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ITEM No. 22
FILE No. XXVII-85

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by Col. E. W. Gruhn.

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RESTRICTED

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

Kern, Murray, Sudhoff

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

I.G. FARBENINDUSTRIE A. G.

LUDWIGSHAFEN AND OPPAU AM RHEIN

MISCELLANEOUS CHEMICALS

19-30 June 1945

Reported by:

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

27 July 1945

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

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

RESTRICTED

95 p.

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PERSONNEL OF INSPECTION TEAM

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

I.G. FARBENINDUSTRIE A.G.

LUDWIGSHAFEN AND OPPAU AM RHEIN

MISCELLANEOUS CHEMICALS

1. INTRODUCTION

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

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

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

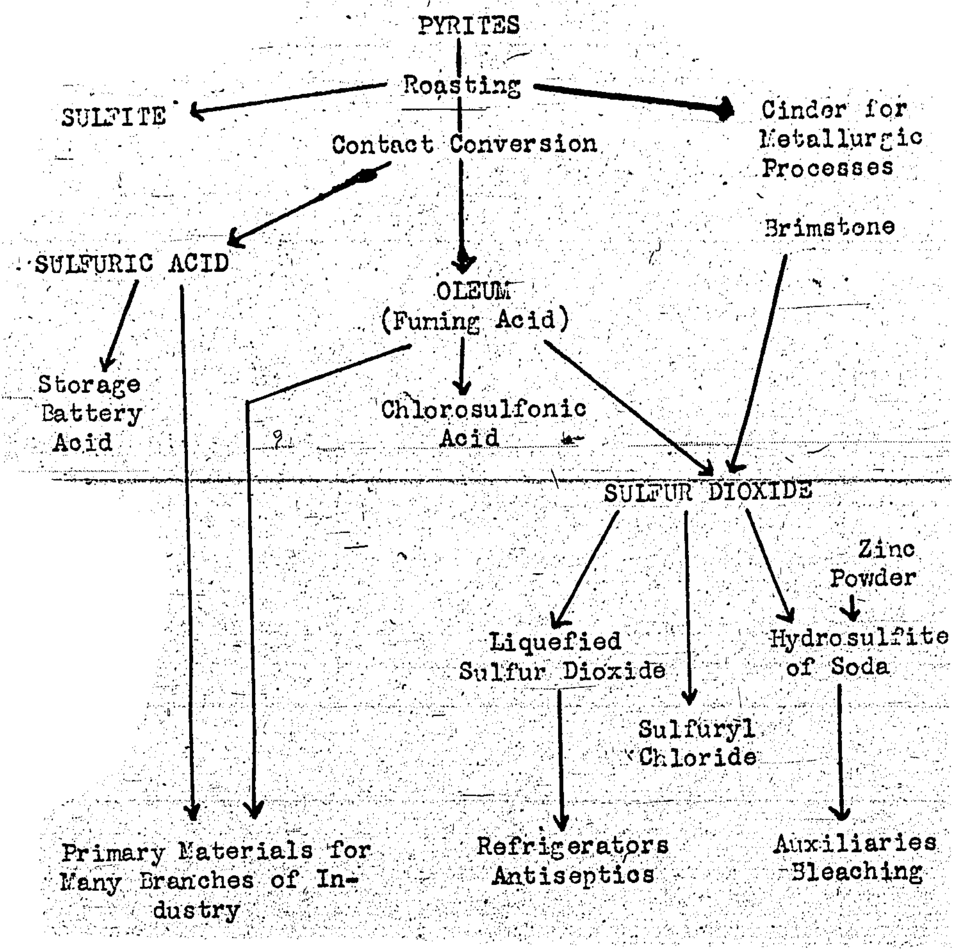
A large room on the 3rd floor of the main office building has been fixed up as an exhibit. Eighteen large charts, showing the groups of products manufactured and their derivation, are hung on the walls of this room. Copies of these charts will be found at the end of this section. Many tables are covered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

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

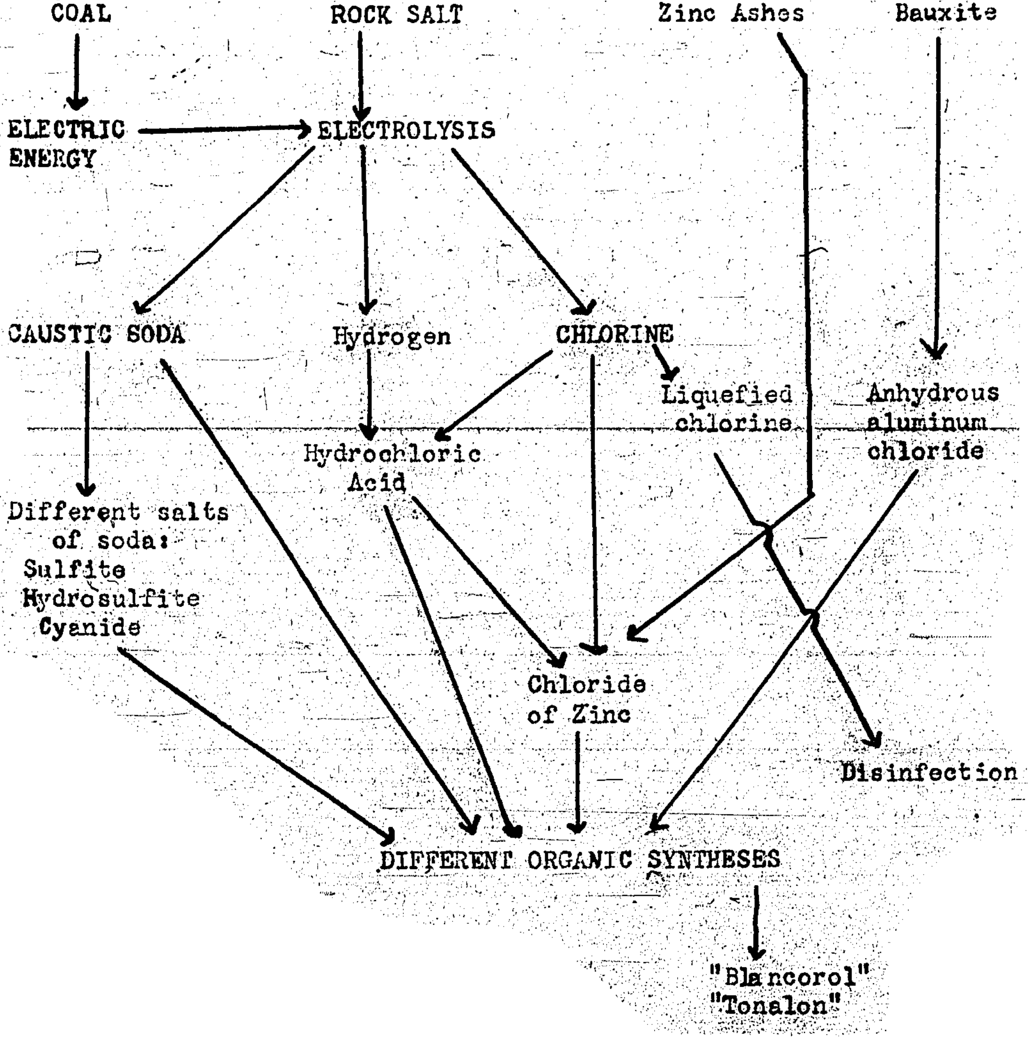
Production capacities (with the plants fully repaired) for some of the more important products of Ludwigshafen and Oppau were stated to be as follows:

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

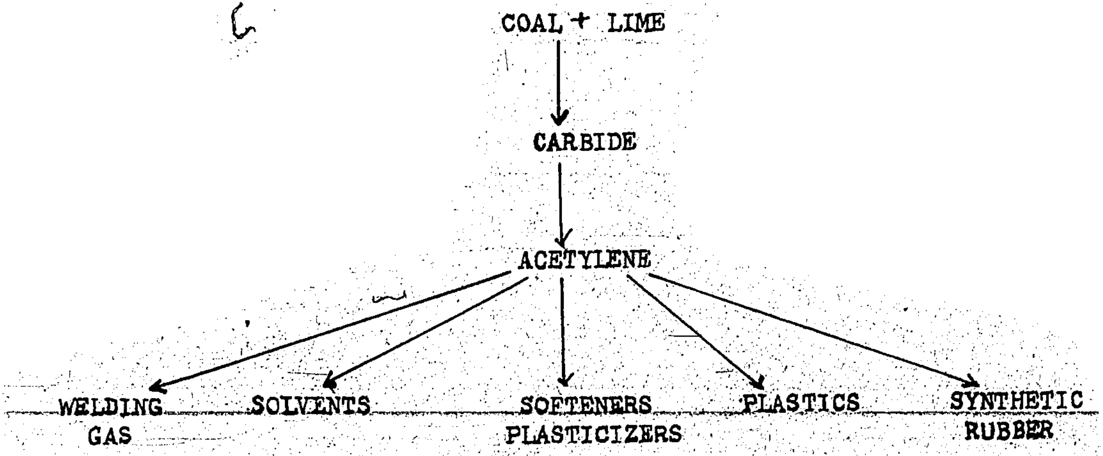
SULFURIC ACID GROUP



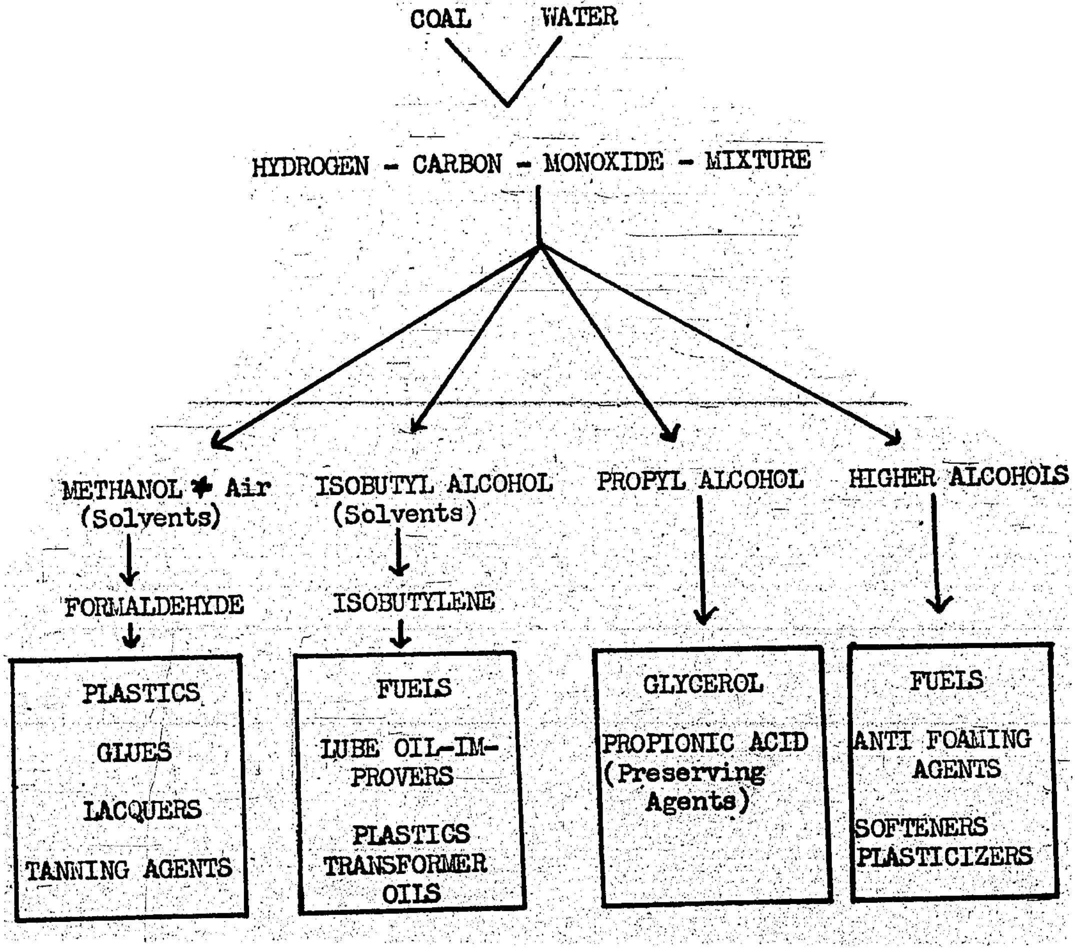
CHLORINE GROUP



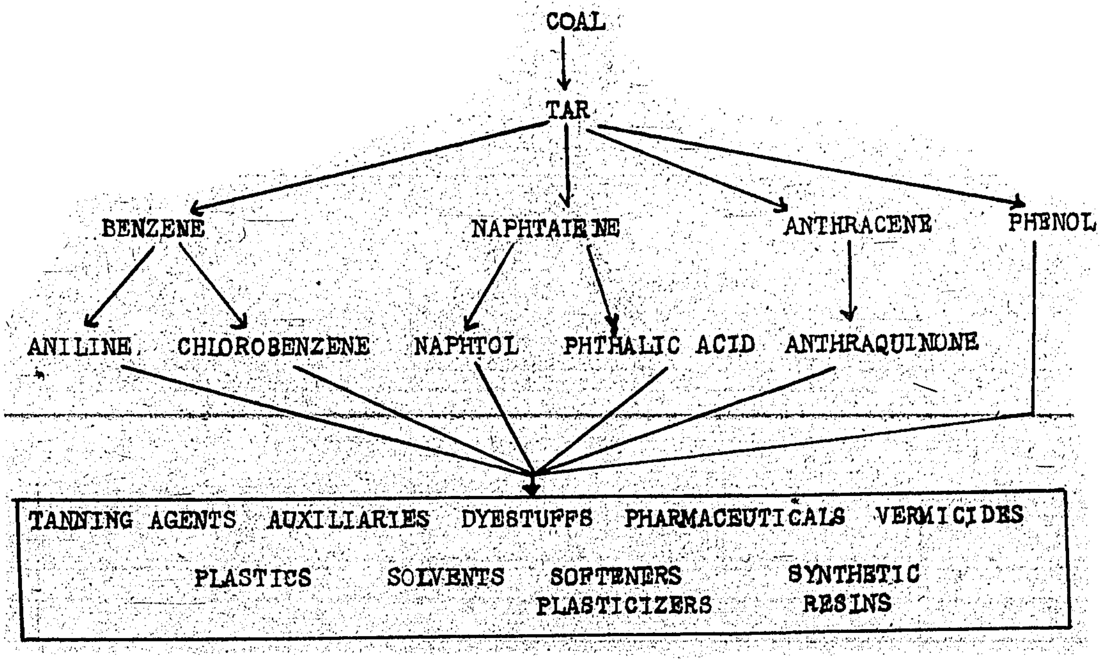
ACETYLENE CHEMISTRY



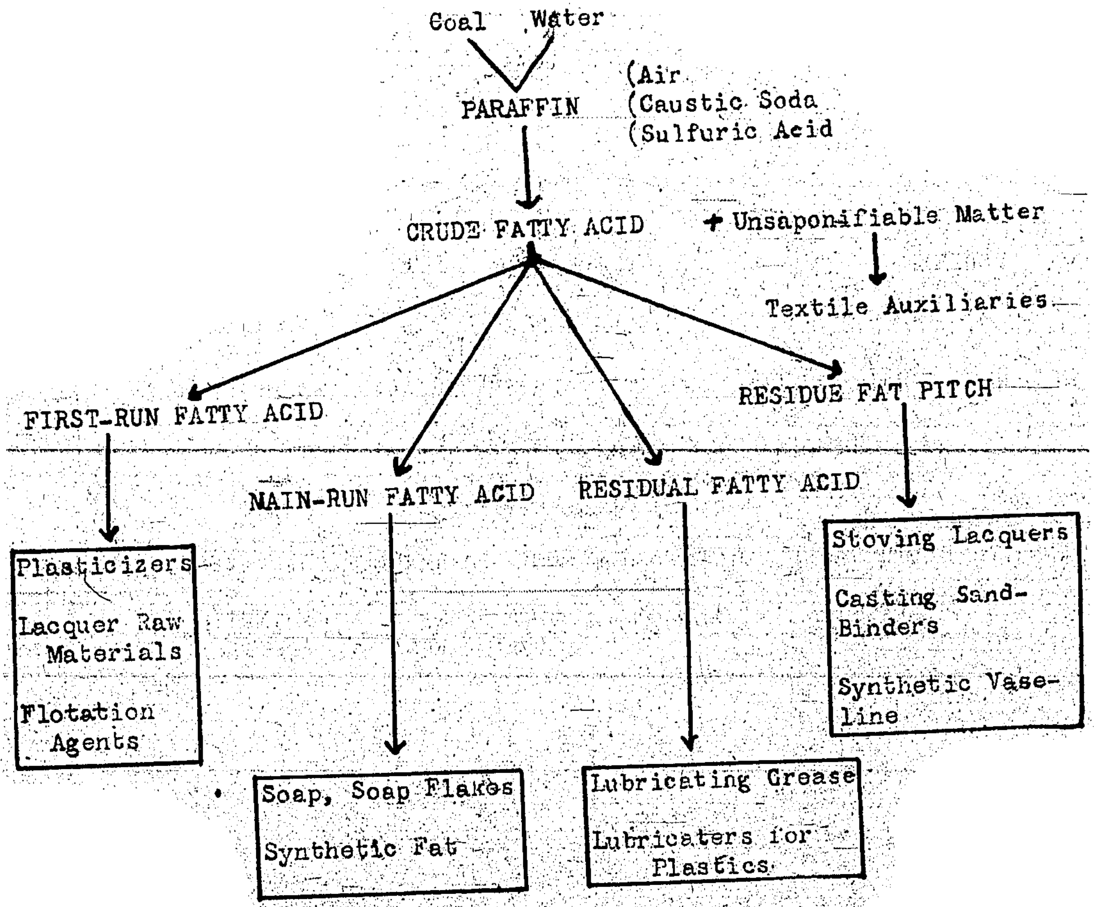
ALCOHOL SYNTHESIS

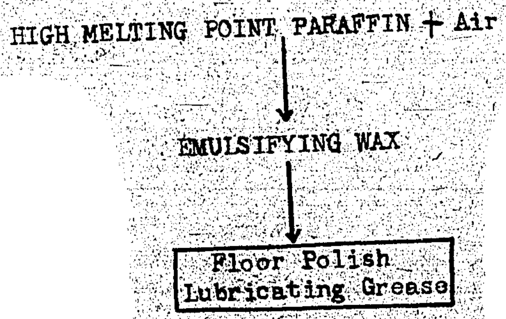


