but found unsatisfactory because (a) Exhaust red, (b) Gets clogged in engine, does not escape with gases.)

13. Special Products.

B-Stoff = HYDRAZIN (possibly for motor fuel) Only small experimental shop, No. 263. Not mixed in OP or IJ.

T-Stoff = Same as B-Stoff, only a new name given to it. (Hydrogen Peroxide?)

C-Stoff = Abbreviation for K-Stoff. (Methyl alcohol?) Only AMBROS knows exactly what this is. WURSTER claims not to have been told of details.

14. EXPLOSIVES
Only primary and intermediate products (Vor- und Zwischenprodukte) at LU-OP, such as Saltpetersaure, Oleum, Diglycol (Bulow knows all details), Anilin, Dimethylanilin, Chlorbenzol, Nitrobenzol, Chlot.

15. Primary and Intermediate Products for V-Weapons.
Possibly some made at LU, but WURSTER claimed not to be certain of that.

16. CW, Poison Gases, etc.
According to WURSTER all "Kriegsgase", literally "wargases", or poison gas, is made by Dr. AMBROS. No one outside of Dr. AMBROS' dept. is told any details, not even WURSTER who opined, however, that poison gas is probably made in DYHERENFURT in SILESIA.
(NOTE: In HEIDELBERG it was discovered that all mustard gas "Gelbkreuz" is made in GENDORG near MUNICH and that the main laboratory is there. In DYHERENFURT a yet more deadly poison gas is said to be made. WURSTER never mentioned GENDORF although he knew that AMBROS worked there. These two scientists were both ordered to cross the Rhine. WURSTER decided to remain as all of his work was in LU and OP, and he agreed that AMBROS should leave as most of his work was "elsewhere")

Deputy of Dr. AMBROS for CWA is a Dr. ULRICH who transferred some time ago from LUDWIGSHAFEN to DYHERENFURT. Others who went from LU to DY are
Dr. PAUM (CHEMISTRY)
SCHMAL, Ingenieur
BILFINGER, Ingenieur
DR. VON BOCK (chemistry)

WURSTER knows that several other assistants of AMBROS had been transferred but he could not remember their names at the time.
(NOTE: As Dyherenfurt is now in Russian hands all these gentlemen are now likely to be in GENDORF.)

For CSA see 11.

SOZIAL (PERSONAL = Personnel)	WEISS X	
Wirtschaftliches, Arzte	HOFFMANN X	
Patent Recht (Legal Dept.)	Von KNIEREM HOLDERMANN) & Kleber)	for patent dept.
	BRENDEL (for legal dept.)	
Fabrikbuchhaltung (Works accounting Dept.)	MAIR Schmidt X	
Koloristische Abt. Hauptlaboratorium	Kollek X) REPPE)	AMBROS
OP	MULLER-CONRADI	
Stickstoff	GOGGEL X GLOTH X	
Technische Op	SCHIERENBECK	
Handwirtschaftliche Abt.	BIEDABOCK (?)	

Copy 1

ITEM No. 5
FILE No. XXVI—83

COPY No.....186

RESTRICTED

BAYERISCHE MOTOR WERKE
(BMW)

Liebhafsky, Norris, Hult

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

BAYERISCHE MOTOR WERKE (BMW)

12 May, 19 June 1945

Reported By

Dr. H. A. LIEBHAFSKY, U. S., ORD.
Mr. R. H. NORRIS, U. S. ORD.
Mr. E. H. HULL, U. S. ORD.

CIOS Target Number 5/74

Jet Propulsion

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

RESTRICTED

10 p. illus.

TABLE OF CONTENTS

SUBJECT	PAGE NO.
I. Target Location	3
II. Subject Covered	3
III. Summary	3
IV. Report	3
V. Photo Titles	6

Figure 1
Sketch of Test Pit

BAYERISCHE MOTOR WERKE (BMW)
Target No. 5/74

I. TARGET LOCATION (Sheet M49 at 11274811)

The main entrance to the BMW plant is 6 km. SSE of Dachau and 0.7 km. SSE of Karlsfeld on the west side of the Munich road. The rocket motor test pits are in the SE corner of the plant.

II. SUBJECT COVERED

Liquid fuel rocket motor testing installation and associated shops.

III. SUMMARY

This report covers an inspection made about 12 May by Lt. Col. G. J. Gellin (British), Squad Leader E. J. A. Kenny (British), 1st Lt. Ozel (U. S., Ord.), and H. A. Liebhafsky (U. S. T/O) of CIOS No. 183 and a later trip made by R. H. Norris and E. H. Hull (U. S. T/O) on 19 June 1945.

The target contains an important rocket motor testing station, briefly described below, which might be studied further if the German operators could be obtained for explanations in order to answer certain questions concerning methods of measurement and operation, safety precautions, reasons for explosions, test results, etc.

IV. REPORT

There is no doubt that the target is one of the outstanding German stations for stationary tests on rocket motors. Stations of comparable importance seem to have been only at Peenemunde and Berlin.

Our first party was conducted through the station by Dr. Hemsath, chief chemist of BMW for rocket fuels, who claims to be the inventor of hypergole fuels utilizing nitric acid as oxidant. He claims further that some 6000 rocket-fuel combinations have been tested at the target. Nitric acid was the only oxidant used in these tests; many reducing agents (fuels) were tried, the choice of these being dictated largely by supply considerations. Hydrogen peroxide has been studied for submarine purposes in the laboratory, but never in a rocket motor.

The station was begun early in 1943. It was to consist of 12 pairs of test pits, each pair having one control room. Most of these pits were built, but not all were operated.

Thrust was measured hydraulically through a membrane. There was also an electrical method of thrust measurement, but this did not

involve a quartz crystal; a reasonable guess is that it involved changing the capacity of a condenser by a mechanical displacement proportional to the thrust. (The CIOS team expects to clear up this matter and to obtain samples of the thrust-measuring devices). The reactants are delivered by pressurizing, air or nitrogen being used. Reaction is begun by having an explosive rupture of a metal membrane, which starts the flow of reactants. (Lt. Col. Gellin says that he is thoroughly familiar with this method, which he uses). The hypergolics are self-igniting; for the other fuels, ignition by means of gunpowder, by means of an electric spark, and by means of hypergolics in small quantity has been used.

Although pressurized tanks, see Photo No. 1, filled by means of electrically driven portable pumps , were used for reactant supply, a more elegant system was practically complete. Four sets of large metal acid tanks and smaller fuel tanks were suspended on scales for accurate weighing. Pipes led from these tanks to a pipe tunnel passing under the floor of the test pits for distribution of the reactants. The acid tanks are cylindrical in shape and laid horizontally on their weighing apparatus (See Photo No. 3). Acid tanks hold about 750 gals. and the fuel tanks, 200 gals., approximately.

Apparently no precautions have been taken to keep the reactant systems separate. Fuel and acid tanks are located in the same room and the supply pipes lead through the same duct. There is no visible protection for these supply lines in the test pits and apparently no means of keeping blast or fire from travelling along the pipe tunnel from one pit to the next, or to the tank rooms.

Exhaust gases from the motor tests are taken care of in an elaborate duct system. A long horizontal brick duct, 5 x 7 ft. inside, is built parallel to the row of test pits. At each pit a short brick section, built at right angles to the main duct, ends in an open-ended telescoping steel tube about 4 ft. in diameter, as shown in Photo No. 4. Exhaust gases collected by this tube run along the horizontal duct to a vertical stack about 50 ft. high, up which they are forced by a centrifugal fan. There is a gate valve in each individual test stand duct. Some of these side ducts have built beside them a brick observation room for looking axially into the rocket motor from the exhaust end.

As mentioned above the test pits are built in pairs with a common observation room between each pair. There are sections between these units for workrooms and the reactant storage spaces. The test pits, 13 x 20 x 12 ft. high, are enclosed by 30-inch concrete walls except on the front, which is covered by a rolling steel door to be opened during tests. Steel T-slots are built into the floor and walls to facilitate fastening equipment. Excellent lighting is provided by lamps near the ceiling covered by safety glass, some of which has been cracked by explosions. Photo No. 5 is a general view of one of these

test pits showing the stand for mounting the rocket and measuring thrust on the right and on the left reading from bottom to top, a reactant supply pipe, observation window, wire screen for the window, the screen being raised at the time the picture was taken, and two lights. In the far corner an entrance door can be seen standing open. This leads into a vestibule opening into the observation room, the test pit on the other side of that room, and to the outside. The T-slots in the floor and walls can be seen also. Each pair of test pits opens on the exhaust side into a paved yard divided by walls at the sides and enclosed by the duct at the rear.

Two long windows lead from each observation room to each test pit (shown in Fig. 1). The glass in these windows contains 4 laminations totaling 2" in thickness. In one of the pits a severe explosion had spalled the concrete walls and cracked the outer glass window but nothing penetrated. Photo No. 5 shows an investigator holding this cracked window. Spalling of the concrete wall between the two windows and above the nearer can be seen as well. During tests these windows are covered by a heavy wire screen which was missing from the cracked window, probably having been removed for repair. The space between the two pieces of glass is either heated electrically or dried with a dehydrating agent to insure non-fogging.

Explosions are not uncommon since nitric acid tends to form explosive organic nitrates if oxidation of the fuel does not proceed rapidly in mixing.

The observation rooms are equipped with neat control boards mounted under the observation windows as well as a large instrument panel which appeared to be arranged for movie photography. On this panel were 2 tachometers, a clock, several pressure gauges and 2 temperature indicators.

Some of the test pits appeared to be arranged for testing the entire propulsion unit of the Henschel 8-117 including tanks. This assumption is strengthened by the fact that several partially destroyed 117 power plants were seen nearby. Also in the shop across the street from the test pits were found several 117 tanks, pistons and a burned-out combustion pot. Experiments were also made in motors of the X-4 type in which the reactant rate is 0.8 kg/sec. for 20 sec. duration. Work has been done on ATO units for rocket planes on a 10 times larger scale than the above, as well as for longer times. Specific impulses of 200 sec. are claimed but this point has not been verified.

Dr. Hemsath feels that nitric acid is the most promising of all oxidants for rocket purposes. He admits, however, that no operational use has yet been made of it in Germany but says there have been trial flights. Most experiments were made with a 5 to 1 ratio of nitric acid to fuel which indicates an excess of acid.

V. PHOTO TITLES

1. Pressurized reactant tank suspended for weighing.
2. Acid supply tank mounted on scales.
3. Fuel supply tank suspended for weighing.
4. Exhaust gas telescoping duct.
5. General view of a test pit.
6. A pit in which an explosion had occurred.

