APPENDIX B

ISO OCTANE PLANT
DESCRIPTION AND FLOW SHEET FOR THE SPECIAL MOTOR FUEL PLANT "AT 244" (INCLUDING PRODUCTION OF BUTYLENE)

The "AT 244" plant, a code name apparently, serves to produce special motor fuel from the C4 hydrocarbons which are produced as a by-product of brown coal hydrogenation. The ratio of iso to normal butane normally pro- The hydrocarbons are puri- duced was said to be about 1:3. fied "according to normal procedure," liquified and separated into the feed tanks (1) for n-butane and (22) for iso-butane, shown on the attached drawing. All numbers hereafter refer to the accompanying drawing numbered "Rh-1414-16."

The entire process is simply a combination of dehydrogenation of n-butane to butylene, followed by sulphuric acid-catalyst-alkylation with iso-butane. All apparatus is more or less conventional for such operations except the moving catalyst arrangement for dehydrogenation. This step will be discussed later in a little detail, but at the moment a translation of a description of the entire plant will be given.

N-butane is taken from storage tank (1), vaporised in a vaporiser (2), and after passing through heat exchanger (3) is led to catalyst chamber (4). This (chromia-alumina on Terano Earth catalyst at 540°C - translator's note) operation dehydrogenates the feed mixture in this catalyst chamber, and the exit gas mixture is cooled in cooler (5), freed of dust in the filter (6), and is sent to gasometer (7). The catalyst in chamber (4) moves downwardly into col- lection vessel (10), and is lifted to the hopper (11) of the regeneration chamber by bucket conveyors (8). After regeneration, during which the catalyst moves downward, the solid passes into collection chamber (12), thence out and back into the entrance chamber (9) by bucket conveyors for the catalyst chamber (4). Gasometer (7) serves as a suction vessel for compressor (13) which compresses the gas to 10 atmospheres, after which condenser (14) liquifies a portion which drops out in separating vessel (15). Uncondensed gas passes to the oil washer (16) where it is scrubbed at the 10 atmpspheres pressure.

This enriched oil is stripped in (18) and the absorbed C_4 hydrocarbon product is sent back to gasometer (7). In the usual fashion, the stripped oil is cooled by cooler (18a) and is sent back for further washing of incoming gas in tower (16). The stripped gas that is outlet to (16) passes to the stripped gas holder (17) from which it is taken in part to heat the burners of the dehydrogenation tower (4). The liquified gas is taken from the collection vessel (15) to the stabilising column (19) which separates the lower boiling hydrocarbons at 25 atmospheres operating pressure. The top of column product from stabiliser (19) is either led to the fuel gas holder (17) or may be used for cylinder butane-propane mixture. The heavier hydrocarbons ($N-C_4-H_8$) emerging as a bottom stream for (19) pass through a water separator (20) into an intermediate tank (21). The contents of (21) together with those of tank (22) already mentioned as holding isobutane, serve as a feed for the alkylation unit. The operation of this unit will now be described.

Products from the two tanks (21 and 22) are mixed in a definite ratio, after which they pass through a heat exchange system (23) into a mixing vessel (24). A part of the mixture is allowed to evaporate in order to produce the required low temperature (translator's note: said to be about 0°C to + 5°C). The gases which evaporate to furnish the cooling are passed through a liquid separator (26), thence to compressor (27), where they are compressed, after which they are condensed again in condenser (28) and led back into the intermediate tank (29). From this tank they are mixed back into the refrigerating and mixing vessel (24).

The cooled liquid hydrocarbons in the mixing vessel (24), which is actually a reaction vessel, are contacted with concentrated sulphuric acid out of the feed tank (25). This catalyst partly converts the mixture into "AT" product. The mixture, consisting of "AT" product, unreacted hydrocarbons and sulphuric acid, passes to the separating vessel (30) where it is allowed to separate over a period of time into an upper layer of butane-"AT"-mixture, and partyly spent sulphuric acid.

Part of the bottom layer of sulphuric acid passes back after admixing fresh acid from (29) to the mixing and reaction chamber (24). A portion corresponding to the fresh acid added is removed from this sulphuric acid circulating system and discarded as shown".

*Reaction vessel (24) was said in conversation to be maintained at 88% H_2SO_4 concentration.

The upper layer from separating vessel (30), consisting of hydrocarbons and "AT" product, passes through the heat exchanger (23), through the pre-heater (31) to the "fine" separating step (32). Here again, at elevated temperature, sufficient time is allowed to make an almost complete separation between the butane mixture and the remaining sulphuric acid. This residue sulphuric acid from the "fine" separator (32) is removed batchwise from separator (32) and delivered to collection vessel (33). The butane and "AT" product (top layer) from (32) now almost free of sulphuric acid passes to an intermediate tank (34) and into the caustic washing system.

Dilute caustic from tank (37) is mixed with the hydrocarbon mixture in orifice mixer (35), after which it is separated in the separator (36). The bottom layer caustic which collects in this separating vessel is circulated until it is substantially used up, and is then removed batchwise as very dilute caustic, and led away.

Returning now to the hydrocarbon mixture which emerges as a top layer in separator (36) it may be noted that this passes through two stages of water washing, which removes all of the caustic by means similar to the caustic washing process. Thus, orifice mixer (38) serves to mix the water which is separated in separator (39). The water layer passes to the condensate vessel (40) and from the upper layer mixture butane and "AT" product is run from the intermediate tank (41) into the distillation operation.

Here the distillation pump (42) feeds the mixture to stabilisation column (43), where butane is separated for recirculation in the process, and the true "AT" product is obtained as a bottom-of-column product. A pump taking suction from the bottom of column feeds the redistillation unit (45). The special "AT244" stream is taken as a top product from this redistillation unit and led to the finished product tank (46). "The AT" product was said, in conversation, to show 92 octane no. (motor method). The bottoms from the redistillation column (45) are passed to the C_4 separating column (47). Bottoms from this pass to the feed tank No. 1 directly. Distillate from column (47) passes to a connecting column (48) which thoroughly frees same from lower boiling hydrocarbons, after which the heavier residue portions are mixed with the bottom product of stabilising column (1a) and recirculated back to the "AT" operation just before the point where n-butane is dried in (20).

All the above material, with the exception of a few notes indicated as such, is translated from a seized document, purporting to be a description of the "AT" plant. This document is undated and it is not known whether the flow diagram indicated actually corresponded to the plant which was nearly built though never operated at Wesseling.

At this writing no drawings or other diagrams have been discovered to indicate the mechanical nature of the most interesting feature of the process, namely, the catalyst chamber (4) and regenerator (8). However, in Appendix F, giving the preliminary report made by the investigators, there is a description, on page 133, of this apparatus which was obtained in oral discussion with previous employees at the plant. For the present this will have to serve as the only information on the catalyst reaction chamber and regenerator.

It must be noted, however, that the batchwise operation there described does not seem to correspond very well with the description just given above which would tend to indicate a truly continuous process. The explanation of this anomaly will undoubtedly come when other plants are uncovered which actually have the "AT" process in operation. From information gathered by the team which went to Ludwigshafen it appears that such "AT" plants do exist at Leuna, near Merseberg, at Scholven in the Ruhr, and at Pölitz, near Stettin. It was also stated that there may be three other plants which have the "AT" installations.

OPERATING REQUIREMENTS OF THE "AT" PLANT

In a letter dated April 12, 1944, to Director Dr. Müller von Blumencron of U.R.B.K.A.G., the following data were given as to yields from the alkylate plant which von Blumencron had apparently wanted for some time to insert in the contract to be signed in connection with this unit. Data given by Leuna Werke/Krs. Merseburg but the copy available had no signature.

The following is a translation of the pertinent parts of the letter:

"The figures given below are operating data and are corrected to current yields of 80% alkylate, referred back to the butane introduced. All figures refer to 1 ton (metric) of aklylate.

Yield	80%
Contact introduced	5-7 kg
Sulphuric acid used	20% referred to alkylate
Fresh sulphuric acid introduced	15% of the above amount
Usage of NaOH	ca 0.4% basis alkylate
Steam required	7.4 tons High Press 8.0 " Low "
Water required	533 cu. meters employed (10% fresh water)
Electricity	200 KW High Tension 235 KW Low Tension, exclusive current for recirculated water cooling
Fuel gas required	2.1 Mio WE
Personnel required	170 operators for the entire plant
Credits	9.7 cu. meters "Condensate" (presumably referring to steam condensate from above quantity of steam)

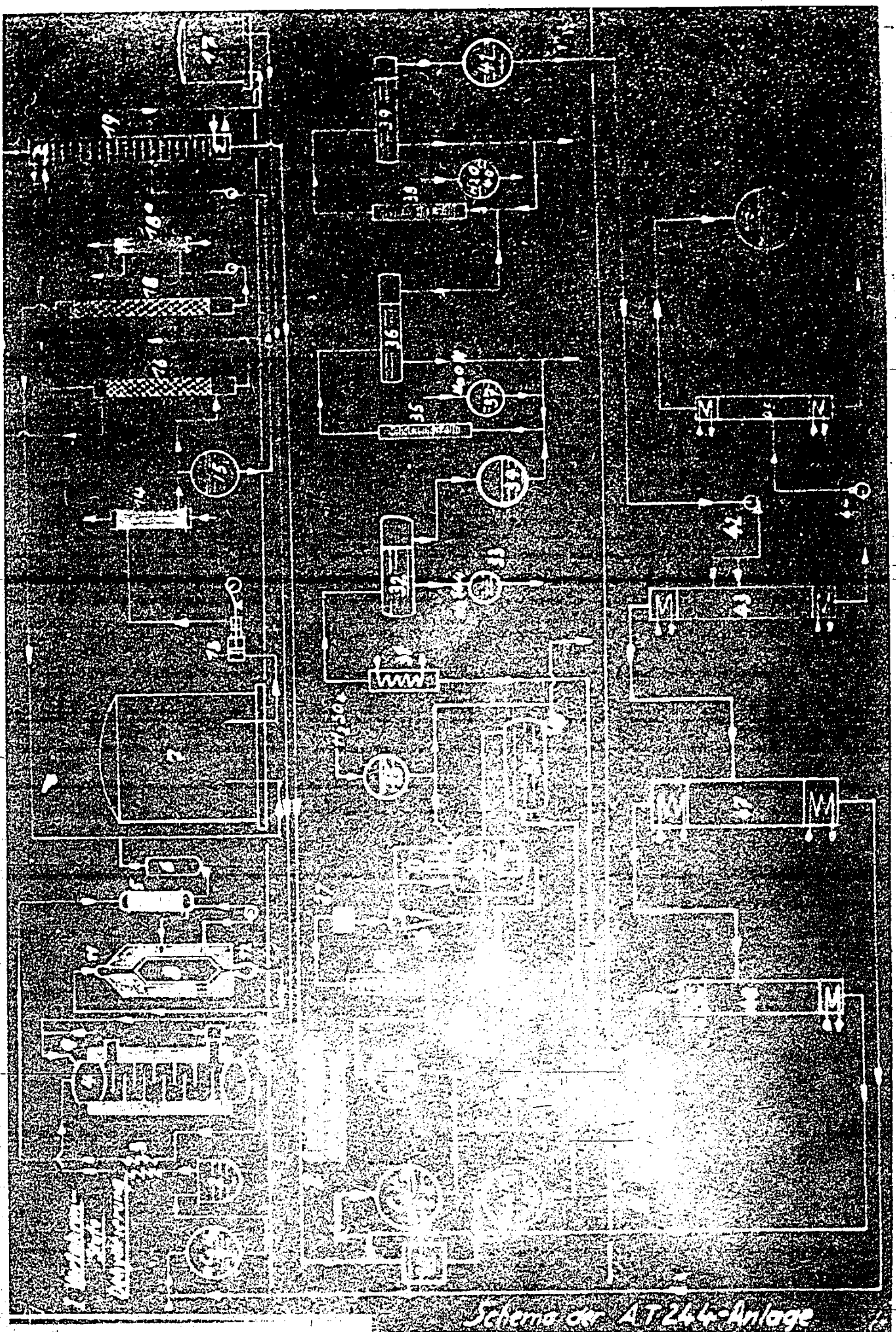
"We note that these figures refer to the particular conditions of our plant. Energy usage in your case may be different. We recommend that you have your own engineers look into the matter.

Heil Hitler, etc.

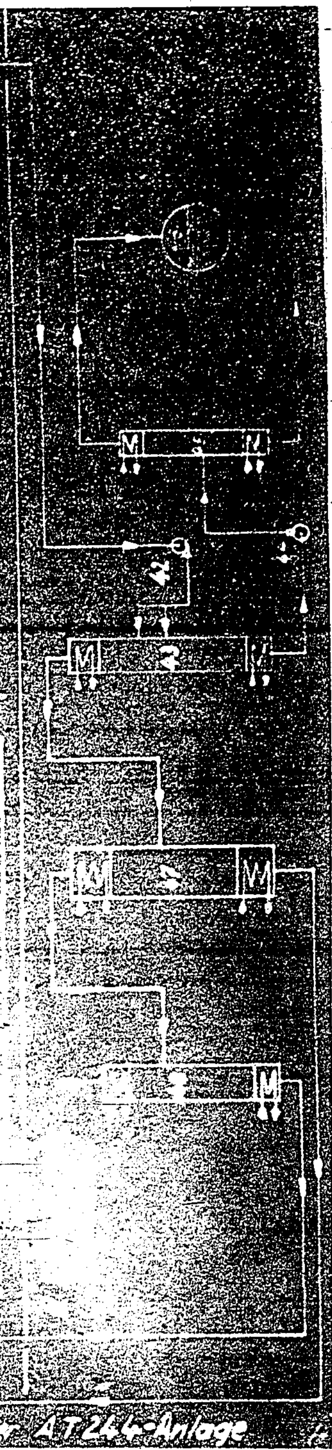
(no signature)

While the above is a free translation, the matter clearly refers only to "alkylate". It will be obvious, however, that the figures must refer to the entire "AT" plant, as this term is used in the rest of the manuscripts we have seen; hence both the dehydration and alkylation steps are discussed, otherwise the terms "Contact introduced" and the usage of gas would have no meaning.

Apparently, 5-7 kg of the chromia-alumina catalyst are used per ton of alkylate finally produced and 2.1 million WE heat units in form of gas are used for both the conversion and regeneration steps. The sulphuric acid figures are ambiguous in the original. The figure of 20% must refer to the volume of acid used with hydrocarbons in the alkylation, whereas the figure of 15% is the actual consumption of fresh acid. No mention is made of disposition of used acid and no credit shown for this material.



Flow Sheet of the
Alkylation Plant
at
Wesseling.



r AT244-Anlage

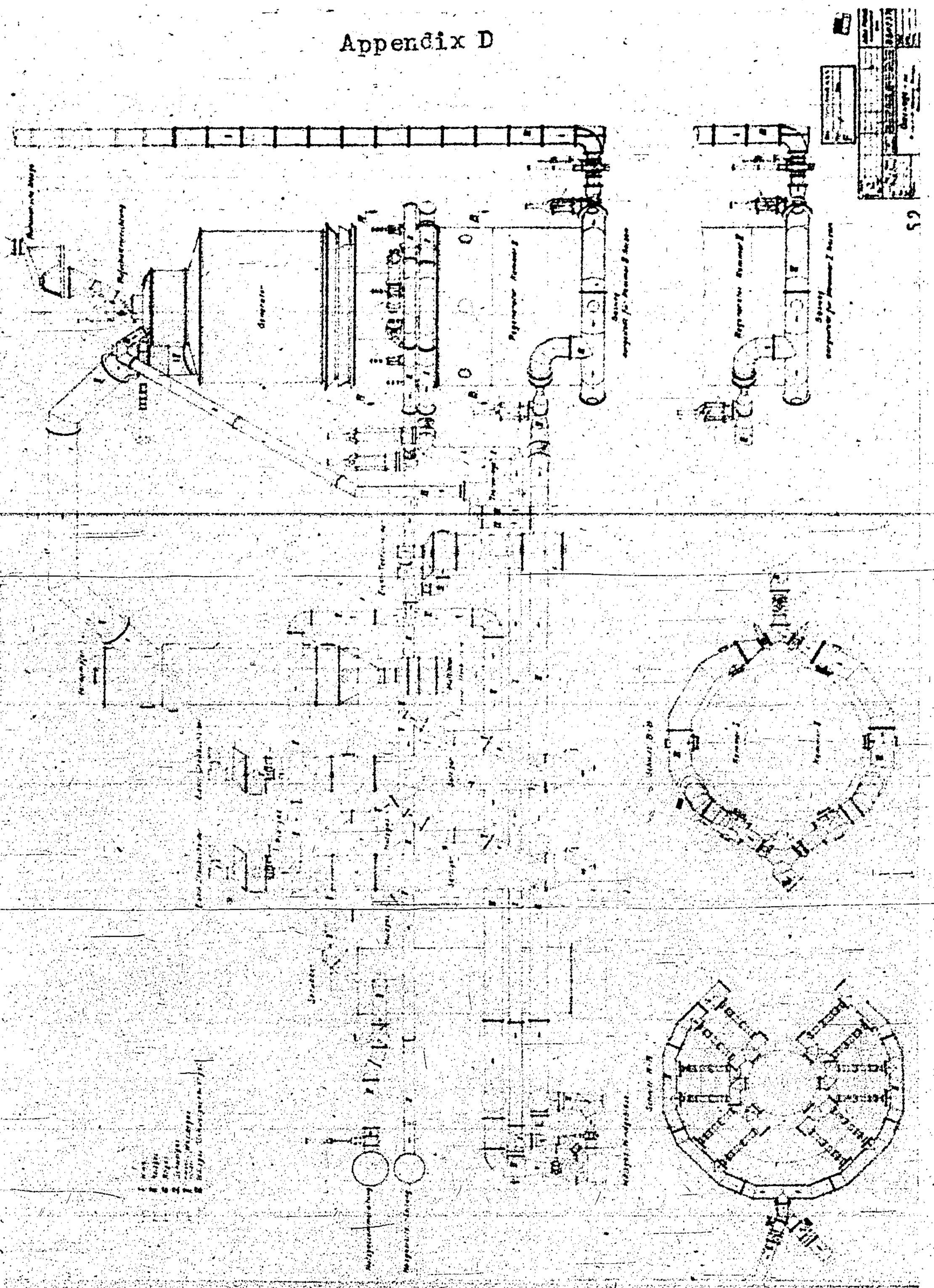
APPENDIX C

Personnel of the Wesseling Plant of the Union Rheinischen Braunkohlen Kraftstoff Fabrik, A.G.:

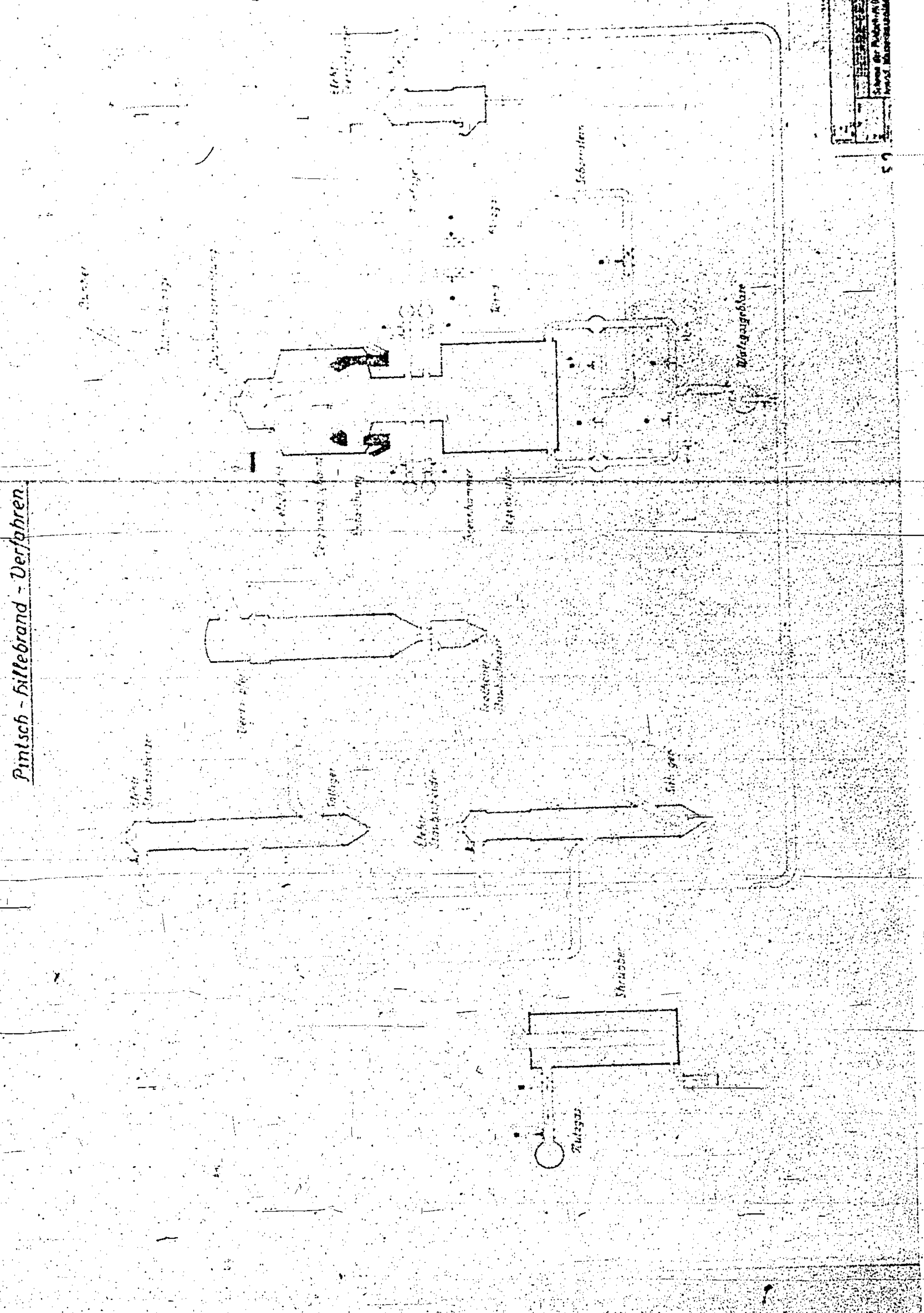
* 1. Dr. Müller von Blumencron, General Manager
2. Dir. Dr. Moll, Production Manager
* 3. Dir. Dr. Peukert
4. Dr. Kerzillius
5. Dr. Nedelmann
6. Dr. Schilling
7. Dr. Neubauer
8. Dr. Abegg
* 9. Dr. Schuh
* 10. Dr. Heinz Sustman, Chief Chemist
11. Dr. Meissner
12. Dr. Erdmann
13. Dipl. Ing. Wörner
14. Dr. Ing. Jaeger
* 15. Dr. Fischer, Dispatching Manager
* 16. Dipl. Ing. Gerhard Feldhoff

* Interrogated

Appendix D



Appendix D (continued)



APPENDIX E

The following is a translation of a document from the I. G. Farbenindustrie and signed by Pier, seized at Wesseling, dated 15 July 1939 and relating to the preparation of Benzine and Diesel Oil from the Middle Oil produced by the liquifaction of Rheinish brown coal. It contains the following details:

Summary - 15 July 1939:

For the production of Diesel Oil and Benzine, the middle oil of the liquifaction and having an end-point of 350°C. and including also the Sumpf-phase benzine is given a preliminary hydrogenation over catalyst 5058 at 250 atm. pressure and from the resultant middle oil by means of catalyst 6434 auto-benzine and L-benzine are produced. The Diesel oil in the preliminary hydrogenation product has Cetene number of 46-50 and according to the degree of hydrogenation, a pour-point of -26 to -34°C.; (1) the viscosity of the Diesel oil fraction having a first drop of 200°C. was too low; however, this was easily adjustable to the proper value by raising the first-drop temperature of such fraction. The throughput was 1.0 kg/liter/hour of catalyst; the gas produced amounted to 1.5-3% (average 2.2%) of the injected hydrocarbon oil. The product of the preliminary hydrogenation had 39% below 180°C. and 27% below 150°C.

For the production of auto- or L-benzine, the benzine fraction was distilled off the product of the preliminary hydrogenation and the middle oil was treated over catalyst 6434 at 200 atm. The benzine fraction obtained from this 6434-treated fraction was admixed with the benzine fraction produced in the preliminary hydrogenation in the proportion in which they are produced; the so-obtained auto-benzine had an end-point of 180°C. with 37% over below 100°C, and its octane number was 68. By operating to obtain a higher

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(1) By the use of catalyst 6719 only, a Diesel oil having a Cetene number of about 35 is obtained.

content of material boiling up to 100°C., the octane number of the resultant benzine can be improved. In those cases where no Diesel oil needs to be produced, the preliminary hydrogenation can be made milder so that the octane number of the so-formed benzine can be raised by 1 to 2 units.

The L-benzine (benzine produced during the preliminary hydrogenation step + 6434 - Benzine) has an octane number of 69 (motor method) and 49% distills below 100°C. and 95% distills at 150°C; with 0.1% addition of lead, it has an octane number of 87.5. The Benzine is cut relatively high and has an end-point of 145°C. and 58% at 100°C. an octane number of 73.5 (motor method) and with 0.09% lead, this is raised to 88 and with 0.1% lead, to 89.

The throughput in the 6434-step during operation to produce auto-benzine was 1.4 with 9% production of gas. When operating to produce L-benzine, the throughput was 1.15 with 16% of gas produced including stabilization losses.

1. Preliminary Hydrogenation of Middle Oil from Rheinish Brown Coal with Catalyst 5058.

In the preliminary hydrogenation of the middle oil of brown coal liquifaction with about 10% of Sumpf-phase benzine added, there is obtained, by cutting 27% of benzine, a product having an octane number of 69 (Research Method) and an end-point of about 100°C.

The Diesel oil obtained has a cetene number of 46 to 50 depending upon the degree of hydrogenation and has, in the event that the first drop is too close to 200°C., a somewhat too low viscosity; the first drop must be therefore at a somewhat higher temperature. According to the material balance worked out in 1938, 10% Diesel oil must be altered to benzine by use of catalyst 6434. If this fraction is distilled out below the Diesel oil, it will have the proper viscosity of about 1.2°E at 20°C (compare Table IV, tests of January 29 and February 10, 1939). Another possibility of further increasing the viscosity of the Diesel oil may lay in a higher end-point of Sumpf-phase middle oil.

Experimental Data

Sumpf-phase benzine without the gas benzine and with Sumpf-phase middle oil in the ratio of 1:10 from Rheinish brown coal is prehydrogenated at 250 atm in a 1.5 liter gas-phase convertor over catalyst 5058. By means of the fractionating column connected with the catch-pot, the hydrogenated product was continuously separated into benzine and B-middle oil:

Operating conditions were:

a. Pressure 250 atm.

b. Temperature, 382/381°C.

c. Throughput, 1.0 kg/liter/hour

d. % P471-addition o.5

3. Cbm gas per kg. oil injected 3.0

The resultant catch-pot product has the following characteristics:

Specific Gravity	0.830
Aniline Point °C.	- 48
First drop °C.	78
% - 100°C.	4.0
% - 120°C.	14.8
% - 150°C.	29.0
% - 180°C.	41.0
% - 200°C.	49.5
% - 225°C.	61.0
% - 250°C.	74.0
% - 300°C.	92.0
End Point % C°	322°/98.8 cc.

On the average, the gas produced amounted to about 2.2% of the injected oil. By means of the fractionating column, benzine products of different end-points were cut. The important characteristics of the so-obtained benzine are given in the following table.