TAR CHEMISTRY

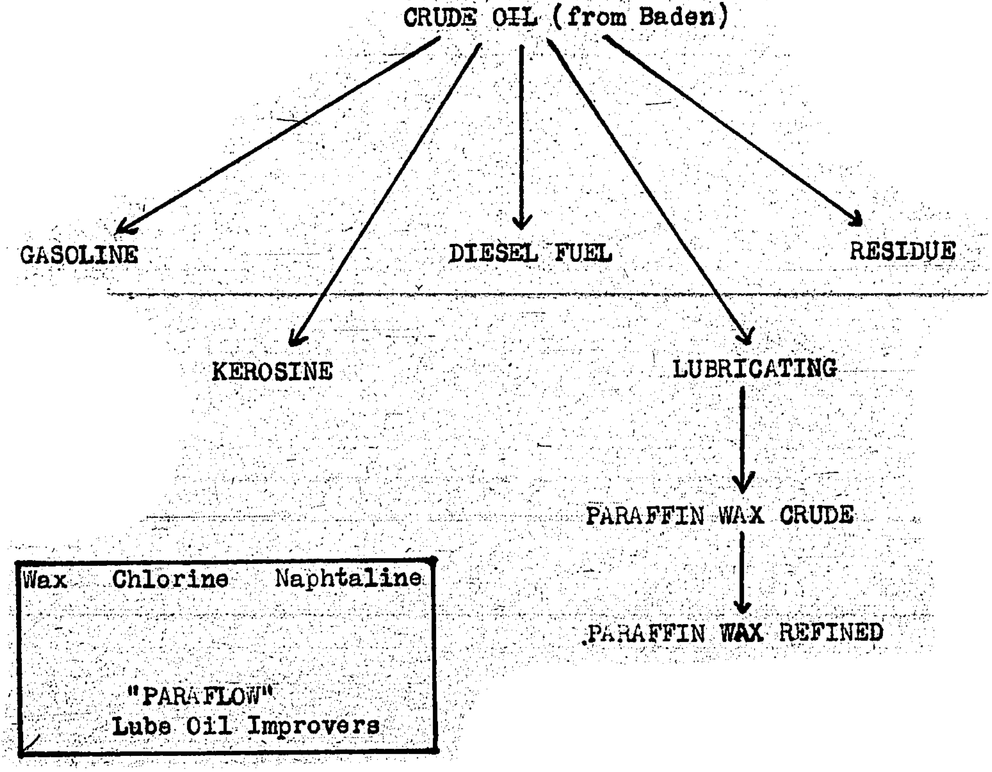


PARAFFIN OXIDATION

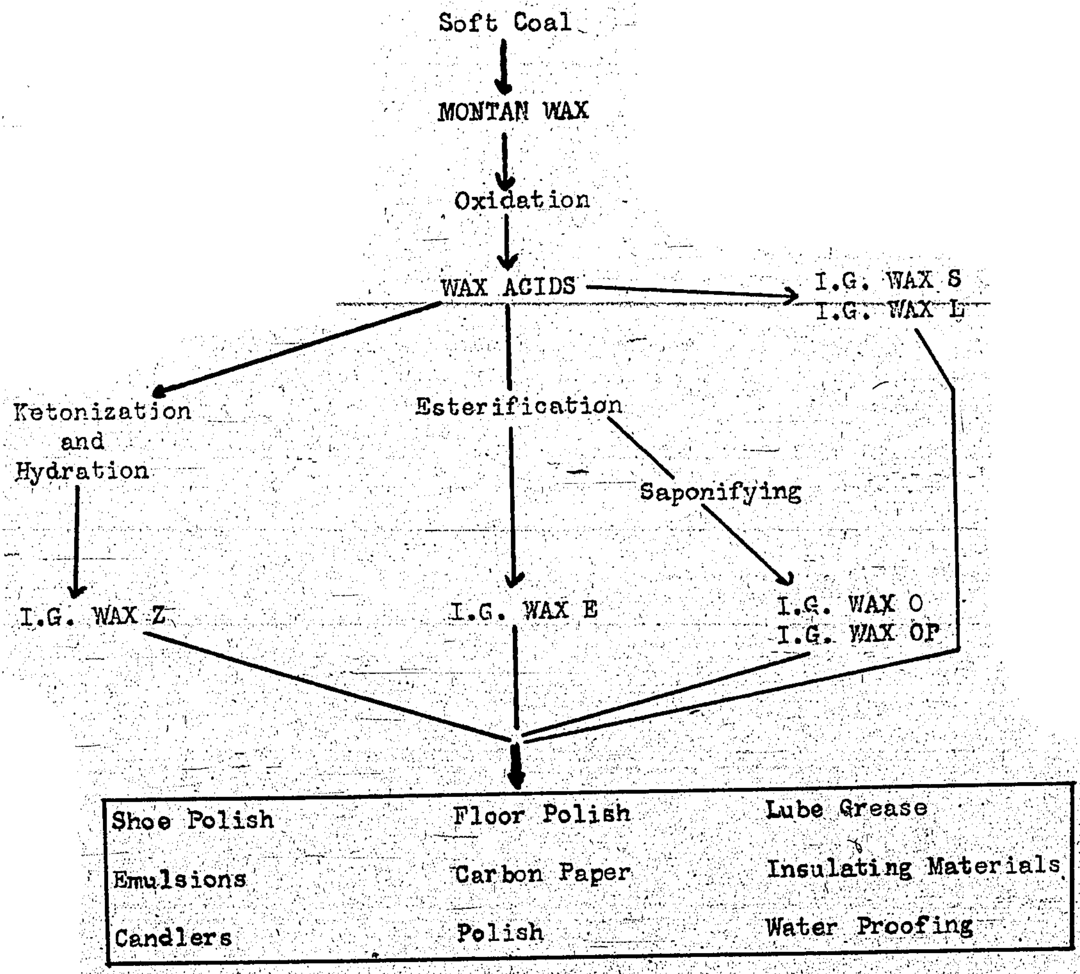




OIL PLANT

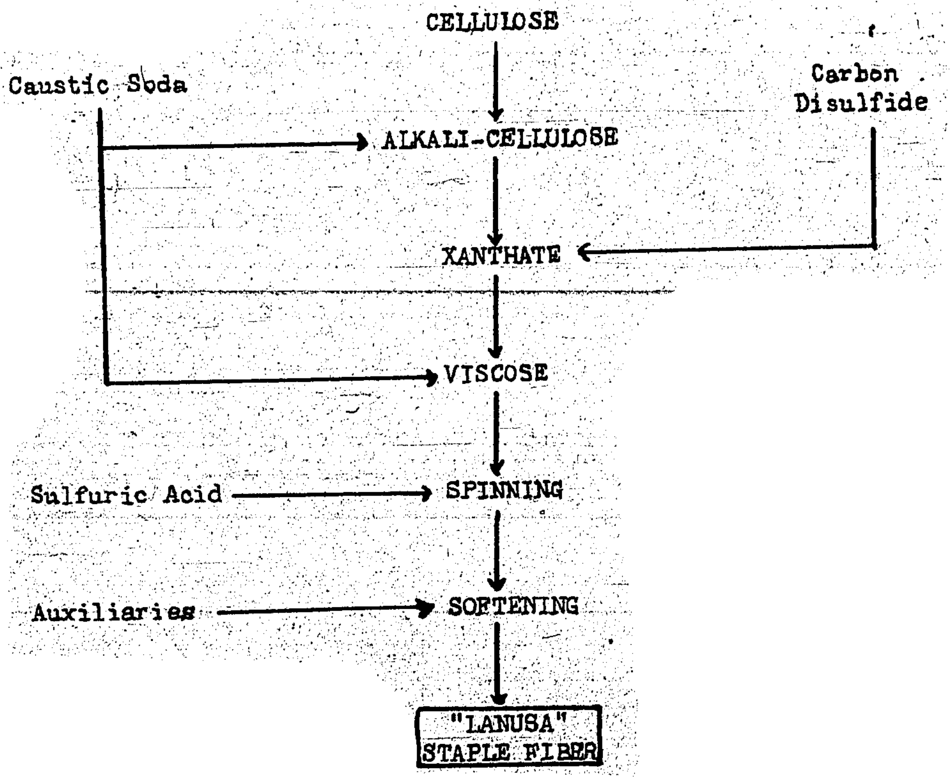

CRUDE OIL (from Baden)
GASOLINE
DIESEL FUEL
RESIDUE
KEROSINE
LUBRICATING
PARAFFIN WAX CRUDE
PARAFFIN WAX REFINED
Wax
Chlorine
Naphtaline
"PARAFLOW"
Lube Oil Improvers

SYNTHETIC WAXES