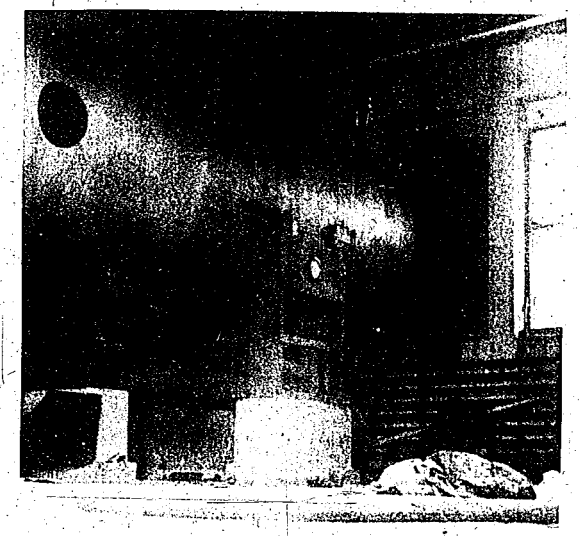

Photo No. 1

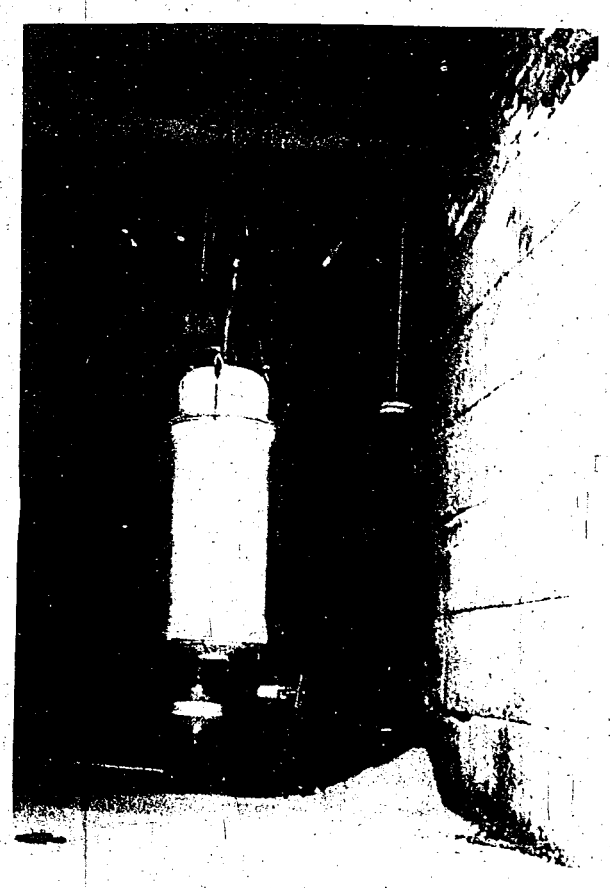

Photo No. 2

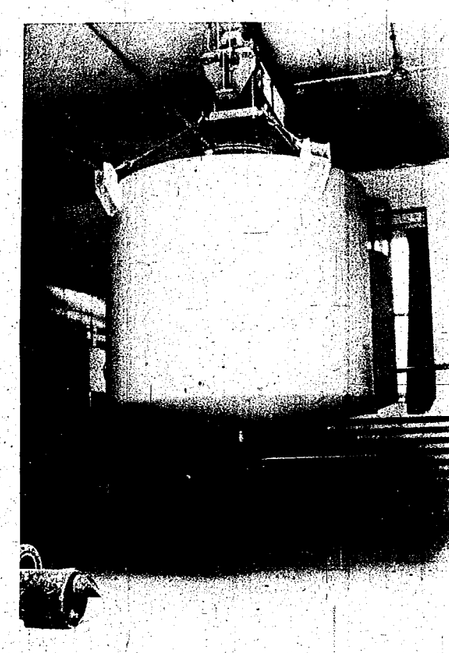

Photo No. 3

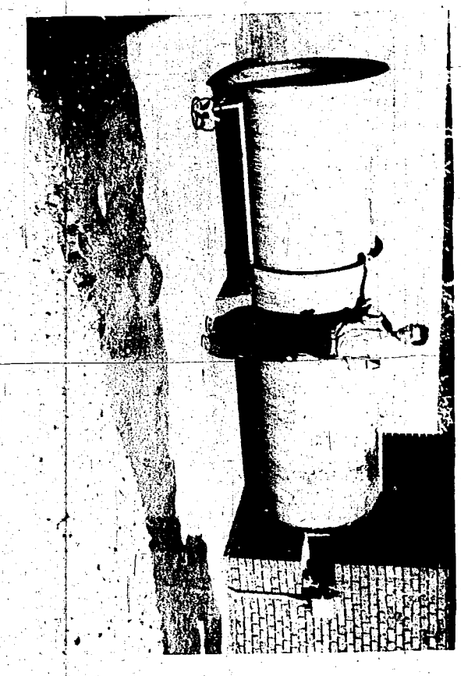

Photo No. 4

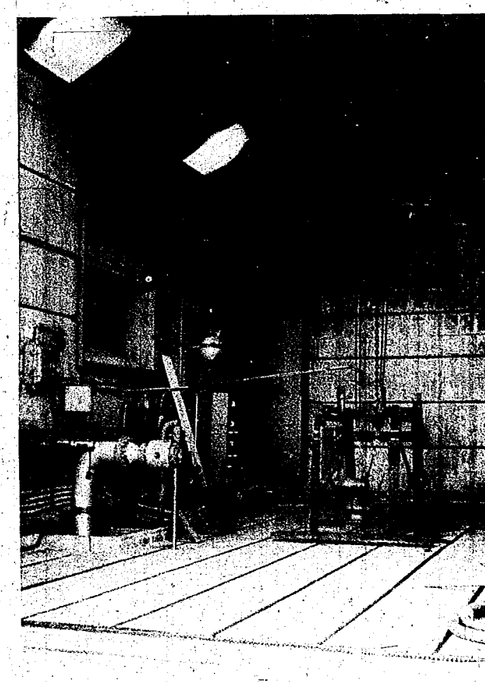

Photo No. 5

Photo No. 6

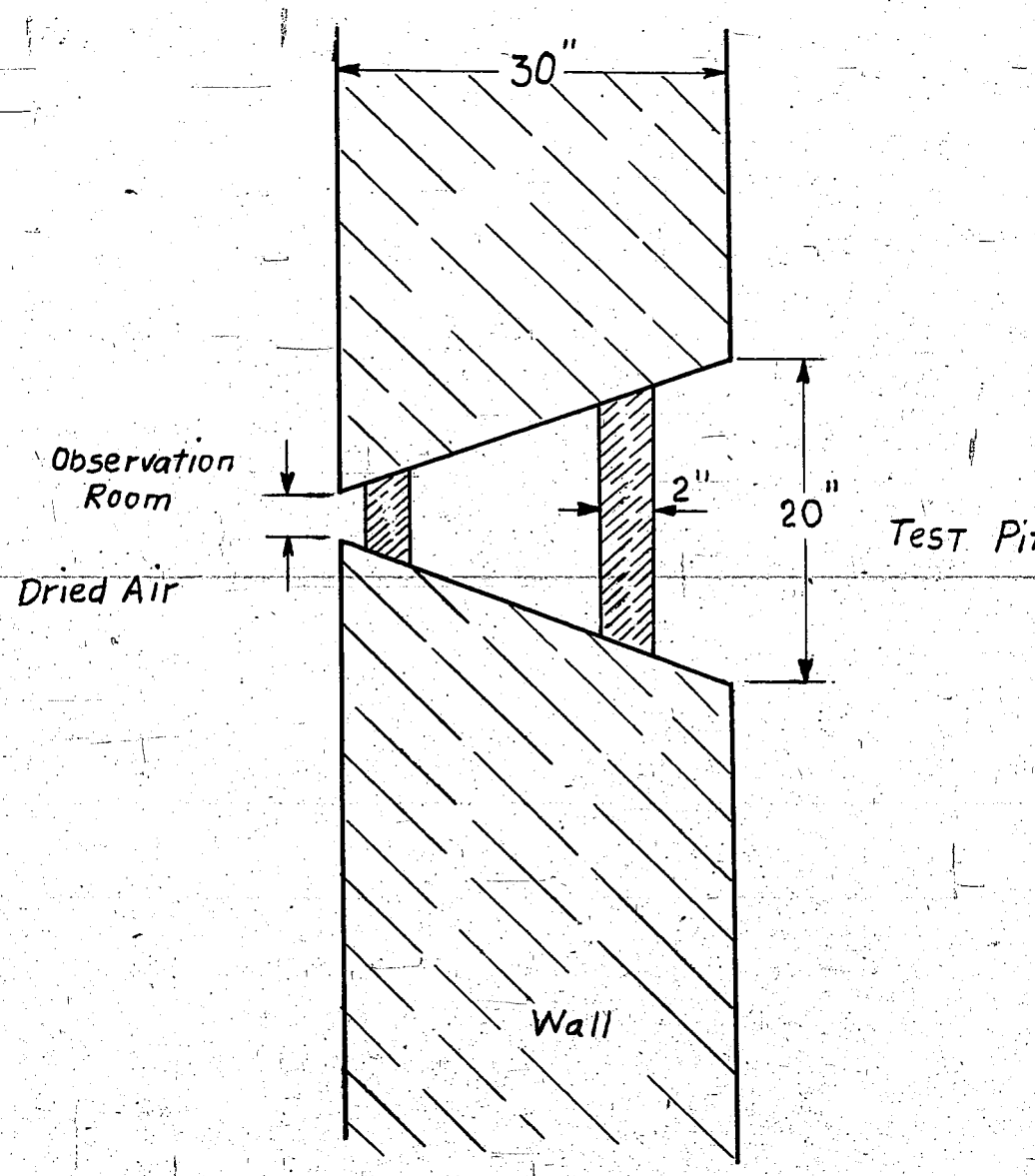

FIG. 1

ITEM NO. 30
FILE NO. XXXI - 27
Solid Fuels 21

COPY NO. 1

~~RESTRICTED~~

COAL EXTRACTION PLANT

OF

RUHROL G.M.B.H.

Lowry, Newman, Rose

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

COAL EXTRACTION PLANT OF RUHROL G.m.b.H. AT THE HUGO STINNES WERKE OF MATHIAS STINNES GEWERKSCHAFT IN WELHEIM NEAR BOTTROP 1. W

Reported by

H. H. LOWRY
H. J. ROSE

On behalf of

U. S. Technical Industrial Intelligence Committee

CIOS Target Nos. 30/4.11 and 30/86
Fuels and Lubricants

June 29 and 30, 1945

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

RESTRICTED

10 p.

CONTENTS

SUBJECT	PAGE NO.
Date of Trip	1
Location and Condition of Target	1
Object	1
Personnel Interviewed	1
Conclusions	1
Introduction	2
Extraction Process at Welheim	4

RESTRICTED

COAL EXTRACTION PLANT OF RUHRÖL G.m.b.H. AT THE HUGO STINNES WERKE OF MATHIAS STINNES GEWERKSCHAFT IN WELHEIM NEAR BOTTROP 1. W.

Date of Trip: June 29 and 30, 1945.

Persons Making Trip: H. H. Lowry (U.S.)
L. L. Newman (U. S.)
H. J. Rose (U.S.)

Location and Condition of Target:

The coal extraction plant is located in Welheim near Bottrop in Westphalia and is associated with a hydrogenation plant with which it is integrated. The plant occupies an area of 350,000 sq. meters (86.5 acres) and was first bombed on July 21, 1944. There were 10 raids, the heaviest damage being done on Oct. 31, 1944, and since which the plant has not operated. The coal extraction equipment could be mostly salvaged but it is highly improbable that it could be operated without starting up the hydrogenation plant which was largely destroyed.

Object: To determine advances made in large scale coal extraction.

Personnel Interviewed:

Dr. Hans Broche, Director of Mines, Mathias Stinnes, Essen and co-inventor with Dr. A. Pott of the extraction process.
Dr. Erich Frese, General Manager of Welheim plant.
Dr. Helmut Schmitz, Head of Extraction Division.

Conclusions: The extraction process is feasible mechanically. It is uncertain that, even in Germany, the process could be justified without having available the special solvent oils from hydrogenation of pitch. One of the major advances in the technical operation of the process during the war was a new filtering system using specially developed ceramic filters of high porosity that permitted recovery of an extract containing only 0.05% ash. The filters and filtering system might have other industrial uses.

Introduction:

The Pott-Broche process has been under development for many years although only one plant was built. This plant was built in 1937, but it was not operated continuously. At first there were many difficulties. It was the original intention to hydrogenate the coal extract to produce fuel oil, but it was found that the capacity of the hydrogenation plant was greater when operating on coal-tar pitch (of which there was a large surplus in war-time Germany) than on coal extract. Consequently the coal extraction plant was shut down for some time. Then it was discovered that the middle oil from the hydrogenation of pitch was an excellent solvent for coal extraction, and it was used instead of the original tetralin-cresol mixture. Furthermore, after use in the coal extraction process, the recovered middle oil was better for vapor-phase hydrogenation, because the motor-fuel produced contained a higher amount of aromatics. The coal extraction plant had been operating since 1941-42 until it was bombed out late in 1944. The coal extract was coked for the manufacture of high-grade electrode carbon of exceptionally low (0.1 to 0.15%) ash content. The important patents are: Ger. Pats. 633,391; 633,693; 663,497; 687,898; 691,529. Brit. Pats. 462,478; 464,337; 480,214; 480,644; and U. S. Pats. 2,123,380; 2,241,615.

Coals having more than 25% volatile matter (Muck method) are suitable for the process. Those of lower volatile matter content yield less extract. Dr. Broche said that the process was also suitable for higher-oxygen bituminous coals like Saar coal, which gave as high yields as Ruhr coal. The bright components (clarit and vitrit) of bituminous coal are extracted well; the dull coal (durit) is extracted in part, while the fusain is not extractible. Brown coal is not suitable on account of the large amount of decomposition.

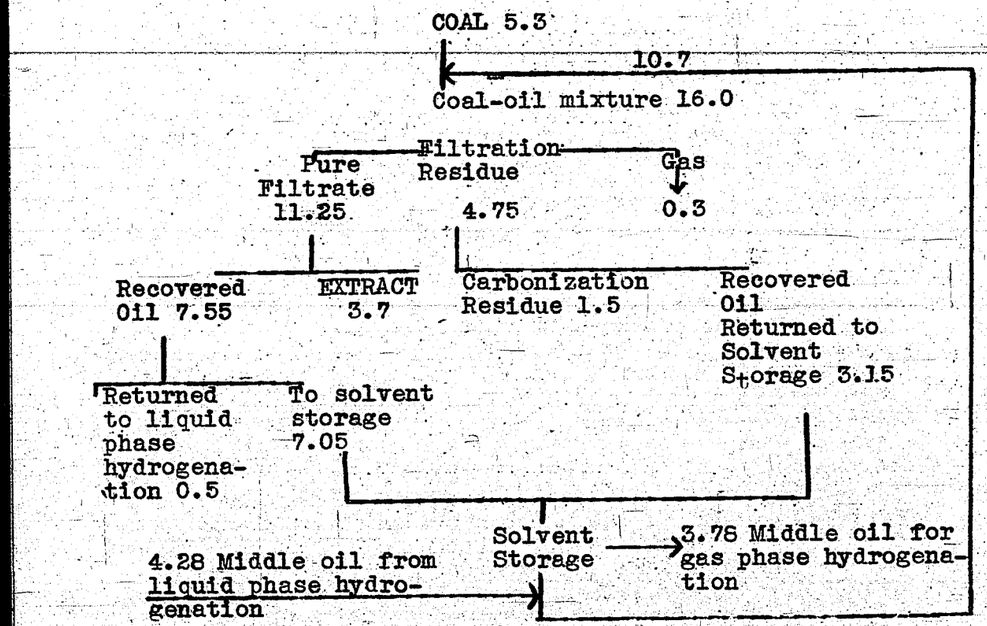
The original solvent was 4 parts of tetrahydronaphthalene and 1 part of a mixture of the 3 isomeric cresols boiling from 190 to 210°. This solvent was used with half its weight of coal as the mixture to be treated in the extractor. The same ratio of solvent to coal was

used later but the solvent was changed to a middle oil with a boiling range from 200 to 320°C and about 9% hydrogen, from the hydrogenation of coal-tar pitch. The pitch had a melting point of 67° and was obtained from tar produced by normal high-temperature carbonization of bituminous coal. It is important that the solvent contain hydronaphthenes with disposable hydrogen as furnished by the tetralin in the original solvent. The tetralin originally used was reduced to naphthalene in the process and had to be recovered and regenerated for economical operation. The regeneration was the stage that ruled out this solvent since the sulfur in the recovered liquid product poisoned the Ni catalyst used for hydrogenation.

Earlier papers on the process emphasized the necessity of a definitely predetermined and controlled temperature schedule in the process. It has now been determined that this is unnecessary and it is only important that the maximum temperature does not exceed the decomposition temperature of the insoluble residue (Restkohle). This temperature differs for different coals and for Stinnes coal of 28% volatile, on a dry, ash-free basis is 410°, A higher temperature such as 440 to 450°C would give much trouble from coke formation in the tubes. This coal would begin to yield tar at 350°C when heated under ordinary conditions. Broche stated that early work indicated the need for using a high enough temperature. For example, only part of a coal may be extracted at 380°, with increasing amounts at 390° and 400° but still more complete extraction at 410° C, in which case the latter temperature would be used. Extracts made at too high or too low a temperature would be hard to filter. The optimum temperature for processing a particular coal would be determined by laboratory extraction tests at a series of temperatures. Broche referred to the process as the "Aufschluss," i.e. the decomposition or "unlocking," of coal. In reply to questions, he said that he did not know how to dissolve a large percentage of coal without decomposing it, nor did he know how to extract a large percentage while working at atmospheric pressure. The maximum temperature and the vapor pressure of the oil determine the maximum pressure - which ranges from 100 to 150 atmospheres.

Extraction Process at Welheim:

The following description is prepared from notes taken in the plant and from a flow sheet (1511-8) obtained at the plant and a print of a schematic layout (BK16-2) of the preheater and extractor equipment, which have been deposited in bag 1481. These two items have also been microfilmed on P.R.W. Series "B", Reel 25, as number 000895 near the end of the reel. The flow sheet is for an annual production of 26000 tons of extract calculated on the basis of 7200 hours per year, and is reproduced in part as follows where the numbers are tons per hour. The figures do not balance exactly in every case.



The coal used in the process as outlined is from the Stinnes I/II and Stinnes III/IV mines with a volatile

matter content on a dry ash-free basis of 27-28%. On the same basis, a typical elementary analysis is C, 86.7%; H, 5.1%; S, 1.2%; N, 1.6%; and O (by diff), 5.4%. The raw coal has a water content of 5 to 10% and an ash content of 5 to 7%. It is bunkered and fed to air-swept Büttner ball mills where it is both ground and dried by flue-gas to about 0.5% water content. The product is about 95% through 180 mesh (4900 mesh per square centimeter) and 65% through 240 mesh (10,000 mesh per square centimeter). So far as the extraction is concerned, the fineness of the coal is not very important - they could use 0 to 10 mm size for example. However, in order to pump the mixture they found it necessary to pulverize the coal. The pulverized coal is stored in bunkers and fed by volume (on a rotating plate) to agitated mixing kettles as the solvent is added.

The mixing kettles are steam-heated, of 50 cubic meters capacity each, and are maintained at 60 to 100° C. This temperature is not critical. The mixing is a batch process and four kettles are available. The coal concentration is determined in each batch before being transferred to the extraction tubes. A new batch is started about every 3 hours. The coal-oil mixture is taken from the kettles by Atlaswerke transfer pumps to high pressure pumps (150 atm) each having 15 cu. meters per hour capacity for introduction to the preheating and extraction tubes. The three high pressure pumps had been destroyed, but were said to have been of conventional design.

The preheating and extraction tubes are assembled in a fire-brick furnace heated by flue-gas circulation. The temperature of the gas is maintained at about 550°C and the gas is only in direct contact with the preheater tubes which at the entrance of the coal-oil mixture are at about 100°C and at the end of the preheating zone about 430°C. The preheater tubes completely surround the extraction chamber itself which is thus effectively thermostated. The material entering the extraction chamber is at about 430° and it leaves at about 415°C, the drop in temperature being explained as heat necessary for the depolymerization reactions. The total time from entrance to preheater to outlet of extraction chamber is about 1 hour, 20% of the time being in the preheater.

If a much shorter time of treatment were used, the product could not be filtered, because of insufficient depolymerization.

Both preheating and extraction tubes are hairpins or inverted "U"'s about 17 meters high. The preheating tubes are of uniform diameter and are Mannesmann finned tubes of N-8 steel, 70 mm i.d., and 102 mm o.d. designed for withstanding 300 atm pressure which is higher than necessary. Forty of these preheater tubes are shown in Ruhröl drawing BK 16-2. The extraction tubes have the down-leg 120 mm i.d. and the up-leg 185 mm i. d. and a wall-thickness of 8 mm. The up-leg was made of larger diameter because of anticipated effects due to gas evolution but this is not now believed necessary. As last operated there were 24 hairpins in the extractor sections of the furnace. Originally 48 extraction hairpins were provided but experience showed 24 were sufficient and one reactor tube chamber was empty when observed. With 48 tubes bad coking occurred in the last tubes. There appears to be an optimium time in the extractor section, too long a time causing excessive coking and too short a time giving a product not readily filtered. It is necessary to close down every 2 to 3 months and remove the extraction tubes for cleaning. Replacement by spare tubes takes 5 days. The fouled tubes are cleaned by a mechanical borer since the coke formed on the inner surfaces is very hard. No sludge traps or boots were considered necessary at the bottom of the hairpins.

From the extraction chamber, the material goes to a vessel where it is cooled by water to 160 to 170°C and discharged thru a pressure-reducing valve which drops the pressure from 100 atm to 1 atm. The gas formed in the process is mixed with other gas in the plant. The gas is about 70% saturated hydrocarbons - mostly CH_4, 20 + % hydrogen, the balance being CO, CO_2, N_2, and H_2S, this latter being 1 to 2 grams per cubic meter. No ammonia appears in the gas. The product is stored in tanks at 150°C ahead of the filters. There has been no trouble from sludge settling out in the pipe lines of the plant.

The filtering operation is one of the most important steps. The filters consisted of pressure vessels each containing 32 filter "candles" in a vertical

position with a filtering surface about about 2 meters long. Each "candle" consists of an assembly of coarsely porous ceramic rings put together with washers. The individual rings measure:

Outside diameter	122 mm (4 13/16 in.)
Inside diameter	81 mm (3 3/16 in)
Wall thickness	20 mm (13/16 in.)
Height of ring	32 mm (1 1/4 in.)

and were said to have been manufactured from quartzite material by Schuhmacher Fabrik at Biettigheim, near Stuttgart. Dr. Broche did not know the details of manufacture, which were said to be a trade secret of Schuhmacher. Each ring was reinforced by two external welded wire bands. Experimental filter rings of more-finely-grained ceramic material with a corrugated external surface, and about 8 inches high were seen in the plant. These were said to have been less satisfactory.

Each filter vessel with 32 candles provides 22 square meters of surface and was said to have a thruput of about 16 cubic meters (or tons) of liquid per hour which is equivalent to about 90 tons of recovered solid extract per 24 hours. The plant had three filters of this type, any one of which was sufficient to handle the whole plant output. There was also an experimental filter of different design. The life of the ceramic filter rings was about 4000 filtrations, which is equivalent to 1000 hours or two months of continuous operation. They could be regenerated to some extent by washing and scraping (but not by burning) but it was preferred to replace them with new rings.