Benzine Product	0.48	0.31	0.29	0.27
% Concentration	49	39	31	27
Benzine:				
Sp. gr.	0.790	0.780	0.776	0.768
% below 100°C.	19	20.5	24.5	37
End Point °C.	190	178	153	144
Octane Number:				
Research Method	63.5	66	69	69
Motor Method	62	63.5	65	67
" + 0.09% Pb.	80	-	-	84

In the scheme for Rheinish brown coal (Mar. 7, 1938), it is anticipated to separate the 5058 catch-pot product into 26% benzine, 20% heavy benzine for use over catalyst 6434, 10% Diesel oil for catalyst 6434 and 44% Diesel oil itself.

As provided, benzine would be cut out of the prehydrogenation product at about 150°C. and it would have an octane number of 69 by Research Method (see also Table II).

After the heavy benzine is separated, the residue has a Cetene number of 46 to 50, depending on the degree of hydrogenation, the pour-point is in all cases good; however, it has too low a viscosity with 1.14°E at 20°C. Consequently, it seems proper in the operative scheme which provides for a 10% Diesel oil cut for 6434 treatment, to make the cut somewhat narrower in order to bring the viscosity of the Diesel oil up to 1.2°E at 20°C. (See Table IV, tests of January 29 and February 10, 1939). Tests on the heavy benzine and Diesel oil are set forth in Tables III and IV.

TABLE I

Characteristics of the Injected Oil

Sumpf-phase Benzine and Sumpf-phase Middle Oil from Rheinish Brown Coal (1:10)

Sp. Gr.	0.952
First Drop °C	90
% below 100°C	2.8
" 150°C.	7.0
" 180°C.	13.0
" 200°C.	20.0
" 250°C.	47.5
" 300°C.	70.5
" 325°C.	83.8
" 350°C.	95.5
Residue	4.5

TABLE II

Benzine Tests

Atm. Pressure	250	250	250	250	250
Kg/ltr/hr	1.0	1.0	1.0	1.0	1.0
Temp. °C.	382/391	382/391	382/391	382/391	382
Cbm gas/kg/oil	3	3	3	3	3
Operating days	5	7	7	13	17
Benzine Output	0.48	0.31	0.31	0.26	0.27
" Concentration	49	39	39	27	27
% Gas/Prod. & Gas	-	-	-	1.4	2.9
Benzine					
Sp. gr	0.790	0.780	0.776	0.776	0.768
Aniline Pt. °C.	33.8	+ 33.7	+ 34.8	+ 32	+ 35
First Drop °C.	73	68	71	74	72
% below 100°C.	19	20.5	24.5	28.5	37
" 150°C.	68	78.5	97.5	-	-
" 180°C.	92	-	-	-	-
95% - Point °C.	184	173	147	144	141
End Point °C.	190	178	153	148	144
Octane No.					
Research Method	63.5	66	69	-	69
Motor Method	62	63.5	65	-	67
" - 0.09% Pb	80	-	-	-	84

Composition.

% Paraffins	-	-	-	-	26
% Naphthenes	-	-	-	-	61
% Aromatics	15	-	-	-	12.5
% Unsaturateds	-	-	-	-	0.5

Fractions.

80-100°C	-	-	-	-	0.750 + 35
110-140°C	-	-	-	-	0.780 +35.2
150-180°C	-	-	-	-	-

Elementary Analysis.

% C	-	-	-	-	86.02
% H	-	-	-	-	13.78
% O	-	-	-	-	0.08
% N	-	-	-	-	<0.01
% S	-	-	-	-	<0.01
H available/100gC.	-	-	-	-	16.00

TABLE III.

Investigation of the Heavy-Benzine Fraction.

Atm. Pressure	250	250
Temp. °C.	382/391	382
Throughput Kg/Ltr/hr.	1.0	1.0
M^3 Gas per kg. Oil	3	3
Operating Days	12	17
Benzine produced	0.29	0.27
" concentration	31	27
% Gas/product + Gas	1.4	2.9
% Total Catchpot	14	16.5
% of b-Middle Oil	20	25
Sp. gr.	0.836	0.837
Aniline Point °C.	+ 42.6	+ 40.5
First Drop °C	158	167
% to 170°C.	5.6	3.5
% to 180°C.	31.2	45
% to 200°C.	86	83
% to 225°C.	97	96
End Point °C./%	235/98.8	240/99

Ultimate Analysis

% C	-	86.53
% H	-	15.25
% O	-	0.20
% N	-	0.01
% S	-	0.01
Available H/100 g C.	-	15.28

TABLE IV

Diesel Oil - Investigations

Pressure Atm.	250	250	250
Temp. °C.	382/391	382/391	382
Throughput Kg/ltr/hr.	1.0	1.0	1.0
M^3 gas per kg. oil	3	3	3
Operating Days	5	12	17
Benzine Conversion	0.48	0.29	0.27
" Concentration	49	31	27
% Gas/Product + Gas	-	1.4	2.9
Diesel Oil:			
% of total catchpot	40	55	50
% of B-middle oil	78	80	75
Spec. Grav.	0.870	0.866	0.874
Aniline Point °C.	+ 61.8	+ 57.7	+ 54
% Phenols	0.03	-	0.07
% unsatur. hydrocbns	1.5	3	0.5
Cetene No.	51	49.5	46
Pour Point	-26	-28	-34
Visc. °E at 20°C.	1.205	1.145	1.14
Ignition Pt. °C.	100	86	86
% to 225°C.	-	26.8	22
" 250°C.	24	53	55
" 300°C.	84	89.8	91.5
" 325°C.	93.5	96.6	97
End Point °0/%	338/98.9	331/98.8	336/99
Fraction			
210-230°C.	-	0.85 + 49	0.860 + 46
240-270°C	-	0.87 + 56.2	0.876 + 53
280-310°C.	-	0.872 + 65.5	0.888 + 64.1
Ultimate Analysis:			
% C	-	-	86.85
% H	-	-	13.13
% O	-	-	0.01
% N	-	-	-
% S	-	-	15.11
% N exactly	-	-	0.008

II. Benzination of the Pre-Hydrogenated Middle Oil by means of Catalyst 6434.

The b-middle oil was hydrogenated in a 50 cc oven over catalyst 6434 at 200 atm. pressure to Auto- or L-Benzine. The injected material had the following characteristics:

Sp. gr.	0.856
Aniline Point	+ 54°C
First Drop	187°C
% to 225°C	40
% to 250°C	60.5
% to 300°C	89.0
% to 325°C	95.0
End Point °C/%	345/98.5
Phenols	0.12%

The operating conditions were:-

Temperature	370-375°C.
Pressure	200 atm.
Throughput (Kg/ltr/hr)	2.0
Cbn Gas/kg oil	2.5
Addition	0.75% CS_2

With return of material
boiling over either 150 or 180°C (see Table V)

The b-middle oil of the prehydrogenation and derived from Rheinish brown coal can be with good yield "benzinated" over 6434 to Auto- or L-Benzine. The gas production is normal at about 9%. The benzine fraction up to 180°C. has an octane number of 71 (Research) when it distills 47% below 100°C. In admixture with the benzine produced during the prehydrogenation of the b-middle oil, the so-formed benzine distills 37% below 100°C and has an octane number of 68 (Research). The benzine that distills below 150°C., and contains 58% boiling below 100°C., has an octane number of 72.5 (Motor Method) and with 0.09% Pb an octane number of 88. In admixture with the benzine product of the prehydrogenation of the b-middle oil, its octane number is 69 (Motor) with 0.09% Pb 86, and with 1% Pb 87.5; it should be here observed that the above mixed benzine had too high an end-point, and consequently, a new sample having an end-point of 145°C was taken - this product had an octane number of 73.5 (Motor Method) with 0.09% Pb 88, and with 0.1% Pb 89.

The characteristics of the above benzine products are given in Table V. The test operation ran 20 days without reduction in yield.

TABLE V. **RHEINISH BROWN COAL.**

- Benzination of 5058-b Middle Oil from

Injection Product Catalyst.	180°C. Benzine. Benzine from the preliminary hydrogenation up to 180°C.	180°C. Benzine. B-Middle Oil >180°C. 6434	180°C. Benzine. Mixture: 51 parts benzine of the prelim. hydrogenation; 2 parts Sumpf pentane; 47 parts 6434 benzine.	150°C. Benzine. Benzine from the prelim. hydrogenation up to 150°C.	150°C. Benzine. B-Middle Oil >150°C. 6434	150°C. Benzine. Mixture: 33 parts benzine of the prelim. hydrogenation 2 parts Sumpf pentane; 65 parts 6434 benzine.	150°C. Benzine. The same mixture having a 145°C. end point.
Pressure atm.		200			200		
Temp.°C.		374			370		
Kg/ltr/hr.		2.0			2.0		
Gas : Oil		2.5			2.5		
Addn.(CS_2)		0.75%			0.75%		
Method of Operation		Recycle >180°C.			Recycle >150°C.		
Sp.gr.of Pdct.		0.744			0.742		
Benzine Conc.		78%			62%		
" Leistung		1.40			1.15		
Gas/Benzine + Gas.		8.7			16 (stab)		
Benzine:-							
Sp.gr./20°C.	0.776	0.722	0.750	0.768	0.728	0.738	-
Aniline P+I/II	36/-	52/55	44/52	34/-	52/55	47/53	+ 47/-
First Drop °C.	67	31	42	67	50	47	47
% to 100°C.	23	48	37	28	58	49	58
% to 150°C.	80	84	82	96	96	95	-
% to 180°C.	99	99	99	-	-	-	-
End Point °C/%	180/99	180/99	180/99	157/99	155/99	158/99	145/985
Paraffins %	-	49	36	-	49	39	-
Naphthenes %	-	47	55	-	47	54	-
Aromatics %	15	3	8	-	3	6	-
Unsaturateds %	-	1	1	-	1	1	-
Test:-							
Sulphuric Acid	-	1	2	-	2	2	2
Doctor Solution	-	Neg.	Neg.	-	Neg.	Neg.	Neg.
Vapor Pressure	-	-	-	-	0.47	0.48	0.48
Octane Number:-							
Research Method	66.0	72	68	69	73.5	71.0	-
Motor Method	63.5	71.5	-	65	72.5	69.0	73.5
" - 0.09% Lead	-	85.5	-	-	88.0	86.0	88.0
" - 0.10% Lead	-	-	-	-	-	87.0	89.0
Middle Oil:-							
Sp.gr./AP	-	0.838/55	-	-	0.822/52	-	-
First Drop °C	-	188	-	-	158	-	-
% to 250°C	-	88	-	-	87	-	-
End Point °C/%	-	293/99	-	-	288/99	-	-

APPENDIX F

PRELIMINARY REPORT

VISIT TO UNION RHEINISCHE BRAUNKOHLEN KRAFTSTOFF A. G.

(WESSELING) B. KOLN

This report is written to present the single most importent and urgent fact uncovered, namely the existence of five or six underground plants for oil production, termed "Schwalben." The exact location of Schwalbe I is given in a form we believe is suitable for air survey, etc.

In addition, brief notes are given on the nature of the plant at Wesseling. The same hydrogenated pulverised Rheinland brown coal to make intermediate cuts of petrol, suitable for incorporation by others in aviation gasoline. Production at various rates continued from 1940 to July 19th, 1944, when a bombing raid destroyed it past repair, according to the assessment of Herr Dr. Geilenberg. The nominal production of the plant was 20,000 tons per month.

Complete details, including history of construction, operation, methods used to overcome difficulties, etc., will be given after the original documents, now presumably en route, are actually received.

John A. Oriel
Irvin H. Jones
H. M. Weir.

REPORT ON A VISIT TO THE HYDROGENATION PLANT AT WESSELING ON MARCH 10th, 11th AND 12th, 1945

(Hydrogenation Plant of the Union Rheinische Braunkohlen Kraftstoff A.G. (Wesseling) B. Köln

This is not intended to be a detailed report, which can only be prepared after the arrival of the documents, but such information as we were able to bring away with us is being detailed below.

The report naturally falls into two parts: one - and in this case, the more important - part, deals with other German activities outside of Wesseling, and is information gleaned by interrogation; the second deals with technical information regarding the plant itself.

PART I

We interrogated:

The General Manager	Herr Mueller von Blumencron.
The Production Manager	Dr. Ernst Peukert.
The Head of the Laboratory	Dr. Heinz Sustmann.
The Product Despatching Manager	Dr. Fischer.,
A Diploma Engineer	Gerhard Feldhoff.
A Chemical Engineer	Dr. or Dipl. Ing. K.H.Schuh.

Fortunately we were able to interrogate all these people before they were able to collect their wits after the plant had been captured, and before they were able to prepare any sort of story. Of course, the possibility must be borne in mind that the preparation of a story that hung together might have been going on for some time before the occupation.

None of the above personnel confessed to being a member of the Nazi Party. In the cases of Drs. Peukert and Schuh they expressed a strong distaste for anything connected with the party. In the case of the former, the attitude was quite rebellious, and the latter hoped to leave Germany in the immediate future to return to his plantation in Africa, having been apprehended when in Germany for medical treatment for his wife, and refused permission to leave. The General Manager, von Blumencron, had been a Major in the First World War, and was a member of the General Staff of the German Army.

He said that he had been approached many times and pressed to join the Nazi Party. He always claimed to have declined, and that his sole interest was for the good of Germany itself, and not for the Party, and that any insignia which he wore on his garments had little to do with that emotion. He confessed to having been engaged in counter-espionage in the Wesseling district. He had visited Billingham in connection with hydrogenation, and was at one time a member of the staff of I. G. Farben. Dr. Peukert was the most outspoken anti-Nazi of the above listed. He seemed to be generally the best informed as to plant operations and processes, and the most co-operative in divulging technological facts concerning them. He delivered to the team, and they will be found in the list of confiscated documents sent to C.I.O.S. in London, two copies of his scholarly description in detail of all plant operations and processes. These copies had been buried in different secret places and under different custodies, to prevent their falling into the hands of the Nazis - probably for the purpose of having at hand a text-book of instructions in anticipation of the time when the plant could be returned to operation in the interest of the local civilian economy, and in the event no key men remained on the left bank of the Rhine who were sufficiently acquainted with such details as to operate the units. A complete analysis of the damage done by the Allied bombing raid and the location of the bomb hits are shown in the document on a map in considerable detail; of the more than 1,000 bombs dropped in July 19th, 1944, 221 hit the Gas Production Plant alone. We were also told that over 200 dud bombs had fallen on the plant during this raid on July 19th. It is important to note that a copy of this account, prepared by Dr. Peukert, was sent to Dr. Pier and Dr. Krauch.

Certain members of the staff of the plant entertained the hope that the Allies would see fit to restore the same to operating condition. One member estimated that this could be done in about five months' time if equipment could be procured.

It is interesting here to note that in the event of its possible capture by the Allies, the plant was to be completely destroyed, according to a dictate by the Nazi

Party. However, this order was superseded by one signed by Armaments Director General Erdmann of the German Army (a copy of which we have) who wished to preserve the plant for possible use after its recapture by the Germans. The officials at Wesseling were thus ordered to hide all essential and key parts that were critical to the operation of the plant, and could not be easily procured. Among these are 21 insulators, and possibly some other minor parts that are in the possession of a certain Ringhausen, owner of a tile works at Alster, somewhat west of the city of Bonn; others are at Waldbrohl, about 50 km from Wesseling in the care of a Fabricant Projahn, where also all duplicates of documents have been sent.

An interesting sidelight on activities at Wesseling was given by Dr. Peukert to the effect that the German labor experience in the plant was very unfavorable to the Nazi system. In contrast he had analyzed the absences, vacation, sickness, leaves etc. of the imported foreign labor, which showed practically continuous presence at the works, in comparison to extraordinarily frequent absences on the part of typical German workmen.

The matter of outstanding interest which we discovered was the work being carried on at Wesseling in connection with the underground Hydrogenation Plants, known by the code name of Schwalbe. They understood that it was originally proposed to build five or six of these underground Hydrogenation Plants, but although they had no direct information, they were under the impression that some of these projects had been abandoned. The sites of these were as follows:-

(a) At Menden, which we shall deal with in greater detail later.
(b) At Bueckeberg; this plant was to have been operated by the Nordstern-Gelsenberg A.G. The location was in some natural caves in the Bueckeberger mountains.
(c) A third was near the station at Berga Kelbra in Thüringen.
(d) Another was in the Erzgebirge mountains near Bruex, somewhere near the German border in Czechoslovakia. This one was to have been operated as a satellite of Bruex.
(e) Another one in the Hartz mountains near the I.G. Gypsum quarries at Nieder Sachswerfen. It is said that this last one already exists, but the alkylation plant which was to be attached to it has not yet been completed.

There is also a possibility of two plants somewhere between Dresden and Aussig, but their whereabouts are not known.

All of the above plants are to be assisted in their construction by the I. G. Farben.

All of these plants are being built under what is known as the Geilenberg plan. Geilenberg apparently has powers directly from the Führer for the programming of the production of all gasoline, and it is in his hands to decide if plant should be repaired, abandoned, or new ones built, and for this purpose he apparently has direct access to the highest quarters and can by-pass, if necessary, both Kehrl, the President of Planning of the Armaments Industry and Krauch, who is responsible for the general production of all oils, aluminium, nitrogen and explosives. The building of these places is being carried out under the Organisation Todt.

The following seems to be the organisation in the Reich for production directly connected with oil. Dr. Sperr is in general charge, and supervises the oil production interests of the "Wirtschafts Ministerium" under Dr. F. R. Fischer, and the War Department where Dr. Kehrl is in charge of the Planning Division. On a par with these two executives is Dr. Krauch, formerly with I.G., who now correlates planning of the two departments with respect to the following:

Oil production,
Hydrogenation,
Aluminium production
All nitrogen chemicals, including explosives.

Dr. Geilenberg has direct contact with "der Führer", and there is a Geilenberg plan for both the erection of new plants and the repair of bombed-out production facilities. Apparently Geilenberg can over-rule any of the above on anything connected with hydrogenation. His organisation in respect to the repair of bombed-out plants was lauded by Dr. Peukert, who maintained that, almost invariably, the estimates which Geilenberg made after survey of a plant were met in respect to the time of re-initiating operations. We were also told that within the last three or four weeks Geilenberg had been called upon to defend his organisation on the grounds that although he had had every facility placed at his disposal the production of gasoline was nevertheless not coming up to expectations. We understood that his defence took the line that things would have been very much worse if it had not been for the powers entrusted to him.

Schwalbe I, near Menden

This plant was under the special care of the people at Wesseling, and was being built under the Organisation Todt, employing at present 4,000 men. The Chief Engineer is Heinrich, and the Chief Technical Engineer is Dr. Moll, and both Meissner and Nedelmann from Wesseling are at present at Hönnethal working on this plant. Nedelmann is the previous Technical Director of the Gelsenberg benzine producing plant.

The exact location of the installation is in a quarry south of Menden. Co-ordinates from the map Dortmund Sheet Q2 are Across 077, Up 104. For further identification, the following information may be of interest. 300 to 400 metres north is the Rheinische Westphalische Kalkwerke. To the west is a landing-ground. 500 metres south is an inn near a small railway station, called Klosenstein. In front, and on the road, a brick building has been erected as an administrative office. The old chalk quarry is 200 metres west of the road, and the ground is level for the first 150 metres and then gently slopes up to the quarry for the next 50 metres. Part of the installation (the reaction chambers) is to be erected on the slope and not buried, but covered by a concrete deck. Between the administrative building and the quarry is the River Hönne. Either south or north of the administrative building is a brook running into the Hönne, coming from the hill above the quarry, and a small bridge spans the Hönne just north of the administrative building. On the hill directly behind the quarry is a village called Aprike (or Rienke) and about two kilometres west of this village is one with either of these names. The entrance is approximately opposite the middle of the bend in the road leading from Menden to Volkringhausen.

The above information was given us by the above Diploma Engineer, Feldhoff, who was to have charge of the high pressure, the low pressure and the Alkazid apparatus. The plant was designed to produce only ordinary motor fuel, and no alkylation process was anticipated. Feldhoff was at the actual plant site in December, and at Menden in January, at which time no material had arrived on the site, and in his opinion they would be ready for the machinery on 1st April, and the date for completion was given as some time in October.

Whilst we will give pinpointed co-ordinates when our material arrives, it should be borne in mind that the above information was an approximation from memory on the part of the man who had visited the plant on several occasions.

The entry for the Alkazid process had been finished on December 1st. The total length of the leads, or entries, in December was 60 to 80 metres. Their total length was to be ultimately 200 metres and there were also to be 10 to 15 such entries, when the face of the escarpment would have a height of 6 to 7 metres.

Between 500 and 1,500 men were to have been sent from Wesseling to work at this site, and we have a complete list of the material which has already been sent there, but which we understand is at present in the sidings at Soest. The size of the plant is about a quarter of that of Wesseling.

Jacob

This is the code name for cracking plants, probably underground. Wesseling had been instructed to forward all compressors to Jacob 11 (eleven) at Pintsch Kosswig, near Dresden, but the instructions came too late for them to be carried out.

The new benzine for the new jet-propelled aeroplane is known by the code identification J. 2. It is a product intermediate between ordinary benzine and diesel oil and boils within the range of about 140° to 310°C.

PART II

Hydrogenation Plant at Wesseling

No technical details of this plant can be presented until the official bag of documents arrives, but it is sufficient for this report to record that it is a conventional I.H.P. plant operating on brown coal, said to work at about 700 atmospheres. It has not operated since the bombing attack on the 19th July, 1944.

It was intended to manufacture the alkylate from butene, and a plant was practically complete for the production of 28,000 tons per annum alkylate, but was never operated owing to the destruction last July. The butane separated from the hydropetrol consists of 1.2 parts of iso-butane to one part of n-butane. These are separated by distillation and the n-butane is dehydrogenated over the usual chromia alumina catalyst at a temperature of about 540°, and approximately atmospheric pressure. The process is batch-continuous, and four converters were installed.

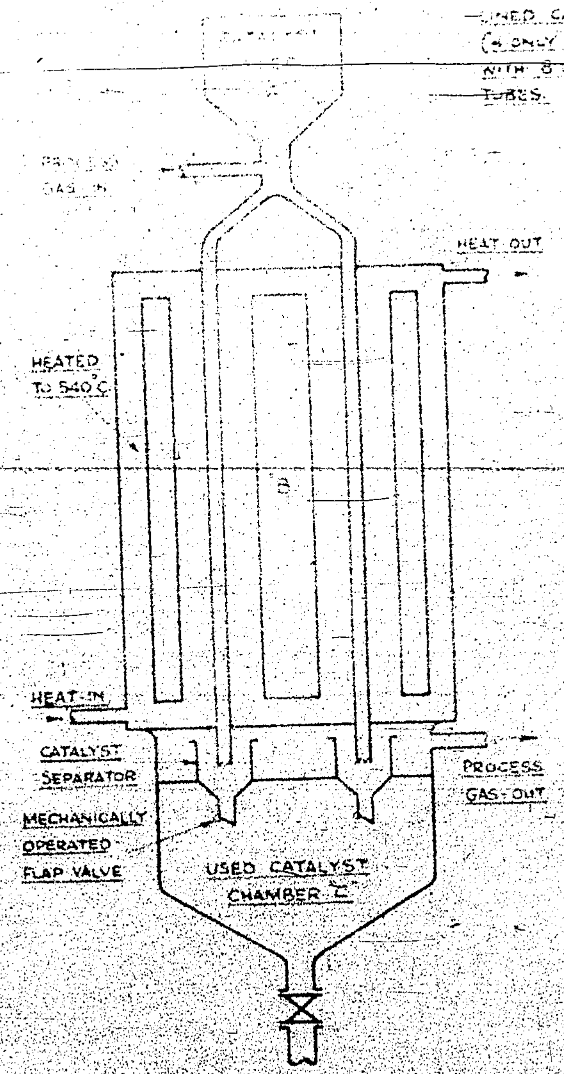
The vessel A shown in the attached flow diagram is filled with fresh catalyst, and the pellets fall by gravity on to a distributor at the top of vessel B. Vessel B was about two metres diameter, and contained eight refractory lined cylindrical tubes, about 65 to 70 centimetres diameter. Inside each of these tubes were eight tubes 12 centimetres diameter, disposed out of contact with each other. The heating arrangements were such that the whole vessel was heated by means of a jacket outside, whilst hot gases also passed through the larger tube and around the smaller tubes, which smaller tubes were filled with catalyst. The hot gases were recirculated and kept up to temperature by the addition of a small amount of air and fuel gas. The butane was admitted at the top and flowed down the tubes concurrently with the catalyst. The ends of these tubes were serrated, and entered into a cup-like member of larger diameter, which supported the catalyst in the tubes. (See fig. 2). From this cup-like vessel the butylene was drawn off at the top, whilst the catalyst descended intermittently through a mechanically-operated flap into the used catalyst chamber C. When the whole of the catalyst had been transferred from A to C, the plant was shut down, purged with nitrogen, and the catalyst from C transferred by means of a belt to the regenerating stoves, of which there were at least two. Here the carbon was burnt off and the regenerated catalyst returned to vessel A. This cycle occupies two hours.

The n-butylene was mixed in the proportions given above in the presence of cold sulphuric acid, which was a normal cold acid alkylation process, operated at 0°C. with sulphuric acid at 88% concentration. The final materials were alkylates (known as A.T.) with Motor Method octane number of 92.

Another point of interest in connection with the plant is that from time to time the hydropetrol is sent to Ludswigshafen for the manufacture of D.H.D., which is, as far as they know, a dehydrogenated product of the hydropetrol up to 165°C. This was in order to convert the naphthenes present to aromatics.

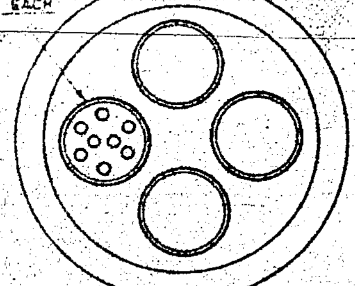
John A. Oriel

21st March, 1945



FLOW DIAGRAM

FIGURE 1.



DIAGRAMMATIC SECTION THROUGH VESSEL 'B'

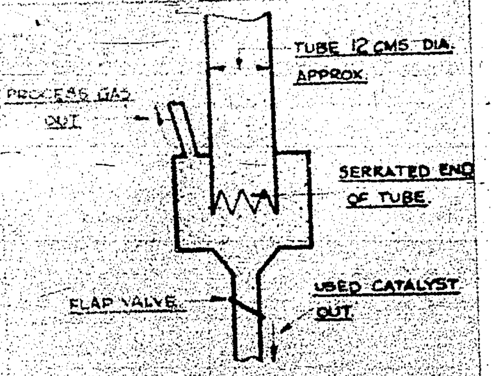


FIGURE 2.

APPENDIX G.

The following documents were seized at Wesseling and have been placed in the files of M.I.R.S. for safekeeping in Document Bag No. 1677 for Black Target No. 30/4.10 after having been reproduced in microfilm for transmittal to the Secretary of the Interior, Washington, D.C.:-

1. Tagebuch for 1942 to 1944, inclusive, giving an account of important daily operations, disturbances, changes and problems of plant operations.
2. Beobachter-Bericht über die Herstellung einer geschweissten Mehrteil-Ofenmantels, 1000 mm. diameter, 18 m long. A document prepared by Fried. Krupp, A. G., Essen, explaining the fabrication of high pressure catalyst ovens. Important photographs.
3. Betriebs-Ergebnisse for 1943. A document of 127 pages giving the most important operating results such as raw materials input, yields, energy consumption, gas analyses, product analyses, etc., for the year 1943.
4. A file of Specifications and Analytical Methods of the Reichsminister der Luftwaffe and Oberbefehlshaber der Luftwaffe für Treibstoffe in der Wesseling Anlage.
5. Specification of the Oberkommando der Luftwaffe for September 1944 for Aviation gasoline.
6. A file containing Analyses of Divers Products and Intermediates produced in the Hydrogenation of Brown Coal at Wesseling in 1943 and 1944.
7. Flow Diagram of Gas-Recirculating Pumps in the S-phase 700 atm. at Wesseling.
8. Diagrammatic Flow Sheet of Brown Coal Hydrogenation Plant at Wesseling.