MANUFACTURING

OF "LANUSA" STAPLE FIBER



PLASTICS

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

SYNTHETIC
TANNING AGENTS

INORGANIC

ALUMINUM COMPOUNDS	CHROMIUM COMPOUNDS
"Blankorole"	Chromium Alum

ORGANIC

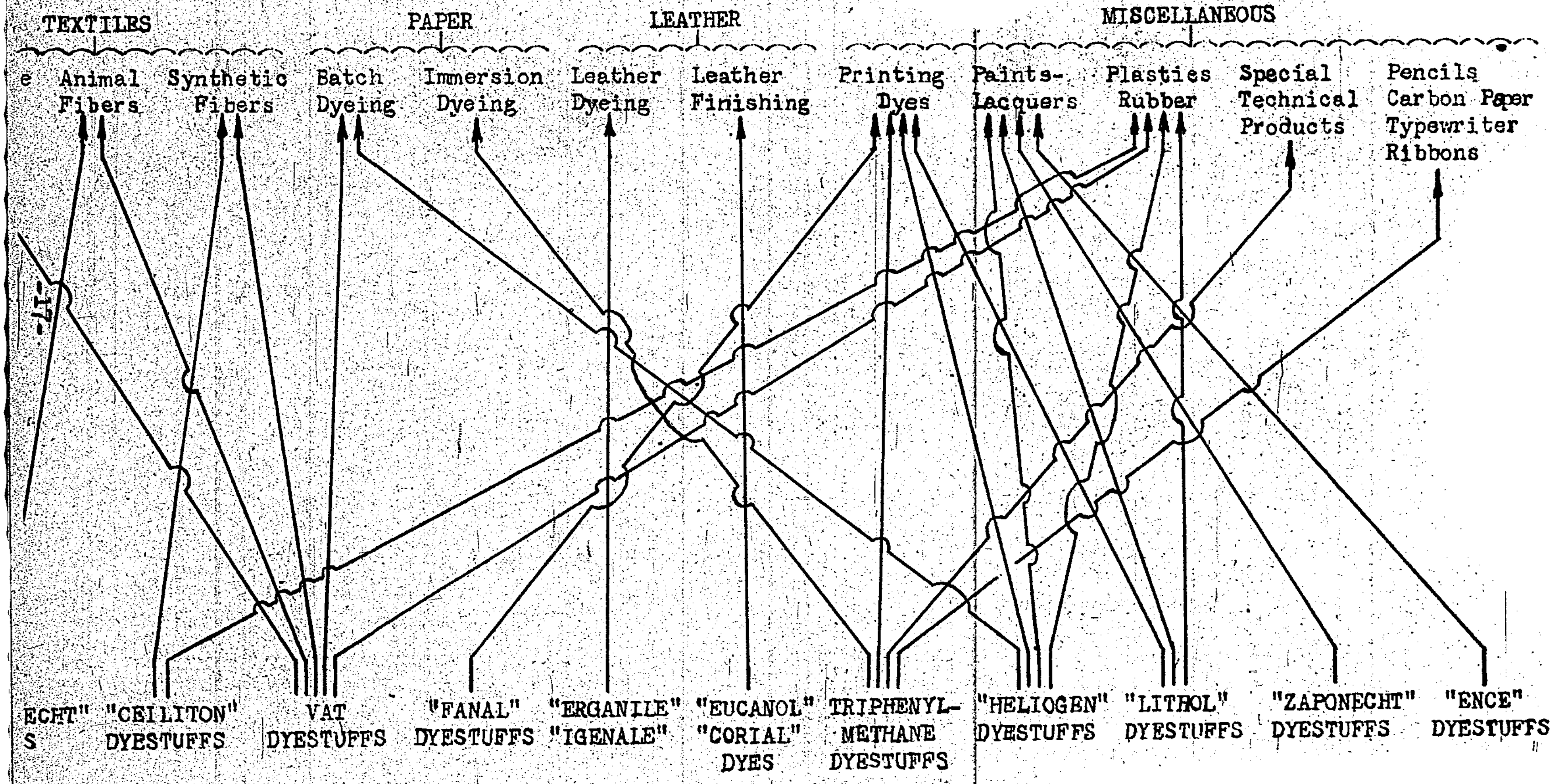
PHENOL AND NAPHTOL DERIVATIVES	COMPLEX METAL COMPOUNDS
"Tannigane"	"Terrigane"