The solution of coal is forced around the outside of the "candles," the pressure being about 4 to 6 atm and the temperature being about 150°C, at a rate about 10% greater than the rate of filtration so there is some recirculation to storage. The throughput per filter is 16 cubic meters per hour. When the rate of filtration becomes low, cleaning is necessary and this occurs from 3 to 4 times per hour. The material in the pressure vessel is withdrawn and returned to storage. Fresh solvent at 150° is passed through the sludge layer on the outside of the filter and the sludge is dried to a shell on the outer surface of the "candle" by CO_2 supplied at ordinary temperature and traveling the same direction as the solution being filtered. The cake of

"Restkohle" is then broken off by a sudden increase in pressure of CO_2 to 6 or 7 atm. inside the candle. The residue falls into the conical bottom and is then transferred by conveyor to the rotary kilns for distillation. As constructed, the filtering station has a capacity several times greater than the earlier stages of the process.

The 3 rotary kilns provided also have excess capacity. The largest unit has a capacity for trating the residue from 100 tons of coal per day, fer recovery of the oil, and there are two smaller kilns. The kilns contain 6 tubes of 350 or 500 mm in diameter and 12 meters long. The tubes are heated by flue-gas so that the final temperature of the "char" is 350°C. There are chains in the upper end of the tubes for breaking up the char. As discharged, the powdered char has about 0.2% oil content, an ash content of about 30% and is used for boiler fuel.

The filtered solution - "reinfiltrat" - is stored in tanks at 150° and kept agitated. (If cooled to 20°C it could still be stirred. Dr.Broche did not know of any possible commercial use for this filtrate containing both the coal extract and solvent oil). From the storage tanks the filtrate goes to stills for separation of the solvent from the extract. The filtrate is first heated in a pipe still to about 250°C at 10 to 12 atm and is sprayed into a vacuum chamber having 40 to 50mm pressure, where the extract is concentrated from 25% to 50% content of solids. It leaves the vacuum column at about 200° and is reheated in a pipe still to about 350 to 360° at 10 to 15 atm and then goes to the final distillation in a vacuum column at 30 mm pressure. The extract discharged from the bottom of the vacuum column at 300° is said to be completely oil free, and to be as fluid as water at this temperature. It is discharged thru an electrically heated outlet onto a steel conveyor belt, where water cooling may be used.

The recovered oil is redistilled, a small residue being returned to the liquid-phase hydrogenation plant. This redistilled oil is about 1 or 2% greater in amount than the solvent used, due to some distillation of the coal during the extraction stage which more than balances oil losses in the process. The recovered solvent is a better raw material for

vapor-phase hydrogenation for gasoline than the original solvent. As shown in the flowsheet, a part of the recovered solvent is returned to the hydrogenation plant and replaced by fresh middle oil. This is necessary to maintain an adequate supply of disposible hydrogen in the solvent. If the same oil was re-used 4 or 5 times, it would no longer work well. Dr. Broche recommends this coal extraction process only in connection with a hydrogenation plant.

The coal extract has a volatile matter content of more than 40% (the exact percentage is hard to determine because of foaming) and a melting point of 210 to 220°C. (This softening temperature is determined by placing a fragment in a capillary tube and heating in a liquid bath. The softening temperature is not sharply defined). The extract has 0.2 to 0.3% more hydrogen than the original coal, this hydrogen having been obtained from the middle oil used as solvent. Analyses have shown the following ranges: C, 88.50 to 89.90%; H, 5.20 to 5.30%; N, 1.50%; S, 1.00 to 1.10%; O (by diff.) 3.75 to 2.15% and ash, 0.05%. It is 100% soluble in pyridine, cresol, and cresol-tetralin mixtures, and 50% soluble in benzene. Recovery on the basis of the starting coal is about 70%. When nitrated to destroy caking properties and to lower the ignition temperature, it gives a product suitable for carbon-dust Diesel engines. It was said to work very well for this purpose. However the actual commercial use was to produce carbon for electrodes by high-temperature carbonization, in which it was charged to regular by-product coke ovens as a solid. It was not necessary to melt it and spray it in, as in the carbonization of pitch.

The yield of coke or carbon is about 66% based on the extract. The ash content of the coke ranges from 0.10 to 0.15%, thus being lower than either petroleum coke or pitch coke (the latter having 0.4 to 0.5% ash). The carbon sold for 180 M per ton, while pitch coke sold for only 90 M per ton. (These figures were confirmed by the A. G. der Kohlenwertstoff-Verbände at Bochum, which is a sales organization). The raw coal cost 20 marks per ton. Dr. Broche stated that they figured the price could be reduced to less than 100 M per ton of coal extract before coking, for a plant with an annual capacity of 75,000 tons of extract. Most of the carbon was used for electrode manufacture for the aluminum and ferrous industries. However it was stated that it was an "excellent graphitizing agent" for electric steel.

The cost of this first plant was stated to be excessive - seven to eight million marks - primarily because the capacities of the different stages were not completely integrated. For instance, 3 commercial filters were available, any one of which had enough capacity for the plant output; and 3 rotary kilns were provided, the largest of which was sufficient for the plant output. Some standby equipment was doubtless desirable.

For information on the hydrogenation plant at this target, and some additional data on the Pott-Broche coal-extraction process, see the report:

"A visit to Bottrop-Welneim Hydrogenation Plant" Target No 30/4.11 Reported by C. Cockram, British Ministry of Fuel and Power, 8 August, 1945.

which covers the earlier visit of a team which removed a large number of drawings and documents.

ITEM NO. 30
FILE NO. XXXI - 30
Solid Fuels 27

Copy 1

COPY NO. ~~188~~
Solid Fuels Rept No 27

~~RESTRICTED~~

KRUPP - LURGI LOW-TEMPERATURE CARBONIZATION PLANT WANNE - EICKEL

Linny + Rose

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KRUPP-LURGI LOW-TEMPERATURE CARBONIZATION PLANT OF FRIED-KRUPP A.G. AT WANNE-EICKEL NEAR BOCHUM.

Reported by

H. H. LOWRY, T.I.I.C.
H. J. ROSE, T.I.I.C.

CIOS Target No. 30/5.02 and 30/88

FUELS and LUBRICANTS

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

RESTRICTED

8 p.
m.d.

TABLE OF CONTENT

Subject	Page No.
Location & Condition of Target	1
Object	1
Personnel Interviewed	1
Conclusions	1
Introduction	2
The Low-Temperature Carbonization Plant At Wanne-Eickel	3
Coal used	3
Charging the Ovens	3
Construction of the Ovens	4
Heating the Ovens	5
Time for Carbonization	5
Coke	5
Byproduct recovery	6
Cost of Plant and Operation	7
Use of Coal-Washery Refuse in Boiler Plant.	8

KRUPP-LURGI LOW-TEMPERATURE CARBONIZATION PLANT OF FRIED. KRUPP A.G. AT WANNE-EICKEL NEAR BOCHUM

PERSONS MAKING TRIP:

H.H. Lowry (U.S.)
L.L. Newman (U.S.)
H.J. Rose (U.S.)
E.T. Wilkins (Brit.)

LOCATION AND CONDITION OF TARGET

Low-temperature carbonization is only one of a group of operations carried out in Fried. Krupp plant at Wanne-Eickel about 4 miles north of Bochum. While there was considerable bomb damage to the plant as a whole, the low-temperature plant, outside of the by-product recovery system and accessory coal and coke handling equipment, was not badly damaged. Dr. Müller estimated that the new block of ovens built in 1943 could be put back into operation in 3 to 4 months with an annual coke production rate of 80,000 to 100,000 tons.

OBJECT

To obtain first hand information on the construction and operation of the Krupp-Lurgi low-temperature carbonization plant.

PERSONNEL INTERVIEWED

Dr. Fritz Müller, a director of F. Krupp A.G. and inventor of the process.

Dipl. Ing. Erich Combles, Gen. Mgr. of Wanne-Eickel.

Dr. Ing. Wolfgang Junkermann, Chief Engineer for Coal "Veredlung", F. Krupp A.G. Essen.

Dr. Ing. H. Wittig, Engineer for Coke-oven Plants, F. Krupp, A.G. Essen.

CONCLUSIONS

The Krupp-Lurgi low-temperature plant can be used for producing a semi-coke from a wide variety of coals or briquets. Improvements in design were incorporated in the 6 blocks of new ovens built in 1943 from

experience gained with those built in 1937. Further improvements would be made in a new plant. The method of charging the ovens was being changed when operations ceased due to bomb damage. The semi-coke is a 50% porosity fuel which is a highly reactive, easily ignited, smokeless product of 8 to 10% volatile matter content, that may have many applications.

Dr. Müller stated that it was estimated that a 1000 ton per day plant could be built at approximately the same cost as a high-temperature carbonization plant of the same capacity. Some cost figures are included in this report. The heat requirements of low and high-temperature plants are essentially equal.

INTRODUCTION

It was stated that 11 "commissions" had previously visited the plant and that original records and drawings were not available, but might be secured from Lurgi Gesellschaft für Warmetechnik in Frankfurt am Main. A report on the plant is included in the "Report on Plant of Krupp Triebstoffe Werke G.m.b.H., Wanne-Eickel, Germany", Target No.30/5.02 Fuels and Lubricants by A.R. Powell dated 22 June, 1945.

Dr. Müller, who throughout was mot co-operative, stated that the following papers gave a background both of laboratory testing of coals for the Krupp-Lurgi L.T.C. and development of the process:

Ref. 1. "Uber Betriebserfahrungen mit der Steinkohlenschwellanlage Bauart "Krupp-Lurgi" auf Schachtanlage Amalie der Fried. Krupp Aktiengesellschaft, Bergwerke Essen by K. Brüggemann in Technische Mitteilungen Krupp, 1938, Heft 3, pp. 50-58.

Ref. 2. "Laboratoriumsapparatur für Steinkohlen-schwelung nach dem Heizflächenverfahren" by K. Scheeben in Technische Mitteilungen Krupp, 1940, Helft 1, pp. 39-44.

He also stated that a paper on the process, with detailed description of the equipment and results, was being prepared and should be ready for publication, if permitted, by the first of August, 1945.

The first ovens embodying the principles used at Wanne-Eickel were built at Zeche Helene, Essen-Altenessen, with a throughput of 4 tons of coal per 24 hours. In

April 1936, a larger plant with a throughput of 40 tons per day was built at Zeche Sälzer-Amalie. This was followed by Wanne-Eickel where 32 ovens were built in 1937 and 24 ovens in 1943. Each oven has 6 cells which hold about 0.5 tons apiece. The rated capacity of Wanne-Eickel is 17,000 tons of semi-coke, 100 tons of fuel oil (Heizöl) and 160 tons of motor fuel (Schwelb-enzin) per month, of which 7,200 tons of semi-coke, 500 tons of fuel oil, and 97 tons of motor fuel were obtained from the 1943 ovens. A plant had been built at Velsen with a rated capacity of 50,000 tons per year which it had been intended to increase to 200,000 tons per year.

The Low-Temperature Carbonization Plant at Wanne-Eickel

Coal Used:

The coal charged to the ovens was a mixture of 25% from the Hannibal (F. Krupp A.G.) mine of about 22% volatile matter content (Muck method) and 75% from the Bismarch (Gelsenkirchener Bergwerks-A.G.) mine of from 33 to 34% volatile matter content. On the average, the mixture contained about 5.4% ash, 8 to 10% water and 30.0% volatile matter. Fine grinding was not desired since a high density of the charge gave increased through-put and a better product. Normally, the size analysis of the charge was: 0 to 1 mm, 30 to 40%; 1 to 3 mm. 30 to 40%; 3 to 6 mm. 20 to 30%; and 6 to 10 mm. about 5%. The bulk density of the charge, unstamped, was 0.770 tons per cubic meter (48 lbs. per cu.ft).

Charging the ovens:

Each oven has 6 cells, with an average width of 84 mm. and the 6 cells were charged simultaneously. The correctly predetermined volume of coal was fed in a stream into each cell by passing through rolls. As the coal was fed in, a stamping bar, the length of the oven and of somewhat smaller width, was raised and lowered. The density of the charge was thus increased by about 8%. The time required was about 1.5 mm. The top surfaces then had to be cleaned before the cover was replaced on the oven; thus cleaning took about 2 min. and was a disagreeable operation since within about 2 minutes after the coal first entered, the tar fog began to be liberated.

A new charging machine had been built and a full-scale model tested. With this machine charging could be made in 15 seconds and the increase in density above that

of the unstamped coal was 15%. This was obtained by a "free" fall of the coal charge of 15 feet from a hopper through guiding slots into the individual cells. It was claimed that a uniform density from top to bottom of the cell was achieved by this method and stamping was not required. A "free" fall of 25 feet was said to give a 25% increase in density but the charging machine became too unwieldy. With this method of charging, the tar fog nuisance was avoided.

Construction of the ovens

Each oven contained 6 cells, 3,200 mm. long and 2,100 mm. high. The width at the top was 76 mm. and at the bottom 100 mm. The capacity per cell was 0.585 cu. meters and per oven 3.51 cu. meters. The cells were separated by heating flues, the walls being 24 mm thick "II" steel boiler-steel plate. An all-welded construction was used. The heating flues were of a cellular construction where the maximum dimension of a cell was not more than about 3 times the thickness of the webbing. Due to the taper of coal cells, a taper in the reverse direction existed in the flues which were narrower at the bottom than at the top. Since the heat requirements at the bottom were greater than at the top, the hot gas entered at the bottom and the average temperature at the bottom was about 10°C higher than at the top.

The steel used had a strength at room temperature of about 50 kg per mm^2 and this rapidly decreased above about 300° to about 0.5 kg per mm^2 at 600°C. Some difficulty had been encountered with distortion of the walls of the end flues but this was remedied by adding special supports within the refractory housing that surrounded the metal chambers for heat insulation. It was stated that no difficulties due to carburization, decarburization or oxidation were encountered. Some of the ovens were not cooled down for 5 or 6 years. The wall thickness decreased about 0.5 mm per year and experience indicated a life of 10 or 12 years could be anticipated.

Sometimes local buckling of the wall occurs, and they have developed two types of equipment, one mechanical and the other hydraulic, to flatten the metal walls. They start to use this after the ovens are 2 or 3 years old.

The cover plate was water-sealed and did not make a tight seal against the top of the metal structure, thus providing a plenum chamber connecting to the gas-offtake. The bottom door stood about 10 feet above the floor level below, permitting a railway car to be moved under the oven for receiving the discharged coke. The bottom door was

also water-sealed. Inside the bottom door was a movable metal grid or grating which completely closed off the bottom openings of each cell. The grid could be moved to one side by a chain and pulley so that the coke could be pushed.

Heating the ovens

The heating of the newest ovens was by recirculation of flue gas obtained by burning the tail gas (Restgas from the Fischer-Tropsch plant. This tail gas had a net calorific value of 1800 to 2000 kcal per normal cubic meter (192-213 Btu per cu. ft. at 60°F. dry). It is important to avoid excess air for combustion so as to maintain a reducing atmosphere in the heating flues. The gas entering the bottom of the flues was at about 620° and leaving the top of the flues at about 570 to 580°C. On the average the gas recirculated 12 times, i.e. make-up gas for maintaining temperature was about 8.5%. Both the heating gas and the air for combustion are preheated by the waste gases. There was a separate burner for each block of 4 ovens. The heat requirement per kg of coal with 10% water content was stated to be 540 to 580 kcal, i.e. 972 to 1044 Btu/lb. When starting up a plant, they allow a week to heat up the ovens.

Time for Carbonization:

The total time for carbonization is 5.34 hours, including 1.5 min. for charging (the new method will reduc this to 0.25 min), 2 mins. for cleaning the top surface of the ovens and closing the top cover, and 3-5 mins. for discharging the coke. With this time of carbonization the capacity per oven per day, using stamped coal with a density of coal of 835 kg. per cu. meter, is 11.2 tons per day. With the new charging device the capacity is expecte to be increased to about 12.0 tons per day owing to the greater density of coal charge in the oven.

Coke

The coke is pushed mechanically and received in a car for quenching with liquor and delivery to the coke wharf. The coke is collected as slabs that have no center parting line. It is fed by conveyor belt to a breaker specially designed to produce a minimum of fines under 10 mm. in size. The slabs are carried over a set of eccentric rolls and as they pass, pusher bars are thrust by a system of cams against the slabs cracking them into large lumps. It is stated that this procedure produced on 7% material less than 10 mm. as compared with 20% when a roll crusher is used.

The yield of dry coke based on dry coal charged at Wanne-Eickel was 84%, of approximately the following size distribution: 40 to 90 mm. 70%; 20 to 40 mm. 11%; 10 to 20 mm. 7%; and below 10 mm. 12%; (this latter figure includes the fines from discharging and handling as well as those produced in crushing). The large coke contained about 6.5% ash, 3 to 5% water, and 7 to 8% volatile matter. Its porosity was approximately 50% and it had a high reactivity and was easily ignited. In the Micum drum test for coke strength, the percentage of coke greater than 40 mm. in size was about 65%.