9. Diagrammatic Flow Sheet and Elevational and Vertical Cross-Sectional View of the Pintsch-Hillebrand Water-Gas Plant.

10. Document relating to Operating Results with the new Vorhydrierungs Catalyst at the Pölitz plant, dated October 12, 1942.

11. Same as item 10 for the Scholven and Leuna plants.

12. Test Methods for Gasoline supplied to the Zentralbüro for Mineralöl, issued November 1940.

13. Correspondence re:- Ceramics for the Pintsch-Hillebrand Generators.

14. Analysis of Costs of 1000 kg. Liquid Products at Wesseling for the first quarter of 1944.

15. Analyses of Brown Coal employed in Wesseling Hydrogenation Plant.

16. Drawing of Grinding Plant for Coal Paste.

17. Analysis of a Suggestion for Obviating Caviar Formation in Coal-Hydrogenation Plants.

18. Process for recovering oil from Shale at Schömberg, Würtemberg.

19. A file of documents relative to Alkylate Production and including:

    a. - Plant Design.
    b. - Flow Sheet.
    c. - Operating Requirements.
    d. - Plant Costs.
    e. - Description of similar operation at Leuna.
    f. - Minutes of Conferences.

    g. - Materials Consumption
    h. - Required Laboratory Tests
    i. - Operating Precautions.

20. File on Problems of Materials of Construction in Coal-Hydrogenation Plants, including Problems of resistant Materials.

21. File on Proposed DHD-Plant at Wesseling including:-

    a. - General Questionaire
    b. - Project details - Material Requirements.
    c. - Special Equipment and Energy Consumption.
    d. - Nature of DHD-benzine produced at Wesseling.
    e. - Composition of DHD-outlet gases at Ludwigshafen.
    f. - Reports of Operation on Wesseling Benzine in the DHD plant at Ludwigshafen.
    g. - Apparatus requirements for DHD-Plant.
    h. - Operating Conditions and Yields.

22. Operating Data on DHD-plant at Scholven.

23. - Documentation of Operating Improvements developed in Wesseling Operation from 1941 to 1944 by Dr. Peukert.

24. - Drawings of Underground Hydrogenation Plants for Liquid Fuels. (Schwalben).

25. - Comments on F. Fischer's Patent Application for heating coal to 300°-350°C. for its aging and to remove O_2 before its hydrogenation.,

26. - A chart drawing of Mineralöl-Baugesellschaft-No. 49999-2, showing input and output of products on an hourly basis; this chart was made as a basis for designing Wesseling tankage requirements.

27. - Document of indeterminate origin found at Wesseling mentioning patent application that relates primarily to the chemistry of metal alcoholates and their use for divers purposes including preparation of catalysts, ordnance, and medicinals.

28.- Two copies of a black-bound typewritten report of about 220 pages in German by Dr. Ernst Peukert of the Wesseling Plant.

APPENDIX H.

A document found in the Wesseling files dated January 7, 1942 and of unknown origin gives interesting information on research developments and filed patent applications in divers fields of catalyst preparation, plastics, and the manufacture of metallic alcoholates and their uses.

The content of this document is as follows:-

(1) Dehydrogenation of hydrocarbons, especially propane and butane by chromium and aluminum oxides catalysts developed for this purpose.

In this study, about 60 catalysts were prepared of which the following have been demonstrated to be highly active and technically usable:-

a. K33b: a mixed catalyst of 10% Cr_2O_3 on synthetic Dawsonite;

b. K57: a mixed catalyst with 18% Cr_2O_3 which is technically especially simple to prepare since it is obtained by mixed precipitation of an aluminum-chromium solution with ammonium bicarbonate. (See patent application St 59796 and St 61012 IV b/12 g entitled "Verfahren zur Herstellung von Aluminumoxyd- und Aluminumoxyd-Chromoxyd-Misch Katalysatoren".

c. 58/K61: a mixed catalyst of high activity and extraordinary mechanical strength prepared from aluminum secondary butylate by decomposition with water and subsequent direct sorption with chromic acid. (See patent application IVb/12 m entitled "Herstellung und Verwendung reinster Hydroxyde und Oxyde des Aluminiums und Magnesiums" as well as also the application-of-addition St 59894 entitled "Verfahren zur Herstellung von aktivierten Aluminum oxyd-Katalysatoren".

(2) Conversion of alcohols to ketones. A process has been developed whereby, by means of a zinc catalyst (K67) having a content of zinc of 7-9%, secondary alcohols and especially sec. butyl alcohol is thermally dehydrogenated to the

corresponding ketone. The process was practised technically with a production of 30 tons per month. A process has been found for refining by distillation in the presence of CaO methyl-ethyl ketone that has a tendency to turn yellow in storage.

(3) Preliminary Work on Synthetic Resins: Preparation of ethylacrylic methyl ester, B methyl-gamma keton Butanol. Production and purification of methyl isopropenylketone and its plexigum-like polymerization products. Decoloring of methylisopropenylketone before its polymerization was attempted in research methods and it was found that barium hydroxide amongst other weak alkalis were suitable. (See patent application St 60877 "Verfahren zur Reinigung von Methylisopropenylketone". In addition, there was produced cyclohexanone resin (AW-2-Harz), methylvinylketone, amongst others.

(4) Development of the Keton resin "Emekal" from methylethylketone and formaldehyde as well as the completion of a plant for production of about 4 tons per month thereof. Further works on the "Emekal" resin to produce as colorless as possible a product and especially a type soluble in hydrocarbons (for example, Emekal 350) for the varnish industry. (See application St 60911, "Verfahren zur Herstellung von hellen leichtlöslichen Kunstharzen").

(5) Production of sec. Butyl Stearate as a plasticizer. Production of Aluminum Alcoholates. Tests on various catalysts for the reaction of aluminum with alcohols. (See patent application St 59625 IV c/12 o and St 59626 IV c/120 - "Verfahren zur Herstellung von Alkoholaten des Magnesiums und Aluminums").

(6) Use of aluminum alcoholates (butal and propal) for:-

a. Pyrotechnical purposes (see application St 59322 IV d/78d "Verwendung von Metallalkoholverbindungen für pyrotechnische Zwecke").

b. Ignition agent for carbon (See application St 59424 IV b/78d, "Verfahren zur Verbesserung der Entzundlichkeit und Verbrennungsgeschwindigkeit von Kohlenwasserstoffen").

c. Varnish industry and other purposes especially preparation of emulsions (See application 60217 IV d/12c "Verfahren zur Herstellung von Emulsionen und Suspensionen mit Hilfe von Aluminiumalkoholaten).

d. Medicinal Purposes (Prof. Engelhardt, Tübingen, and also Prof. Frey, Düsseldorf).

(7) Development of the Carbon Dioxide addition product of Aluminum alcoholates especially of Butal. (See application St 59783 IV d/12o, "Verfahren zur Stabilisation von Metallalkoholaten"). Preparation of the product "Carbutal" and "Rh_5" and its use as a gelatinizing medium for lacquer technology and army purpose (see application St 60358 VI/10b, "Verfahren zur Verdickung and Verfestigung von flüssigen organischen Verbindungen). Also suggestion for a medicinal use of Carbutal. (Prof. Engelhardt, Tübingen, and Prof. Frey, Dusseldorf).

(8) Development of apparatus for the production of 30 tons per month of aluminum alcoholate. (See application St 61255 IV d/12c, "Verfahren zur Herstellung von Metallalkoholaten", as well as St 59783, see above).

(9) Preparation of active Aluminum Hydroxides and Oxides from aluminum alcoholates and their technical and medicinal use; also a plant for producing said hydroxides and oxides.

(10) Development of a process for recovery of pure aluminum from residues and alloys. (See application St 61237 IV b/12 m, "Verfahren zur Abtrennung von Aluminium aus Aluminiumlegierungen").

(11) Preparation of a new gelatinizing medium (RH_6) from Butal and fatty acids (C_6-C_9) as well as the first fractions of the fatty acids produced at Witten.

(12) Developments for the High Command of the Army (OKH. Wa Prüf 5):-

(a) Development of smoke pipes (Parachlorit 7) *

(b) Development of water-resistant friction settings.

(c) Development of an ignition fuse for oil (Parachlorit 7) *

(d) Development of a storage-stable delay-fuse (Parachlorit 7) *

(e) Development of a membrane as a safety-valve for flame throwers.

(f) Oils for filling flame thrower shells.

In this connection: -

(g) An aluminum alcoholate plant (see above)

(h) Development of Combustion Pipes (parachlorit 7) *

(i) Development of a chemical time-fuse (see application W 109,820 XI/72 i, "Chemischer Zeitzünder")

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* See application St 59425 IVb/78 i, "Verfahren zur Herstellung von feinst aufteilbaren pyrotechnisch wichtigen Stoffen aus Hartparaffinen der Fischer-Tropsch Synthese".

APPENDIX I

Photographs, taken at the Wesseling Plant from March 10-12, 1945, are shown ~~in the~~ following figures:

Fig. 1

Fig. 2

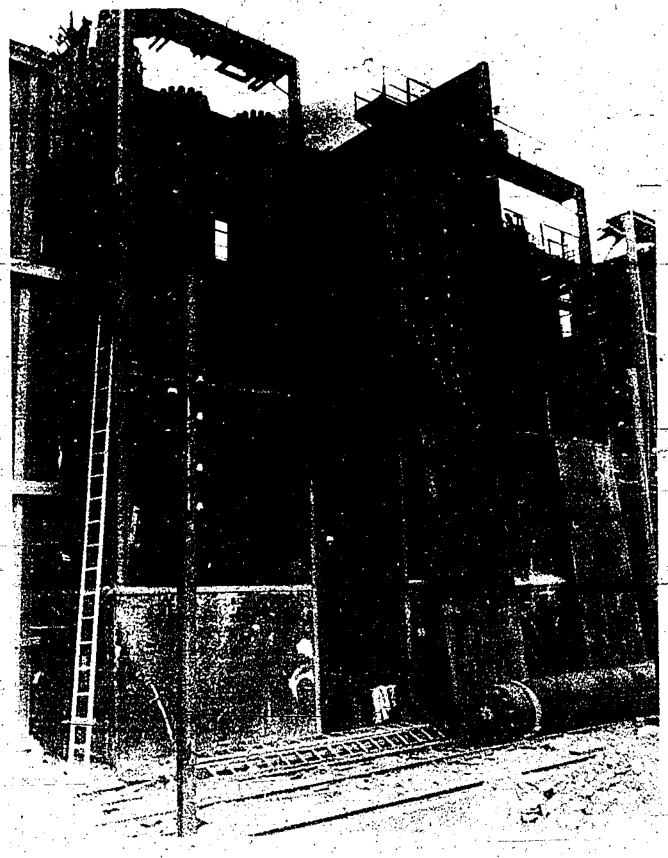

Fig. 3

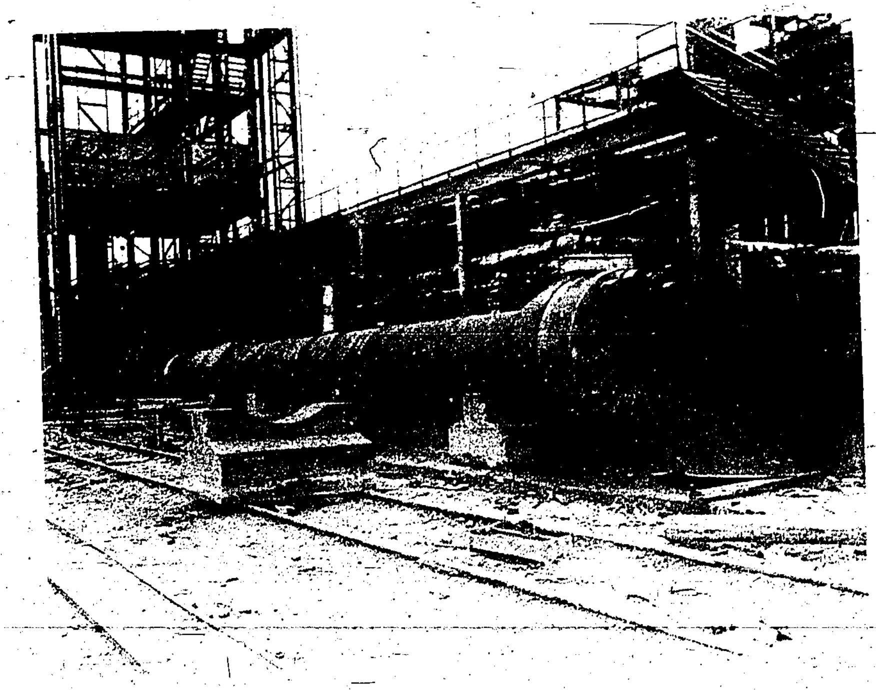

Fig. 4

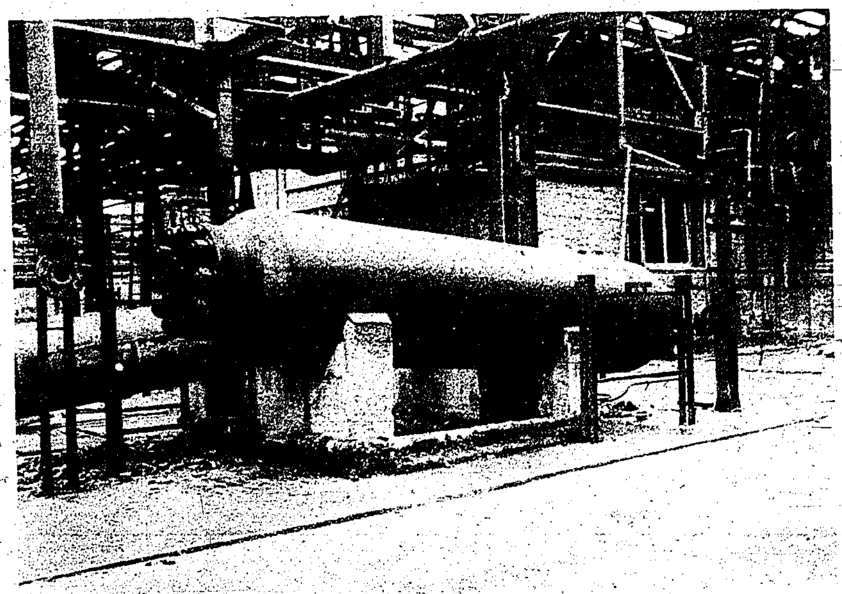

Fig. 5

Fig. 6

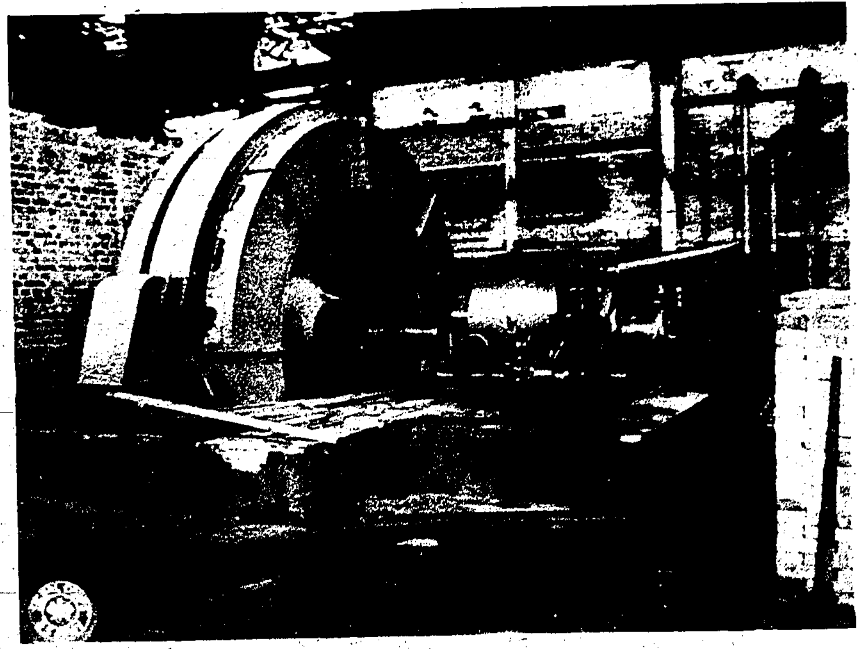

Fig. 8

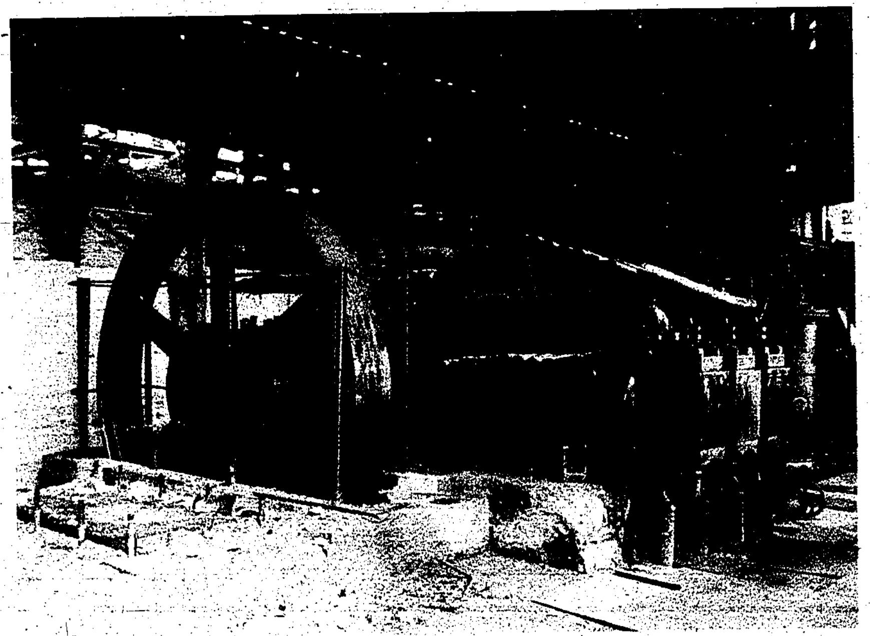

Fig. 7

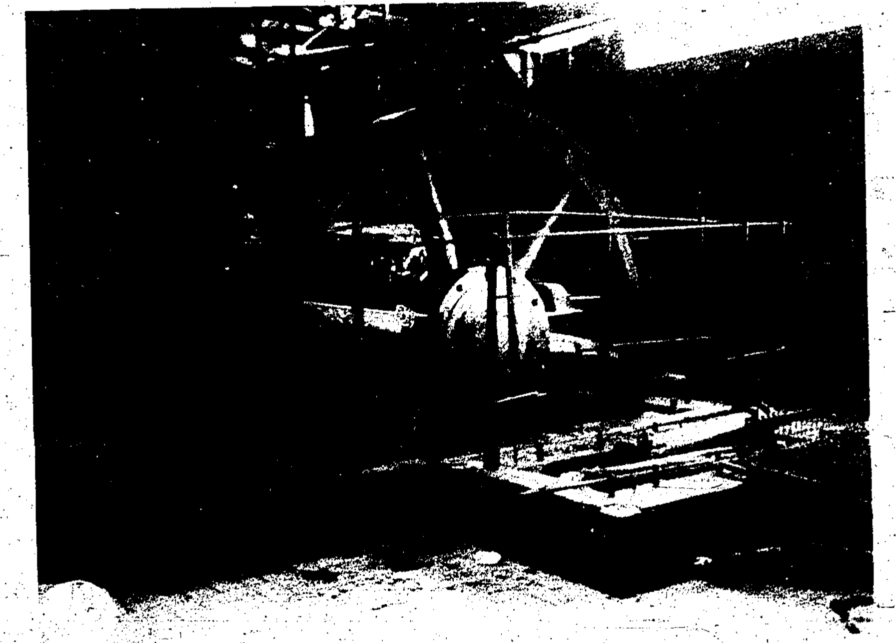

Fig. 9

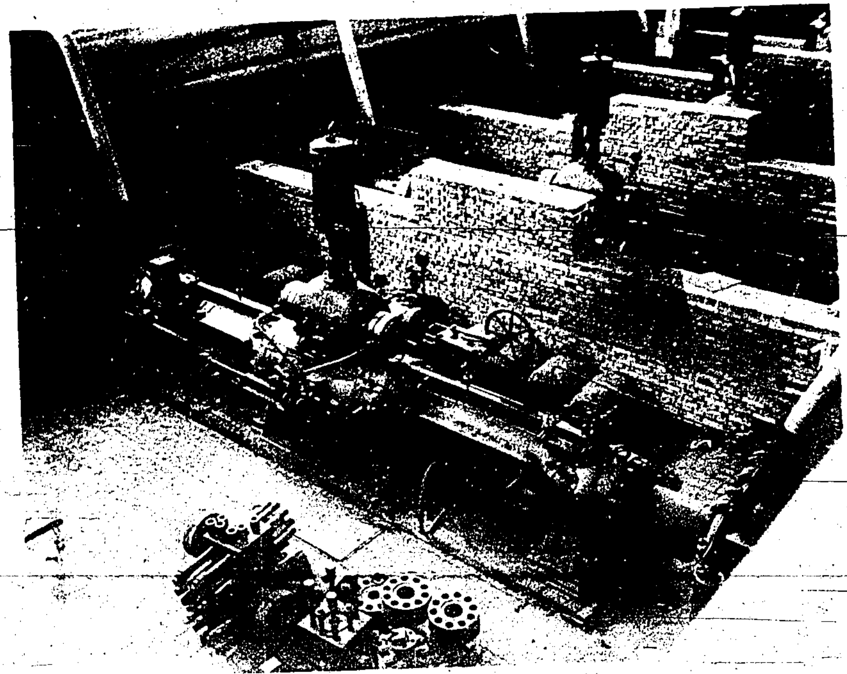

Fig. 10

Fig. 11

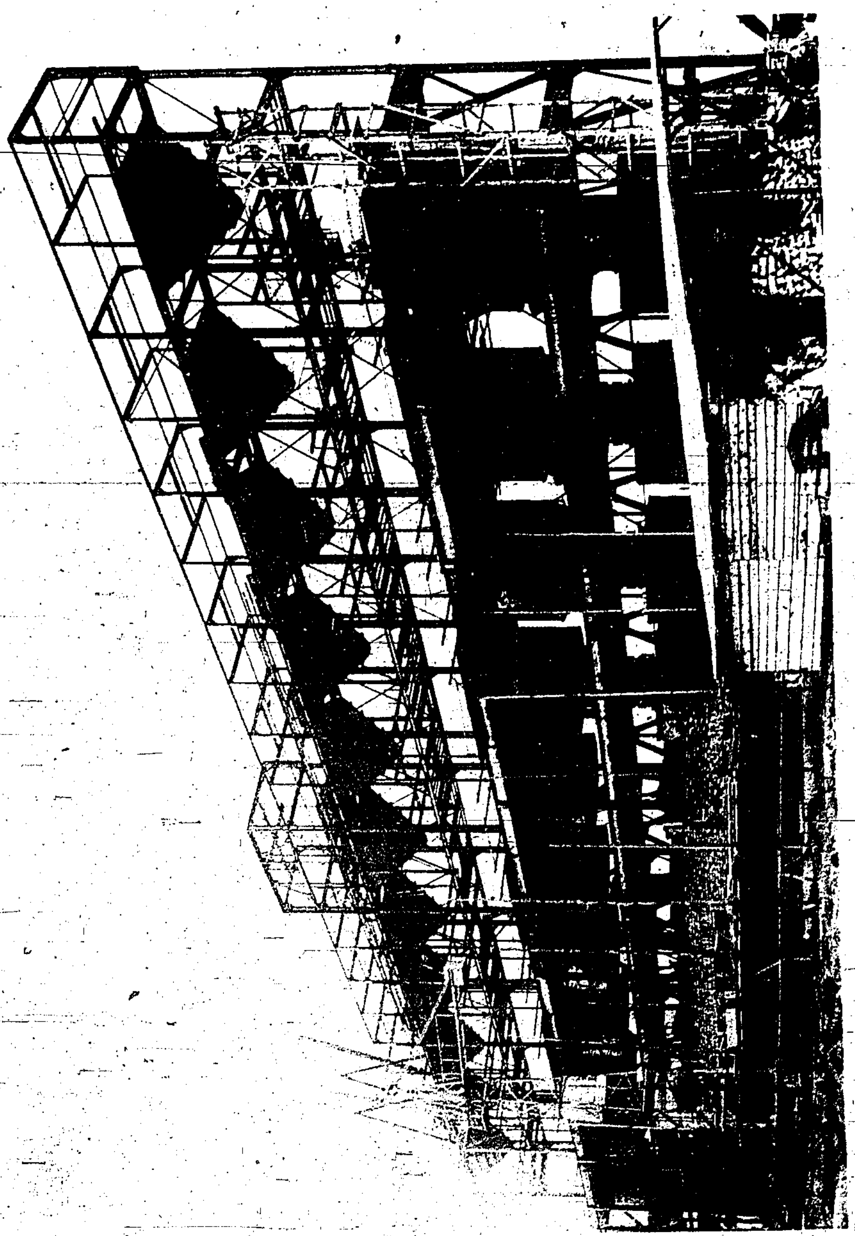

Fig. 12

APPENDIX J.

This Appendix is a copy of Dr. Ernst Peukert's report in German on Wesseling operations including a discussion of the chemical reactions, products, features of apparatus and technology, and changes of operational procedure, both successful and unsuccessful, more especially directed to improving operating results with particularly Rheinish brown coals. The original of Dr. Peukert's report has been depositied, along with a substantially duplicate copy, with MIRS in Bag No. 1677.

copy 1

ITEM No. 22.
FILE No. XXX - 10

COPY No 0167

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

~~RESTRICTED~~

I. G.
Farbenindustrie,
Hoechst.

Ozol + Chaffee

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

I. G. FARBENINDUSTRIE - HOECHST GERMANY

Reported by

Lt. R. J. OZOL, U.S. Ord.
Capt. C. C. CHAFFEE, U.S. Ord.

9 July 1945

CIOS Target No. 22/1g
Miscellaneous Chemicals

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

RESTRICTED

10 p.

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PERSONNEL OF TEAM
(PART OF CIOS PARTY 551)

Mr H.Schindler, TIIC, Oil Team
1st Lt. R. J. Ozol, U.S. Ord.
Capt. C.C.Chaffee, U.S.Ord.
Maj. D.A.Howes, Ministry of Fuel & Power.

I. INTRODUCTION

The offices of I.G. Farben, Hoechst, CIOS No.22/1g, Target of Opportunity for Group 30, were visited by a detachment from CIOS party 551, 9 July 45, to obtain further information on synthetic additives used in cutting and metal drawing oils, by interrogation of Dr. Hans Lange, Manager of the Dyestuff dept. who had worked on these materials.