SOLVENTS, PLASTICIZERS AND SYNTHETIC RESINS

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

DYESTUFFS

for



AUXILIARIES

AUXILIARIES FOR GENERAL USE

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

DYEING AUXILIARIES

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

TEXTILE PRINTING AUXILIARIES

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

WOOL and WORSTED INDUSTRY

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

COTTON INDUSTRY

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

MANUFACTURING OF RAYON AND STAPLE FIBE

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

LEATHER AND FUR INDUSTRY

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

BASICS FOR DETERGENTS

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

PHARMACEUTICALS, DISINFECTANTS AND VERMICIDES

PHARMACEUTICALS

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

PRESERVING AGENTS

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

DISINFECTANTS

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

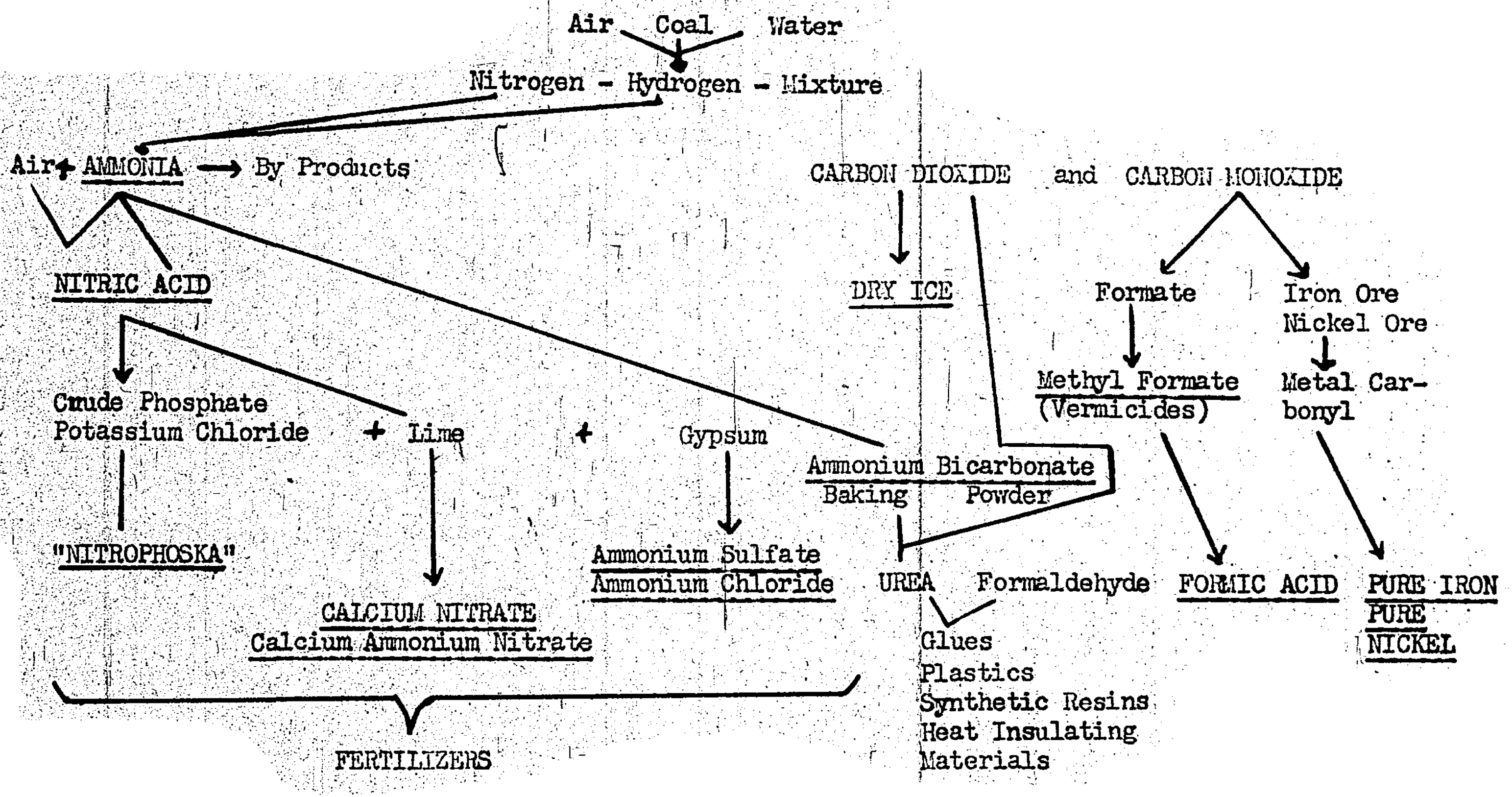
VERMICIDES AND ANTIPARISITES

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

BUILDING MATERIALS AND AUXILIARIES

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

AMMONIA SYNTHESIS



2. INORGANIC DIVISION

a. Chlorine Plant

(1) Brine Department

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

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

(2) Horizontal Mercury Cells

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

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

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

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

(3) Chlorine Cooling, Drying, Compression and Liquefaction

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

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

sulfuric acid plant and the diluted drying acid could be fortified very cheaply with contact SO_3.

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

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

(4) Miscellaneous (Horizontal Cell Plant).

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

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

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

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

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

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

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

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

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

Ba, Ca, Mg not detectable

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

(5) New Rotating Vertical Mercury Cell

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

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

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

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

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

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

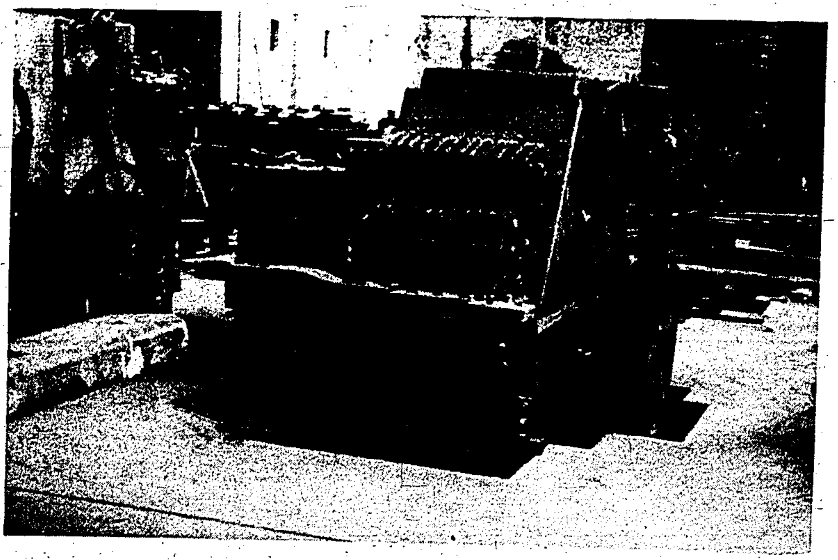
The current flowed from bus bars on each side of the cell through 96 leads, half on one side and half on the other side of the cell, to the graphite anodes. 72 of these leads passed through the top section of the cell and were not insulated from it ~~whereas the 24 leads passing through the central section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

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

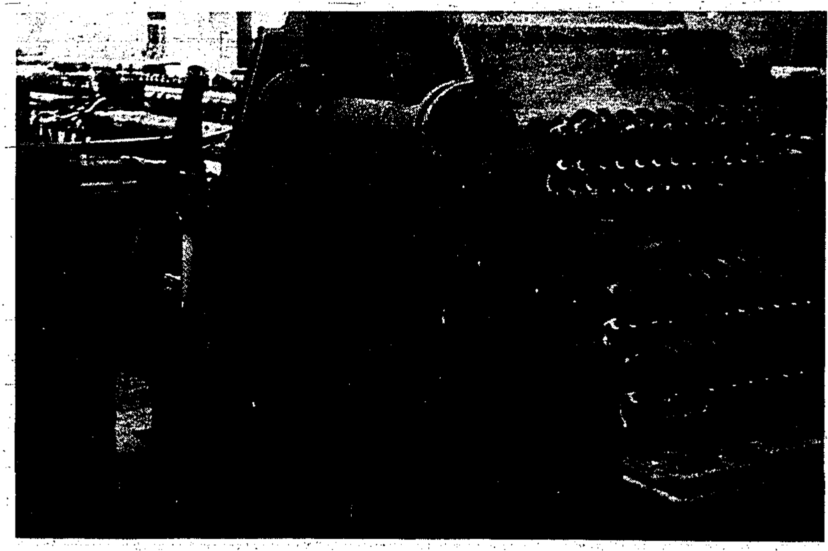
This vertical rotating cell has not yet been operated for a long enough period of time to thoroughly establish such factors as over-all power consumption, voltage, graphite life and durability of parts, particularly the rubber lining. The chlorine plant superintendent, Dr. Honsberg, as well as Dr. Pfannmüller, were most enthusiastic about it and it must have shown real promise or it would not have been used as the basis for the major expansion of the plant. The operation of an earlier version of this cell as installed at Hüls and Heydebreck is not a fair basis to appraise this improved design, according to Dr. Honsberg. In this connection it is noted here that the cost of making 100 kg of electrolytic product was 13.26 RM at Hüls in 1943, and 17.65 at Heydebreck during the first half of 1944 as compared to an average of 8.26 RM per 100 kg for all the other I.G. chlorine plants in 1943. This is probably an unfair comparison because of other factors.