Because of its properties, the coke was regarded as having special value for production of gas. Its high reactivity permits water gas formation at lower temperatures than high-temperature coke. It was stated that the $CO:H_2$ ratio in the gas from the semi-coke was 1:1.5 as compared to 1:1.25 when H.T. coke is used, thus providing a more favorable gas for Fischer-Tropsch synthesis. It was claimed that in their experience a combination of L.T.C. with Fischer-Tropsch gave a total oil yield of more than 30% greater than H.T.C. with Fischer-Tropsch. Another use suggested was in production of ferro-silicon. It was claimed to be an excellent smokeless domestic fuel and could be used advantageously by blending with H.T. coke for central heating. The smaller sizes were an excellent fuel for mobile gas producers.

Two papers published in 1937 were recommended for information on use of semi-coke:

Ref. 3. "Steinkohlenschwelkoks als Rohstoff für chemische und metallurgische Prozesse" by W. Demann in Glückauf, 1937, Heft 49, pp. 1101-1106.

Ref. 4. "Wassergaserzeugung aus Steinkohlen-Schwelkoks" by G. Wilke, in Technische Mitteilungen Krupp, 1937, Heft 2, pp. 44-49.

Byproduct Recovery

The tar and gas enter the primary cooler at about 190° and heavy tar is collected therein. They then go to a Lurgi-Cottrell precipitator at about 150° for removal of tar fog and to an indirect cooler for collection of light tar. These three tars are combined into low-temperature tar (Heizöl "5) and, after removal of the benzin, amount to 6.4% on the dry coal basis. The yield analysis, and physical properties depend on the coal charged, and/or the coal mixture described in an earlier section of this report, were said to be as follows: sp. gr. at 20°, 1.06; viscosity at 20°, 40° Engler and at 50°, 5° Engler; softening temp. (Stockpunkt) 5°C;

flash point, 96°; insoluble in benzene, 0.7% by weight and in amiline 0.15% by weight; tar acid content, 30% by volume; pitch of 70° softening point by Krämer-Sarnow, 35% by wieght; heating value 9250 kcal per kg (gross) and 8900 kcal per kg (net). Distillation analysis:

Start 98° to 170°	1.5% by volume
200°	4.2
230°	23.0
270°	40.0
300°	53.0
360°	66.0

The raw heavy tar when dried to less than 1% water content was used by the Navy without further refining as a fuel. The mixability of the L.T. tar with other fuel oils has been studied and the results published in

Ref. 5 "Mischbarkeit von Heizölen"

by W. Demaun in Glückauf, 1940, Heft 5, pp 61-68.

After tar removal the gas goes to the ammonia washer and the dilute ammonia liquor is used for quenching the coke. The gas may then either be sent directly to a gas holder or compressed to 10 atm, cooled, freed of sulfur, and then pass to a Feld washer for recovery of benzine. The wash oil used in the Feld washer is the light tar condensate from the indirect cooler which has been debenzinized. The benzine recovered amounts to 1.25% based on the dry coal charged and, at Wanne-Eickel, had a sp. gr. at 20° of 0.820; octane number 90; phenol content 0.8% by volume; base content, 0.5% by volume; aromatic content, 50% by volume; olefin content, 15% by volume; distillation begins at 50° and 25% by volume distills up to 100° and 96% up to 195°C. The Feld washer reduced the benzine content of the gas from 70 grams per normal cubic meter to 3.

The gas yield amounted to 95 normal cubic meters per ton of dry coal and a typical analysis of the gas produced at Wanne-Eickel is: CO_2, 2.6%; sat. hydrocarbons, 2.4%; O_2, none; CO, 3.8%; H_2, 25.7%; CH_4, 59.5%; N_2, 6%. The gross heating value is about 830 Btu per cu. ft. and the net, about 750.

Cost of Plant and Operation

The following incomplete information was given from memory by Dr. Müller and concurred in by Dr. Junkerman

The entire cost of the Krupp-Lurgi plant at Wanne-Eickel was about 5,000,000 marks. Thirty-two ovens were built in 1937 when labor was relatively cheap and 24 ovens in 1943 when labor was relatively expensive. The new plant of 24 ovens and the direct equipment for this operation cost about 2,000,000 marks.

About 100 men are required for the operation: 8 men on each of 3 shifts for the 24 new ovens, an equal number on the 32 old ovens, one man on each of 3 shifts in the bunker house, and the balance in the byproduct plant. The wages paid were 8 to 11 marks per day.

Use of Coal-Washery Refuse in Boiler Plant:

Dr. Müller stated that the boiler plant at Wanne-Eickel had 3 boilers. Two of these were fired with gas, while the third was fired with coal washery refuse of about 60% ash. This was burned on a travelling-grate stoker with special agitating device which gave the refuse a rotary motion on the grate, to ensure the burning out of the combustible.

ITEM NO. 22
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GERMAN CARBIDE, CYANAMIDE AND CYANIDE INDUSTRY

McBurney, Sinclair & Sutherland

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COMBINED INTELLIGENCE OBJECTIVES
SUB - COMMITTEE

XXVII-92

RESTRICTED

GERMAN CARBIDE, CYANAMIDE AND CYANIDE INDUSTRY

Reported by

Lt.-Col. W.G. McBurney
Lt.-Col. G.W. Sinclair
Lt.-Col. H.S. Sutherland

CIOS Black List Item 22
Miscellaneous Chemicals

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

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TABLE OF CONTENTS

Subject	Page No.
Calcium Carbide for Acetylene Generation	
Alexander Wacker Werke - Burghausen	
Investigating Personnel	1
Personnel Interviewed	1
Present State of Factory	1
Production Capacity Carbide Furnaces	1
Activity During War Time	1
Electrical Characteristics, General	2
Electrode Adjustment	3
Furnace Data	4
Generation of Acetylene	5
Calcium Carbide for Cyanamide	
Süd Deutsche Kalkstickstoff Werke - Hart, Bavaria	
Investigating Personnel	6
Personnel Interviewed	6
Present State of Factory and Equipment	6
Present Activity of Plant	6
Activity During War Time	6
Destination of Carbide Produced	7
Number and Capacity of Furnaces	7
Gas Collection from Furnaces	7
Transport of Carbide	8
Operating Data	8
Calcium Carbide for Acetylene	
I.G. Farbenindustrie - Ludwigshafen	
Investigating Personnel	10
Personnel Interviewed	10
Present State of Factory	10
Furnaces Installed	10
Design of Furnaces	10
Particulars of Electrodes	11
Special Tapping and Cooling Equipment	11
Operating Data	12
Activity During War Time, see Exhibit 2	31
Acetylene Generation	12

RESTRICTED

TABLE OF CONTENTS

Subject	Page No.
Calcium Carbide	
A/G für Kalkstickstoffdünger, Knapsack	
Investigating Personnel	13
Personnel Interviewed	13
Present State of Factory	13
Furnaces Installed	13
Design of Furnaces	14
Activity During War Time	14
Operating Data	14
Acetylene Generation	15
Calcium Cyanamide	
Süd Deutsche Kalkstickstoff Werke - Trostberg, Bavaria	
Investigating Personnel	16
Personnel Interviewed	16
Present State of Factory	16
Use of Linde Oxygen-Nitrogen Plant	16
Description of Process	17
Operating Data	18
Other Activities Suspected	18
Calcium Cyanamide	
A/G für Stickstoffdünger - Knapsack	
Investigating Personnel	19
Personnel Interviewed	19
Present State of Factory	13
Description of Granulating Process	19
Description of Powdered Process	20
Nitrification	21
Operating Data	21
Capacity of Plant	21
Calcium Carbide	
Société Electrométallurgique de Montricher France.	
Investigator	23
Personnel Interviewed	23
Object of Investigation	23
Electric Supply Porto-Marguera	23

RESTRICTED

TABLE OF CONTENTS

Subject	Page No.
Calcium Carbide	
Société Electrométallurgique de Montricher France (contd.)	
Characteristics Miguet Furnace	24
Transformer Details	25
Furnace Details	26
Electrode Adjustment	27
Electrical Contacts to Electrode	27
Operating Data	28
List of Installations	28
Remarks on Miguet System	29
General Remarks on Carbide and Cyanamide	30
Sodium Cyanide	
I.G. Farbenindustrie - Ludwigshafen	
Investigating Personnel	32
Personnel Interviewed	32
Present State of Factory	32
Nature of Process Employed	33
Capacity of Plant	34
General Remarks on German Cyanide Industry	34

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Calcium Carbide and Acetylene Generation

Dr. Alexander Wacker Werke, Burghausen

Co-ordinates 788640

Map Sheet No.X7

CIOS Trip 399

Investigating personnel: Lt. Col. W.G. McBurney
" " G.W. Sinclair
" " H.S. Sutherland

Personnel interviewed: Dr. Hess, Manager
Ing. Kallas, Plant Superintendent

This plant was visited and inspected on June 10th and 11th, 1945, and both buildings and equipment were found to be undamaged.

The works comprise two independent sections, both on the same site. The one deals with the manufacture of calcium carbide and the transformation of this to acetylene, whereas in the other acetylene is transformed into other products comprised in the field of synthetic resins and plastics.

At the time of our visit the carbide section was operating intermittently on a very reduced scale due to the lack of raw materials, namely, lime, coke and anthracite coal.

The carbide furnace equipment comprises three units designated Nos. 2, 3 and 4. These three furnaces have a total potential capacity of approximately 100,000 metric tons of carbide per annum, but since 1942 production appears to have fallen short of the full capacity, namely, for 1943, 56081 metric tons. For 1944, 67644 metric tons and for 1945, up to May, only 7614 metric tons.

All three furnaces are equipped with the Söderberg system of continuous electrode, the external sheet steel shells for which are made on the site but the plastic mass is imported from elsewhere already prepared.

No.2 furnace was constructed in 1922 and is rated at 8000 KW. The three electrodes are arranged in line and are hand

operated. The construction may be regarded as somewhat out-of-date, giving a power factor of only 0.88.

No.4 furnace is rated at 11000 KW and represents an improvement in design and construction on No.2. In this case the axes of the electrodes are equidistant from one another on the three points of a triangle. The power factor is 0.94.

No.3 furnace, which is rated at 20000 KW, is worthy of special study, inasmuch as the construction and general layout embody some unusual features, particularly as regards the electrical features, as the result of which the high power factor of 0.95 is obtained.

The primary tension on all three furnaces is 10,000 volts at 50 cycles, separate transformers with tappings for adjustment of the secondary voltage being used.

All three furnaces are of the open type and their construction does not embody the use of devices of more or less recent origin for the partial or complete collection of fumes and carbon monoxide.

Referring particularly to furnace No.3, certain features of design and construction call for special remark.

In the first place the high power factor, namely 0.95, is due, firstly to the arrangement of the electrodes, equidistant from one another on the points of a triangle, and secondly, that the busbars from the transformers to the flexibles are symmetrically interlaced, and the phases separated only where the busbars join the flexibles. To this end three sets of busbars consisting of copper tubes, water cooled, are led to points midway between the electrodes. These tubes are of flat section for the greater part of their length, which permits of close grouping, and are separated by solid insulating material about half an inch thick. In spite of the relatively long busbars the symmetrical interlacing enables an exceptionally high power factor to be obtained.

The flexibles connecting the extremities of the busbars to the electrodes consist of bundles of flat copper strip, nickel plated to prevent oxidation.

The method of adjustment of the electrodes as also the

periodic displacement of the ring carrying the contact plates, is unusual. It should be remarked that the downward feed of the electrode is controlled by an hydraulic cylinder, the movement of which can be either effected by hand operated or electrically controlled valves from a constant pressure reservoir. Automatic control following voltage variation is effected by means of a device based on the Thury principle.

In order to make the periodic adjustment of the contact plates as the electrode is consumed, an abutment is lowered to bear on the top of the upper section of the electrode casing. Upward movement of this abutment is prevented by means of iron rods inserted into holes in two vertical channels fixed to the structure of the building. The plunger of the hydraulic cylinder is provided with a heavy cross frame from which two insulated rods descend. These rods are attached to the ring which carries the contact plates, and by the upward movement of the hydraulic plunger the contact ring and plates can be moved upwards for a space of 1600 m/m. In this operation the employment of the "Wisdom" ribbon is unnecessary. It is claimed that the copper contact plates suffer practically no wear and last indefinitely.

In the case of furnace No.3, eight contact plates are used, and for furnaces Nos. 2 and 4 six are used. These plates are pressed tight up against the sheet steel casing of the electrode by heavy volute springs inserted in recesses in a massive steel ring surrounding the electrode.

An exceptionally high output of carbide per KW day is claimed for this furnace, when anthracite alone is used, namely 8 Kg. of 300 litre grade, whereas when using all coke the output might fall below 7 Kg.

In the following tables all essential data relating to the three furnaces are given:-

Characteristics	No.2	No.3	No.4
Transformers			
Number and KVA	3 x 3400	3 x 10000	6 x 2000
Makers	B.E.W.	S.S.W.	A.E.G.

Characteristics	No.2	No.3	No.4
Transformers (continued)			
Type	WEO 4000/15	EMU 1524/10	OT.ak
Primary volts	10,000	10,000	1,000
Secondary volts	123/143/163	115-165 170-190	112/152/156
Primary amps	340	1000	200
Secondary amps	20800	60000 52600	12800/15300 17880

Furnace	No.2	No.3	No.4
Max load KW	8000	20000	11000
Full normal load KW	7800	19000	10800
Electrode amperes	40500	64000	41500
Volts to neutral	68	105	92
Secondary volts	123	185	156
Power factor	0.88	0.95	0.94
Electrode centres m/m	1930	2550	2200
Electrode dia. m/m	920	1250	920
Electrode section c/m^2	6650	12250	6650
Amperes per c/m^2	6.1	5.23	6.25
Weight of electrode Kg/M	1150	1900	1150
Contact plates	6	8	6
Length of contacts m/m	1500	1350	1500
Width of contacts m/m	360	400	380
Electrode travel m/m	1500	1620	1500
Max. spring pressure tons	20	20	20
Free movement springs m/m	50	60	60
Lifting speed cm/min.	50	35	45
Down pressure tons ca.	12	16	10-12
Fixed secondary conductors, pipes m/m	8 x 60/45	16 x 75/45	12 x 60/45
pipe section	round	flattened	round
Section flexibles m/m	100 x 1.3	150 x 1.3	100 x 1.3
Flexibles per packet	20	13	10
Packets per phase	12	32	24

The carbide produced at this plant was used exclusively for the production of acetylene. It was reported that some had been

shipped to other factories but always for the production of acetylene.

The largest acetylene generator of the I.G. "dry" type is installed in this factory. At least 150 metric tons of carbide crushed to 0 - 2 m/m can be treated per day in this single unit.

The generator consists of a cylindrical steel vessel some 12 feet in diameter and 20 feet overall depth. The axis of the vessel is vertical and the interior is provided with several horizontal trays, as also with a heavy central shaft, operated by geared electric motor. To this shaft horizontal arms are fixed furnished with scraper plates so arranged that the carbide from the centre of one tray is slowly scraped to the periphery, where it falls to the tray immediately below and is then scraped to the centre. The principle of operation is precisely the same as that adopted in the well-known stage furnaces for the roasting of pyrites.

Several pipes for the supply of water are fitted on the upper cover, each pipe being provided with appropriate regulating valve, but the greater part of the water is supplied to the upper trays, and a temperature maintained between 85° and 90°C. Under these conditions the tendency to form organic sulphur compounds is diminished and after passage through scrubbing towers a relatively pure acetylene results.

The hydrated lime resulting from the decomposition of the carbide leaves the generator with a water content of from 5% to 6%. It can be briquetted and for this purpose an extrusion type of briquetting machine with a daily capacity of about 100 metric tons is installed. After calcining the briquettes may be used for further carbide production. This course, however, is not to be recommended as the impurities in lime used repeatedly in the operating cycle have a decided tendency to build up. Wherever possible, therefore, such lime is disposed of in the neighbourhood for agricultural purposes.

Calcium Carbide for Cyanamide

Süd Deutsche Kalkstickstoff Werke
Hart - Bavaria

Co-ordinates 623608

Map Sheet No.X7

CIOS Trip 399

Investigating personnel: Lt. Col. W.G. McBurney
Lt. Col. G.W. Sinclair
Lt. Col. H.S. Sutherland

Personnel interviewed: Dr. Krämer, Commercial Director
Ing. Reppmann, Plant Superintendent

The carbide plant of the above-named company at Hart was visited and inspected on June 12th, 1945.

The damage to buildings and equipment was of a minor nature, capable of easy repair, and would not prevent the rapid re-establishment of manufacturing operations.

At the time of our visit no carbide was being manufactured, owing to the lack of raw materials and the difficulties of transport. There was, however, on hand a stock of some 7000 metric tons of carbide stored in transport containers referred to later.