II. MANUFACTURE OF EMULPHORS STH AND STX (HOECHST)

A. Preparation of Raw Material (Mersol).

The starting material was KOGASIN II, a special cut from the Fischer Tropsch synthesis having a distillation range of 220 - 330°C and having an average chain length of 15 carbon atoms. This material was first hydrogenated over a nickel tungstate catalyst then redistilled in order to remove olfinic and ocygenated compounds. The product resulting from these operations was termed MEPASIN and was then converted into the sulfone chloride derivitive by reaction with SO2 and chlorine in the presence of artificial light, according to the Reed process. This reaction was carried out at 30°C to obtain a maximum addition of SO_2Cl at the end of the hydrocarbon chain and a minimum substitution of chlorine elsewhere on the chain. This type of reaction was further assured by allowing the reaction to proceed only to approximately 50% completion. This product containing 50% unreacted oil was termed MERSOL and was normally reacted with caustic soda to make detergents.

B. Preparation of Emulphors.

A variety of emulsifying agents were made by reacting MERSOL with Ammonia to make an amide, which was reacted with monochloracetic acid before saponification with NaOH:

$$R\text{-}SO_2Cl + NH_3 \text{-------} R\text{-}SO_2\text{-}NH_2 + HCl$$

$$R\text{-}SO_2NH_2 + ClCH_2COOH \text{----} R\text{-}SO_2\text{-}NH\text{-}CH_2COOH$$

$$R\text{-}SO_2\text{-}NH\text{-}CH_2COOH + \text{------} R\text{-}SO_2\text{-}NH\text{-}CH_2\text{-}COONa - H_2O$$

The pH was adjusted so that the emulsified water

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$$R\text{-}SO_2\text{-}NH\text{-}CH_2COOH + \text{ ------ } R\text{-}SO_2\text{-}NH\text{-}CH_2\text{-}COONa - H_2O$$

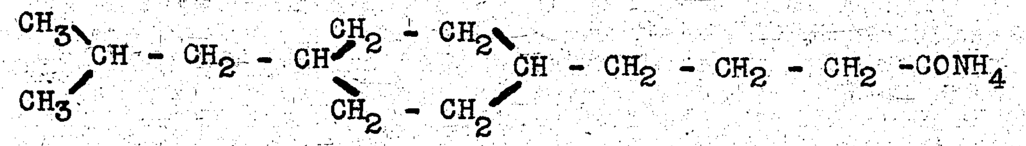
The pH was adjusted so that the emulsified water solution was slightly above the neutral point. The commercial product contained 30-50% of the Na salt with 70-50% of mineral oil, MEPASIN. These compounds were marked as Emulphor STH and STX containing 50 and 30% mineral oil respectively.

III. PROPERTIES AND USES OF EMULPHORS STH AND STX.

For metal drilling and light cutting operations 1-1½% of the emulsion of STH (Borhrmittel H) was stated to be as effective as a 5-10% emulsion of fatty acid soaps and oil previously used. Since soaps were in very short supply, 500 tons per month of Bohrmittel H was being manufactured at the end of the war. For heavy cutting 60% of the compound is mixed with 40% of mineral oil (3-5°E, preferably unrefined) and an intended production of 600 tons per month was contemplated at Hoechst. Several small purchasers were already using this type of blend. For rust prevention in gasoline containers they used 0.1% by weight of Bohrmittel H in the gasoline. This material was effective for the purpose but as expected aggravated engine deposits.

Since it was desired to combine the advantages of rust prevention and the injection of a small amount of water into the engines, further work was in progress to develop products in which the inorganic radicals were eliminated. Among some 200 products tested for the dual purpose, two proved most promising which are represented by the following formula.

$$C_{12}H_{25} - C_6H_4 - O - NH_4$$



The first compound was obtained by the condensation of the sodium salt of dodecylphenyl with chloracetic acid and neutralization of the product with ammonia to form a salt. The second compound was formed by neutralizing iso-butyl-cyclohexyl-n-butyric acid with ammonia. The first compound was considered most promising, but test data from field trials was not available.

IV. USE OF METAL DRAWING OIL - "SAURE E".

"Saure E" is MEPASIN sulfamido acetic acid which is obtained by acetone extraction of the unreacted MEPASIN from Bohrmittel H. Plant scale tests have been made on the drawing of bonderized metals, starting with metal discs. Full-scale production tests were also made on the final draw of 3.7 cm. steel shells. The tests were only partly successful and no definite conclusion on the characteristics of the material can be made at present. The difficulties encountered when working with "Saure E" included the following:-

a) Material treated with "Saure E" must be drawn immediately since the effective film tends to shrink, thereby leaving some metal areas uncovered;

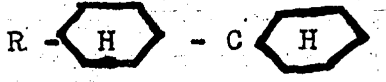
b) The solution of "Saure E" causes reddening and peeling of the skin.

According to the limited experience obtained, it seemed possible to overcome these difficulties by adjusting the pH of the working solution to values between 5 and 7. This was done by the addition of a zincate solution (sufficient to neutralize one-half of the "Saure E" used) to a 0.5% solution of "Saure E".

Better results, without the above-mentioned disadvantages, are expected from the use of isopropylcyclohexylbutyric acid which can be used in form of its Na salt and in exactly the same way as the ordinary soap. No production scale tests on this material have been made but laboratory tests indicate that it is about 5 times as efficient (calculated from the amount of chemical required for covering the metal surface) as the soap solution.

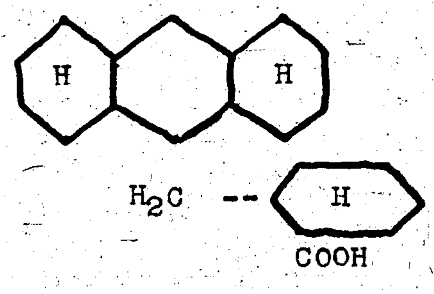
V. RESEARCH TRENDS IN SYNTHETIC EMULSIFYING AGENTS.

The raw material for the emulsifying agents was KOGASIN II obtained from the Fischer Tropsch synthesis. In order to be less dependent upon this source of material, a research program was inaugurated and consisted of condensing alkyl benzene or anthracene with phthalic anhyride in the presence of $AlCl_3$ and then hydrogentating this type of compound. The chemical structure of the compound from alkyl benzene was of the type



Where R is C_3 - C_8

The compound from anthracene had the formula.



Laboratory scale work on the preparation of these compounds was underway and no conclusions may be made as to the additive properties.

VI. INFORMATION CONCERNING THE INTRODUCTION OF THE BOHRMITTEL H

A document from Hamburg, dated 5/2/44 issued by the Technical Advisory Committee for the Reich Station for Mineral Oils, entitled "Concerning the Introduction of the New Boring Medium "Ho", gives full information concerning the introduction and mode of use of the compound. A copy of this article is appended.

VII. SAMPLES.

A drum sample of Bohrmittel H has been obtained for test purposes either as a cutting oil, as a gasoline additive, or as a metal drawing oil in the extracted acid form.

18 July 1945.

APPENDIX A

Instructions for use of "Ho"

APPENDIX "A"

Hamburg 5.2.44.

TECHNISCHE GUTACHTER - KOMMISSION BEI DER REICHSSTELLE FÜR MINERALOEL.

(Technical Advisory Committee for the Reich Station for Mineral Oils).

CONCERNING THE INTRODUCTION OF THE NEW BORING MEDIUM "Ho".

All previous communications concerning introduction and mode of use are hereby superseded.

The supply position in the mineral oil industry renders it necessary to exert the utmost economy in the use of fats and mineral oils in metal-working. As a result of careful research in preparation and application, a new boring medium has been developed that contains no fats and allows of considerable saving in mineral oil.

Not only does this new product replace earlier boring oils, but it shows a whole series of favourable properties of considerable importence under present working conditions.

The boring medium "Ho" is made by the I.G.Dye Industry and has been in use for many months in several works. The amount of fats and mineral oils that can be saved in this way justifies the wide-spread introduction of the new medium.

The boring medium "Ho" has the following special properties.-

1. It can be used, without treatment, with mains water up to 20°DH. In the case of harder water the appropriate use of soda or permutit for softening is indicated, or condenser water may be used. Excess soda should be avoided; for 20°DH 0.4 gm./lt., for 30°DH 0.6 and for 40°DH, 0.8 gm. of soda ash is sufficient (after addition allow to stand a few hours, with occasional stirring). The water hardness can, if necessary, be obtained from the responsible water works.

To obtain as stable an emulsion as possible, boring medium "Ho" should first be agitated with 2-3 parts of cold water (base solution). The water should be added gradually, i.e., each portion added only when the preceding one has been well mixed in. This base solution can then be diluted in one operation with the main bulk of water, either by addition of the latter or by pouring into water. The final emulsion should not be very milky but translucent (opalescent)

The common salt content of most water supplies is below 200 mg./litre and is thus without any harmful corrosive action. Salt concentrations above 500 mg./litre render the water unsuitable for emulsification, the rust-protection of the emulsions then falls sharply with increasing salt content. In such cases a suitable water supply, among others condenser water must be used. The appropriate water-works will also give information as regards NaCl content.

2. In general the addition of special protectives against corrosion is unnecessary, since boring medium "Ho" protects tool, job and machine against rust. However, if rust appears, the supplier and the Lubricants-Society should be informed. Often the addition of 1-2% soda-ash helps (calculated in the weight of boring medium Hö, i.e., add 10-20 gm. soda-ash per kilogram and stir well and only then dilute with water, as described above. The soda-ash is thus not added to the water or to the finished emulsion). Protectives against corrosion such as sodium nitrite etc., can be used, but, as with soda, excess should be avoided, since otherwise the essential stability of the emulsion is endangered.

3. Consumption is small since the "activity" towards metal is high. The mixing ratio must therefore be kept much lower than with previous boring oils. On the average, for all operations previously undertaken with aqueous emulsions the ration 1.100 should not be exceeded. For grinding work 1.150 to 1.200 is sufficient. For tough material the ratio can be increased to 1.50 if necessary, when shavings are being taken off (zerspanen). Higher concentrations and increased soda addition cause strong foaming of the cooling liquid.

4. The boring medium "Ho" emulsion alters during use only when it becomes unstable, because of too hard water or excessive additives. It then runs off on the work or cuttings and the emulsion becomes thinned. In addition, it may become acid after lengthy circulation. It is useful to test the reaction of the emulsion with a suitable indicator (see below) from time to time and when necessary, to render it weakly alkaline by the slow addition of 1:10 soda solution. A pH of about 8 should be maintained, and under no circumstances should the neutral point (pH = 7) be passed.

5. Hö does not attack the human skin. "Hö" is unsuitable as a lubricant. On the contrary, it washes away lubricating oil from surfaces gliding in contact, so that it cannot be used to replace cutting oil with automatic machines. The lubricating oil collecting on the surface in the cooling liquid sump should be removed from time to time and after settling can be used for lubricating railway-beds etc. With shavings of grey cast pig iron separation of the boring medium emulsion sometimes occurs In this case a considerable addition of rust protective must be made, on in case of need another boring oil can be used.

Before using with the new boring medium emulsion, all deposits should be removed from the machines as far as is possible. An intermixing of the boring oil previously used with the new product should not be made, but the emulsions can be mixed.

The immediate introduction and appropriate use of the new product is essential from the point of view of war economy. The change over to the new medium should be so arranged that while the previous stock of boring oil is being used up, no confusion or mixing is possible.

Estimation of the Concentration of Boring Medium Hö and of the pH value.

The estimation of the concentration of boring medium "Hö" can be carried out as for boring oils. A boring oil tester can be conveniently used for the purpose.

The procedure is as follows.-

The flask of the boring oil tester is filled up to the mark with 100 c.cm. of the Hö emulsion to be tested. Then 30 c.cm. of a solution of 100 g. conc. sulphuric acid and 100 g. of common salt in 1000 c.cm. of water is added, up to the upper filling mark. The use of common salt is advantageous for obtaining better separation of the boring medium from the emulsion which is spilt up by the acid. Separation is also helped by standing the flask in a water bath at 60 - 80°C. Splitting up and separation are complete after about 30 minutes. This can be seen from the clearness of the liquid. The flask should now be cooled.

If oily liquid still clings to the walls, aggregation can be effected by repeated rotations. The quantity of oily liquid separating is read off on the calibrated neck of the flask.

The number so obtained gives the quantity of "HO" present in the 100 c.cm. tested and thus gives directly the percentage content of the emulsion. The estimation of the pH value can be made with Lyphan paper or with Merck's reagent paper.

Technical Advisory Committee
of the Government Station for Mineral Oil.

Sgd . E. Thiessen.

N.B. Differences from the communication of 11.10. 43 are shown by vertical margin lines.

Item 22
File XIX-1

Copy 1

Report No. 176

OFFICE OF THE PUBLICATION BOARD

DEPARTMENT OF COMMERCE

WASHINGTON, D. C.

SYNTHETIC RUBBER PLANT
LUDWIGSHAVEN

Lt. Col. P. D. Patterson
E.A.B., F.O./M.E.W.

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

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14 p. diagrs.

SECRET

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MEMBERS OF TEAM

Mr. R. Hopkinson	U.S.	Leader
Lt.Col. W.C. Davey	Br.	Dep. Leader
Lt.Col.P.D.Patterson	Br.	
Mr. E.W. Glen	U.S.	
S.Ldr. A.C. Gruneberg	Br.	
Mr. Handley	U.S.	
Mr. C.C. Monrad	U.S.	

INTRODUCTION

Within the I.G. plant at Ludwigshafen-Oppau there are the following targets of interest from the point of view of rubber:

a. A large scale synthetic rubber plant
(including carbide plant)

b. A plant for making polyiso butylene (Oppanol).

c. A research laboratory for synthetic rubber.

d. A plant for making Koresin, a special tackifier for synthetic rubber.

In addition, Dr. Ambros, the Managing Director, has been a pioneer of the I.G. achievements in the production of synthetic rubber and has played a large part in the general planning of the German synthetic rubber industry.

This report summarises the economic aspects of the investigation only. A separate report from the technical angle is being compiled by other members of the team. A large number of documents were set aside for despatch to London and eventual study. It is probable that these will provide material upon which a further report will be made. In the meantime this report should be regarded as preliminary.

SUMMARY

Although the I.G. chemical plant at Ludwigshafen is on the whole very badly damaged the synthetic rubber plant has escaped more lightly. Providing outside supplies of styrene could be brought in it seems possible that half-rate production might be restored in some four months' time. This would provide about 10,000 tons of rubber per annum until full production could be restored. Power and carbide plants are virtually undamaged and there would appear to be a sufficiency of labour and skilled personnel. In addition to styrene, coal and limestone would be required for the power and carbide plants.

Valuable information on the layout of the German synthetic rubber industry was obtained which, in general, confirms M.E.W. estimates. Total capacity in 1944 was 141,000 tons of Buna S type rubber from four plants. It was learned that a fifth underground plant was in course of construction in south central Germany.

BUNA PLANT

Size of Plant

The construction of the large scale Buna plant was commenced in 1941 and completed in 1943. It was planned for a capacity of 30,000 tons per annum but this was never achieved. The greatest rate of production was 20,000 tons per annum which was obtained during the second quarter of 1944. Thereafter production diminished due to bombing. Although the Buna plant itself was not seriously damaged production was undoubtedly affected by the general disorganization of the chemical plant as a whole, which suffered very severely.

General Description

The process used is not quite the same as was generally believed. It goes straight from acetylene to aldol, thus eliminating the acetaldehyde stage, as indicated below. This process was only used at Ludwigshafen and not at the other plants.

Calcium carbide - Acetylene
Acetylene + Formaldehyde - Aldol
Aldol - Butylene glycol
Butylene glycol - Butadiene

The efficiency from carbide is high, 1.5 tons of carbide being required per ton of Buna S.

The production of carbide and acetylene is carried out in a different part of the plant and is dealt with separately in this report. The main units of the Buna plant itself are:-

Unit	I.G. Building No.	C.I.U. Plan No.
See separate technical report		388-389
		390
		386
		391
		392
		395
Polymerization	193	427
Finishing	195	401

The polymerization unit has space for 40 reactor chambers arranged in 5 lines of 8 each. Two lines, i.e. 16 reactors, have been removed for safety to some unspecified dispersal point. They were not sent to another Buna plant immediately although they may have gone there since. The total number of 40 reactor chambers were never all used at once. The original plan called for a sixth line of reactor chambers which was never installed. The polymerization process is arranged so as to be a continuous one through each line of eight reactors.

The finishing unit consists of four lines each comprising coagulant unit, forming belt, dryer, chalking plant and batching off equipment. One line is incomplete and existing production has been from two lines with one line in reserve. The latex (Buna SIII), is treated in the presence of sodium chloride with calcium chloride and acetic acid which produces an agglomeration of particles forming a fine sludge. This sludge is fed by gravity over a weir on to a wire mesh belt with small suction boxes at the far end of the belt and on through the dryer and chalker.

Incidentally the finishing plant looked very new and hardly used but had apparently been in operation since early 1943, according to Dr. Neiman the production superintendent.

Condition of Plant

On July 31st, 1943 there was a big explosion at the plant due to leakage from a tank car of butadiene. This caused a fire and the plant was out of operation for 8 to 14 days.

Following on the peak production in the second quarter of 1944 production was disturbed due to bombing. However, the plant continued working up to December 15th. It does not seem to have been damaged during the recent fighting or by sabotage, except that many of the control panels have been removed. There were no stocks of finished material in the finishing plant but a more thorough search of the plant might possibly have brought some to light. It seems likely however that all finished material had been evacuated as there was plenty of time to do so.

Without a detailed survey it is impossible to state how long it would take to put this plant back into production. Further details regarding the condition of the various key units will be found in the technical report. It is however possible to say that the Buna section of the Ludwigshafen plant is much less badly damaged than the rest of the factory and is probably the least damaged section of all. The finishing plant is virtually intact and the polymerization unit only slightly damaged. At a rough guess the plant might be restored to half-rate production in a matter of some 3 to 4 months. This however would entail a fresh supply of styrene up to about 5,000 tons per annum since the Ludwigshafen styrene plant is very severely damaged.

Many key personnel are still available at Ludwigshafen. There are also living in the air-raid shelters inside the works a considerable number of foreign workers, mostly Russian and French, but also including Italians, Poles and others. There seems to be a large population remaining in the towns of Ludwigshafen and Frankenthal so that sufficient labour should be available to rebuild and operate the plant. The power stations are still operating. The essential raw materials needed to re-start the plant are therefore coal, limestone and styrene.

Products Made

Ludwigshafen only produced Buna S III. There was however some need to dispose of off-grade material and this was called Buna SV. Experiments proved that it was unsuitable for tyre manufacture but could be used for other products such as footwear.

Records were found which indicated the existence of a new type of rubber Buna MV. This was recorded as needing no thermal breakdown or long working up. From other sources it is believed to be made by a new and simpler process which has been kept secret. Although it was clear from documents that experiments with this product had been made at Ludwigshafen the personnel questioned dismissed it as an experimental development having no future.

CARBIDE PLANT

This is situated some distance from the Buna plant and down by the river. The production of carbide is to some extent controlled by the Buna production superintendent Dr. Nieman.

Size of Plant

There are 4 high pressure boilers working at 130 atmospheres and 500° Cel. There are 4 generators, one of 25,000 kw., one of 20,000 kw., one of 18,000 kw. and one of 16,000 kw. Half of the power generated is used for carbide production and the rest fed into

the main chemical plant to supplement the output of the other two stations. There are two arc furnaces each of 20,000 kWh rating and each capable of producing 45,000 tons of carbide per annum One of these furnaces is normally held in reserve; a further furnace has been planned but not installed.

The bulk of the carbide produced is used for Buna production (via acetylene) but some is used for other purposes at Ludwigshafen and some exported to Hoechst.

The acetylene for Buna production is generated at the carbide plant.

Condition of Plant

Of the boilers one is destroyed, two slightly damaged and one intact.

The 20,000 kW and the 18,000 kW generator are intact and the others only slightly damaged.

Although the buildings housing the carbide plant are somewhat damaged the main damage to the plant consists of derangement of wiring etc. and it is estimated by the personnel in charge that the entire carbide-acetylene plant could be restored within a matter of 3 weeks.

MISCELLANEOUS

Oppanol

It was not found possible to visit the Oppanol plant during the time available.

Koresin

This important tackifier is specially produced at Ludwigshafen for use in the production of tyres from Buna. It is made in building No. 926 (I.G. number) or building No. + (C.I.U. plan)

+ Further details are given in the technical report

Research Laboratory

A fairly well equipped research laboratory is housed in building 178 (I.G. number), or building 620 (C.I.U. plan). The laboratory has been considerably damaged by bombs. It appears to carry out quality and compounding tests on the Ludwigshafen Buna. Further details are given in the technical report.

Pilot Plant

There has been a small pilot plant at Ludwigshafen but this only made Butadiene and Styrene; no co-polymerization was carried out. It seems probable that the early work on co-polymerization was carried out at Leverkusen.

GENERAL LAYOUT OF GERMAN SYNTHETIC RUBBER INDUSTRY

Appendix I shows the German synthetic rubber programme for 1943. It consists of a basic and an emergency programme, the latter being introduced as a special measure. At the end of the year the programmed output was to be as follows:

			Tons per Annum
Schkopau			60,000
Hüls			
	Basic	45,600	
	Emergency	3,000	
		48,600	48,600
Ludwigshafen			
	Basic	24,000	
	Emergency	6,000	
		30,000	30,000
		Total:	138,600

Auschwitz is not shown in this table (which was prepared at the end of 1942) since it was still in an early stage of construction at that date.

It is clear from this programme that the Schkopau plant had reached a static rate of production but that Ludwigshafen and Hüls were still in course of expansion, particularly the former.

This chart showing the 1943 programme was an appendix to a detailed report which it is hoped will be available for study at some future date. Some notes taken from this report are given below:

Schkopau	Capacity planned for 5,000 tons/month (60,000 tons/year)

Hüls	Capacity planned for 3,300 tons/month (39,600 tons/year) increasing to 48,600 by the end of 1943. To make the grades Buna S, Buna SS and Buna SR; also to supply Leverkusen with 300 tons of Butadiene per month for the manufacture of Perbunan.
Leverkusen	For polymerization only starting from Butadiene. Capacity planned to be 250-500 tons/month (3,000 - 6,000 tons/year).
Ludwigshafen	Planned for 2,500 tons/month Buna S (30,000 tons/year).
Auschwitz	Planned for 30,000 tons/annum as a dispersal measure in case of damage to Schkopau and Hüls. Part of the aldehyde plant was due to commence operations in the 2nd half of 1943.
Ferrara	Planned for 600 tons/month Buna S (7,200 tons/year)

This report also gives considerable space to a detailed study of the labour requirements for Hüls and Ludwigshafen.

Appendix II consists of an exact copy of a diagrammatic plan of the German synthetic rubber industry dated 18.11.44. It was taken from the personal files of Dr. Ambros, managing director of the I.G. Ludwigshafen Plant and one of the leading personalities in the German synthetic rubber industry. The plan shows the location and relative size of all plants, expressed in terms both of finished Buna and acetaldehyde production. A completely coloured circle obviously shows a completed plant and a coloured segment an uncompleted plant.

The following figures show the capacity of the plants as shown in the table, compared with E.A.B. and F.E.A. estimates:

		(tons/annum)	
	1944 E.A.B. Estimates	1944 F.E.A. Estimates	1944 Figures from German Diagrams
Schkopau	43,000	65,000/85,000	72,000
Hüls	30,000	43,000/56,000	21,000
Ludwigshafen	20,000	45,000/55,000	24,000
Auschwitz	20,000	16,000/21,000	24,000
	113,000	169,000/217,000	141,000

E.A.B. estimated total synthetic rubber capacity (see Section P. Economic Survey of Germany July 1944 and M.E.W. Int. Weekly No.157 8.2.45 p.9) is therefore 20% lower than the figures shown in the German diagram. The original E.A.B. estimate, largely based on ground reports (see M.E.W. Int. Weekly No.31 19.9.42 p.9) gave Schkopau as having 50,000 tons capacity but the figure for this plant was reduced on the advice of C.I.U. Using the higher Schkopau figures E.A.B. estimates are 9% too low.

The emphasis which the diagram places on Acetaldehyde production is interesting. In addition to the acetaldehyde production at the buna plants themselves there are shown four completed and two uncompleted plants producing acetaldehyde only, as indicated below:

Plant	Yearly Production capacity of Acetaldehyde (tons)
"Mü" (Mückenberg?) (middle Elbe region)	43,200
Burghausen (southern Germany)	28,800
Gendorf (southern Germany)	24,000
Waldshut (Swiss border)	10,200
Total from completed plants:	106,200
Knapsack (Rhineland)	72,000 (planned for 216,000)
"Fü" (? Fünfeichen or Fürstenberg) (middle Oder)	18,000
Total from uncompleted plants:	90,000

Arrows leading from these acetaldehyde plants all point to a new location in south central Germany north of the Danube. It is clear from the diagram that this is a partly completed underground plant in forest country. Although it is possible that this is a mere storage depot for acetaldehyde and finished buna it is

far more likely that, starting with acetaldehyde, a new underground buna plant is in course of erection designed for a capacity of 24,000 tons per annum. From indications received during interrogation it is possible that this plant may be at Eckstein, but this should be treated with considerable reserve. It seems probable that this new plant is not owned by the I.G. but by the German government.

One further point arising from this diagram is that Hüls was originally planned for a capacity of 42,000 tons per annum but had not been completed beyond 21,000 tons per annum in November 1944. The 1943 programme shown in Appendix I in which Hüls was shown with a maximum planned capacity of 48,600 tons per annum was obviously never carried out, probably due to the bombing in June 1943.

Schkopau is also shown at 72,000 tons per annum as compared with 60,000 tons per annum in the 1943 programme. Whether this is due to additional plant or to increased efficiency is not clear.