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

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

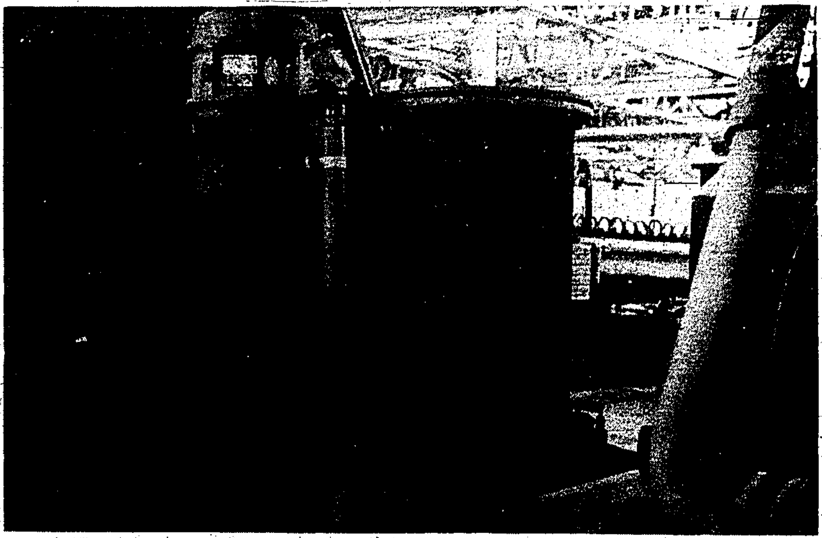


General View of Rotating Vertical Mercury Cell, Showing Amalgam Decomposer (left) and One Anode Bus.



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

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



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

b. Aluminum Chloride

(1) Summary

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

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

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

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

Capacity per Chloridizer

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

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

(2) Chloridizing Step

Dr. Pfannmüller stated that their information was very incomplete as to whether it really was necessary to convert the gases to phosgene before feeding to the chloridizer and he was sure that complete conversion was unnecessary as they had occasionally operated with very little carbon in the gas contact chamber and the conversion to phosgene must necessarily have been low.

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

(3) Condensers

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

(4) Sublimation of Crude Product

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

c. Sodium Hydrosulfite

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

$$Zn + 2SO_2 = ZnS_2O_4$$

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

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

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

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

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

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

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

d. Calcium Carbide and Acetylene Generation

(1) Introduction

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

Salient operating data on the units are as follows:

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

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

(2) Production of Carbide

Coke and anthracite coal were crushed to minus 1½" and blended with minus 1½" lime (CaO) received from a nearby plant. The materials were elevated to an overhead storage bin from which they were fed manually to the furnace at a rate sufficient to keep the top of the charge burden about 5' above the level of the molten reaction mixture. The entire top of the furnace was surrounded by a 5' high wire screen barrier and ventilated to take care of dust losses which were discharged to a very tall stack by means of a blower.

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

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

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

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

(3) Generation of Acetylene

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

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

(4) Miscellaneous

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

Capacity 1943 -

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

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

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

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

e. HCl

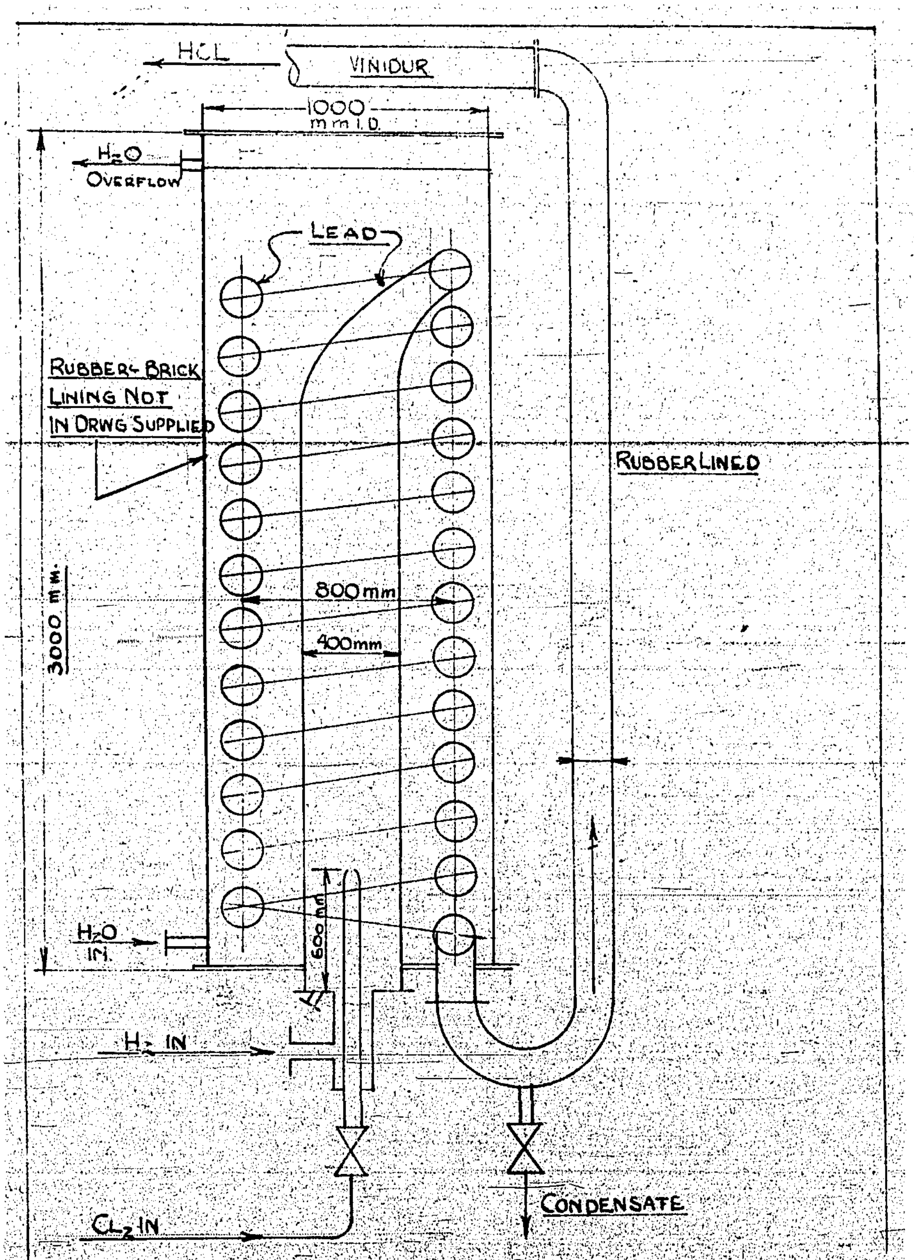
(1) General

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

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

(2) Burning of Hydrogen and Chlorine

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



HYDROGEN-CHLORINE BURNER.

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

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

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

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

(3) Hydrochloric Acid Production

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

(4) Hydrogen Chloride Compression and Liquefaction

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

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 re-compression 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 (motol) ~~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-O 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.

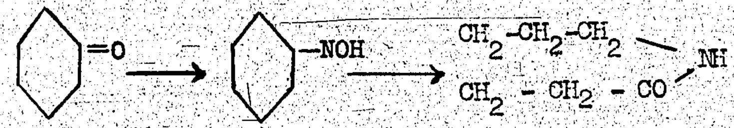
The bulk of the above data were given by Dr. Kollek, head of the Coloristic Department.