The full year capacity of the plant is approximately 230,000 metric tons of carbide of 80% grade. In 1943 the production reached 211,342 tons, but in 1944 only 190,148 tons were manufactured. In January 1945 the output was 5,930 tons, after which manufacture ceased completely.

The power is normally drawn from hydro-electric stations in the vicinity, and we were told it was usual to shut down for about six weeks during the winter, due to lack of water power. The records for 1943 show no such break, but in 1944 no carbide was produced in the months of January and February.

The entire make of carbide was formerly shipped to the company's other factory at Trostberg, and converted into calcium cyanamide. During the last few months of the war, however, much of the carbide produced was diverted to the I.G. Factory at Gendorf for the manufacture of organic chemicals produced from acetylene.

The furnace equipment consists of six units as follows:-

1	furnace of	24500 KW
2	" "	18500 KW
1	" "	21500 KW
2	" "	9500 KW
Total		102000 KW

One of the foregoing furnaces was under repair and a seventh furnace of 24000 KW was in course of construction.

All furnaces are fed from three phase transformers installed above and very close to the electrodes, so that the conductors are very short. In spite of this, however, the power factor is low, namely about 0.76.

The electrodes on all furnaces are of the solid pre-baked type, supplied by Plania Werke and Siemens, and are of rectangular section. In the case of the large furnaces the section of each electrode is 3000 x 600 m/m. In all cases the electrodes are arranged in line, and when burnt down the short "stubs" are thrown to waste.

In each furnace an arrangement for the partial collection of furnace gases is installed. This consists of four inverted troughs, two placed between the electrodes and two between the outer electrodes and the side walls of the furnace. These troughs, which are of rooflike section, are made up of closely spaced water cooling pipes embedded in a cement-asbestos mixture. The troughs are connected to a common header which is coupled to a suction fan by which the fumes and gas are exhausted and blown into a chimney stack. The furnace charge is piled up so as just to cover the angular tops of the troughs, thereby making a more or less gas tight seal in contact with the electrodes and the furnace walls. Not more than 70% of the carbon monoxide liberated is caught, and the device cannot be considered as highly efficient. Moreover, explosions have

from time to time occurred, due to cavitation of the furnace charge under the troughs.

As already mentioned, the crushed carbide is shipped from the factory to other plants. For this purpose steel containers, each of 40 metric tons capacity, are employed. These containers are of cylindrical form, with one conical end fitted with a bolted cover with air tight jointing. For filling the containers are placed vertically, and the crushed carbide fed in through the conical end. The closed containers are then placed on special flat cars for transport, and on arrival at their destination the sealing covers are opened, the containers lifted, and by means of a specially constructed crane the containers are tipped and the contents discharged into storage hoppers. The system has been well thought out and offers not only a cheap method of handling large quantities of carbide in bulk, but also ensures complete protection against hydration during transport.

Operating data

Grade - 79% (Taphole) 75.42% (shipped)

Raw materials per 1000 Kg. crude carbide

Lime	923.68 Kg.	Analysis CaO - 94.34, CO_2 - 1.22 H_2O - 0.71
Coke	393.96 Kg.	Analysis H_2O - 1.92, Ash 9.67 C - 89.41
Anthracite	146.63 Kg.	Analysis H_2O - 3.42, Ash 5.78, C - 90.80
Mixed Carbon	540.59 Kg.	
Electrodes	31.22 KG.	
Pure Lime/ Crude CaC_2	871.34 Kg.	
Crude CaC_2/KWD	7.546 Kg.	
Pure CaC_2/KWD	5.594 Kg.	
KWH/Crude CaC_2	3187 KWH per Kg. (1000).	
KWH/Pure CaC_2	4291 KWH per Kg. (1000).	
C/Crude CaC_2	466.59 Kg. per ton	

The lime used is purchased in the burnt state, and brought into the factory in heavy steel rectangular containers provided with weatherproof hinged steel covers. The containers are furnished with shackles to facilitate handling by crane. It is estimated that each container will carry about 15 metric tons of burnt lime in the form of pieces averaging five to six inches

cube. The containers are carried in pairs on specially constructed flat cars.

With the exception of the means provided for the transport of carbide, the equipment of this factory calls for no special mention. Indeed the whole installation, although in good shape, may be considered as somewhat out-of-date.

Calcium Carbide for Acetylene

I.G. Farbenindustrie, Ludwigshafen

CIOS Trip 399

Investigating personnel: Lt. Col. W.G. McBurney
Lt. Col. G.W. Sinclair
Lt. Col. H.S. Sutherland

Personnel interviewed: Dr. Ambros, Director, Organic Section
Dr. Alt, Chief Assistant to Dr. Ambros
Herr Huber, Charge Engineer

This plant was visited and inspected from 14th - 18th June, 1945, inclusive. The factory forms one of the huge collection of various chemical plants of the I.G. Farbenindustrie which extends along the west bank of the Rhine, and is located at the juncture of the Meckar river.

Electrical power is supplied from independent steam power station in the vicinity of the carbide plant, and within the I.G. factory boundary, but provision is made for the supply of power from outside sources if necessary.

No carbide is packed, and the entire output is normally utilised for conversion to acetylene as the starting point for the synthesis of many organic chemicals.

The plant which has been installed since the commencement of the war consists of three carbide furnaces, each of 20000 KW capacity and has suffered so little damage that it could be re-started with practically no delay.

The design of the furnaces appears to have been the subject of very careful study, due to the fact that the molten carbide is handled in a manner developed only in Germany, and which differs from the procedure adopted in other countries. An essential feature of this system is that a single tap hole shall be used and that this shall be arranged as close as possible to the hottest zone of the furnace. To this end electrodes in line

are adopted, the tap hole being in the line of the centre electrode. Moreover, the electrodes are of rectangular section rounded on the narrow sides facing the front and back of the furnace. These electrodes are of the Söderberg type.

The conducting mass for the filling of the electrode shells is not prepared at the factory, but procured ready mixed from elsewhere. It is simply pre-heated and dropped into the shells without tamping. The electrodes are slipped by means of the "Wisdom" ribbon, provision being made to exercise a downward pressure when necessary. The height adjustment of the electrodes is affected by gearing operated electrically but controlled by hand.

The molten carbide is run from the furnace at approximately half hour intervals, from a tap hole of normal pattern. The spout of this tap hole is prolonged, however, into the form of a steeply inclined chute, which dips below the tapping floor, and enters the mouth of a long rotary kiln-like drum which is slightly inclined towards the far end. The molten carbide entering the drum, which is both air and water cooled, rapidly forms itself into a semi-solid ring, which as it cools shrinks and breaks up into relatively small fragments, and due to the inclination and slow rotation of the drum is progressively conveyed to the far end, at which point it is sufficiently cool to permit of transport by elevators and conveyors to the acetylene generating plant. It may here be mentioned that the mouth of the drum where the molten carbide enters consists of a massive copper cone, forming an integral part of the drum and tapering from the diameter of the drum, some two metres, to an opening approximately 1300 m/m diameter. This cone is also water cooled.

The drum, which is of steel, mounted on bearing rollers and gear driven, would appear to be about 80 feet overall. The construction follows very closely that adopted for cement kilns. The cooled carbide as it leaves the drum is in the form of more or less regular lumps, the major dimension of which is between 2 and 3 inches.

Inasmuch as the chute from the taphole and the cooling drum are all below the tapping floor level, piercing electrodes of the usual type are employed.

With the cooling system referred to it is of supreme importance that the entry of ferro-silicon into the drum be

avoided, as otherwise this would attack the steel shell. To avoid this contingency a small tap hole, level with the floor of the furnace, is provided, and from this the ferro-silicon is withdrawn from time to time.

It may here be remarked that the cooling system described, so far as is known, was developed and perfected at the carbide works at Piesteritz some time before the war. Indeed, the prints of the Ludwigshafen furnaces bear the stamp of Piesteritz and are dated December 1940. Although the arrangement of the furnace, with rectangular Söderberg electrodes in line, may be criticised, trial and experiment at Piesteritz may have shown that this was the best means of ensuring that tapping from one hole would not be interrupted.

The capacity of the cooling drum is approximately 6 metric tons of carbide per hour, based on tapping at half-hourly intervals. It is claimed that the fines produced do not exceed 12% and there is practically no loss in "grade".

Each furnace is fitted with a gas collecting system of the type referred to in the description herewith of the Hart factory. Approximately 200 cubic metres of gas containing 60% - 70% of carbon monoxide are collected per metric ton of carbide. This gas, however, is not utilised.

Operating data

Grade of carbide 80% to 86% CaC_2

Raw materials per 1000 Kg. of 80% CaC_2

Lime	1000 Kg.
Coke + up to 10% anthracite	630 Kg.
Electrodes	10 Kg.
KWH per Kg. of 80% CaC_2	3200
KWH per Kg. of 86% CaC_2	3500
Voltage	100 - 125
Current density in electrodes	4 - 5 Amps/cm^2

Due to the fact that the carbide leaving the cooling drum is not further reduced in size, it has been necessary to adopt a type of acetylene generator which differs from the usual I.G. form, such as described under Alexander Wacker Werke. The actual apparatus used consists of a single rotary drum, so arranged that carbide of greatly varying size can be treated. This system, however, has the defect that the acetylene generated contains a considerable proportion of organically combined sulphur, which must later be removed if the gas is to be used for organic synthesis.

Calcium Carbide

A/G. für Kalkstickstoffdünger, Knapsack

Co-ordinate 370520

Map Sheet No.R.1

CIOS Trip 474(399)

Investigating personnel: Lt. Col. W.G. McBurney
Lt. Col. G.W. Sinclair

Personnel interviewed: Dr. Bachmann, Managing Director
Dr. Maier, Director
Herr Arnet (Norwegian) Engineer
Herr Loesch, Chemist

This plant was visited and inspected on the 20th and 21st June, 1945.

The carbide section of the plant was scarcely damaged and full production could be resumed in a matter of six weeks, assuming that the necessary raw materials and electric power were available. One small furnace was actually in intermittent operation, the carbide being used to make cyanamide.

The factory lies alongside the large power plant of Knapsack, which has a generating capacity of some 500,000 KW, produced from steam, the fuel being brown coal obtained from a rich deposit in the immediate neighbourhood of the plant.

The carbide plant normally derives its power from its own steam station, but this has been leased temporarily to the power company, so that at present electric power comes from the plant of the latter.

The installation is classed under three sections as follows:-

Section No.	Type of Furnace
No.1	2 old (1915) 10,000 KW 1 new (Union Carbide type) 10,000 KW
No.2	2 large 20,000 KW 4 old 10,000 KW
No.3	2 new (Union Carbide type) 24,000 KW

All the furnaces are equipped with the Söderberg type of continuous plastic electrode, the construction and method of adjustment of which follows more or less closely the arrangement adopted in the other German carbide factories. One innovation, however, was noted, namely, the housings containing heavy volute springs, whereby pressure is brought to bear on the contact plates, are provided with pneumatic pistons, so arranged that the pressure on the plates may be wholly or partially relieved when it is necessary to alter the position of the contacts with respect to the electrodes.

In the case of all the furnaces the electrodes are of circular section, equidistant from one another, and arranged in triangular formation. The transformers are also symmetrically arranged and occupy a position above the upper platform. The phases are interlaced, but not so completely or effectively as in the case of the Alexander Wacker plant, consequently the power factor is not quite so high, namely 0.85 for the old type and 0.92 for the new furnaces.

The most interesting feature of this plant is the two large furnaces, each of nominally 24,000 KW. These furnaces are of the completely closed type, following the design developed by Union Carbide Company of America. The details of construction would appear to have been most carefully thought out, and according to reports the operating results are entirely satisfactory. The carbon monoxide and other fumes are collected by a suction fan from only one point on the furnace cover, and are at present discharged into a stack and burnt. In the operation of such closed furnaces there is always a certain danger of explosion, which may be caused by the accidental entry of air into the space containing the hot carbon monoxide under the cover. The possibility of such accident would seem, however, to have been carefully provided for.

The estimated total yearly production of this plant is approximately 300,000 metric tons. According to records, 271,808 tons were produced in 1943, but the official figures for 1944 show only eight months production, totalling 152,809 metric tons.

Operating data for all furnaces per 1000 Kg. CaC_2

Basis Carbide of 280 litres Acetylene

	All furnaces	Covered furnaces 8 & 9
Lime	982.1 Kg.	
Coke	533.1 Kg.	

	All furnaces	Covered furnaces 8 & 9
Anthracite	105.0 Kg.	
Electrodes	32.9 Kg.	22.6 Kg.
Electric current	3531.1 KWH	3334.0 KWH
Light + power	24.9 KWH	
Gas	0.22 cubic metre	
Fresh water	0.72 cubic metre	
Treated cooling water	116.08 cubic metres	
Nitrogen	7.61 " "	
Compressed air	19.68 " "	
Steam	3.15 " "	
Repairs	0.94 man hours	
Wages	4.86 R/M	

The greater part of the carbide production from this plant is employed for the manufacture of calcium cyanamide, but a certain proportion is used for conversion to acetylene, which is subsequently transformed to other chemical products.

For the production of acetylene two generators are installed. One is of the "dry" I.G. type and has a capacity of approximately 100 metric tons of carbide per day. The construction follows very closely that described under Alexander Wacker Werke.

The second generator is of the wet type, and although from the operating point of view it is satisfactory, it presents the disadvantage that the hydrated lime discharged is in the form of a slurry, and must be dried before it can be put to further use.

All the lime produced from the generation of acetylene is briquetted, and burnt for further use in three small vertical kilns, one of which is a high temperature calcining kiln.

It is admitted that the repeated use of the same lime in the process, which promotes a cumulative effect on impurities, is not to be recommended, but apparently there is no ready sale for lime for agricultural purposes in the district.

It was noted that the plant for the subsequent conversion of acetylene to other chemical products had been almost completely destroyed by a bombing raid in 1943.

Süd Deutsche Kalkstickstoff Werke

Trostberg - Bavaria

Calcium Cyanamide Plant

CIOS Trip No. 399

Investigating personnel: Lt. Col. W.G. McBurney
Lt. Col. G.W. Sinclair
Lt. Col. H.S. Sutherland

Personnel interviewed: Dr. Kramer, Commercial Director
Herr Braun, Production Superintendent

This plant was visited and inspected on June 11th, 1945.

The cyanamide plant of this company had suffered little damage and was confined to the roof of one building and to some of the electrical equipment.

No cyanamide was in process of manufacture at the time of the visit and in fact production had been suspended since November 1944.

The plant normally used for the production of nitrogen and installed by the Linde Gesellschaft of Munich had been turned over to the production of liquid oxygen, which was shipped to the Linde headquarters near Munich to make up for shortage caused by serious damage to the Linde Oxygen factory.

The carbide produced at Hart, which normally would have been used at Trostberg for the manufacture of calcium cyanamide had been diverted to Gendorf, as already mentioned, for the production of synthetic derivatives of acetylene.

The factory at Trostberg was one of the first to manufacture calcium cyanamide in the early days of the industry and although the quality of the product has progressively improved, the actual plant now used does not differ greatly from the type originally installed.

The carbide broken into relatively small lumps is received in the 40 ton rail transported containers from the carbide factory

at Hart. The contents of the containers are discharged into storage bins from which the carbide is fed to fine crushers and rotary tube mills in which it is reduced to fine powder, namely 80% through 4900 meshes per c/m². Finished but unhydrated cyanamide to the extent of 10% of the weight of carbide treated, as also 1% of fluorspar, is added before fine milling. As a protection against possible explosion the mills are kept under a constant small pressure of nitrogen.

The process of nitrification of the finely milled carbide is effected in cylindrical steel ovens lined internally with refractory tiles. The ovens are provided with luted steel covers also lined with refractory material.

The ovens are of two sizes, the smaller taking a charge of about one metric ton, and the larger 5.6 metric tons of milled carbide. The charges are contained in perforated steel baskets paper lined.

After the basket and its contents have been placed in the nitrating oven, a taper rod is withdrawn from the centre, and after closing the oven a carbon resistance pencil is placed in the tubular orifice and heated electrically. The initial heating from the centre rapidly promotes the exothermic reaction which spreads to the whole mass.

In the case of the larger ovens the procedure is such that a cylindrical cavity of about one foot diameter is provided in the centre of the contents. Moreover, provision is made for the placing of eight resistance pencils, although this number need not necessarily be used. It would appear that the combination of the large central cavity and the initial heating from several points causes the reaction to spread rapidly throughout the mass and enables the total reaction time to be very considerably shortened.

The cooling, breaking and fine milling of the finished cyanamide call for no special remarks.

The finely ground cyanamide is lastly treated with a small proportion of water, in order to eliminate the final trace of free carbide. This operation is effected in a closed cylindrical vessel provided with internal screw agitator. The vessel is kept under a pressure of nitrogen and the operation is continuous.

Before packing, the finished cyanamide is diluted with finely ground calcium carbonate and its nitrogen content adjusted to between 20.5 and 21.5% N.

Although no cyanamide was in process of manufacture, a part of the Linde nitrogen plant was in operation, and gas was being circulated through several parts of the equipment. This precaution had been taken to avoid the absorption of moisture from the air in various parts of the equipment.