APPENDIX I

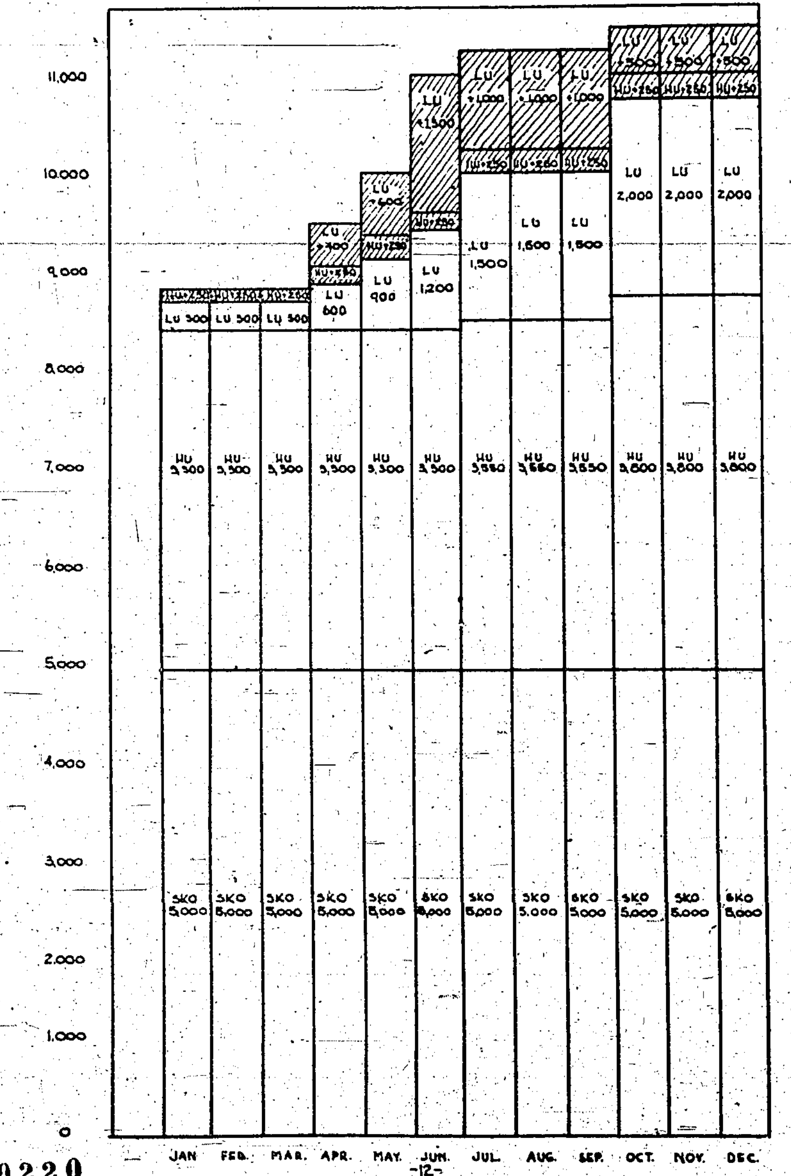
BUNA PRODUCTION – 1943 (PLAN)

(Without Perbunan, Plasticator 32 and Italian Buna)

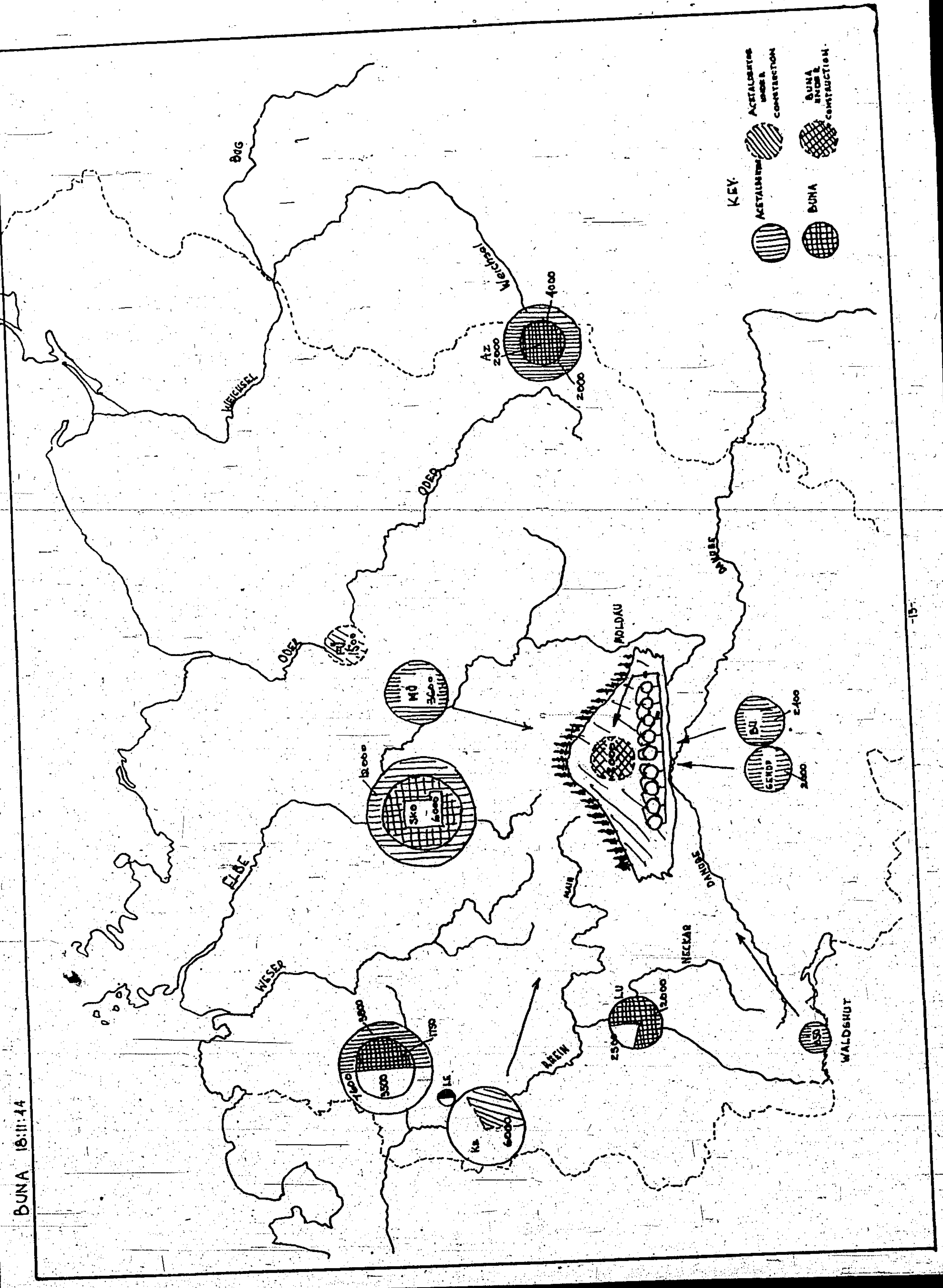
TOTAL PLANNED PRODUCTION 1943	Tons Per Month.											
	JAN.	FEB.	MAR.	APR.	MAY.	JUN	JUL.	AUG.	SEP.	OCT.	NOV	DEC.
NORMAL	8.600	8.600	8600	8.900	9.200	9.500	10.050	10.050	10.050	10,800	10.800	10.800
Inclusive of Urgent Programme	8.850	8.850	8.850	9,550	10.050	11,050	11, 300	11, 300	11, 300	11,550	11.850	11,550

KEY:
☐ Normal Production without special measures.
▨ Production increase in accordance with urgent programme.

NOTE: CHART EXTRACTED FROM DR. NIEMAN'S FILES N.B: THIS IS CLEARLY A PLAN AND NOT REALISED PRODUCTION



APPENDIX II



BUNA 18:11:44

APPENDIX III

PERSONALITIES ASSOCIATED WITH SYNTHETIC RUBBER AND ALLIED PRODUCTION AT LUDWIGSHAFEN

Dr. Wörster	Chairman of directors	Interviewed by Lt.Col. Phelps - little information about rubber.
Dr. Ambros	In charge of synthetic rubber developments at Leverkusen in 1938 and now managing director at Ludwigshafen. The key man for synthetic rubber.	Evacuated together with many of the more important documents. The latter were believed to have been sent first to Dr. Ambros' private house and then to Heidelberg.
Dr. Nieman *	Production superintendant of the Buna plant.	Interviewed; attitude correct but no information volunteered.
Dr. W. Bulow	Director of Organic Products (including Buna)	Particularly concerned with Koresin. Interviewed by other members of the team.
Dr. Goggle) Dr. Gloth)	Oppanol	
Dr. Hopff	Perlon	
Dr. Wurthe	General Director	
Dr. Stechl	Engineer in charge of all power plants.	
Dr. Fees	Engineer in charge of carbide power plant	Interviewed.
Dr. Wesly	Engineer in charge of acetylene production.	
Dr. Pünkel) Dr. Staübel)	Buna finishing plant.	
Dr. Schnell	Chemical technician.	
Dr. Flanmer	Chemical technician.	
Dr. Franke	Polymerization plant.	

* Under interrogation Dr. Nieman revealed that he had buried in waste ground near the buna plant a barrel containing important documents concerning synthetic rubber. These were dug up and examined. They proved mostly technical and will eventually be available for study. The chart in Appendix I and other information on plans for the German synthetic rubber industry came from the buried documents.

ITEM No. 22
FILE No. XXVIII-35

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COPY NO. 196

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PRODUCTION OF FATTY ACIDS FROM BY-PRODUCTS OF THE FISCHER-TROPSCH PROCESS

Pavcik, P. L.

CONFIDENTIAL

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

CONFIDENTIAL

Report on

PRODUCTION OF FATTY ACIDS FROM BY-PRODUCTS OF THE FISCHER-TROPSCH PROCESS

Reported by:

P.L. PAVCEK

CIOS Target No. 22/1(i)
Food & Agriculture

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

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3 p.

n.d.

I.G. FARBENINDUSTRIE, LEUNA. FATTY ACID PRODUCTION BY FISCHER-TROPSCH PROCESS.

Dr. Paul Herold, Director of Research, indicated that Dr. Müller-Cunradi or his assistant Dr. Wietzel at the I.G. Farbenindustrie in Oppau (Ludwigshafen) were directly concerned with the production of synthetic fatty acids from by-products of the Fischer-Tropsch process. This process, for the catalytic synthesis of hydrocarbons produces paraffins as a by-product. These paraffins have a m.p. of 50-55°C. and consist of C_{20}-C_{26} hydrocarbons (average chain length is C_{22}).

The paraffins are oxidized with air @ 130-150°C. using $KMnO_4$ as catalyst in aluminium towers. The oxidation is not complete and the Manganese salts of the fatty acids must be separated from the unreacted paraffin. This is accomplished by use of Alcohol and Benzene.

The crude fatty acids are neutralized with NaOH or Na_2CO_3. The crude soaps are then subjected to steam distillation at 250°C. (Pressure). The lower fatty acids such as formic, acetic, popionic and butyric acid, come off immediately and the hydroxy acids are converted to unsaturated acids. Keto acids are also removed at this point. (Hader process.)

The olefinic and saturated acids, which remain as the sodium salts from the above distillation, are liberated with HNO_3 and the $NaNO_3$ removed. The free acids are steam distilled by the "Wecker" method of forcing water into the hot fat. This method avoids polymerization and keto acid formation and high grade fatty acids are obtained.

The fatty acids are esterified with glycerol to form soaps or edible tri-glycerides. Polymerized residue is used in pitching beer barrels by the brewing industry.

Glycerol is made at the I.G. Farben plant in Heydebreck of which a pilot plant is available in Oppau. Propylene is used as the starting material and the usual steps of alcohol → chlorhydrim → glycerol are employed. Glycerol can also be made by direct hydrogenation (nickel catalyst) of glucose or "Invert" sugar. A mixture of glycols results by this procedure.

20,000 tons annually of paraffin are utilized at the Oppau plant and at Witten the Märkische Seifenindustrie uses even larger quantities. The overall yield of fatty acids is of the order of 50%.

The C_6-C_{10} alcohols obtained as by products from the above process are not found in nature and when esterified with phthalic anhydride form excellent plasticisers.

"Tylose" is a detergent made from cellulose which because of its high molecular weight has similar properties to the natural soaps, i.e. high affinity for organic dyes and will produce a "white" yarn as contrasted to yellow or graying observed when sulfonated oils are used.

copy 1

ITEM NO. 30
FILE NO. XXVIII - 36

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H. KOPPERS G.M.B.H., ESSEN

Peck, E. B.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB - COMMITTEE

②

RESTRICTED

REPORT ON
H. KOPPERS G.m.b.H. ESSEN

Reported by:
Dr. E. B. Peck
on behalf of
United States Technical Industrial Intelligence Committee.
and
Dr. A. Parker
on behalf of
British Ministry of Fuel and Power

CIOS TARGET No. 30/11.11 (also 30/6.12)
Fuels and Lubricants
28 June 1945

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

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7 p. diagrs.

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Personnel of Team

Dr. A. R. Powell, - U.S. Petroleum Administration for War
Dr. E. B. Peck, - U.S. Petroleum Administration for War
Dr. A. Parker, - Brit. Ministry of Fuel and Power
Dr. H. Hollings, - Brit. Ministry of Fuel and Power

Target visited on

15 April 1945

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H. KOPPERS, B. m. b. H., ESSEN

Object of Visit:

This company is well known as designers of coke ovens and gas equipment. The present investigation was directed to those activities that relate to synthetic oils, i.e., the low temperature carbonization of coal and the gasification of coal to make synthesis gas.

Sources of Information:

The interrogation of Dr. Hans H. Koppers, son of the founder of the company, and a preliminary examination of confiscated documents.

Information Obtained:

The Koppers process for low temperature carbonization of coal was well known before the war and there have been no new developments since the war.

The process has been developed for the partial combustion of low grade coals with oxygen to produce synthesis gas ($CO + H_2$). The importance of using brown coal fines for producing synthesis gas is shown by the value put on various grades of fuel by the Brabag Company (Braunkohle Benzin A. G.) at the Schwarzheide, synthetic oil plant:

	RM/Metric Ton
Dry fine coke (brown coal)	2.00
Dry Brown coal coke	20.00
Dry hard coke (bituminous coal)	30.00
Power per KW hr.	0.02
Oxygen Nm^3 95%	0.025

The files revealed an estimate prepared by Koppers for Brabag of which the essential features are:

(1) Brabag (letter of 17 May 1943) required a plant (8000 hr/year) to produce 100,000 Nm^3/hr. of synthesis gas ($CO/H_2 = 1.65/1$) from upper Silesian coal or low-temperature coke for medium pressure Fischer synthesis over an iron catalyst. The coal and coke specifications were not given except that it would be ground so that 75% would pass through a 49000 mesh sieve. The finished gas must be free of condensible hydrocarbons and the sulphur removal must present

no difficulties (such as are caused by pressure of dust or condensible tar or hydrocarbons).

Koppers submitted the following proposal:

For a coal dust of analysis H_2O 1.95%, ash 8.75%, volatiles 22.3%, residue 77.7%, and heating value 7650 WE/kg., there would be produced a gas meeting the above Brabag requirements and with composition: CO_2 - 11.0%; CO = 54.0% H_2 = 34.0%; N_2 1.0% (conc. of CO + H_2 = 88%); lower heating value of gas 2505 WE/Nm^3.

The consumption of materials per Nm^3 of synthesis gas would be:

Coal dust	Kg/Nm^3 of syn. gas	0.475
Oxygen	Nm^3/Nm^3 " " "	0.27
CO_2	Nm^3/Nm^3 " " "	0.066
Steam @ 2 atm.	Kg/Nm^3 " " "	0.19
Heating gas	WE/Nm^3 " " "	167.0
Steam recovered at 16 ats. and 350°C.	Kg/Nm^3 " " "	0.339

For the production of 100,000 Nm^3 of synthesis gas for 8000 hours per year Koppers would build six (6) units (one reserve) each costing 2.7 million R.M. or a total cost of 16.2 million R.M. It was estimated that the gas would cost 1.7 pfg. per Nm^3 (@ 5.2 R.M./$ this would be 9.27¢/MCR). The unit costs used for this estimate were as follows:

	RM
1 ton fine coal in bunker	14.00
1 Nm^3 of 95% oxygen	0.025
Labor 1 man shift (8 hrs.)	10.00
Power 1 Kwhr	0.02
Fresh water 1 M^3	0.025
Recycle cooling water 1 M^3	0.025
Treated boiler feed water 1 M^3	0.025
Heating gas 1 x 10^6 Kcal	4.75
Steam at 16 ats 1 ton	3.00
Steam at 3 ats 1 ton	1.50
Amortization and interest	12%
Maintenance and repairs	2%

A comparison of the powdered coal gasification using air instead of oxygen and producing a heating as of 1250 Kcal/Nm^3 (140 BUT/C F) is estimated for three cases for a daily production of 700,000 Nm^3 or 875,000,000 Kcal:

		Capital Cost R.M.
A.	Coal Dust or Fine Coke	6,000,000
B.	Hard Coke, rotating-grate producers, 12 units 2.6 m. in diameter	2,100,000
C.	Brown Coal Coke, rotating-grate producers, 12 units 2.6 m. in diameter.	2,400,000

The operating costs for each case are estimated as follows:

A.	300 t. fine coke @ R.M. 2 ($0.385/ton)	600 R.M.
	1200 KWhr @ 0.02 R.M.	240
	30 Man shifts @ 12 R.M.	360
	Supervision 20% of labor	72
	Repairs 5% of investment	860
	Amortization and Interest 15%	2,570
		4,702

Cost per 1000 Kcal. 039 pfg.

¢ per MMBTU* 19.0

B. Hard Coke.

184 t. coke @ 30 R.M. ($5.77/ton)	5,520
1200 KWhr @ 0.02 R.M.	240
24 shifts @ 12 R.M.	288
Supervision 20% of labor	58
Repairs 5% of investment	286
Amortization and Interest 15%	860
	7,252
Credit for 74 tons L.P. steam @ 2.50 R.M.	184
	7,068

Cost per 1000 Kcal 0.81 pfg.

¢ per MMBTU* 39.3

*5.2 R.M./$.

C. Brown Coal Coke (Grude).

	Capital Cost. R.M.
200 tons @ 20 R.M. ($3.85/ton)	4,000
1200 KWhr @ 0.02	240
Labor 30 men shifts @ 12 R.M.	360
Supervision 20% of labor	72
Repairs 5% of plant cost	330
Amorization and Interest	990
	5,992
Credit 74 tons of L.P. steam	184
	5,808

Cost per 1000 Kcal 0.66 pfg.

¢ per MMBTU* 32

Dr. Koppers produced detailed information on two other processes: (a) conversion of coke oven gas to synthesis gas (CO + H_2), and (b) low temperature carbonization of bituminous coal with gasification of the semi-coke in the form of flow sheets, copies of which are attached to this report as Fig. 1 (process a) and Fig. 2 (process b).

E. B. PECK
A. PARKER

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*5.2 R.M./$.

Electricity Consumption: ca 370 Kwh
= ca 38.5 KW/1000 Nm^3 Coke-Oven Gas
Fresh Water Consumption: ca 25 m3/hr.
(Make-up Water) = ca 2.6 m^3/1000 Nm^3
Coke-Oven Gas

Refactories:			
Silica	1360 ≠ 80	= 1440	Tons
Fire Clay	1180 ≠ 160	= 1440	"
Insul. Mat.	600 ≠ 100	= 700	"
		3580	"

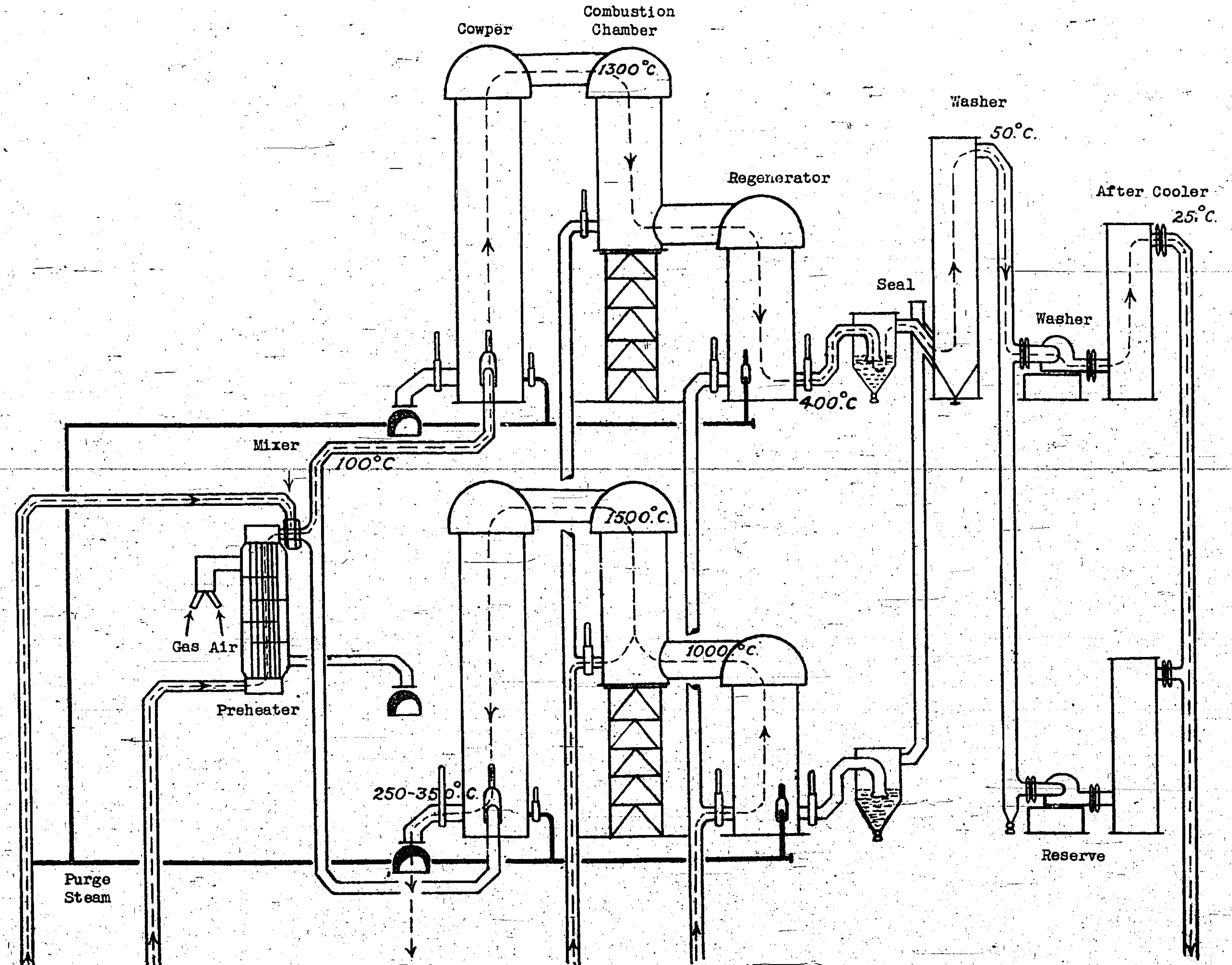


FIG. 1

CONVERSION OF COKE-OVEN GAS TO SYNTHESIS GAS

Steam
2.5 ATS.
8200 Kg/hr.
incl.
Purge Steam
(0.85 Kg/Nm^3
Coke-Oven Gas)

Coke-Oven Gas	
CO_2	6.8%
Cn Hm	2.5%
O_2	0.2%
CO	11.5%
H_2	46.5%
CH_4	24.0%
N_2	8.5%
9600 Nm^3/hr.	

Tail Gas

Fuel Gas
2500 Kcal (Lower Heating Value)
Residual Synthesis Gas
Heating Gas Input:
14,700,000 Kcal
(Lower Heating Value)
/hr. - 1515 Kcal
(Lower Heating Value)
/Nm^3 Coke-Oven Gas
(Of this about 3% for Preheater)

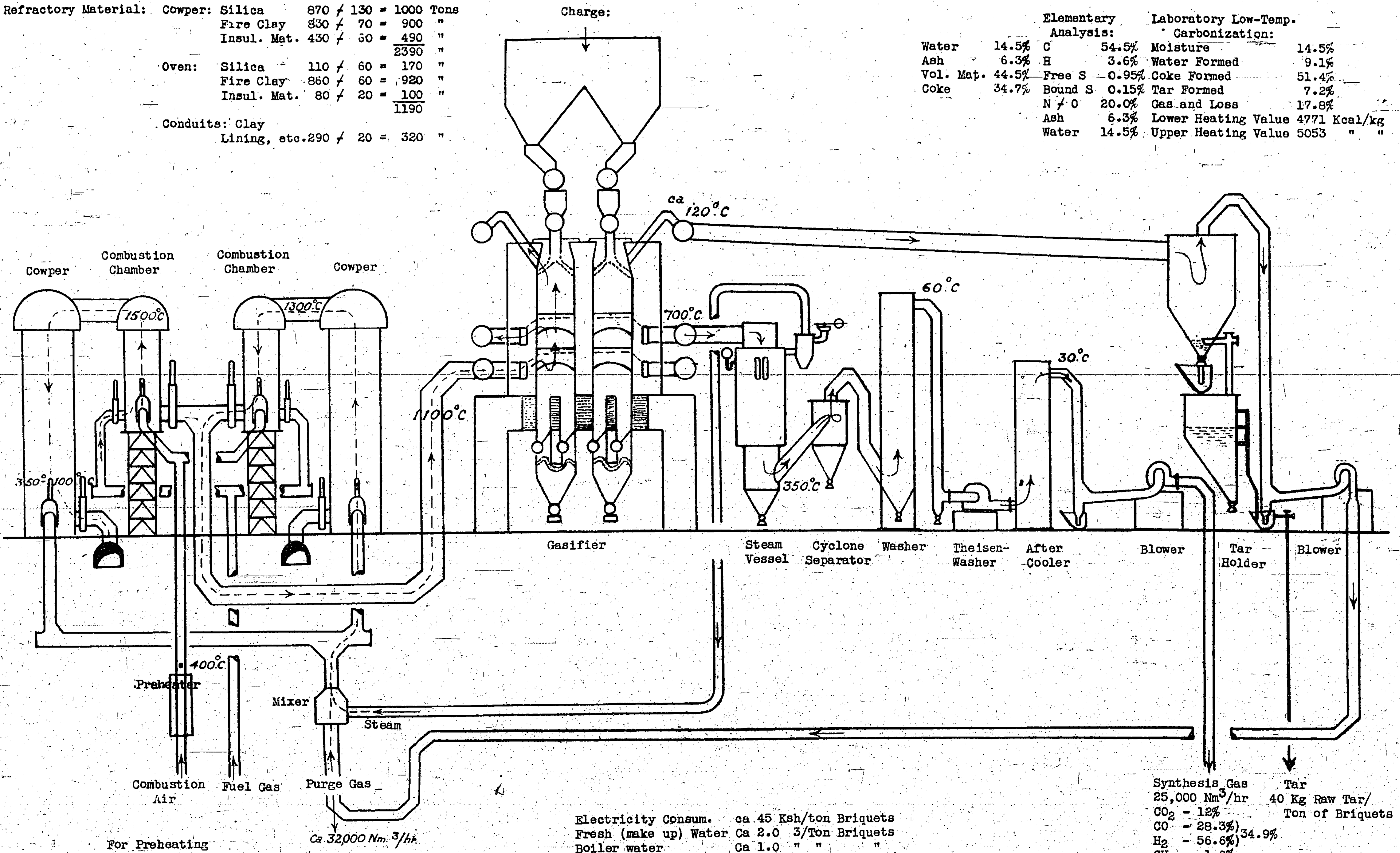
Combustion Air
30,000 Nm^3/hr.

Coverted Gas
CO_2 5.1%
CO 19.7%)
H_2 69.1%) 88.8%; CO:H_2 - 1.5.5
Ch_4 1.0%
N_2 5.1%

17,700 Nm^3/hr.
(From 1 Nm^3 Coke-Oven Gas
1.85 Nm^3 Synthesis Gas)
Dust Content: 30 mg/Nm^3

Refractory Material:						
Cowper:	Silica	870 ≁	130 =	1000	Tons
	Fire Clay	830 ≁	70 =	900	"
	Insul. Mat.	430 ≁	60 =	490	"
				2390	"
Oven:	Silica	110 ≁	60 =	170	"
	Fire Clay	860 ≁	60 =	920	"
	Insul. Mat.	80 ≁	20 =	100	"
				1190	
Conduits:	Clay Lining, etc.	290 ≁	20 =	320	"

		Elementary Analysis:		Laboratory Low-Temp. Carbonization:	
Water	14.5%	C	54.5%	Moisture	14.5%
Ash	6.3%	H	3.6%	Water Formed	9.1%
Vol. Mat.	44.5%	Free S	0.95%	Coke Formed	51.4%
Coke	34.7%	Bound S	0.15%	Tar Formed	7.2%
		N ≁ O	20.0%	Gas and Loss	17.8%
		Ash	6.3%	Lower Heating Value	4771 Kcal/kg
		Water	14.5%	Upper Heating Value	5053 " "



Synthesis Gas
25,000 Nm^3/hr
CO_2 - 12%
CO - 28.3%)
H_2 - 56.6%) 34.9%
CH_4 - 1.0%
N_2 - 2.1%

Tar
40 Kg Raw Tar/
Ton of Briquets

Dust Content: 20 mg/Nm^3
Synt. Gas free from Tar & Oil Vapors
" " " " Resins, etc.
Synt. Gas Yield: 1200 Nm^3/Ton Briquets

For Preheating
1300 Kcal. (Lower Heating Value) per Kg. Briquets
- 1200 Kcal. (L.H.V.) per Nm^3 Synt. Gas
As Fuel Gas-Generator Gas from Res. Coke
Fuel Gas Heating Value: 1300 $Kcal/Nm^3$

Electricity Consum. ca 45 Ksh/ton Briquets
Fresh (make up) Water Ca 2.0 3/Ton Briquets
Boiler water Ca 1.0 " " "
Steam Requirements Produced in Plant.