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 ethylene alone
With fumaric ester - hard product
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

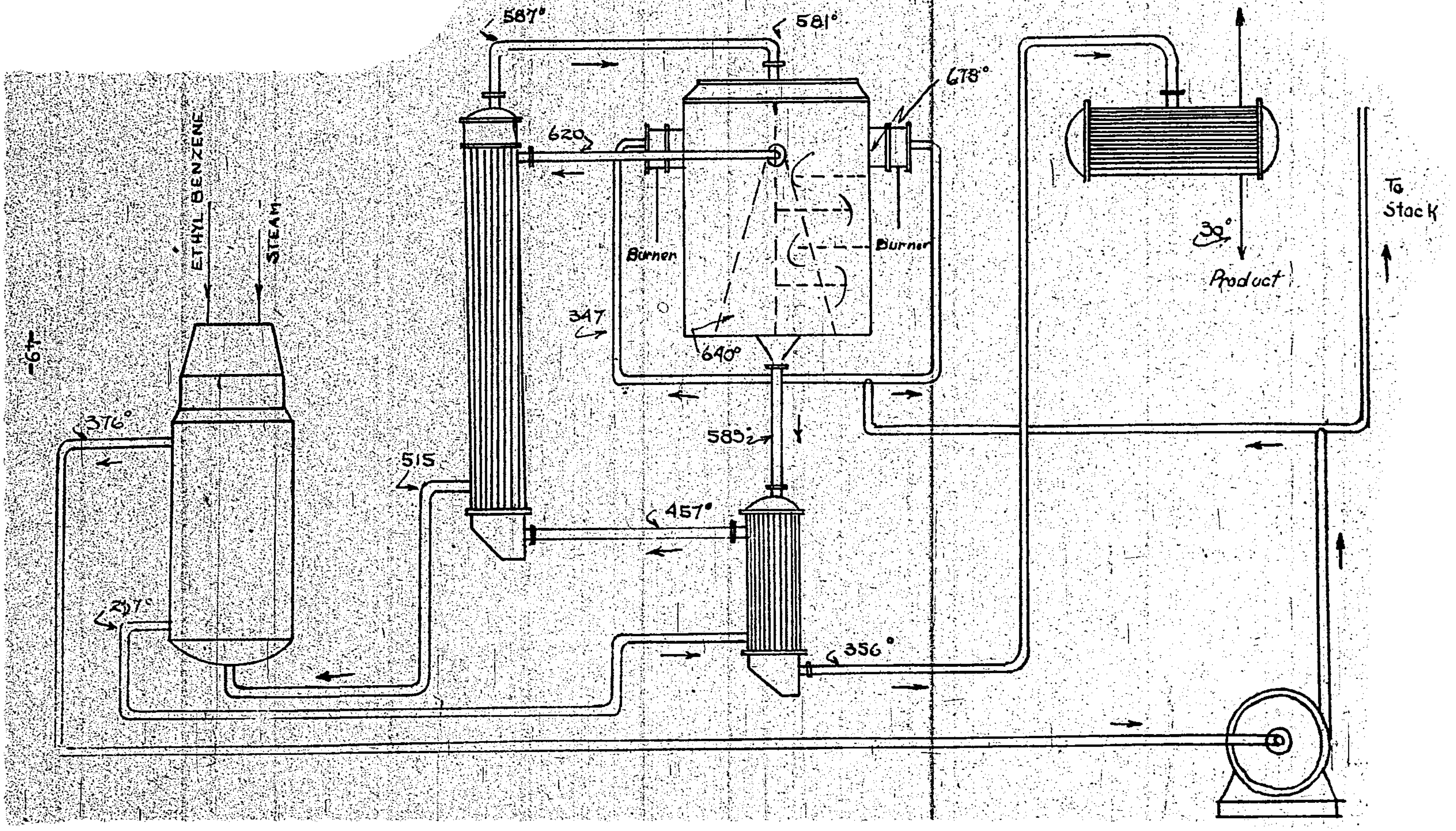
Styrene, in addition to being a key component of synthetic rubber, found considerable use as a polymer. Production of monomeric styrene was begun at Ludwigshafen in 1928, based on the development work of Mark and Wulff (now works manager at Schkopau).

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.

SKETCH OF
STYRENE CONVERTER



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

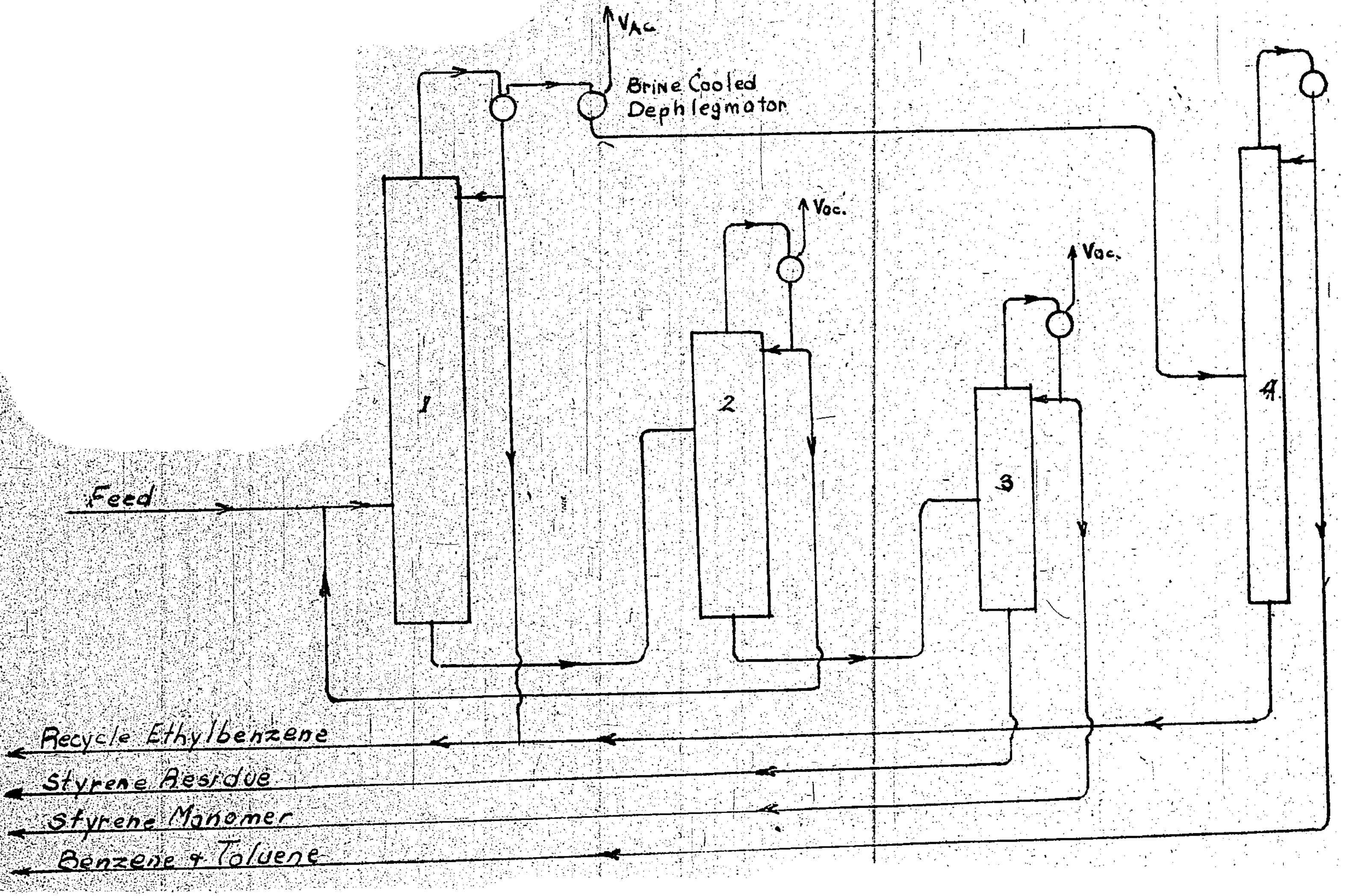
The Ludwigshafen units, each designed for a rated capacity of 100 tons of styrene per month, have been operated at rates of 130 tons under the same conditions of conversion with no change in yield. From the data which were available it is believed that this study was not completed.

(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

STYRENE DISTILLATION SYSTEM.



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	Ca1.0
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.

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 prepolymerized 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. Chlor~~inated 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.

<u>Oppanol C</u> 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.