It was stated that due to many improvements in the Linde system for the fractionation of air and the production of oxygen and nitrogen, the fractionating columns and their accessories could be kept in continuous operation for periods up to 300 days. In this plant high pressure compressors, ammonia refrigeration, and highly efficient apparatus for the absorption of carbon dioxide and moisture from the air are used.

Operating data

Grade of carbide, approximately	75%
Nitrification efficiency	90%
Cyanamide added to carbide during fine grinding	10%
Fluorspar added	1%

Daily capacity of plant, approximately 700 metric tons

The general upkeep of the plant has been good and manufacture could be restarted at short notice, providing supplies of carbide from Hart were available.

In the course of the inspection a party of American soldiers arrived and enquired if the company had ever engaged in the manufacture of aeroplanes or their accessories during the war. To this question Herr Braun gave an emphatic denial. Later in the day, at American Headquarters Dr. Kramer was questioned and he explained that the Government authorities had ordered the company to place certain storehouse accommodation at the disposal of a neighbouring factory manufacturing aero motors, and in this space machine tools and other mechanical appliances were installed. The space so utilised was separated entirely from the cyanamide factory, and the staff of the latter had nothing whatever to do with the motor manufacturing side. At the time of the visit two large centreless grinders were observed, one of which was quite new, and these had presumably formed a part of the machine shop equipment referred to.

Calcium Cyanamide Plant

A/G für Stickstoffdünger Fabrik

Knapsack near Cologne

CIOS Trip No.474(399)

Investigating personnel: Lt. Col. W.G. McBurney
Lt. Col. G.W. Sinclair

Personnel interviewed: Dr. Bachmann, Manager
Dr. Maier, Director and Chief Engineer
Mr. Arnet, Production Superintendent

This factory was visited and inspected between June 20th and 21st, 1945.

The carbide is crushed and reduced to fine granules, which are sized and separated from dust, the fines being subsequently milled to uniform fine powder.

The granular material is now nitrified in four independent rotary kilns of special construction. These kilns, of which four are complete, and a fifth in course of construction, consist of a heavy steel shell mounted on bearing rolls and rotated by heavy gearing at a speed of about four revolutions per minute. These drums are provided with a series of transversal fins in order to disperse excess heat.

The drums are slightly inclined and are fitted at the gear end with gas tight feeders by means of which the granulated carbide, mixed with about 2.5% of calcined calcium chloride, is introduced. The discharge end of the drum rotates in a gas tight collar, forming part of a fixed preliminary cooler, from which the hot granules are finally discharged into a small cooling drum at a lower level. The whole equipment is kept charged with nitrogen under a small pressure.

When once the reaction has been started, by a preliminary heating of the main drum, the necessary temperature is automatically maintained, by reason of the exothermic nature of the reaction, and as nitrification proceeds the material, which maintains its granular form, gradually passes from the feed to the discharge end

of the drum. There is, however, a tendency during the course of the reaction for the granules to build up a ring at a certain part of the drum, and thereby prevent the steady flow of the granules. To avoid this the nitrogen is introduced at a pressure of 10 atmospheres, by means of a fixed pipe coinciding with the axis of the drum, and which pipe is provided with branches and nozzles whereby a strong stream of nitrogen is directed to the periphery of the drum, and thereby serves to break up the ring of granules which would otherwise form. The operation of nitrification, once started, proceeds continuously.

The gramulated material, after thorough cooling, is packed in strong paper bags and marketed under the trade name of "Kornka".

The carbide fines from the granulating process already mentioned, are reduced to fine powder and mixed with about 2.5% of calcined calcium chloride, in accordance with the practice established by Paulsonius, as also with about 0.33% of fluorspar, and is then nitrified in what are termed tunnel ovens. These consist of gas tight chambers of rectangular cross section, lined with refractory brick. The chambers, which are six in number and about 100 feet overall length, have their floors approximately flush with the floor of the building in which they are situated.

At each end of these tunnel ovens a gas lock chamber is arranged, through which the carbide to be nitrified is introduced, and from which the finished cyanamide can be discharged.

Throughout the whole length of the tunnel oven tram rails are provided.

The milled carbide is charged into steel containers of rectangular form, constructed of perforated plate. These containers are lined with corrugated paper.

The containers are mounted on small four-wheeled trucks, and are propelled from one end of the tunnel furnace to the other by means of an intermittently operating mechanical device controlled from the exterior of the tunnel oven.

The interior of the tunnel oven is kept under a low pressure of nitrogen, and the exothermic reaction is sufficient to maintain the optimum temperature, without any recourse to external heating. The process of nitrification is continuous and each tunnel oven can be kept in operation without any major overhaul

for several months.

The rectangular boxes containing the finished cyanamide are lifted by a crane and the contents crushed and milled to relatively fine powder in the usual manner.

The potential capacity of the cyanamide plant can be taken at about 130,000 metric tons per annum.

Operating data

Granulated Cyanamide

Per 100 Kg. of fixed nitrogen

Granulated carbide	330.7	Kg.
Calcium chloride	8.6	Kg.
Nitrogen to furnace	32.9	cu/M
Pressure nitrogen	35.7	"
Power	15.7	KWH
Treated water	2.4	cu/M
Compressed air	11.7	cu/M
Repairs, man hours	0.15	
Wages	0.35	R/M

Powdered Cyanamide

Per 100 Kg. of fixed nitrogen

Milled carbide	346.25	Kg.
Calcium chloride	8.44	Kg.
Fluorspar	1.15	Kg.
Nitrogen for furnace	140.00	cu/M
Calcium nitrate	0.28	Kg.
Tar oil	3.23	Kg.
Power	9.10	KWH
Water	0.10	cu/M
Compressed air	9.9	cu/M
Wastage of steel containers	17.86	Kg.
Repairs, man hours	0.17	
Wages	0.71	R/M

The nitrogen content of the granulated cyanamide averages about 22.27% with a content of free CaC_2 of 0.6%.

The nitrogen content of powdered cyanamide, which is mixed with a small proportion of tar oil to diminish dustiness,

averages 20.24% with a content of free CaC_2 of 0.54.

Both types of cyanamide are packed in waterproof paper sacks and sold for use as fertiliser.

It was reported that during the latter period of the war a monthly supply of some 30 metric tons of powdered and un-oiled cyanamide was shipped to the factory of Dr. Jacobs at Bad Kreutznach for transformation to other chemical products, the nature of which was not known to the management at Knapsack, and that a small quantity was also shipped to Firma Kalle at Beabrech for experimental purposes.

Calcium Carbide

Société Electrométallurgique de Montricher, France

CIOS - Trip - Opportunity

Investigator: Lt. Col. G.W. Sinclair

Personnel interviewed: Monsieur Miguet, Director
Monsieur Chabasseur, Director

This investigation took place in Paris between the 9th and 14th July, 1945, and included interviews with French carbide makers.

In the course of the investigation in Germany conducted by Lt. Col. W.G. McBurney, Lt. Col. H.S. Sutherland and the writer, references were made to the Miguet system of furnace construction, and although there was no evidence that this system of construction had been adopted in the territory to which we had access, it was evident that it had been carefully studied by the Germans, who, during the period of hostilities, had had access to the plants actually operating in France, as also to the large installation at Porto-Marguera in Italy. In view, therefore, of the interest of the Germans in the Miguet system, and the claims made for it, the writer was authorized to make a trip to Paris, and by the courtesy of friends was enabled to get in touch with the exploiting company, Société Electrométallurgique de Montricher, as also with the inventor, Monsieur Miguet.

Although, as will be seen from the list of installations included in this report, the system has been rather widely exploited, the outstanding example is that at Porto-Marguera in Italy, near Venice, and the following detailed description of the furnaces relates to this installation.

The carbide plant at Porto-Marguera forms part of a group of industrial undertakings established on reclaimed land, and is controlled by Societa San Marco, filiale of Societa Adriatica di Elettricita, which in turn controls the supply of electrical power from the following central stations:

Central Stations	Capacity
Fadalto	87200
Nove	54500
S. Floriano	4440
Castelletto	5180
Canave	44650
Livenza	7000
	202970

Main supply of water is from Falls of Piave and Lago Santa Croce in the Alps, minor powers from river Cellina and river l'Adige. In addition a steam power station of 100,000 H.P. is installed at Porto-Marguera.

The installation at Porto-Marguera is intended to absorb excess power which might otherwise be wasted, and it is claimed that the carbide furnaces can operate efficiently on very variable load to suit the power available. High tension transmission is at 150,000 volts, transformed at Porto-Marguera to 10,000 volts. Current is 42 cycles per second.

Two carbide furnaces are installed, each rated at 15,000 KW, but it is doubtful if they have ever operated successfully over 10,000 KW.

Characteristics

1. Furnace closed and gas tight with means for recuperating the carbon monoxide.

2. Feed of different raw materials by screws automatically controlled by electric contactors.

3. Elimination of the usual current conductors to the electrode and the furnace base by the use of a new system employing conducting walls in the construction of the well of furnace.

4. The employment of a special type of transformer whereby a very great variation in secondary voltage by many steps is attained.

The transformer is placed immediately below and in line with

the vertical axis of the furnace. The conducting bars from the transformer radiate outwards. These bars are interlaced and insulated from one another. The outer shell of the furnace is of bronze and is connected to one pole of the transformer, as also to the system of adjustable contact plates surrounding the electrode. The other pole of the transformer is connected to a second shell of bronze, which is embedded in the refractory lining of the furnace and is connected to conductors buried in the floor of the furnace, as also to the other pole of the transformer. Both the bronze shells referred to are water cooled. It is claimed that the arrangement of transformer and conductors ensures a power factor of at least 0.96.

The current is supplied to the two furnaces by a group of two monophase transformers composed of two units, each of 16,000 KVA, with Scott coupling, and operate at 42 cycles per second. The current is received at 10,000 volts and transformed in the secondary windings to voltage varying between 25 and 55 in 57 steps.

The primary current is 1800 amperes and that of the secondary 410,000 amperes.

Each transformer unit comprises a main as also an auxiliary transformer, both contained in the same casing. The combination of these two transformers enables the wide range of regulation above-mentioned to be obtained. The apparatus by which the secondary voltage is regulated by hand or automatically is enclosed in an oil filled casing, which also forms part of the shell of the main transformer.

The exterior wall of bronze, water cooled and 2200 m/m high, which conducts the current to the electrode, and the interior wall of the same metal, also water cooled, are separated from each other by insulation 10 m/m thick. Between the inner shell and the refractory lining is a lead shell in order to render the construction air tight. The floor of the furnace consists of two upper layers of carbon blocks 500 m/m thick, under these a layer of powdered carbon, next a bed of silicions sand and finally a water cooled bronze disc resting upon a concrete base.

The interior dimensions of the furnace are 5750 m/m diameter by 1500 m/m depth.

The tapping electrode is of the usual suspended type and is fed with current at 70 volts by a transformer of 140 KVA capacity.

The raw materials are fed to the furnace by twelve pairs of enclosed screws, the axes horizontal and the pairs arranged symmetrically at the same height around the furnace. On the floor above the feeding screws an annular hopper is arranged which surrounds the furnace. This hopper is divided into twenty-four compartments, each alternate compartment being charged with a measured mixture of coke and lime, and those between with lime only. Each screw is driven by an enclosed geared electric motor and controlled by a contactor. The electric circuits are so arranged that all screws may be driven simultaneously or the group for lime or for lime-coke separately, and if necessary each screw may be operated individually. On the same floor level and below the aforesaid screws, twenty four pneumatically operated and inclined pokers are arranged. These pokers are brought into action simultaneously after each tapping and are furnished with ends which can be changed without affecting the gas tightness of the furnace. Under normal conditions the operation of the feed screws is controlled by an electrically driven commutator following a pre-arranged order, but as already mentioned, the groups and individual feed screws may be operated independently.

On the third or top floor the suspension for the electrode is arranged, as also the four suction fans for exhausting the gases from the furnace. These have a capacity of 10 cubic metres each per second and suction head of 125 m/m water column.

The electrode, measuring 4045 m/m diameter and weighing some 80 metric tons, consists of an external shell composed of twenty four pre-baked carbon sectors per layer. These sectors are locked to one another by dovetails and attached to a circular steel basket-like core by means of transverse bolts. The joints between the sectors are made with sugar paste, protected on the outside surface by a layer of silicate and powdered asbestos, penetrating to a depth of about 2 c/m. The interior of the carbon shell is filled with a mass consisting of coke and tar compacted by means of pneumatic tampers. The diameter of the paste core of the electrode is 2750 m/m.

The electrode is consumed under normal load at the rate of 10-12 c/m per day, and new sectors and paste are added every 6 to 8 days. The operation is performed without interrupting the working of the furnace.

The work of filling in the paste core is easily performed by three or four workmen and artificial ventilation is unnecessary. It is usual to add to the electrode about one metre of shell, core and internal steel basket at the time interval above-mentioned.

The steel cage or basket in the interior of the electrode, by which it is suspended, consists of twenty four vertical members, placed equidistant around a circle, and held in place by iron hoops at intervals. These vertical members are each coupled to a long screw provided with a nut in the form of a gear wheel. These nuts or pinions rest each on a ball race, supported on a part of the framework of the furnace. An endless gear chain meshes with all the pinions so that any angular movement given to one is transmitted to all. Two further gear chains are fitted and these are connected to suitable operating gear, whereby the aforesaid pinions can be rotated in the sense required either by hand or automatically by a Thury electric regulator.

The electric current is fed to the electrode from the exterior bronze shell of the furnace through the closure papels, the protecting cone and finally by means of the flexibles to the contact plates. These plates, of which there are forty eight, are of bronze, water cooled. The plates consist of two parts. The inner part is shaped to make contact with the wall of the electrode, whereas the outer part, which is inclined to the vertical, rests in a ring of conical section, completely surrounding the electrode. This ring is held by twelve spring suspensions from the upper part of the frame of the furnace, and is capable of up and down movement. Between the two parts of each contact is a wedge-shaped piece, which can be displaced vertically by means of a right and left hand screw accessible from the outside of the furnace at the level of the top platform. By means of this screw the contact plate may be made to press on the electrode or released as required. To raise the contact plates as the electrode is consumed, the afore-mentioned screws are released, thereby allowing the suspension springs on the conical ring to raise both ring and contact plates to a new position, where the plates can there be clamped by means of the left and right hand screws aforesaid.

It is to be remarked that in view of the great bulk and weight of the electrode, as also the fact that the furnace is operated completely closed with full recuperation of the gases, it is desirable that the electrode shall not be displaced oftener than is absolutely necessary. To avoid frequent displacement, recourse is made to the large range of voltage regulation provided, namely 57 steps between 25 and 55 volts.

According to M. Miguet, the following results may be taken as representative:-

2800 KW per 1000 Kg. carbide using the most recent improvements in the furnace.

2900 KW using Porto-Marguera type.

These figures refer to carbide of 285-290 litres acetylene grade, using raw materials:-

CaO	94 - 95%
Coke containing	10% - 12% ash

It is advantageous to mix good anthracite with the coke in the proportion of 20% to 33%.

With materials as referred to above, carbide has been produced continuously up to 340 litres acetylene per kilo, particularly when operating at about 50 volts.

M. Miguet stated that the bottom of the electrode approaches to about 85 c/m from the bottom of the furnace, and is about 15 c/m clear of the molten carbide layer.

With raw materials of the grades above-mentioned, the furnace can be kept in continuous operation for approximately five months without any major overhaul, and with raw materials of first class quality up to one year.

It would appear that the Société Electrometallurgique de Montricher has installed a large number of furnaces according to the Miguet and Miguet-Perron system, of which the aggregate power amounts to approximately 250,000 KW. The various installations are as follows:-

France	Mines de Lens, Wenglas near Lille	2 x 6000 KW
France	Soc. St. Gobain, Modane	2 x 6000 KW
France	St. Julien - Montricher	1 x 5000 KW
France	Chateau Feuillet	3 x 6000 KW
France	Rioupéroux	2 x 3000 KW
France	Montricher	2 x 5000 KW
France	Uckange	2 x 4000 KW
France	Sabart, Pyrenees	1 x 6000 KW
Belgium	Langerbrugge	2 x 4000 KW
Holland	Amsterdam	2 x 6000 KW
Russia	Donoi-Postroi	9 x10000 KW
Russia	Near Leningrad (constructed by the Russians)	3 x10000 KW
Italy	Porto-Marguera	2 x15000 KW
Portugal	Setubal	1 x 3000 KW

The opinions derived from conversations with some of the French carbide makers on the merits of the Miguet system vary considerably, and may be summarised as follows:-

(a) It is considered that the system is not economically applicable to very large units, and that 10,000 to 12,000 KW is probably the maximum economical size.

(b) With first rate raw materials an exceptionally high grade of carbide can be produced.