FIG. 2
SYNTHESIS GAS PRODUCTION
FROM BROWN COAL BRIQUETS

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FILE No. XXX—34

COPY No. ~~196~~

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by Col. E. W. Gruhn,

TECHNICAL ASSISTANCE ON SYNTHETIC OILS RENDERED THE JAPANESE BY THE I. G. FARBENINDUSTRIE A.G.

Peck & Jones

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

Report On

TECHNICAL ASSISTANCE ON SYNTHETIC OILS RENDERED THE JAPANESE BY THE I.G. FARBENINDUSTRIE A.G.

Reported by:

Dr. E. B. PECK
Irvin H. JONES

On Behalf Of

U.S. Technical Industrial Intelligence Committee

CIOS Target Number 30/4.03

Fuels and Lubricants

July 26, 1945

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

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/8/45

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Personnel of Team:

Dr. E.B.Peck - U.S.Petroleum Adm. for War
Mr.Morley J.Ayearst - U.S.Foreign Economic Adm.
Irvin H. Jones - U.S.Bureau of Mines.

TECHNICAL ASSISTANCE ON SYNTHETIC OILS RENDERED THE JAPANESE BY THE I.G.FARBENINDUSTRIE

Introduction

The report sets forth information on the extent and the quality of the assistance given the Japanese in their problems of synthetizing oils and motor fuels from coal. The information was obtained by the reporters in interviews separately with Dr. Fritz Ringer and with Dr. Mathias Pier along with two of the latter's associates, Frl. Dr. Hoering and Dr. Donath. Dr. Ringer is a prokurist in the oil department of I.G.Farbenindustrie in Berlin and had conducted most of the negotiations with the Japanese for synthetizing oils in anticipation of the contract signed between them as well as also in many similar negotiations on related subject matters with others. More recently he had charge for the German Government of bomb-damage repairs on oil installations in Roumania and later in Hungary from which latter country he had only recently returned to Germany. Dr. Pier is a director of the I.G. Farbenindustrie and has been the principal inventor in the field of the hydrogenation of coal, oils and related substances. The interview with Dr. Ringer took place in Fischbach, near Bayreuth, on 24 May 1945, and with Dr.Pier at Heidelberg, Germany, on 25 May, in part in the presence of said Drs. Hoering and Donath.

Summary

The I.G.Farbenindustrie gave a Japanese Commission early in 1945 limited information on its technology of converting coal, coal tars, and the like, to liquid fuels. The interviewed, Drs. Ringer and Pier of the above organization, were separately questioned in different parts of Germany and both seemed in agreement that any oil production in Japan, derived from solid fuels by their direct hydrogenation or hydrogenation of derivatives, could have only a minor influence on the outcome of the present war. The Japanese Commission discussed with the representatives of I.G.Farbenindustrie nothing relating to the present status of Fischer-Tropsch plants in Japanese-held territory or their capacities. The locations of some low-temperature carbonization plants are given as well as some data on a combined-operations plant projected for installation on

Sakhalin Island for production annually of 128,000 kiloliters of aviation gasoline. A list of twelve hydrogenation projects considered in 1939 as described in seized documents, is also included.

The Interviews.

There was substantial agreement in all statements made by the interrogated; they all agreed that insufficient information had been given the Japanese by the I.G.Farbenindustrie to have any marked effect on their output of oils from coal, and the like, by way at least of I.G.Farben's processes of direct hydrogenation of such materials. Dr. Ringer's personal opinion is that, in as far as hydrogenation is concerned, there could be little practical synthetic production of gasoline, or of aviation fuel in Japan in the near future; there could, however, be produced some fuel-oil from coal. This situation may possibly result from the fact that the contract-negotiations with the Japanese extended over such long period that there was quite limited contact with the I.G.Farben before the capitulation of Germany, and also from the fact that the Japanese were seemingly desirous of making their own processes operate properly, without disclosing much, if any, of their details to the I.G.Farben.

The contract between the Japanese and the I.G. Farben was signed by the Military Attaché of the Japanese Embassy, and Dr. Ringer believes that the negotiations with the Japanese went so very slowly also largely because of jurisdictional disputes between the Japanese Army and Navy that seemed to be each developing hydrogenation processes competitively. During their negotiations with the I.G.Farben, the Japanese also were trying to circumvent the I.G.Farben and to procure hydrogenation apparatus from probably such concerns as Krupp.

Mr. Matsoka, who was probably Minister of Internal Affairs of Japan, began the negotiations with I.G.Farben in 1941. He however returned to Japan in 1942 and thereafter the negotiations were undertaken by others. The I.G.Farben was attempting to avoid giving exclusive rights for the processes of hydrogenation to the Japanese Army and Navy. However, the German Government gave orders to the Company to reveal to the Japanese the "know how" on hydrogenation processes as they were related to the manufacture of Diesel oil and gasoline, and the I.G.Farben attempted to limit the disclosed information precisely to these orders. In other words, such processes as are used in the preparation of isooctane and aviation gasoline, or in any hydro-cracking procedure of the DHD (Druck-Wasserstoff-Dehydrierung) process; or in the preliminary hydrogenation process step (Vorhydrierungs Verfahren) and in the complete operations with catalyst 6434, were at no time discussed with any of the Japanese negotiators or their visiting technicians. Neither was information relative to the manufacture of synthetic lubricating oils such as Paraflow inquired of by the Japanese.

Eventually, a contract between the I.G.Farben and the Japanese was ready to be signed in December 1944 and was actually signed in January 1945. The negotiations which actually led to the signed contract included the following negotiators:-

General Komatsu - Military Attaché;

General Atani - who was probably responsible for successful culmination of the negotiations. He was later captured by the American Forces in S.Germany;

Colonel Yoshida - took some part in negotiations but returned to Japan in 1944;

Staff Engineer Mikami (Army) - A glass chemist who bought alkalis in Germany;

Colonel Ishige - who did not understand the processes, and was merely amongst those present;

Major Kinoshita - Army engineer who spoke German and carried on much of the discussions;

Dr. Kani - A salesman from the Mitsubishi Company who joined in the pre-contract discussions;

Dr. Fukao - also a salesman from the Mitsubishi Company who had some experience in a refinery near Tokio where a U.O.P. poly-plant was operated.

Before the above contract was signed, Japanese visitors were frequently in the I.G. plants, but Dr. Donath had the impression that they were either not experts or dissembled well. Both Drs. Ringer and Pier stated that the Japanese technicians who were commissioned to obtain the hydrogenation information from the I.G.Farben after the signing of the contract were not well-informed or clever technologists and that it is doubtful that they could have accumulated sufficient information to be of practical advantage to Japan.

The exchange of information between the contracting parties started after the preparation of the contract and all real exchange of information took place this year. The Japanese Commission was actually in Heidelberg for this purpose up till eight days before the city was occupied by the American troops.

During this period of exchange of information, Dr.Pier gained the impression that the Japanese Army had 3 hydrogenation plants for Low-Temperature Tar (Urteer) that had a nominal capacity of 50,000 metric tons per year of gasoline. These plants operated with only "Sumpf-phase" and gas-phase steps. The Japanese Navy has a hydrogenation plant for coal at Tokuyama near Tokio. Its capacity is not known, but it is believed to be a small pilot plant producing mainly naval fuel oil and it probably operates at 200-300 atm. pressure. Tungsten and molybdenum catalysts were probably being used in this Navy plant, but long life of catalyst requires special talent in its preparation. Tungsten gives a better catalyst than does molybdenum, but it must be known how to operate it.

The Japanese inquiries suggested that the principal difficulties they had met in developing their own hydrogenation processes were: (1) coking-up of heating coils and heat-exchangers, and (2) operation of the gas-phase step of the hydrogenation for the conversion of Middle Oils to gasolines. It is also known that they were employing chlorine in their processes and were having trouble with corrosion as a result. (Incidentally, Dr. Pier said that 300 atm. hydrogenation operation plus chlorine was the equivalent of 700 atm. operation without it. Operation at 700 atm. is also better with chlorine but, during the war, Dr. Pier never risked its use because of the necessity of keeping all hydrogenation installations at their full capacity in such times)

The difficulties experienced by the Japanese with gas-phase operations were very probably traceable to the employed catalysts and preparation thereof, since Dr.Ringer emphasized that the Japanese wanted especially the "know how" of catalysts manufacture and also to have despatched two or three experts of the I.G.Farben to Japan to give assistance. It was intended to send these specialists in May of this year by submarine which was an eight weeks' trip. This however was not done. Plant designs and information on catalysts were given the Japanese beginning December 1944, but Dr. Ringer does not know whether they ever reached Japan because they were probably sent by U-boat. It was also thought by Dr. Ringer that the Japanese did not plan to expand their hydrogenation operations until at least the existing Navy plants were brought into successful performance.

A Herr Ruhl, an I.G.Farben representative, is in Japan; he is specialist in nitrogen-fixation plants and does not have the latest information on hydrogenation processes for oil from coal. He also was of the opinion that it was preferable to work with the Japanese Navy rather than with the Army. Herr Ruhl sent no reports and was not in close contact with the I.G.Farben men in Germany; all communications with Germany were direct by wireless telephone every week or ten days. The I.G.Farben heard from Herr Ruhl that the Japanese were not going to build any new plants and he also did not indicate other locations, although Dr. Ringer personally believed them to be in Manchuria. Herr Ruhl was also said not to be the type of man to head a business and his information was limited almost solely to fixed-nitrogen processes, but in this connection he was able to assist the Japanese in ways of producing hydrogen which may be made in Winkler generators.

Dr. Pier said that the Japanese discussed nothing about any Fischer-Tropsch plants or processes they may have had in operation.

The information the Japanese received from the I.G. Farben was the technique of operating hydrogenation plants employing, as primary material, either ordinary high-temperature bituminous coal tar or tars produced by low-temperature distillation of especially brown coals. (It is known that Lurgi, of Frankfurt-am-Main, has assisted the Japanese in building Low-Temperature Distillation plants for coals).

Both Drs. Ringer and Pier were apparently completely cooperative with the interviewers. The former spoke entirely from memory, whereas the latter and his associates had specific information at hand, but they stated that most of their Japanese files had been evacuated both to Unter Loquitz - a small town south of Erfurt and near Saalfeldt on the main railway line between Munich and Berlin - and to Hassmansheim (Neckar). At Unter Loquitz, the files were stored in a mine-entry of a slate quarry and they were in charge of a Herr Reichler. The files at Unter Loquitz do not however carry all papers that extend up to the conclusion of the contract with the I.G.Farben. Dr. Pier suggested that if these documents could be brought back to Heidelberg, he and his staff would undertake to study them to the end that they could give complete and accurate information in as far as it was in their possession. While it is doubtful that any valuable information could be obtained, it is recommended that these documents of Dr. Pier's be assembled for study at Heidelberg by him and his associates.

Shortly after initiation of the exchange of technical information with the Japanese, I.G.Farben, on 8 February 1945, received from the above-mentioned Major Kinoshita, statements relating to the existence of three Japanese plants for the hydrogenation of tars produced by low-temperature distillation (Urteer); these plants are named as follows:-

(1) Kinsei in Manchuria, located on the Asiatic mainland opposite Koro Island, southwest of Mukden;
(2) Mukden; and

(3) Hokkaido, on the Japanese mainland.

The above three plants were designed by the Japanese for operation at 300 atm. pressure and each for a yearly production of 50,000 tons of gasoline.

A commission of Japanese representatives went to Heidelberg, Germany, in December 1944 to collect full information for the building and operation of a plant for the production of 128,000 kiloliters (93,000 tons) per year of aviation gasoline from Utibuti coal (Sakhalin) (see below). A prior project had been considered for Kinsei (above-mentioned), but was later abandoned for this undertaking on Sakhalin (Karafuto) Island.

Of the various proposals made by the I.G.Farben to the Japanese, the one decided upon projected the consumption of 600,000 tons of Utibuti coal to produce the 128,000 kiloliters of gasoline per year. Considering capital investment and coal consumption, the most economical operation was to be achieved by direct hydrogenation of a portion of the above amount of coal in combination with low-temperature carbonization of the remainder coupled with hydrogenation of the thereby-formed low-temperature tars. The hydrogenation was to be performed at 300 atmospheres pressure following the same procedure used at Scholven in the Ruhr. Thus, the Japanese received from the I.G.Farben actually only substantially the Scholven plant and its operation along with data on the hydrogenation catalysts 3510, 5058 and 6434; as aforementioned, Dr. Donath states his doubts that the Japanese know how to operate with catalyst 6434 which is adapted to provide a gasoline product having an octane number of 91 when admixed with Tetraethyl lead.

The Utibuti coal is a young bituminous coal that had not been tested by the I.G.; however, the Japanese submitted the following information:

1. <u>Analysis of Raw Coal</u> (Japanese analysis).

Water	-	8.17%	by wt.
Ash	-	15.9%	" "
Volatile matter		34.54%	" "
Fixed carbon		41.39%	" "
Total		100.00	
Heating value		6655 Kcal/kg.	

<u>Ultimate Analysis</u>

Carbon	-	60.69%	by wt.
Hydrogen	-	5.18%	" "
Oxygen	-	16.78%	" "
Nitrogen	-	1.32%	" "
Sulphur	-	0.46%	" " (combustible 0.14; non-combustible 0.32.

MeltingPoint of ash - 1230°C.
Sintering Point - 1160°C.

In 1943, data were submitted by the Japanese on another coal, as follows:

2. Analysis of Raw Coal

Source	-	Not given
Water	-	6.05% by wt.
Ash	-	11.5% " "
Volatile matter	-	41.0% " "
Fixed carbon	-	41.0% " "
Sulphur	-	0.5% " "
Total		100.0%
Heating value	-	6655 Kcal/kg.

Ultimate Analysis

Carbon	-	74.0% by wt.
Hydrogen	-	5.5% " "
Oxygen	-	13.5% " "
Nitrogen	-	1.5% " "
Combustible Sulphur		0.4% " "
Ash	-	5.0% " "
Total		99.9%

Yield from the above coal by its low-temperature carbonization:

Semicoke	-	62% by wt.
Tar	-	18% " "
Water	-	13% " "
Ash in coke	-	8% " "

The above (2) coal has been washed with 80% yield of a coal product having the following composition; this washed coal was intended for use in the direct hydrogenation:

Water	-	6.0%
Ash	-	5.05%
Carbon (amf)	-	72.0%
Volatile matter	-	45.0%

"amf" = ash and moisture-free coal or "reinkohle".

The hydrogen consumption for converting the coal to aviation gasoline is estimated to be 3000 Nm^3 per ton of gasoline, and the product would have an octane number of 70-72 clear and of 88-90 with 0.1% vol. of T.E.L.

The best washing tests gave an 83% yield of washed coal with 2.1% ash.

Low-temperature carbonization of the Raw Coal (2) by the Lurgi process was reported by the Japanese to yield:

Semicoke	-	63.0% by wt.
Tar (Urteer)	-	12.25% " "
Gasoline	-	1.50% " "
Gas	-	9.00% " "
Water	-	14.30% " "
Total		100.05% " "

Fischer-Hempel assay shows 16.4% by weight of the coal as tar.

Hydrogenation of coal (2) gave the following results, as reported by the Japanese:

Yield	?
H_2 consumption	?

Assay of oil:

First drop	40°C.
Off at 180°C.	8.05% by vol.
Off at 320°C.	52.92% " " (53.92)

Analysis of the Light Oil shows:

Sp.gr./20°C.	0.8633
Off at 180°C.	38.9% vol.
Off at 280°C.	97.4% vol.
Phenols	23.0%
Unsaturateds	14.8%
Aromatics	16.3%
Saturateds	45.9%
Total	100.0%

It is believed that the Japanese Navy process operates under conditions that give much less Middle Oil than is shown by the above results, and produces mostly fuel oil. These conditions are reported to be operations at 220 atm. pressure and 425°C.

According to Dr. Pier, no new coals from Japan were recently tested by I.G.Farben. He said that he was not acquainted with the Japanese method of producing hydrogen, but suspected that Winkler generators were employed.

In so far as the manufacture of Tetraethyl Lead is concerned, both Drs. Ringer and Pier said that the I.G. Farben gave the Japanese representatives no information on Tetraethyl lead, nor did the Japanese ever visit any plants for its manufacture.

Dr. Ringer who, as aforesaid, handled all negotiations with the Japanese, stated that they obtained no information on the manufacture of Oppanol.

From the I.G.Farben, the Japanese got no data on fuels for jet-planes, but they may have obtained such information from the Reichsministerium or outside firms. Both Drs. Ringer and Pier said that they were not aware that the Japanese secured any advice or data on motors for jet-planes although they had contact with such firms as Junkers and also Messerschmidt. The Japanese General Otani, who was involved in the contract negotiations, was much out of Berlin on aviation business. Incidentally, in this connection, Dr. Pier stated that brown-coal middle oil was the fuel used for the jet-planes; such fuel should have a low pour-point (stock punkt) and neither too many aromatics nor phenols. The best fuels for planes of this type were never completely developed because the models changed so frequently.

Survey of captured documents of the I.G.Farben stored in the Library at Heidelberg under guard of the American Army disclosed the following statements which are of importance in this connection:

a. In the last paragraph of the minutes of a meeting in Ludwigshafen on 3 November 1941 between the Japanese and Dr. Pier, there stands the following statement:

"The production in Sakhalin amounts to about half a million tons. The Japanese hydrogenation plant in Tokuyama (Navy) is in production; it is small and still giving trouble".

b. A document dated 3 May 1939 mentioned the following hydrogenation projects under consideration:

(1) Ogura Sekiyu

200 tons/day anthracene-gas oil (200-300°C) to a special gasoline having an End Point of 150°C. This should give a gasoline that, in admixture with 0.09% tetraethyl lead has an octane number of 90 or above. This was a Japanese Army project.

(2) Project North China

Under the leadership of Admiral Godo, there was requested a bid on plants for the production of 50,000 and 100,000 tons per year of gasoline from bituminous coal.

(3) Project Nissan Kagaku (Dr. Endo)

This company closed a contract with Lurgi of Frankfurt-am-Main for the low-temperature distillation of 100,000 tons per year of bituminous coal. The plant was projected for operation in the summer of 1940. Herr Ruhl (I.G.Farben) gave a cost estimate on a hydrogenation plant for 13,500 tons of the low-temperature tar per year to 10,000 tons of gasoline.

(4) Japan Gasoline K.K.

a) Production of isooctane. At the same time a licence for cracking of CH_4 was declined because the project was too small;
b) Hydrogenation of 100,000 tons/year of crack-gasoline to aviation motor fuel having an octane number of 82;
c) Hydrogenation of 41,000 tons/year of "lube stock" (360-385°C) to aviation motor fuel.

(5) Project Nippon Yuka

Mr. Haga, of New York, requested a plant for the recovery of 10,000 tons/year of gasoline from bituminous coal. Ovens for the NH_3 synthesis at Showa Hiryo were let to the Bethlehem Steel Co.

(6) Project Uba Chisso

Uba Chisso was interested in tar and coal hydrogenation. In 1937 a bid was submitted by the I.G. Farben for treating 20,000 tons/year. In December 1938, new projects were bid upon for the hydrogenation of 40,000 tons/year of tar to gasoline for automobiles, and to 28,400 tons/year of aviation gasoline.

(7) Project Tokio Gas

This company contemplated a plant for hydrogenation of 20,000 tons/year tar to about 16,000 tons automobile gasoline.

(8) Sumitomo Kagaku

Messrs. Nakao, Kodama, and Shioya in contact with Messrs. Patrick & Tillman in London.

(9) Showa Seiko

Costs were submitted on the following projects:

a) Production of 125,000 tons/year of gasoline from Fushun coal;
b) Production 80,000 tons/year gasoline from 100,000 tons/year of coke-plant tar;
c) Production of Synthesis Gas from coal in Winkler generators for the Fischer-Tropsch reaction.

(10) Manshu Yuka

The Manshu Yuka has a plant for low-temperature distillation of bituminous coal. The tar is hydrogenated according to its own process (Kuroi). Mr. Hama, during a visit to Berlin, said on 31 October 1938, that his company would produce in Manchuria 1,000,000 tons of which he would take over the production of 350,000 tons and that, of the latter amount, one-third would be produced according to the Fischer-Tropsch process, and another one-third would be according to the SMR (Navy) process. It is planned by Manshu Yuka to increase the present production of 10,000 tons/year gasoline to 50,000 tons.

(11) Project Manshu Tanko

Coal samples (six) submitted by this organization can be easily hydrogenated.

(12) On 23 June 1942, the Japanese asked the Krupp organization for a bid to supply them with: 18 ovens, 18 m. long and 1 m. in diameter; 12 vessels 6 m. long and 0.8 m. in diameter; all adapted respectively for operation at 300 atm. and 450 atm. pressure operation.

These project data are here included because, since the writing of the letter wherein they were described, many, if not all, of the projects may have developed into producing plants.

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by Col. E. W. Gruhn.

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GAS UTILITIES IN GERMANY

Pfeiffer, Getz, Osborne

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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GAS UTILITIES IN GERMANY

Reported by
Mr. B.V. Pfeiffer, T.I.I.C
Dr. C.A. Getz, T.I.I.C
Mr. A, Osborne, T.I.I.C

CIOS Target No. 33/151
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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

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MANUFACTURE OF GAS AT LEIPZIG GAS WORKS, LEIPZIG

1. Introduction.

The Leipzig Gas Works located in Leipzig is a municipal operated and owned property. It purchased approximately 5% of its gas requirements from the Energie A.C. with headquarters at Markleeberg. The company manufactures the balance of its gas requirements. The director of the company is Earnst Homborg, and the plant engineer is Paul Thieroff. Both showed us through the plant.

2. Carbonizing Plant

This consists of:

a. Two batteries of Koppers Ovens, each battery containing 18 ovens. The ovens are heated by 6 detached Koppers Producers. These ovens can carbonize 300 tons of coal per day and can produce 100,000 m^3 (4800 Kg. Cals. per m^3) of gas per day.

b. Two batteries od Didier Inclined Ovens, each battery containing 18 ovens. The ovens are heated by gas produced by the ovens. The ovens can carbonize 200 tons of coal per day and can produce 140,000 m^3 (4800 Kg. Cals. per m^3) of gas per day. One battery is out of operation awaiting complete refilling.

3. Water Gas Plant

This consists of:

a. Two Bamag machines, equipped with automatic controls and self-cleaning generators. Each machine can produce 70,000 m^3 (2600 Kg. Cals. per m^3) of gas per day.

b. Two Pintsch Company machines are under construction and are 90% completed. They are equipped with automatic controls and self-cleaning generators. It is estimated that each machine will be able to

produce 100,000 m^3 (2600 Kg. Cals. per m^3) of gas per day.
Coke produced in the carbonizing plant is used in the water gas generators.

4. Fisher Tropsch Plant

In June 1944 the company started the erection of 12 Fisher Tropsch ovens for the production of synthetic oil. The plant was completed about 75% in April 1945, when heavy bombing of the gas works stopped all work on this installation. It is estimated that this plant will handle 220,000 m^3 of 4300 Kg. Cals. per m^3 of gas and 250,000 Kilos of synthetic oil per day. This oil when refined will produce 50% motor fuel, 30% Diesel oil and 20% lubricating oil. All synthetic oil will be shipped to a central refining plant at Zeitz in Central Germany. Other Fisher Tropsch Plants located at Nurenberg, Furth, Erfurt and other cities in Central Germany will ship their synthetic oils to Zeitz for refining. The Fisher Tropsch Plants use activated carbon for complete sulphur removal and a cobalt catalyst heated to 200°C for producing synthetic oil.

5. General Comments

Ammonia has not been recovered in the carbonizing plant since 1937 due to competitive conditions brought about by the numerous low price synthetic ammonia plants, and the high prices of sulphuric acid to produce sulphate.

A mixture of 70% Lux and 30% Bog Ora (Natural iron oxide) are used for H_2S removal. Spent purifying material is sold to chemical plants for sulphuric acid production.

Coal, known as hard coal, is received by rail from Zwickau. Due to the present coal shortage and plant damages, the use of gas is limited and consumers can only secure sufficient gas for their use during the

following hours:

3:00 to 5:30 o'clock (Bakeries only)
7:00 to 9:00 "
12:00 to 14:00 "
17:00 to 19:00 "

During all other hours of the day the gas pressures throughout the city are reduced to 1/2" water pressure. Consumers are notified through radio broadcasts as to the actual hours during which gas will be available. All automatic gas appliances such as gas refrigerators, water heaters, etc., are not permitted to be used.

The plant was heavily bombed with fire bombs in December 1943, and in May 1944, causing some damage to structures, buildings and holders, most of which have been repaired. About 15 high explosive bombs were dropped on the plant in February 1945, damaging holders and coal handling equipment which are now being repaired.

The gas main distribution system throughout the city was severly damaged by bombs. These breaks are gradually being repaired.

There is nothing of unusual interest to the gas industry at this plant.

MANUFACTURE OF GAS AT
BÖHLEN GAS WORKS
BÖHLEN

1. Introduction

The Böhlen Gas Works located in Böhlen is a privately owned company. It sells all the gas produced to the Energie A.G. (located at Markleeberg). This latter company operates a gas grid system and resells the gas purchased to approximately 20 cities extending from Zwichau to the south of Böhlen and to Magdeburg to the north of Böhlen. The director of the company is A. Böhn with whom we discussed various plant operating features. Hans Otto, plant engineer showed us through the plant and explained operations.

2. Gas Generating Facilities

In 1940 five Luvgi gas generators were installed. In January 1945 five additional Luvgi gas generators were put into operation.

Eight generators are usually in operation and produce 480.000 m^3 of 4200 Kg. Cals. per m^3 per day. The generators have an internal diameter of 2.5 meters. Each generator can produce 60,000 m^3 per day.

3. Oxygen Plant

A Linde-Frankel air liquifaction plant is installed for the production of oxygen. It consists of two small machines each having a capacity of 1000 m^3 of O_2 per hour, and two larger machines each having a capacity of 2000 m^3 of O_2. The oxygen is 95% to 97% pure and contains from 3% to 5% N_2. One large and one small machine is usually in operation. Oxygen is produced at 20 to 22 atmospheres pressure.

4. Cost of Plant

The total cost of the plant was as follows:

Machinery and apparatus........	8,180,000 marks
Buildings and structures	1,920,000 "
Miscellaneous	629,000 "
Total cost	10,729,000 "

It is estimated that the Linde-Frankel oxygen plant cost 3,600,000 marks.

5. Operating Results

Brown coal shipped by railroad from Kulkwitz is used. The coal as received contains from 50% to 55% water. This moisture is reduced to 15% in steam driers after which the coal is crushed to 2 to 10 m.m. in size before it is charged to the generators.

Plant operating results are as follows:

Oxygen used................	0.15	m^3 per m^3 gas made
Coal "	1.45	Kilos per m^3 gas made
Steam "	1.46	" " " " "
Electric power used	.27	Kwh. " " " "
Tar made	128	Grams " " " "
Light oil made	52	" " " " "

The cost to produce oxygen is from 2.0 to 2.4 pfg per m^3 which includes the fixed charges on the plant. The capacity of the oxygen plant is 4000 m^3 per hour. It requires a total of 6 men per shift 3 shifts per day to operate the oxygen plant.