<u>Oppanol O</u> 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 develoment 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 D, 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		C_2H_2 in feed Vol. %	Approx. Annual Prod.-Tons
			C_2H_2	Alcohol		
Methyl	160	20 - 22	90	90	55	200
Ethyl	155	18 - 20	92	92	60	1000
Isobutyl	150	4 - 5	92	95	90	2400
Butyl	150	4 - 5	90	92	90	50
Decahydronaphthol	170	0	88	85	90	20
Octadecyl	175	0	88	65	90	10
1.4- Butandiol 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.

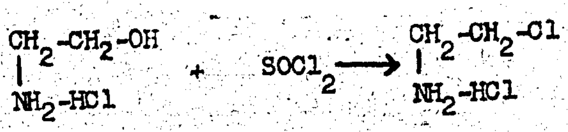
Commercial anhydrous potassium hydroxide and pure methanol were boiled to remove traces of water and prepare a potassium methylate solution. This catalyst solution, together with fresh methanol, was pumped into the reactor as necessary to maintain the proper concentration, about 5% KOH, and to keep the 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.

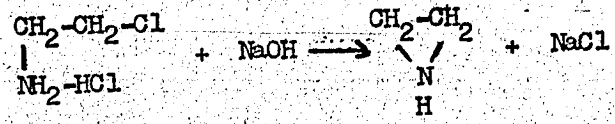
1. Ethylene Imine

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:

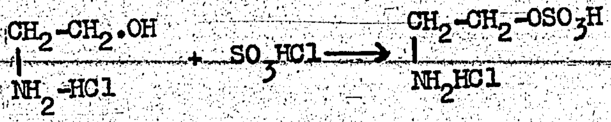


$$\begin{matrix} CH_2-CH_2-OH \\ | \\ NH_2-HCl \end{matrix} + SOCl_2 \longrightarrow \begin{matrix} CH_2-CH_2-Cl \\ | \\ NH_2-HCl \end{matrix}$$

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

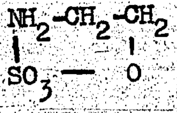


Since acids catalyze the polymerization, the product was stored in carbon dioxide free atmosphere. Another method of synthesis, employed in the original research by Dr. Ulrich, was the reaction -



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

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



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 $CH_2 = CH-NH_2$ 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.

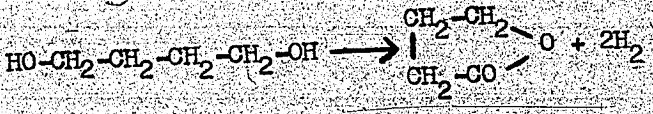
m. Vinyl Benzoate

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

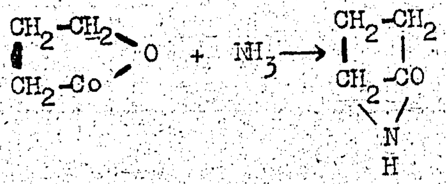
Vinyl pyrrolidon is a new polymerizable product from the I.G. developments in acetylene chemistry. It was introduced in 1942. The starting product was 1,4-butanediol, the intermediate in the synthesis of butadiene. This was dehydrogenated to gamma butyrolactone as follows:



$$HO-CH_2-CH_2-CH_2-CH_2-OH \longrightarrow \begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CO \end{matrix} \!\!> O + 2H_2$$

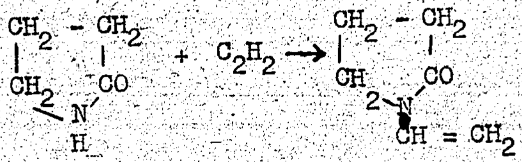
Butandiol was vaporized at 200°C and passed together with a stream of hydrogen over a copper on silica catalyst maintained at 200-230°C. A feed rate of 20 gm of diol and 350 liters of hydrogen per hour per liter of catalyst was used. The hydrogen split off in the reaction was scrubbed with water and 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 carboazole 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
No. 90		Glycerine + 6 mols ethylene oxide		5
--		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.

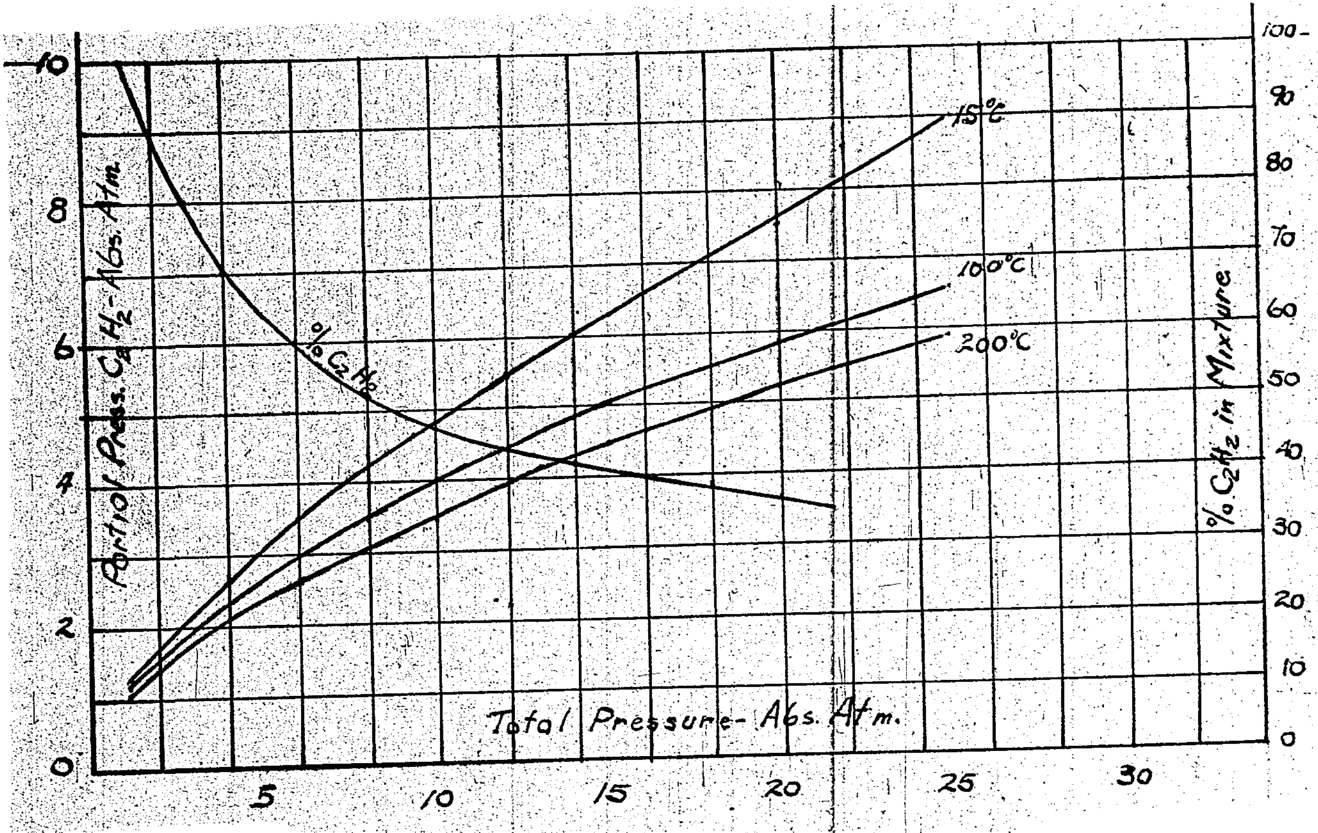
Igelite PC was ground to 300 mesh and milled with 1 to 2% I.G. wax at 160°C on a 4 high calender rubber mill to give a 0.040 mm sheet. The wax was added only to facilitate the milling. The sheet was then given the Luvitherm treatment which is a mechanical stretching in two directions. The sheet was drawn 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 FG	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 Trilon 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.

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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 14 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.

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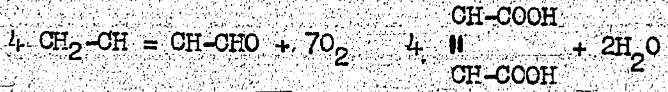
d. Maleic Acid

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 hydraulic 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 single 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 free-board 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	$C_{10} - C_{18}$
	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.

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