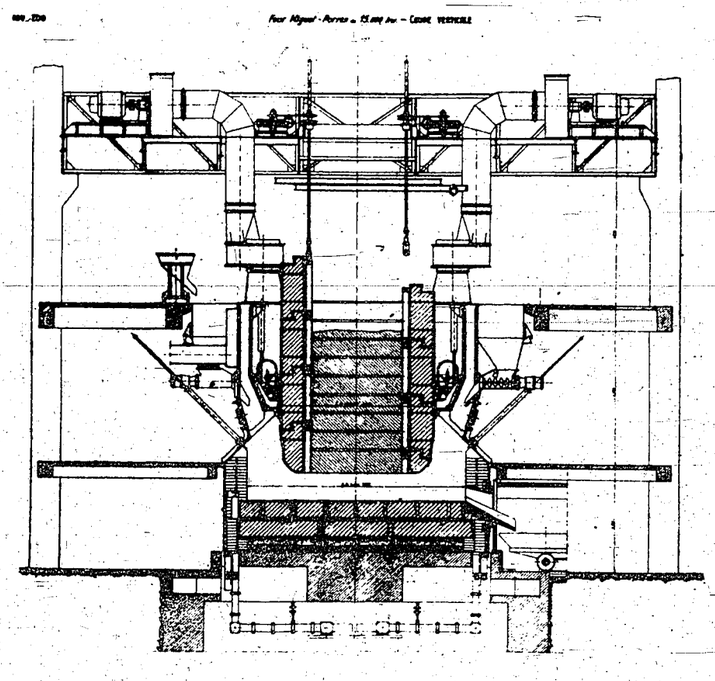
(c) Due to the special arrangement of transformer and conductors the electrical efficiency is exceptionally high.

(d) The system, which is extremely ingenious, involves a great deal of gear, much of which is of a more or less delicate type and involves more expert supervision than is the case with the commoner types of furnace.

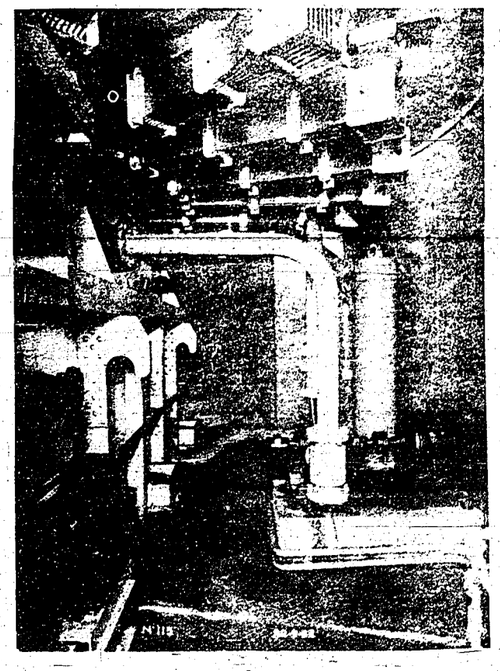
(e) Reckoned on the basis of carbide tonnage the Miguet system is more costly in installation than the more common three phase furnace with Söderberg type electrodes.

(f) It is suggested that it is dangerous to place a large oil filled transformer and intricate high tension electrical gear immediately below the furnace.

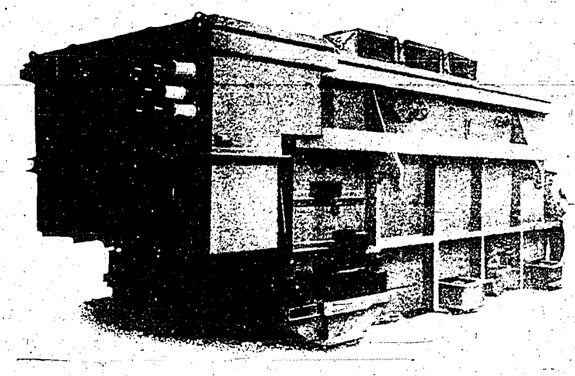
The following six reproductions from photographs of the Miguet furnace will serve to give some idea of its appearance as installed at Porto-Marguera.



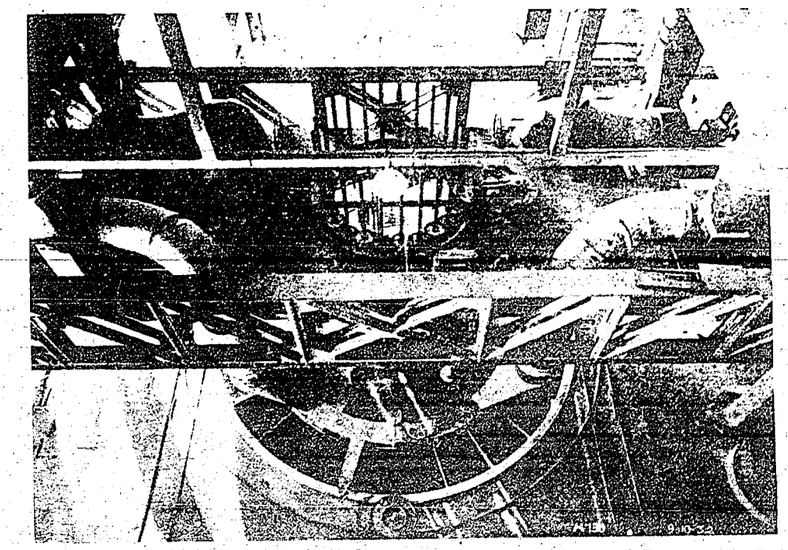
I. Cross Section through Furnace



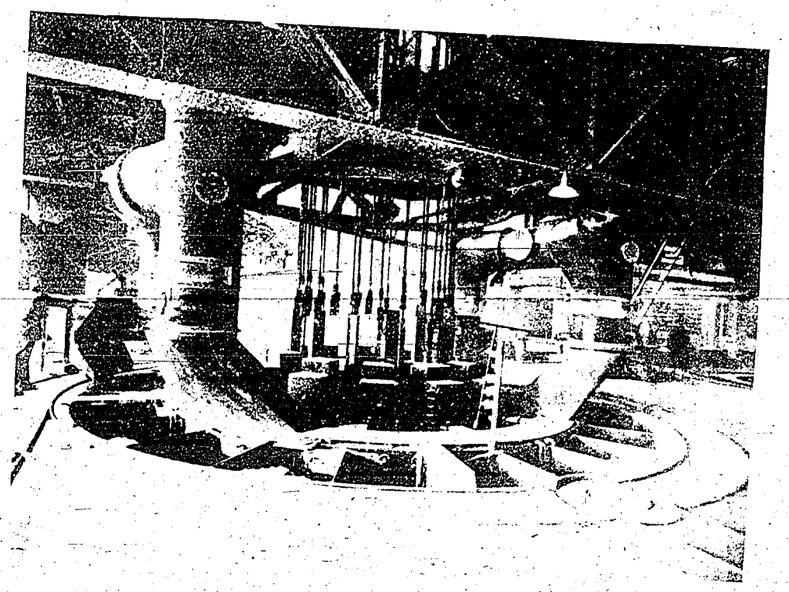
II. Conductors, Transformer to Furnace



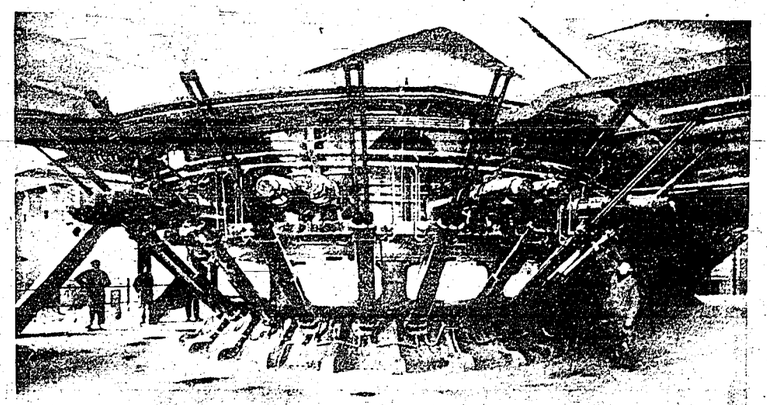
III. Transformer and Voltage Regulator



IV. Electrode Adjustment Gear



V. Raw Material Hoppers and Electrode



VI. Charging Screws, Pokers etc.

General Remarks on Carbide and Cyanamide

The carbide and cyanamide industries in Germany are both old established. Indeed, calcium cyanamide was discovered in Germany by Drs. Frank and Caro, and the first industrial plants date from about 1908. From this date up to the present day the most noticeable features are the great increase in the size of carbide furnaces, as also in total production of carbide. This has been brought about by the discovery of processes by which acetylene may be synthesized into a large number of organic compounds, some of which are of great importance in the manufacture of artificial rubber and rubber-like compounds, as also plastics and resins. All such products were of paramount importance to Germany in her war effort, hence the great increase in the establishment of new factories for the manufacture of carbide.

Among the factories of large capacity built shortly before or during the war period, the following may be cited:-

Location	Metric tons production 1943
Schkopau	298,256
Mückenberg	99,015

The total tonnage available to Germany from factories within the Reich or in occupied territories was 1,513,190 tons.

It is reported that attempts have been made to construct carbide furnaces of up to 40,000 KW capacity, but that results have indicated that the most economical and convenient units should not exceed 25,000 KW.

In the case of the German furnaces, no radical departure from what may be termed standard practice was observed. Some of the details, however, to which attention has been drawn in this report merit consideration. The special method of cooling the carbide described under Ludwigshafen would appear to be decidedly advantageous.

Under the conditions existing before the war, with carbide factories located near the power plants, and using current produced from cheap braun coal, the cost of carbide undoubtedly fell well within the economical limits. For instance, over 500,000 metric tons of cyanamide were produced per annum and sold for use

in Germany in competition with cheap ammonium sulphate produced from ammonia and anhydrite. It is very doubtful, however, if the new plants, and many of the older ones which have been extended, could be operated economically, and presumably a great part of the German carbide industry will be permanently shut down.

Documents annexed

Exhibit 1	Data relating to German carbide furnaces up to 1930
Exhibit 2	Data relating to carbide production in Germany and German occupied countries for years 1943 - 1944.

German Carbide Production in 1943

EXHIBIT II.

Metric Tons

	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Year Total
Schkopau	24532	22215	25290	23378	24454	23668	24256	24717	25251	27338	26701	27455	298256
Knapsack	21197	19918	24780	25866	27190	25689	22237	23120	21920	20548	19465	20378	271808
Hart	11895	11594	18342	19476	20386	20435	24399	22689	18806	15967	11660	15693	211342
Piesteritz	13569	14256	15313	13650	15254	12490	12027	11024	12921	13748	10194	11128	155574
Auschwitz	-	-	-	-	-	-	-	-	-	-	-	-	-
Königshütte	8729	6504	9702	12522	13561	12731	11195	11568	10298	10123	9053	8425	124411
Mückenberg	8716	8199	9505	8602	8514	8183	7574	4661	7668	8873	9157	9565	99015
Burghausen	1687	3323	6594	8142	8001	8026	8234	4729	2539	2445	945	2316	56081
Waldshut	5900	7400	6700	9100	12060	11500	11100	9550	8400	8500	5550	6500	102260
Spremberg	1837	1890	1966	1960	1990	1864	1855	1826	1800	1850	1850	1950	22548
Ludwigshafen	-	-	2279	2214	-	1442	3303	2894	3039	5168	2695	3266	26500
Falkenau	3163	2679	3181	3066	3190	3130	2968	2253	2320	5049	2917	3081	34977
Bobreck	2477	2787	2767	2752	2888	2896	2901	2876	2957	3152	3060	2904	34417
Maria Rast	-	-	-	1443	2404	2698	2749	2555	1907	2215	324	-	16195
Wyhlen	1088	907	1022	1094	1208	1155	1217	1185	1150	1205	247	-	11478
Ober-Lazisk	716	802	1092	1148	1191	1188	1178	1067	1033	1018	924	762	12119
Hirschfelde	968	919	939	929	931	845	719	976	903	845	936	986	10596
Ueckingen	706	701	959	1020	1303	1604	1036	415	666	632	851	720	10593
Landeck	388	193	630	501	638	670	646	612	618	521	294	349	6160
Freyung	287	287	886	1057	712	587	657	374	386	219	293	318	6065
Zombknwitz	176	230	254	270	275	266	271	167	184	272	253	279	2897
	108031	104814	129299	137690	145950	141068	141522	129258	124766	127688	107049	116055	1513190

These figures apply not only to the German Reich, but also to occupied territory.

German Carbide Production in 1944

EXHIBIT II.

Metric Tons

		Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan. 45	Feb. 45	March 45	Apl. 45	May 45
A	Schkopau			26180	26360	22520	25210	25000	23500	20650	22195	16535	6158	12694				
A	Knapsack			23556	18620	15330	20780	21898	22800	18770	11257	-	-	1914				
A	Hart			16621	21110	22001	21980	20598	18876	19080	16000	21154	13228	5930				
A	Piesteritz			13302	14028	11701	11003	10519	11781	14244	15761	15252	14253	10211				
-	Auschwitz			-	1246	1805	1436	1558	432	78	1115	1859	1668	-				
-	Königschütte			9936	9805	9245	8875	9851	9908	10550	8628	11449	10009	-				
A	Mückenberg	9723	8518	9167	8261	8770	8663	8494	6919	6586	7592	8019	7800	6800	3485	2596	?	?
A	Burghausen	5126	4668	3500	6100	8000	7700	7100	6700	4700	5200	4550	4500	2341	1368	2502	1291	312
A	Waldshut			6500	10750	11500	9400	11100	10300	10700	10100	8400	6300	2160				
A	Spremberg			2000	1950	1950	1700	1920	1700	1700	1820	1639	1795	1544				
A	Ludwigsh.	3224	4229	4139	5634	4245	4585	60004	1691	-	-	++	-	-	-	-	-	-
S	Falkenau			2717	1550	1831	2469	2497	2530	2813	2682	1778	2204	2736				
-	Bobreck			3216	3051	3320	3047	3260	3101	2885	3053	2787	2227	-				
-	Maria Rast			-	453	2308	2128	2759	2161	1006	491	102	115	-				
A	Wyhlen			1222	1173	1186	1174	1210	1250	1154	980	780	921	850				
-	Oberlazisk			1185	1131	1085	1071	1187	1108	1122	1051	958	985	-				
A	Hirschfelde			909	813	896	864	811	980	853	817	787	885	866				
-	Ueckingen			603	645	575	555	562	?	-	-	-	-	-				
-	Landeck			200	614	695	588	727	1053	825	569	494	408	339				
A	Freyung			524	987	1085	892	947	569	380	394	785	819	329				
-	Zombkowitz			284	270	270	269	164	213	174	252	147	168	-				
				125759	134549	130512	134165	137910	126782	117869	109757	86455	74461	48714				

These figures apply not only to the German Reich, but also to occupied territory.

Sodium Cyanide

I.G. Farbenindustrie at Ludwigshafen

CIOS Trip 399

Investigating personnel: Lt.-Col. W.G. McBurney
Lt.-Col. G.W. Sinclair
Lt.-Col. H.S. Sutherland

Personnel interviewed: Dr. Ambros, Director and Superintendent Organic Chemicals
Dr. Alt, Principal Assistant to above
Dr. Pfanmüller, Superintendent of Cyanide Manufacture

This plant was visited and inspected between the 14th and 18th June, 1945.

The cyanide part of the I.G. Plant at Ludwigshafen was partly destroyed by bombing, but a considerable portion of the equipment was intact, and the plant could possibly be re-established in workable shape in a matter of four to five weeks. The resumption of operations would depend, however, on several factors, namely, the supply of fuel, power, caustic soda, formamide and other raw materials.

The plant consists of equipment for the manufacture of sodium cyanide by three modifications of the formamide process.

The formamide process for the production of sodium cyanide has been known for many years, and patents for various modifications in the names of Badische Analin, I.G. Farbenindustrie, Du Pont de Nemours, etc. since 1921 exist.

Formamide is produced by the action of carbon monoxide on methanol in the presence of ammonia, as follows:-

$$CH_3 . OH + CO \longrightarrow CHO. O. CH_3$$

$$CHO. O. CH_3 + NH_3 \longrightarrow CHO. NH_2 + CH_3. OH$$

The manufacture of Formamide, which is carried out in another of the I.G. factories at Ludwigshafen, was not investigated.

In the presence of ammonia, and under definite conditions of temperature etc., formamide splits up into hydrocyanic acid and water:-

$$CHO. NH_2 \longrightarrow HCN + H_2O$$

In two of the plants installed at Ludwigshafen the same general procedure is adopted, although the actual equipment is different, one of the plants being of much older date than the other. In general terms the sequence of operations is as follows:-

Volatilised formamide 3% with ammonia 97% is passed first through a filter filled with Raschig rings, then over a catalyst consisting of aluminium phosphate on Bolus Alba, (2 m/m 50-50) and under a temperature of 350° - 370° C. The gas which then contains HCN, water and ammonia, passes through a cooler from which some condensate is removed, then through an absorber filled with Raschig rings, and fed with 50% caustic soda solution. This absorbs excess moisture and HCN, thus drying the gaseous ammonia which is recirculated. The resulting solution, containing some 30% NaCN then passes to the first evaporator, where the major portion of the ammonia is removed, then to vacuum evaporators, in the first of which the remaining ammonia is evaporated. The solution is finally evaporated to dryness yielding a powder-like sodium cyanide of not less than 90% which is briquetted.