All gas is produced at a pressure of 20 atmospheres. It is washed, cooled, purified, metered through orifice meters and delivered to the gas grid system at this pressure.

6. Miscellaneous

The gas is purified in high pressure steel purifiers 8 meters high and contains 6 cu. meters of Lux purifying material. Each box has 6 layers 1/2 meter deep of Lux and is divided flow and can be reversed in flow. Spent oxide is sold to a chemical plant for sulphur recovery used to manufacture sulphuric acid.

The tar and light oil produced is sold to the Bramag Company in Böhlen.

Because of the damage from extensive bombing and also because of coal shortage the plant was only producing 150,000 m^3 of gas per day. It was estimated that it will require from 3 to 4 months before full operation of the plant will be available.

TRANSMISSION OF GAS BY THE ENERGIE A.G. MARKLEEBERG

1. Introduction

The Energie A. G., with headquarters at Markleeberg, purchase all the gas produced by the Böhlen Gas Works Company at Böhlen and distributes the gas to numerous cities and municipalities around Zwickau, Chemnitz, to the south of Böhlen; Erfurt, Jena, to the west of Böhlen; Halle, Leipzig, Dessau, to the north of Böhlen. Director Bernhart of the Company was interviewed.

2. Description of Grid System

The gas grid system consists of approximately 1100 Km. of steel welded mains varying in size from 4" to 12". Of this amount of mains the company owns 200 Km. on which system they retail gas direct to customers. On the balance of the system they wholesale gas for other companies. There are two 12" mains between Böhlen and Leipzig.

The grid was started in 1928 by extending a main from Magdeburg to Wiederitsch, a distance of 100 Km. Gas is distributed at 20 atmospheres.

All mains are steel welded and wrapped with a tar felt covering to protect them against corrosion. Shut off valves are placed about every 3 Km. In built up areas leakage control tubes are installed at every welded joint.

The grid system is tied in with the Reichswercke Grid System at Magdeberg.

3. Purchase Price and Selling Prices

The purchase price of gas is 2.78 pfg. per m^3. It is resold under contract to the various cities and municipalities from 7.5 pfg per m^3 to as low as 3.5 pfg per m^3 depending upon the quantity sold, etc.

GENERATION OF GAS AND HYDROGENATION BY THE BRAMAG COMPANY BÖHLEN

1. Introduction

Interviewed Director N. von Felbert and plant engineers Frederick Mott and Richard Lachner of the company. Mr. L. Ruckes (Central Germany) representative of the Lurgi accompanied us on our visit to this plant.

2. Generating Facilities

Three Winkler Gas Generators having a diameter of 4.5 feet and 120 feet high are installed. Each generator can produce 25,000 m3 of 1200 Kg. Cals. per m3 of gas per hour.

The Linde-Frankel Oxygen Plant has a generating capacity of 15,000 m3 per hour of 98% oxygen gas and 2% nitrogen. The process is air liquifaction and the cost to produce 1 m3 of oxygen is 2.0 pfg. including fixed charges.

3. Operations

The Winkler Gas Generators are fed at the bottom with a screw conveyor with coke of an average size of 1.5 m.m. The coke is fed on the grates to depth of 2 meters. Oxygen and steam enter below the grate at a pressure of .3 atmospheres which keeps the coke in a turbulent state. Eighty percent of the oxygen required is fed below the grates and the balance of the oxygen (20%) enters 8 meters above the grate. The pressure above the grates averages .1 atmospheres. The ash accumulating below the grate is removed by a screw conveyor. Twenty percent of the ash produced goes through the grate and balance (80%) flows along with the gas stream. Seventy-five percent of the carbon in the coke is consumed in making gas.

The gas leaving the generators at 900°C analysis as follows:

CO_2	25.0%
CO	30.0%
N_2	43.0%
N_2 & CH_4	2.0%

From the generators the gas passes through a Weste Heat Boiler where its temperature is reduced to 150°C. The gas is then passed through a centrifugal water cooler and a brush washer, cooling the gas to 30°C before it enters a relief holder. An exhaustor passes the gas through Lux purifiers where the H_2S content is reduced from 10 grams per m3 to .028 grams per m3. From the purifiers the gas passes through a hot water washer and saturated. Steam is also injected (1 Kg. per m3) at this point and the temperature of the gas is raised to 100°C. The gas is next passed through two reactors which are filled with 1 c.m. long chromium $Fe(OH_3)$ catalysist. The following reaction takes place:

$$CO + H_2O = CO_2 + H_2$$

The temperature of the gas at the outlet of the first reactor is 450°C and by adding water in the second reactor the gas is cooled to 400°C. From here the gas goes to a washer cooler that cools the gas to 30°C before going to a small holder. The gas at this point analysis

CO_2	1.0
CO	.1
H_2	97.0
N_2&CH_4	1.9

The hydrogen so produced is used in a hydrogenation plant where tars, light oils and crude benzine (which are purchased) are treated to produce motor fuels.

It was stated that the cost of producing 1 m3 of compressed hydrogen is 8 pfg.

Because of heavy bombing the plant was not in operation.

LOW TEMPERATUE CARBONIZATION PLANT
A. S. W. SAXONIA WORKS
ESPENHEIM

1. Introduction

Mr. L. Ruckes, Lurgi representative and Dr. E. Thamaraus, chief chemist, went through the plant with me. The plant produces coke, which is sold to the adjacent large electric company and to the Böhlen Gas Works, motor fuels, crude benzine and carbon electrodies.

2. Carbonizing Plant

There are 30 Lurgi Low Temperature Carbonizing Ovens installed capable of carbonizing 9000 tons of brown coal briquettes per day and producing 1,800,000 m^3 of 1800 Kg. Cals. per m^3 of gas per day.

3. Brown Coal Briquettes

The plant has the largest briquetting plant in Germany. Thrity-seven presses compress dried brown coal into 9000 tons of briquettes, under 1200 atmospheres of pressure. The brown coal is received from a large adjoining stripper mine.

4. Products Produced

(a) Coke

Two-thirds of the coke produced, 6,000 tons per day, is used in an adjoining electric station for the generation of steam. The balance of the coke is sold to the Böhlen Gas Works.

(b) Gas

The gas produced, 1,800,000 m^3 per day, is used to heat the ovens 700,000 m^3 and 1,100,000 m^3 in the synthetic oil plant.

(c) Tar Oils and Crude Benzine

The plant produces 765 tons of tar oils per day are refined into Diesel oil, fuel oils, paraffins and pitch. The pitch having no ash is reduced to petroleum coke which in turn is made into electrodes. 135 tons of crude benzine is produced which is shipped to a central refining plant for motor fuel production.

(d) Sulphur

A Koppers Liquid Sulphur plant purifies the gas and recovers the sulphur in cake form from this plant.

5. Miscellaneous

The plant was shut down because of extensive damage from bombing. It is estimated that large quantities of new equipment and materials will be required and that it would take 2000 men four months to put this plant back into operation.

GENERATION OF GAS
ERFURT GAS WORKS
ERFURT

1. Introduction

Interviewed Director Conrad Weiss and then went to the gas plant for inspection. Plant Engineer Willy Schaefer showed us through the plant.

2. Gas Generating Equipment

The gas plant has 9 Vertical Chamber Ovens built by the Deutsche Oven A. G. of Leipzig. The ovens can produce 80,000 m^3 of 4300 Kg. Cals. per m^3 of gas per day and can carbonize 150 tons of coal per day. Ovens are steamed and have attached producers.

3. Operations

The company sells all the coke, tar, light oils and 15% concentrated ammonia liquor. Spent oxide is sold to a chemical company for sulphur recovery.

4. Gas Distribution

Gas is distributed to the city under low pressure. Gas pumped to 6 atmospheres is sent West to Vacha through a 150 mm steel welded main 50 km long and sent South to Saalfeld through a 150 mm steel welded main 150 km. long. The high pressure gas system it connected with the Central Germany Grid System by a steel welded main extending to Miltitz.

5. Miscellaneous

The plant was not in operation. It was badly damaged from bombing. All three holders were severely damaged. The plant has a crude benzole reconvery plant which is protected from fire with an automatic carbon dioxide system. Coal shipped from the Ruhr District is used in the plant.

GENERATION OF GAS
KASSEL GAS WORKS
KASSEL

1. Introduction

Interviewed Herr Richards who is in charge of the municipal operation of Electric Plant, Gas Works and Water System. Director Fritz Graubmann is in charge of all gas operations. He showed us through the plant.

2. Gas Generating Equipment

The plant was 4 batteries of Didier Vertical Chamber ovens. The total ovens installed are 75. Two batteries are fired with attached producers while the other two are fired by 4 Pintsch producers. Each producer can produce 50,000 m^3 of 1800 Kg.Cals. per m^3 per day. Ovens are steamed.

The total coal carbonized per day is 400 tons which produce 220,000 m^3 of 4300 Kg. Cals. per m^3 of gas per day. Coal used comes from the Ruhr district.

Two Pintsch Water Gas Sets can produce 20,000 m^3 and 24,000 m^3 of 2700 Kg. Cals. per m^3 per day of blue gas. These sets are hand operated and are equipped with mechanical generators and Waste Heat Boilers.

The plant has a Benzole recovery plant. The benzole recovered is refined for motor fuel. They can produce 3000 kilos of motor fuel per day. Plant was built in 1940.

3. Operations

Part of the coke produced is used in the Producer Plant and in the Water Gas Generators. The balance is sold.

The tar, light oil, motor fuel and spent oxide produced are sold. Ammonia is not recovered because of its low value. The weak ammonia liquor is sent to waste.

Lux purifying material is used for H_2S removal.

4. Gas Distribution

Gas is distributed to the city through an intermediate transmission system and district gas regulators. Gas is also delivered to Henzchel (5 km. away) at 2 atmosphere pressure where it is recompressed to 20 atmospheres and sent to the Reichswerke Gas Grid System.

5. Miscellaneous

The plant was not in operation because of coal shortage and damage from bombing. All three holders at the plant were damaged by flak from bombs and "straffing" from planes. They were being repaired at the time of our visit.

GENERATION OF GAS
BREMEN GAS WORKS
BREMEN

1. Introduction

Interviewed Director George Meyer and discussed plant operations. Plant Engineer Frederich Armbricht showed us through the plant.

2. Gas Generating Equipment

The plant has 2 batteries od Didier Inclined Ovens having a total of 12 ovens and carbonizing 360 tons of coal per day. The ovens can produce 130,000 m^3 of 4800 Kg. Cals. per m^3 of gas per day. One half English and one half Ruhr district coal is used.

Two Pintsch Water Gas Machines which are hand operated and equipped with mechanical grates can produce 30,000 m^3 of 2000 Kg. Cals. per m^3 of blue gas per day. These generators use coke produced in the plant.

3. Operations

Ammonia Liquor is worked up to 20% strength and sold. Very little profit is made therefrom.

Coke is mainly sold for domestic use. Tar and light oils recovered are sold was well as spent oxide.

4. Miscellaneous

Gas is pumped at 5 atmospheres to Bremen Haven and also to North Deutche Heutte where it is sold at wholesale.

Gas is delivered to the city through an intermediate transmission system and district regulators at .3 atmosphere.

All three holders were severely damaged by bombs. The plant itself was also badly damaged from bombing. Because of shortage of coal and damage to plant it was not in operation.

REPORT ON RUHRGAS, A.G.
21 MAY 1945

Organization

Ruhrgas, A.G. was organized under the laws of Germany in October 1926 by a group of important coal and steel companies in the Ruhr district to effect a more profitable utilization of coke oven gas. The stockholder companies were members of the Rheinisch-Westphalian Coal Syndicate and controlled about 90% of the coal mining capacity and coke oven production of the Ruhr district. About 50 companies participated thru stock ownership. Among these were:

United Steel Works Corporation
Harpen Mining Corporation
Rhine-Westfalia Electric Power Corporation
Rhine Steel Works Corporation
Recklingshausen Mining Corporation ‡
Hibernia Mining Corporation ‡
Fried. Krupp Corporation
Essen Coal Mining Corporation
Good Hope Steel Corporation of Oberhausen
Mannesmann Tube Corporation
Mathias Stinnes Mining Company
Köln-Neuessen Mining Association

‡ Controlled thru stock ownership by Prussian Government

There has been little change in the stock ownership so far as known since incorporation with the exception of the addition of Klöckner-Werke, A.G. and Bergbau, A.G., Lothringen. No Stockholder holds more than 24% of the stock.

The corporation was organized with capital stock of 5,950,000 dollars at the then current rate of exchange. A 6½ sinking fund bond issue in the amount of 12,000,000 dollars was made in October 1928 with maturity date 1 October 1953. The bonds are a direct obligation of the corporation and are secured by the title to pipe lines and other property of the corporation. In addition, the bonds were guaranteed by the stockholders. The shares of the stockholders aggregated 400,000,000 dollars market value at the then current rate of exchange, after adjustment for inter-company holdings. (One RM equals 23,8 cents).

The balance sheet as of 31 December 1943 (balance not yet arrived at for year ending 31 December 1944) shows the following approximate figures:

Capital Stock	RM 28	millions
Reserves	3,6	"
Original cost of plant	125	"
Depreciation	62	"
Quick assets (raw materials, stores, claims, securities)	36	"
Liabilities	37	"

An annual dividend of 5% after all costs and interest has been paid since 1935.

At the outset, the corporation acquired about 185 miles of pipe lines of various sizes from the Rhine-Westfalia Electric Power Corporation. These lines were laid about 1913. A large construction program was immediately started, most of which was completed by the end of 1929. The system now consists of about 900 miles of transmission pipe line of various sizes. Many of the lines are jointly owed with the Thyssen'sche Gas- und Wasserwerke G.m.b.H. The lines extend from Köln thru the Ruhr district to Hannover, and south along the Rhine to Koblenz. A line also extends thru southwest Westphalia to Frankfurt-am-Main. Essen is the heart of the system. Pipe as large as 800 mm. (31 inches) in diameter is used. More than half of the lines are 400 mm. or larger. Including lines jointly owned with Thyssen, but not including Vereinigten Elektrizitätswerke nor Westfälischen Ferngas lines, the system consists of the following quantities and sizes of pipe.

Diameter Millimeters		Length Meters
800		47 090
700		129 300
600		158 680
500		215 550
450		11 640
400		260 287
350		8 400
300		273 530
250		106 825
200		165 120
150		44 360
125		6 960
100		37 090
80		2 780
70		1 180
50		478
	Total	1 469 270

General Description of System

The main western line is located on the east bank of the Rhine. It runs generally from Gelsenkirchen, thru Oberhausen, Duisburg, Düsseldorf, to nearly opposite Koblenz. Most of the line is from 500 to 800 mm. in diameter with a large portion 800 mm. The southern portion is 400 and 300 mm. The line is fed by coke plants in the Essen-Gelsenkirchen area (Prosper, Emil, Nord-Wolfsbank, Consolidation). This line also receives additional supplies from plants near Hamborn and Oberhausen. Numerous smaller lines stem from or intersect this line.

A branch of this line crosses the Rhine north of Köln and extends southward toward Bonn or the West side of the river.

Another line runs from Hamm thru Bielefeld to Hannover. This line was built in 1930 and is about 180 kilometers long. It is mostly of 500 and 400 mm. pipe. It is fed by coke plants near Hamm and by two plants east of the Weser River. An older medium pressure line supplies Münster from Hamm.

A third line runs from Dortmund thru Plettenberg, Siegen, Wissen to Frankfurt-am-Main. This line is from 700 to 300 mm. in diameter with a large portion of 600 mm.

There are other subsidiary or branch lines but the above are the more important. All lines are inter-connected so that it is possible to meet peak requirements in one area by drawing on production in another area.

There are pipe line connections with Thyssen'sche Gas- und Wasserwerke, G.m.b.H. so that gas from the Thyssen coke plant at Hamborn, from the Vereinigte Stahlwerke and from the Aachen district can be utilized. A pipe line inter-connection exists with Saar-Ferngas, A.G. in the Main district. Another inter-connection exists in Hannover with the Ferngasgesellschaft of the Hermann Göring Werke which in turn owns a transmission pipe line from Hannover to Berlin. There are also plants or gas plants which do not normally deliver gas to the grid. Among these are those located at Düsseldorf, Frankfurt-am-Main, Mainz, Dortmund, Bielefeld and with the Gewerkschaft Westfalen in Ahlen.

Method of Operation

Ruhrgas owns no coke oven production of its own. Its business is transporting gas. It buys gas produced by stockholder's coke plants, transports it and sells it to large industrial consumers, distribution companies and municipalities. This constitutes about 50% of the business. The aim always has been to negotiate direct sales contracts with the large industrial consumers even though the consumer actually was located on the lines of a distribution company or even another transmission company. This has resulted in transmission arrangements with such concerns as Westfälische Ferngas, A.G. and Vereinigte Elektrizitätswerke Westfalen. Gas for domestic consumption has without exception been supplied thru distribution companies who purchase the gas wholesale.

In order to obtain a larger volume of coke oven gas, Ruhr-gas installed producer gas equipment at the Robert Hüser coke plant. The producer gas thus made is used to replace coke oven gas for heating the ovens. A similar arrangement was made with the Concordia coke plant but construction was never completed.

The remaining 50% of the business is transmission of gas which the company does not own. This is done chiefly for stockholder companies. As an example, the coke plant of the Vereinigte Stahlwerke delivers gas to Ruhrgas at Gelsenkirchen and the gas is transported thru Ruhrgas lines to plant of Vereinigte Stahlwerke near Siegen. Large users of this service are: Vereinigte Stahlwerke, Krupp, Mannesmann, Rheinstahl (for I.G.Farbenindustrie), Hoesch and Gutehoffnungshütte.

Sources of Supply

Four of the coke plants supplying the company are on the west side of the Rhine, two outside of the Ruhr district near the Hannover pipe line in Obenkirchen and Barsinghausen and the remainder in the Ruhr district. Altogether there are about 50 coke plants which supplied the company during the year ending 30 September 1944. In addition, coke oven gas was obtained from Saarferngas and from the municipal plant at Düsseldorf. Nature gas was obtained from one source. The Wolfsbank, Lothringen and Viktor 3/4 coke plants are connected to the system but did not supply any gas during that period. Details of the receipts of gas are shown in appendix B.

Volume of Gas

The volume of gas handled has shown a constant increase. In 1928, 137 million cubic meters were handled. Figures for the past several years are:

Year	Cubic meters
1938	2 700 000 000
1939	2 949 000 000
1940	2 844 000 000
1941	2 931 000 000
1942	3 127 000 000
1943	3 343 000 000
1944	3 100 000 000 (estimated by the company)

For the year ending 30 September 1944, 3,666,713,350 cubic meters of gas was handled. Of this, 1,767,383,256 cubic meters were gas which the company did not own but merely transported. The allocation of the gas handled is as follows:

Transported only	1,767,383,256	Cu.meters
Purchased and sold	1,814,320,136	" "
	3,581,703,392	
Lost	85,009,958	
Total gas handled	3,666,713,350	

An analysis of the gas transported and purchased and sold shows for the same period:

Transported for or sold to industries	3,085,850,050	cu.meters
Sold to distribution companies or municipalities	495,853,342	" "
	3,581,703,392	" "

An analysis of the industrial gas shows:

Class of Industry	Cubic Meters
Iron and steel	1 053 233 199
Steel fabrication	1 275 699 990
Chemical	501 924 799
Glass and ceramic	70 080 645
Metal manufacturing	146 641 553
Other	38 269 864
Total	3 085 850 050

During the year ending 30 September 1944, the peak day was 25 September 1944, with 11,782,000 cu.meters. The lowest delivery was 8,575,000 cubic meters on 19 November 1943 On 20 September 1944, which is a typical day shows that the peak hour was 1900 when deliveries were at the rate of 480,000 cubic meters. The lowest delivery was at the rate of 391,000 cubic meters at 0300. This is only a proportion of 1 to 1.22 between minimum and maximum loads, which is very low compared with most systems. The 24 hour delivery for the day was 9,751,000 cubic meters.

Operation

The pipe lines taken over from Rheinisch-Westfälisches Elektrizitätswerk, A.G., situated for the most part in the Wuppertal - Solingen district, were chiefly cast iron with lead joints. Lines laid by Ruhrgas are steel with welded joints. Pressures up to 14 atmospheres are carried.

Earlier lines followed the streets and highways. During the past five to ten years lines have been laid thru the fields.

In the mining district, expansion joints are located every 100 meters. Beyond the Ruhr district, expansion joints are placed 150 meters apart in built-up areas and much farther apart elsewhere. Valves are installed usually from three to five kilometers apart depending on circumstances. In built-up areas leakage control tubes are installed at every welded joint.

Guards (pipe line walkers) are stationed along the transmission lines at various points. The intervals vary from 5 to 25 kilometers, depending upon whether the area is built up or rural. Telephone communication is maintained between each guard post. The guards check the leakage control tubes and blow drip pots. Daily inspections are made in some districts and weekly in others.

In case of leakage or line-breaks, the guards inform the motorized repair crews. Repair crews are stationed at greater intervals and are normally equipped to handle all emergency line repairs as well as routine maintenance. There were 12 repair crews subordinated to five engineer districts distributed throughout the system.

Pipe lines are carried across the canals and smaller river on special pipe bridges or on existing bridges. The Rhine is crossed at two points, at both of which there are double lines laid in the river bed. The Ruhr, Wupper and Weser are also crossed by river bed crossings.

Compressors are located at the coke plants. These are usually sufficient to maintain line pressure. With but two exceptions the compressors are owned and operated by the cokeries. The compression equipment at the Robert Müser and the Rheinpreussen coke plants is owned by Ruhrgas. There are intermediate compressor stations owned by Ruhrgas as follows:

Location	Capacity (cubic meters per hour)
Huckingen	36,000
Niederschelden	48,000
Wessen	20,000
Niederursel	10,000

The Huckingen station supplies the territory on the west bank of the Rhine. The Niederschelden station supplies the Main district. The other two stations are located at sites of holder.

Piston type compressors are usually used. Most of the compressors are steam driven. Steam driven piston type

compressors have proved more practicable for handling large quantities of gas at several atmospheres pressure. Gas driven equipment was found suitable only where there was a constant supply of gas in sufficient volume. Some of the smaller plants use electric drive positive-displacement compressors.

Practically all of the coke plants now have equipment for removal of sulphur from the gas. All gas entering the lines is purified except that in the line from Concordia to Teerverwertung. An offiliated company, Arbeitsgemeinschaft zum Entzug con Schwefel (Corporation for extracting sulphur from gas purifying mass) has sulphur recovery plants at Horst and Horten. Plants making synthetic oil also have an interest in these plants. Neither Horst nor Horten are operating at the present time. About 75% of the coke plants have equipment for refrigerating gas and removing napthalene. After compression, the gas is passed thru bath of special oil, heated to 180 C and then refrigerated. None of this equipment is now operating because of a shortage of oil.

Gas is measured at the point of receipt and disposal. In certain instances the output of more than one coke plant is measured at a single measuring station.

Three different types of meters are used; wet meters, crifice meters and rotary positive-displacement meters. Practically all of the gas is measured by one of the latter two types because of the size limitation of wet meters.

Because of a number of factors, including which are large number of suppliers, wide extent of system itself, thereby enabling a certain amount of storage in the lines, fairly constant load and interconnections, much less gas holder capacity is necessary than usually required. Most of the gas holders are in the Ruhr district. They are generally located at coke plants and are usually owned or controlled by the producers. Ruhrgas owns holders at Homberg, Wissen and Niederursel. Most of the holders are of the dry-disk type.

Some of the holders are very large. The largest holder in the world is located at the Nordstern coke plant. It is a dry type holder 149 meters high and with a diameter of 80 meters. It has a capacity of 600,000 cubic meters.

Practically all of the holders have been destroyed or damaged. Appendix A gives data regarding location,capacity, condition and ownership of the holders.

The company has private telephone lines and a telemetric system. Cables for both are laid in the pipe line trench. Telemetric stations are located at the coke plants and at various points on the lines and the readings are automatically transmitted to the gas-central at Essen. Direct telephone communication is maintained to compressor stations, certain heavy consumption points and other key installations.

Quality of Gas

The composition of the coke oven gas is about as follows:

CO_2	2.0%
CnHm	2.0%
O_2	0.5%
CO	5.0%
H_2	55.0%
CH_2	25.0%
N_2	10.5%
	100.0%

The heating valve was 4600 calories per cubic meter but was reduced to 4500 calories. Of late it has been down to 4300 calories. It has been the effort of the company to execute as many contracts as possible on the basis of calorific content rather than volume using 4300 calories as the standard.

During normal times the company employed about 740 people in all categories. Of these, 260 were subject to military or similar service which left the company with 480. Of these 480, 62 were executives, engineers and other principal employees. The remaining 418 (480-62) comprised operating employees, clerical staff and laborers. These are made up as follows:

Employees

Operating employees	- male	230
" "	- female	17
Clerical staff	- male	88
" "	- female	83
		418

About 62% of operating employees and 75% of the clerical employees are present and available.

Damage

The grid system suffered bomb damage several times during the years 1940-1943 but repairs generally could be completed within a day or so. During the early part of 1944 bomb damage to the grid system, the cokeries and the systems of distribution companies increased. However, these difficulties generally could be overcome in a comparatively short time. In the latter part of 1944 bomb damage increased in intensity. The result was a sharp decrease in output as the following figures will show:

Month 1944	Delivery
September	300 million cubic meters
October	250 " " "
November	150 " " "
December	88 " " "

The figures for 1945 are even less.

Prior to the isolation of the Ruhr "pocket" by the U.S.Army the company knew of pipe line damage at about 300 points which had not been repaired. Between that time and the occupation, additional damage occurred. The company estimated that there are probably about 400 unrepaired breaks at the present time. Most heavily hit was the interior Ruhr district between Duisburg and Dortmund.

Many river crossings, especially those on bridges, and these comprise nearly all, are damaged. Certain of the river bed crossings will require extensive repair. For example, replacement of the Weser River crossing on the Hannover line will require some time after it is started. In the meantime, Hannover can only receive such gas as can be produced by coke plants east of the Weser.

J. L. TURNER,
Major CE.

Appendix A

GAS HOLDERS

(a) AT COKE OVEN PLANTS

PLACE:	COKE OVEN PLANT:	CONTENTS X 1000 CBM:	CONDITION:	OWNERSHIP:
1 Gelsenkirchen-Horst	Nordstern	600	destroyed or damaged	GBAG
2 Thyssengas, Hamborn	-	300	same	Thyssen'sche Gas- u. Wasserwerke
3 Dortmund	Hansa	175	same	60% GBAG 40% Ruhrgas
4 Dortmund	Min.Stein	175	same	60% GBAG 40% Ruhrgas
5 Bottrop	Prosper	160	same	Rhein. Stahlwerk
6 Homberg	RheinpreuBen	125	same	Rhurgas
7 Dortmund	Rob.Müser	125	same	Harpen
8 Dortmund	Gneisenau	125	same	Harpen
9 Essen-Karnap	Mathias Stinnes 1/2 und 3/4	120	same	Gewerkschaft Mathias Stinnes
		1905		

(b) IN THE GRID OF RUHRGAS

1 Wissen	-	175	repair probably possible	Ruhrgas
2 Niederursel	-		probably in working state	Ruhrgas

Now all gasometers are badly damaged; in how far repair will be possible cannot yet be said in the most cases.

But for the holder in Niederursel where gas is stored on pipes, the holders are dry.