In view of the very weak concentration of HCN in the gaseous mixture obtained by this process it is not possible to obtain gaseous HCN as a final product and this necessitates the absorption in caustic soda.

In a third plant installed at Ludwigshafen, but only on a pilot scale, the process adopted is different. In this process ammonia is not used. Instead, volatilised formamide is passed rapidly through a battery of iron tubes heated to a temperature of 370° - 400° C. and kept under vacuum of absolute pressure 4 m/m Hg. The tubes are provided for some part of their length with iron cores, so that an annular space is provided for the passage of the gas, thereby promoting good contact with the heated iron, which acts as a catalyst. The reaction is stated to be slightly endothermic (- 25 Kg. Cal. per Kg.) and according to reports conversion to HCN and water is practically complete.

The conversion efficiency of formamide to NaCN of 90% grade is claimed to be 83%, with approximately 2% loss of ammonia. The efficiency of the pilot plant should be greater, inasmuch as HCN is produced in the gaseous state without the use of a mmonia.

According to the figures given, it would appear that the potential capacity of the three units of plant referred to is between 800 and 900 metric tons of sodium cyanide per month.

Formerly the sodium cyanide was made on a relatively large scale by the Kastner-Kellner process, using ammonia and metallic sodium. It is probable that manufacture by this process has continued, but no information was obtained as to the location of plants or as to their output.

Up to the start of the war, a certain amount of sodium cyanide, some 700 to 1000 metric tons per annum, was produced from what is known as "Schlempe". This is the residue obtained from the final treatment of beet sugar liquors by the strontium carbonate process. It would seem that only certain classes of beet contain nitrogen in sufficient quantity to warrant treatment for cyanide. This applies particularly to the crops raised in the neighbourhood of Dessau, as also in Kolin (Czecho-Slovakia), the product from these two centres being marketed by Gold und Silber Anscheide Anstalt, a branch of I.G. Farbenindustrie. The "Schlempe" cyanide compared in all respects with that produced by other processes and was marketed in the same form, namely, flat briquettes.

No information was obtained as to the present state of the plants from which "Schlempe" cyanide was formerly produced.

It was stated that the output of the I.G. plant at Ludwigshafen represents 40% of the total German capacity. The balance is presumably made up by other processes, namely:-

Kastner-Kellner, Ammonia-Sodium
"Schlempe" process from sugar beet.

By-product HCN from the cracking of hydrocarbons to acetylene, ethylene, etc.
By-product HCN from gases distilled from coal.

It was thought that the Germans had probably developed a possible method using methane. There was no evidence, however, that anything more than research and experimental work had been done in this direction, and no definite particulars were available.

The greater part of the equipment for the briquetting and packing of sodium cyanide had been destroyed.

Documents annexed

Exhibit 3.
Flow Sheet of Formamide Process.

Exhibit 4.
Diagrammatic Arrangement of Equipment for Formamide Process.

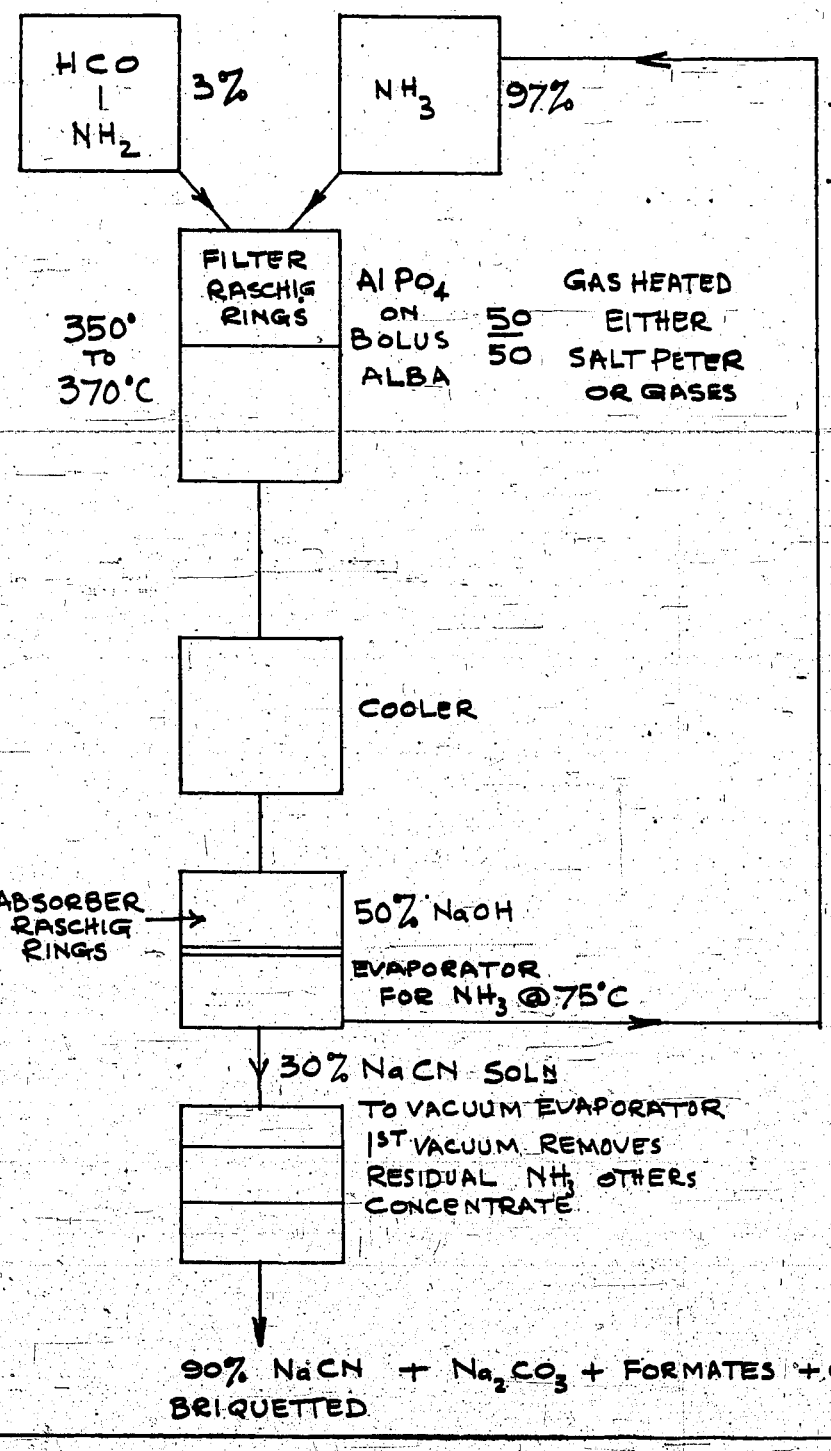
SUMMARY OF MOST IMPORTANT DATA RELATING TO VARIOUS CARBIDE FURNACES

EXHIBIT I

LOCATION OF FURNACES	FURNACE CAPACITY K.W.	FORM OF ELECTRODE	ARRANGEMENT OF ELECTRODES AND CENTRE DISTANCE	SECTION CM^2	TRANSFORMER CAPACITY KVA	POWER FACTOR cos ø	SECONDARY VOLTAGE	VOLTAGE TO NEUTRAL CALCULATED	INST. SECONDARY AMPERES	VOLTS TO NEUTRAL / INST. SECONDARY AMPS.	INDUCED VOLTAGE PER 1000 A	KWH PER Kg CARBIDE	REMARKS
FURNACE II BURGHAUSEN	7200	○ 900 ø		6361·7	3 X 3000	0·80	120	69	43400	$1·59 \times 10^{-3}$	0·96	3370	BUILT 1922/23
FURNACE III(OLD) BURGHAUSEN	9000	○ 900 ø		6361·7	3 X 3330	0·85	140	81	43700	$1·85 \times 10^{-3}$	0·96	3200	REBUILT BY FACTORY STAFF WITH SÖDERBERG ELECTRODES 1924 (JULY – NOV.)
FURNACE III BURGHAUSEN	10500	○ 1000 ø		7854	6 X 3000	0·88	146	84·5	47200	$1·79 \times 10^{-3}$	0·85	3200	QUALITY OF RAW MATERIAL SIMILAR TO WALDSHUT – REBUILT 1927 MEASUREMENTS MADE MAY '31
FURNACE III BURGHAUSEN	11500	○ 1000 ø		7854	6 X 3000	0·88	150	85	50500	$1·68 \times 10^{-3}$	0·85	3200	MEASUREMENTS MADE MAY '31 ELECTRODES PHASES I AND III MOVED 10 CM. TOWARDS II
FURNACE II BURGHAUSEN	8000	○ 900 ø		6361·7	3 X 3000	0·85	140	81	38800	$2·09 \times 10^{-3}$	1·09	3200	ELECTRODE CENTRES SHORTENED FLEXIBLE CONDUCTORS SHORTENED 1929
FURNACE IV BURGHAUSEN	5500	○ 900 ø		6361·7	3 X 2000	0·95	115	66	29000	$2·27 \times 10^{-3}$	0·69	3140	REBUILT 1929 QUALITY OF RAW MATERIAL SIMILAR TO WALDSHUT
FURNACE III BURGHAUSEN	16000	○ 1250 ø		12271·8	6 X 3000	0·95	160	92·8	60900	$1·52 \times 10^{-3}$	0·48	3000	PROJECTED
FURNACE TSCHECHNITZ	5700	○ 800 ø		5026·5	3 X 2000	0·89	119	69	31100	$2·22 \times 10^{-3}$	1·00	3480	BUILT 1925
FURNACE MUCKENBERG	9000	○ 950 ø		7088·2	3 X 2660	0·89	130	75	45000	$1·66 \times 10^{-3}$	0·76	3370	BUILT 1928
LARGE FURNACE MÜCKENBERG	12000	○ 1200 ø		11300	3 X 3330	0·91	155	89·5	49000	$1·82 \times 10^{-3}$	0·76	3080	REBUILT AUG – SEPT 30
PISTERITZ FURNACE NEW TYPE	15200	▭ 2000/600		12000		0·82	158	91	67800	$1·34 \times 10^{-3}$	0·77	3000	
HART FURNACE OLD TYPE	10000	▭ 2000/500		10000	3 ph. 12000	0·72	125	72	64200	$1·12 \times 10^{-3}$	0·78	CA. 3100	
HART FURNACE NEW TYPE	22000	▭ 3000/600		18000	3 ph. 35000	0·71	180	104	99500	$1·04 \times 10^{-3}$	0·73	CA. 2930	SMALL STEP VOLTAGE REGULATION OF I TO IV BETWEEN 100 AND 200 VOLT
KNAPSACK OLD FURNACE	10000	○ 950 ø		7088·2	3 X 4000	0·83	150	87	46500	$1·87 \times 10^{-3}$	1·04	3380	
FURNACE I KNAPSACK	11000	○ 950 ø		7088·2	3 X 4000	0·88	150	87	48200	$1·81 \times 10^{-3}$	0·85	3140	
KNAPSACK NEW FURNACE	22000	○ 1250 ø		12271·8	3 X 8500	0·87	180	104	81200	$1·28 \times 10^{-3}$	0·64	2890	
RUŠE OLD FURNACE	8000	▭ 2000/350		7000		0·77	169	98	35500	$2·76 \times 10^{-3}$	1·76	CA. 3430	
RUŠE NEW FURNACE	13500	○ 1250 ø		12271·8	3 X 6100	0·80	160	92·8	61000	$1·52 \times 10^{-3}$	0·91	3120	RAW MATERIAL NOT PARTICULARLY GOOD LIME 95% – 96% CaO ANTHRACITE 7–9% ASH
VISP NEW FURNACE	13500	▭ 1500/1000		15000	3 ph. 20000	0·81	152	88	63500	$1·38 \times 10^{-3}$	0·81	3350	HIGH MAGNESIUM CONTENT IN LIME (ABOUT 2·5 %)
WALDSHUT	10500	▭ 1500/750		11250	3ph. 11000	0·83	165	95	44500	$2·14 \times 10^{-3}$	1·20	3150	

SODIUM CYANIDE BY THE FORMAMIDE PROCESS AT I.G. LUDWIGSHAFEN

EXHIBIT 3



TOTAL PRODUCTION OLD POTS 600 MET. TONS PER MONTH?

OLD ANNULAR

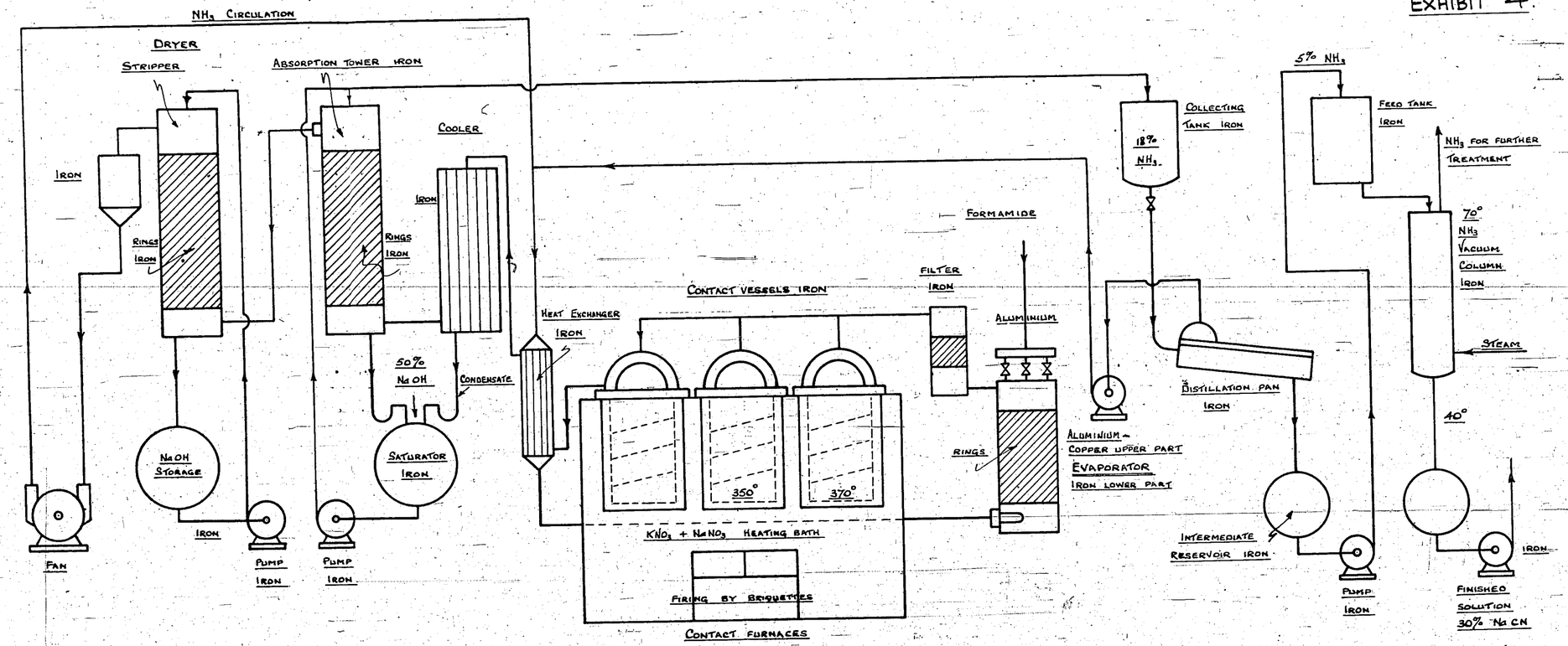
NEW TUBES

WITH SAME CATALYST

4-5 MET TONS DAY

PILOT PLANT FORMAMIDE @ 4 m/m Hg 370°-400°C IN IRON TUBES ANNULAR SPACE 3/16" TUBES 1¼" DIA -25 K PER KG

EXHIBIT 4.



ALL PIPING OF IRON WITH THE EXCEPTION OF PIPES FOR FORMAMIDE

FLOWSHEET OF SODIUM CYANIDE PLANT OF
I.G. FARBEN WERK LUDWIGSHAFEN
PREPARED FOR LT. COL. W.G. Mc BURNEY. 16/6/25

Copy 1

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THE ARC PROCESS FOR ACETYLENE PRODUCTION

Morrow, L. M.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

THE ARC PROCESS FOR ACETYLENE PRODUCTION

Reported by

ENS. G. M. MORROW, USNR

Nav Tec Mis Eu

[1945]

CIOS Target No. 22/6

MISCELLANEOUS CHEMICALS

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

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11 p.

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THE ARC PROCESS FOR ACETYLENE PRODUCTION

SUMMARY

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

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

JUNE 1945

RESTRICTED

TABLE OF CONTENTS

		Page
1.	Introduction	3
2.	Arc Converters	3
3.	Preliminary Purification	5
4.	Acetylene Recovery	7
5.	Acetylene Purification	8
6.	Hydrogen Revovery	9
7.	Ethylene Recovery	11