Appendix B

GAS RECEIVED - CUBIC METERS
YEAR ENDING 30 SEPTEMBER 1944.

NAME OF COKE PLANT:	DELIVERY:
Alma	9 913 729
Bruchstrasse	1 832 264
Erin	146 366 017
Erin an Teerverwtg	37 378 264
Hansa	392 292 702
Minister Stein	222 796 232
Nordstern	206 361 025
Zollverein an Olsberg	6 696 778
Thyssen-Hamborn	23 000 000
Consolidation 1/6	13 576 197
Consolidation 3/4	192 104 203
Königin Elisabeth	55 161 474
Emscher-Lippe	190 708 935
E.-Lippe für Datteln	1 085 269
Hannover	15 475 089
Mont Cenis	95 750 922
Osterfeld	129 116 017
Osterfeld f. Osterfeld +. Sterkrade	3 505 521
Emil	128 165 959
Radbod f.Westf.Union	14 970 279
Radbod f.Hannoverltg.	42 994 468
Gneisenau	247 994 517
Robert Müser	9 825 466
Bergmannsglück	32 541 587
Waltrop	17 687 225
Auguste Victoria	57 190 725
Barsinghausen	23 340 797
Georgschacht	8 980 292
Chem. Werke Hüls (Erdgas)	5 702 584
Consordia	47 338 751
Ernestine	11 018 114
Ewald	164 667 023
König Ludwig	157 087 956
Friedr.Heinrich	66 604 957

NAME OF COKE PLANT:	DELIVERY:
Graf Bismarck	36 357 843
Heinrich Robert	65 542 582
Königsborn	96 755 021
Mansfeld	14 406 639
Minister Achenbach	92 277 252
Monopol	6 490 107
Prosper	221 529 185
Neumühl	23 441 306
Rheinpreussen	1 705 437
Reichsw. Hermann Göring	1 641 400
Sachsen	67 769 624
Mathias Stinnes	26 166 554
Saarferngas	10 439 892
Stadtwerke Düsseldorf	1 901 904
	3 666 713 350

GENERATION OF GAS
HAMBURG GAS WORKS
HAMBURG

1. Introduction

Intreviewed Director Selberg and Plant Engineer Friederich Stief. Both went through the plants with us.

2. Gas Generating Capacity

There are five gas generating plants in Hamburg as follows:

(a) Grasbrook Plant

Five batteries of Didier-Stettine Inclined Ovens having a total of 33 ovens which can carbonize 1200 tons of coal per day and produce 500,000 m^3 of 4800 Kg. Cals. per m^3 per day. These ovens are fired with attached producers and have Waste Heat Boilers.

The plant also has 4-Bamag Water Gas Machines capable of producing 50,000 m^3 of 2600 Kg. Cals. per m^3 of blue gas per day. Coke produced in the carbonizing plant is used in the water gas generators. The machines are hand operated, equipped with mechanical grate generators and Waste Heat Boilers.

(b) Barmbeck Plant

Two batteries of Otto Ovens having a total of 40 ovens which can carbonize 480 tons of coal per day and produce 150,000 m^3 of 4800 Kg. Cals. per m^3 per day. The ovens are heated by 4 Otto detached producers using pea coke and can produce 50,000 m^3 of 1200 Kg.Cals. per m^3.

The plant also has 2 Pintsch Water Gas Machines hand operated and equipped with mechanical grate generators and Waste Heat Boilers. Coke produced in the plant is used in the generators which can produce 5,000 m^3 of 2600 Kg. Cals. per m^3 of blue gas per day.

(c) Tiefstack Plant

Two batteries of Didier Inclined Ovens having a total of 14 ovens, which can carbonize 600 tons of coal per day and produce 200,000 m^3 of 4800 Kg. Cals. per m^3 of gas per day. Six Pintsch (detached) producers are used to heat the ovens. They use 20 tons of stein coal each per day and can produce 60,000 m^3 of 1200 Kg. Cals. per m^3 each per day. Batteries are equipped with Waste Heat Boilers. One-half English and one-half Ruhr coal is used in the ovens.

Two Pintsch Water Gas Machines hand-operated and equipped with Waste Heat Boilers and mechanical grate generators can produce 50,000 m^3 of 2700 Kg. Cals. per m^3 of gas each per day.

In 1932, one Pintsch-Hildebrand Gas Generator was installed. This is a complete gasification unit and uses brown coal briquettes. This unit can produce 100,000 m^3 of 3000 Kg. Cals. per m^3 of gas per day. The plant cost 50,000 marks. Its operation and results obtained are described in an article written in the January 6, 1940 and August 15, 1942 "Das Gas Und Wasser Fach", by engineer Fredrich Stief. The cost to produce gas on this unit is 2.0 to 2.5 pfg. per m^3. It requires 2 men per shift 3 shifts per day to operate this gas generator.

(d) Bahrenfeld Plant

Three batteries od Didier Inclined Chamber Ovens having a total of 18 ovens which can produce 100,000 m^3 of 4300 Kg. Cals. per m^3 per day. Ovens can carbonize 330 tons of coal per day. They are fired with attached producers. Ovens are steamed.

(e) Bergedorf Plant

One battery of Didier-Vertical Chamber Ovens having a total of 4 ovens can produce 25,000 m^3 of 4300 Kg.Cals. per m^3 per day. Ovens can carbonize 50 tons of coal per day. They are fired with attached producers. Ovens are steamed.

3. Operations

One half English and one half Ruhr coal is used in all carbonizing plants.

Purification of the gas is done with 75% Lux and 30% Iron Bog Ore. All spent oxide is sold for sulphur recovery.

All ammonical liquor is worked up to a strength of 15% to 20% and sold. Very little profit is made. Ammonia is not recovered at the Bahrenfeld and Bergedorf Plants.

All tar and light oils recovered are sold. There are Benzole Recovery Plants installed at Grasbrook and Barmbeck Plants. The crude Benzole is sold to a central refining plant.

4. Distribution of Gas

City has pressures are carried at 100 m.m. of water. Gas is also compressed by straight line compressors to 4 atmospheres for distant distribution and outlying holder stations. Rotary compressors deliver gas at .4 atmospheres to a belt-line for distributing gas through district regulators.

The company operates 11 outlying holder stations having a total storage capacity of 121,800 m^3. The 5 plants have a total holder capacity of 739,000 m^3.

5. Miscellaneous

All plants were shut down because of severe damage from bombing and not having coal for operations.

All plant holders were completely destroyed by bombing and will require extensive repairs or complete rebuilding. The total gas storage capacity amounting to 850,800 m^3 had 3 M.A.N. dry type holders having a total capacity of 300,000 m^3. All M.A.N. holders were destroyed.

The gas main distribution system had 1400 breaks, because of bombing.

The Pintsch-Hildebrand complete gasification generator is of interest. It was stated that further development of this generator could be made to reduce construction costs and possibly increase efficiencies.

copy 1

ITEM NO. 2 & 22

FILE NO. V 30 & XII-18

COPY NO. 128

Classification Cancelled,
by authority of
the Joint Chiefs of Staff,
by Col. R. H. [illegible]

~~SECRET~~

CHEMICAL INDUSTRIES IN BELGIUM AND FRANCE DURING GERMAN OCCUPATION

Phelps, H. J.

SECRET

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

SECRET

CHEMICAL INDUSTRIES IN BELGIUM AND FRANCE DURING GERMAN OCCUPATION

September 21st - October 4th, 1944

Reported By
Lt. Col. H.J. PHELPS, E.B. 6 (d)

CIOS Target Numbers 2/59(c), 22/30, 45, 76, 77
Miscellaneous Chemicals

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

55 p.

TABLE OF CONTENTS

Personnel of Team

Lt. Col. H.J. PHELPS, E.B. 6 (d)

I. Chemical Industries in Belgium and France during German Occupation.

A. Summary of targets visited in Belgium.

Arriving in Brussels on September 21st, I found that T. Forces had made arrangements for a party of specialists to visit the Philips Radio Factory at Eindhoven starting on the following day. As I was not specifically interested in any aspect of the work of the Philips factory I visited various industrial targets in Belgium on my own initiative, operating sometimes alone and sometimes in company with officers of the ALSOS Mission whose interests were similar to my own. The most interesting factories and personalities which I visited were the following :-

1. The German Chamber of Commerce, Brussels 230 Rue Royale.

It appeared that this target had previously been visited by a Major Andrews who had removed some reference books and forced the safe. A large bulk of papers remained in the offices of the organisation, including card indices of German firms and their agents in Belgium and of Belgium firms who were members of the German Chamber of Commerce and presumably working for, or in association with, the Germans. There were a number of copies of trade periodicals which appear to have been distributed in Belgium through the Chamber of Commerce. There was also a vast mass of correspondence, some relating to orders placed between Belgium and Germany and vice versa, and others relating to unpaid debts owed by the German firms to the Belgians. There was little of technical interest in these records, but I felt that the card indices and correspondence might be of considerable interest to the right persons. I therefore acquainted Mr. Joint, H.B.M. Commercial Counsellor at Brussels with the type of material available in the German Chamber of Commerce, and passed to him some samples of the trade publications available there.

2. Huilleries de Congo Belge, Lever House, Rue Royale, Brussels.

This firm, which is the Belgian branch of the Unilever combine proved a most valuable source of technical information regarding the production of synthetic detergents and synthetic fatty acids in Germany its raw materials being supplied by I.G. Farben. The firm had made synthetic soap powders with Mersol since early 1942. The Mersol sald could be either solid or liquid, according to the method of preparation. In neutralising Mersol a small quantity of non-salt forming residue is obtained. The Germans were very interested in this residue and the whole of it had to be returned to Germany. Latterly the Germans preferred to send ready neutralised Mersol to Levers. It is thought this was done in order to make sure of getting the unneutralisable fraction to which so much importance was attached. Soap in Belgium was made mainly from recuperated fatty acids, but in July 1944 a first delivery of 200 tons of synthetic fatty acid was received from Germany. Levers gave me samples of acid Mersol, of Mersol salt, and of free and saponified synthetic fatty acids. These have been sent for analysis to the Unilever laboratories in the U.K. Supplies of Mersol came exclusively from the I.G. plant at Leuna, and supplies of fatty acids from the Deutsche Fettesaürewerke at Witten. A detailed report on the information obtained from Levers is attached.

3. **Acieries d'Angleur Athus, Tillieur, near Liege.**

This plant proved to be a liquid oxygen factory of very great size. The plant was new and of German origin. A modified form of the Claude process was employed. Five large compressors were installed with a total electricity load of 6,000 Kw. The estimated capacity of the installation 60/70 tons of liquid oxygen daily. The plant at first operated in December 1943 on a small scale and had come into full activity in May 1944; the plant last operated on 6th September, 1944. The Germans had done considerable damage to the plant before evacuating it. Several tank wagons for the transport of liquid oxygen had been left at the factory. These were of unusual and very interesting design. A detailed report on ly visit to this plant is attached, and it is understood that officers of the ALSOS Mission are preparing a very detailed survey of the technique employed in making liquid oxygen at this place.

4. **Englebert Fils, near Liege:**

This important tyre factory was visited in company with Commander Bullard, U.S.N., of the ALSOS Mission. The plant makes rubber articles of many kinds, including automobile and cycle tyres, belting, rubber hose and moulded goods for civilian and industrial needs, including rubber footwear. This company owns a subsidiary factory at Aachen which has remained under effective Belgian control throughout the war. Very detailed information was given regarding the activities of the plant throughout the period of German occupation, and regarding types of Buna received at different times and the percentage of Buna incorporated in various articiles, also month by month production figures for the whole range of the factories products and certain notes on the technique of manufactured articles containing a very high proportion of Buna. Samples of accelerators, plasticisers, etc. were obtained and have been sent for analysis. A detailed report on the information obtained on this target is attached.

5. **Soc. Belge de l'Azote, Liege.**

The plant belonging to this company at Ougree was not visited personally but was examined in detail by Commander Bullard, U.S.N; who has reported under the following reference:- (a) ComNavEu Orders 15th September., 1944. P16-3/00 File No. 207041, T-5285. I had a long interview with the commercial and technical directors of the company who gave valuable information regarding their experiences under German occupation and the activities of their Liege factory, and also of their factory at Marly. The Marly plant was essentially similar to the Ougree plant in the lay-out of its synthetic ammonia units, but he did not produce any organic chemicals, a moderate range of which were manufactured in Liege. The Ougree plant lies in the neighbourhood of the railway bridge over the Meuse and the Liege/Berlin route, and has suffered considerably from bomb damage (some twenty incidents from 1,000 lb bombs). It was thought that this plant would take about one month to repair. A detailed report on the information obtained from the directors of the Soc. Belge de l'Azote is attached.

6. **Soc. Carbochimique, Tertre.**

The normal business of this company is the manufacture of synthetic ammonia by the Casale process. In the latter part of 1943 the Germans urged the Carbochimique Company to convert a part of their compressor capacity to the production of liquid oxygen, saying that greatly increased quantities were needed for welding purposes. Equipment began to arrive in January 1944, but the Belgians, who were unwilling to undertake the production of liquid oxygen and suspicious that it was not intended for welding purposes as had been stated but for some form of new eapon, managed to temporise until March 1944, at which time the Germans demanded that the liquid oxygen plant should be put into use immediately and the manager of the Tertre factory resigned. The Germans immediately proceeded to erect three Linde type rectifying columns for the manufacture of liquid oxygen. This scale of output would have cut down the production of synthetic ammonia at Tertre almost to nothing, since the Germans were not prepared to provide any new compressors and adapted all the compressors formerly used in conjunction with the sythetic ammonia plant for the preparation of liquid oxygen. It was estimated that the output of the liquid oxygen installation when complete would have been about one ton per hour. The Germans had never been able to complete the liquid oxygen installation and no production had ever been obtained. A detailed account of my visit to this plant is attached.

7. **Poudreries Reunies Belge: Baelen:**

As I was informed that the target factory at Caulilles had been comparitively inactive during the war, while the factory at Baelen had been taken over by the Germans and operated by the Meissner concern, I thought it desirable to visit the latter establishment. The Germans had first proposed to manufacture large quantitites of T.N.T. at this plant but after six months of operation the plant had been almost destroyed by a serious accidental explosion. The washing and purifying section had then been rebuilt on a very large scale, and quantities of captured Allied ammunition was broken down at Baelen and the T.N.T. washed and repurified and despatched to Germany. The factory also had a nitroglycerine unit which had been adapted for the production of diglycoldinitrate, a small RDX plant and a small penthrite plant. For the latter explosive the Baelen factory prepared its own pentaerythritol. The Germans did not show much interest in the production of RDX or penthrite at this plant, but a fair amount of nitroglycol dynamite had been made for use in Belgian mines. I was unable to examine much of the plant at this factory, or at the adjacent and related explosives factory of Arendonck owing to the military situation existing at the time. A detailed report on the information obtained regarding this factory is attached.

8. **M. Dupont**, Director of the **Office des Produits Chimiques** in the Ministry of Economic Affairs.

This gentleman does not appear in the C.I.P.C. Target List, but I was recommended to consult him by the directors of several other companies which I had visited. He provided most useful information regarding the relationship between the German and Belgian chemical industry during the occupation and threw considerable light on the progressive developments of the German chemical industry during the war. A summary of the information obtained from M. Dupont is attached.

B. Summary of targets visited in France.

1. **Distillerie de Deux Sevres** (Usines de Melle), **20 Rue de la Baume, Paris.**

The directors of this firm gave me most useful information regarding the activities of their firm during the war, and German interest in French alcohol production. They also referred me to M. Dubois, director of the French Government Service des Alcools, who confirmed and amplified the information given by the directors of the Distillerie de Deux Sevres. It would appear that the Germans did not make much use of alcohol blended fuels for army purposes. Large quantities of potable alcohol were requisitioned for fortifying low grade wines which were sent to the German forces in Russia. The French used alcohol blends considerably in the early part of the occupation, but by the beginning of 1944 at least 90% of French commercial lorries were run on gasogenes, the remaining 10% using straight alcohol with an auxilliary petrol starting carburettor.

The Germans were interested above all in glycerine, and urged the Usines de Melle to extract all possible quantities of glycerine from their alcohol residues. The Germans were also very anxious to obtain supplies of furfurol and requisitioned two-thirds of Melle's production. Small quantities of butanol were also requisitioned. Despite their experience in this kind of work the Germans had put no pressure on the Usines de Deux Sevres to produce moulds of the penicillin variety. A detailed report on the information of this company is attached.

2. **Poudrerie Nationale et Sevran Livry**

Owing to limitations of time my visit to this factory consisted only of a discussion with M. Medard, the engineur enchef. The Germans appear to have taken little interest in the development work proceeding at Sevran Livry on the production of propellant powders. A considerable manufacture of ignitory detonators of the sulphuric acid/lactose/chlorate type had been established, and a considerable amount of weapon filling, particularly incendiary devices and flares, had also taken place. Dr. Hans Buck had been put in by the Germans as director of that section of Sevran Livry which was kept in operation. It is suggested that further visits to this plant and examination of the German installations there, and of their proofing laboratory, would be valuable.

H.J. PHELPS. Lt. Col.

E.B.6(d) 6.10.44.

C. Report of Information received from targets in Belgium.

2. Huilleries de Congo Belge, Lever House, Rue Royale, Brussels.

This target was visited on 26th September 1944. The visit was made since I had learnt that Levers had done a great deal of work in manufacturing soap powders from synthetic detergents, and that they had also done some work with synthetic fats, the raw materials and the technical information required in the handling of these products being supplied by I.G.Farbenindustrie.

My chief informants relating to this target were M. de Petter (technical director), M. F. Vandenberg (commercial manager), and Mlle. Dascotte (Secretary).

Synthetic Detergents:

The chief synthetic detergent used in the manufacture of washing powders during the war was Mersol. Mersol is made exclusively in the I.G. factory at Leuna. The raw material is known as Mersol sulfa acid. It appears to be a by-product of some large scale process, since it was always in plentiful supply up to June 44 and the Germans were liberal with exports to occupied territories. The Belgians had been informed that Mersol sulfa acid was a by-product of the manufacture of "sulphur gas" which they had interpreted as mustard gas. This explanation does not seem to be very probable, but it does seem probable that Mersol is a by-product of some large scale manufacturing process carried on at Leuna.

In the preparation of detergents the Mersol sulfa acid must first be neutralised with caustic soda. The original sulfa acid is highly acidic and can only be transported in stainless steel or aluminium reservoirs. In the neutralisation of Mersol sulfa acid a 95% yield of Mersolate is obtained: there is a loss of 2% of the starting material and 3% of un-neutralisable residue is obtained.

This un-nuetralisable residue appears to be of great importance. The Germans were extremely insistent that even the smallest amount of residue was returned to them, and latterly the Germans declined to supply Mersol acid, sending instead ready prepared Marsolate. This may have been to some extent prompted by the inconvenience of moving Mersol acid in special containers, but had been interpreted by the Belgians as a further proof of the German anxiety to obtain the un-neutralisable residue. The residue is an inflammable liquid. A sample of this, together with samples of Mersol sulfa acid, and of Mersolate, were obtained. In the process of neutralising Mersol sulfa acid a smell of sulphur is alleged to be produced. It may be of interest that Mersol sulfa acid contains a high percentage of sodium chloride, since this suggests that the product is obtained by the "salting out" process.

Between June 1942 and June 1944 approximately 4,000 tons of Mersolate were sent from Germany to Belgium, and there were clearly considerable exports also to Holland, Scandinavia, and Central and Eastern Europe. I could discover no record of the quantity of un-neutralised Mersol sent to Belgium before June 1944. In June 1944 the Germans informed Levers that no further deliveries of Mersol or Mersolate would be possible.

The most common form in which Mersolate was delivered was as a strong viscous water solution containing 32-50% of sodium mersolate. Higher concentrations in solid flakey form were also delivered from time to time. Mersol sulfa acid was supplied in the form of a 70/75% water solution containing a considerable amount of sodium chloride.

Fatty Acids for Soaps:

The use of Mersolate was restricted to washing powders and detergents for industrial use. Mersolate was too apt to cause dermatitis to be used in toilet soaps. For this purpose Belgium relied entirely on recuperated fats for the first three years of the occupation. These recuperated fats were obtained as free fatty acids recovered in the purification of vegetable oils, and from commercial and domestic waste water, bone grease etc. In the latter part of the occupation period there was much talk of synthetic fatty acids, but the first delivery of 200 tons was in fact received in July 1944. This synthetic fatty acid was delivered from the Deutsche Fettesaurewerke at Witten, this plant being under the control of I.G. Farben.

The synthetic fatty acid was produced in three forms :-

1) Free fatty acid at approximately 100% purity. Three qualities of this were available, knows as pre-production quality, main production quality, and post production quality. The latter was very impure and probably corresponds to the "slops" referred to in 3) below.

2) Saponified acid (e.g. sodium salt) at approximately 73% acid content in the form of dry flakes.

3) So-called "slops" at 60% fatty acid content. This is believed to represent the residue from which pure fatty acids had been extracted.

Synthetic fatty acids were somewhat corrosive and were deliveried in aluminium or tin lined metal drums. The Germans had not solved the problem of rancidity, and the odour of the synthetic fatty acid supplied to Levers was very unpleasant and very persistent. Levers had heard reports of the production of purer forms of synthetic fatty acids and of the production of true synthetic fats by the esterification of synthetic acids with synthetic glycerine. They had not, however, received any samples of these substances, nor had they any knowledge of any other factory producing synthetic fatty acids except that at Witten.

Soft Soaps:

Soft soaps are in great demand in Belgium for household uses, and these were made during the war from a mixture containing 48% of sodium Mersolate with 10% of recuperated or synthetic fatty acid. This mixture was reasonably satisfactory in use.

Synthetic Resin:

The Germans (I.G.Farbenindustrie) provided Levers with certain quantities of a so-called synthetic resin which was mixed to the extent of 10% in hard soaps and in industrial soaps. Levers could not provide me with a sample of this synthetic resin and had little idea as to its nature and composition.

Glycerine:

The Germans were very anxious to obtain supplies of glycerine, and requisitioned most of Belgium's stocks at the time of the invasion. A so-called glycerin-ersatz was sent to Belgium, but this was essentially a sugar solution containing metallic salts (probably magnesium chloride and sugar solution). As mentioned above, synthetic glycerine was believed to exist but was never delivered to Belgium.

Tylose:

This was a hydrolised product made from wood cellulose. It was produced by I.G. Farbenindustrie but the factory concerned was not known. The commercial product was used as a suspension medium in soft soaps etc., and there was also an edible form of tylose which was used in ice cream manufacture and was alleged to have properties similar to those of sodium alginate (a product of seaweed). About 30/40 tons per month of industrial and edible tylose was exported from Germany to Belgium.

Seizure of Factories and Plant:

The margarine factory S.A. Lesieur at Dunkirk was dismantled early in 1944 and sent to Lublin. It was not known whether this had ever been erected on its new site. In Holland a number of dairy products plants had been dismantled and the separators etc. sent to Rumania in payment for supplies of oilseed which Holland had received from that country.

Use of Belgian Firms for Irregular Purposes:

The Huilleries de Congo Belge had been required by the Germans to purchase in the Black Market and deliver rubber and leather belting. This was alleged to be required for a new soap factory under construction at Krasnoder. Levers had also been compelled to purchase a great assortment of equipment including refrigerators, spades, saws and miscellaneous tools to the value of 6,000,000 Francs Belgian, which should have been delivered to Rumania in payment for supplies of Rumanian oilseeds. The transaction had never been completed.

Personalities:

The Controller of the soap section of the Reich-industrielle Fettesvorschung was Herr Reidtsorf; the Refererat für Seifen in Belgium was Herr Aelmann, assisted by Herr Pietsch. The latter was described as a Nazi of the worst type and was believed to have met his end at the hands of the F.I.

3. Acieries d'Angleur Athus, Tillieur, Near Liege:

This plant is not included in the original C.I.P.C. Target List, but it has so frequently been mentioned in intelligence reports as a large centre of liquid oxygen production, particularly associated with the use of new weapons, that I took steps to visit it on 24 & 25.9.44. It appeared that the steel plant of the Acieries d'Angleur Athus was requisitioned by the Germans in May 1942. A very large range of buildings had been cleared and the rolling mills which had been installed there had been sent to Germany or Poland. In their place a liquid oxygen plant of enormous size had been installed. This installation consisted of five large DEMAG compressors feeding five rectifying columns. The liquid oxygen production was effected by a two-stage expansion process which might be described as a modified form of Claude process.

It is estimated that the maximum capacity of the installation was of the order of 60 m.tons of liquid oxygen per day at a purity of better than 95%. It was said that the full electricity load of the compressors was about 6,000 Kw., and it was further reported that the Germans had chosen this site for their plant as a large size high tension electric cable passed through the factory area. It had been hoped to use entirely local supplies of electricity, but in fact these proved insufficient and current was taken from Germany through the LINALUX grid system.

Development of Production:

The plant first came into operation on a small scale on 23.11.43 under the direction of Herr Doktor Schally of Dusseldorf. There were many initial difficulties and continuous large scale production did not start until the middle of June 1944. The plant ceased operation on September 6th 1944. The total quantity of liquid oxygen produced at the plant was about 1,300 m.tons.

Present Condition of Plant:

The Germans had made considerable efforts to scorch the installations. The motors driving the compressors have all been damaged and attempts had been made to sabotage the connecting rods of the compressors with explosive charges. Some of the rods were badly bent. The floor of the building had been heaped with combustible material and a somewhat unsuccessful attempt had been made to destroy the whole by fire. The roofs of the factory buildings containing the liquid oxygen plant was almost wholly wrecked

by blast. It was agreed by officers of the AI and myself that the degree of damage to the plant as a whole might be estimated at 50%.

Transport of Liquid Oxygen:

On a railway siding serving the factory were several very large tank cars of a most unusual design. These were almost certainly identical with the strange tank wagons identified in several air photographs of Peenemunde and Oberaderach which had been thought to be used for the transport of liquid oxygen. These cars consisted of bogey well wagons with an overall length of 61 ft. carried on two four-wheeled bogies. The well section of the wagons carried a rectangular shed-like structure of 28'4" long and 10' wide. This contained a cylindrical tank approximately 8' in external diameter and approximately 26' long. It is estimated that the normal carrying capacity of the tank would be about 18 m.tons of liquid oxygen. Between the cylindrical tank and the shed-like structure on the wagon was a thick lining of very light insulating material which was almost certainly a solid foam made from urea-formaldehyde resin. The tanks were equipped with insulated filling and emptying pipes and with pressure release valves. The tank was designed to carry liquid oxygen under a pressure of 1½ atmospheres.

The wagons carried on their sides the following markings:-

DR Stuttgart (followed by a serial number)
Heimat Bahnhof---------------- Tubingen Hbf.
Ferntransport A.G. Berlin-Charlottenburg 2.
Werner Siemens Str. 19.

GEW d. WAG. mit Aufbau; leer 40400 kg
GEW d. WAG. mit Aufbau bel 71200 kg.
Bremsgen. 31 T.

The wagons were also labelled on the side of the shed-like structure Ladegut Saüre.

Movements of Wagons:

It was generally agreed that the wagons had left Liege in the direction of Aachen and the common belief held by the station staff at Liege was thatthey went to Stuttgart. I think myself that this was probably due to the fact that Stuttgart was painted plainly on the sides of the wagons, but I interpret the phrase Stuttgart Heimat Bahnhof as referring to the home station of the wagons to which they would return for repair and servicing, rather than their normal destination.

The technical details of this plant were examined exhaustively by Lt. R.C. Aldrich U.S.N.R. and Lt.Commander Bullard U.S.N. attached to the ALSOS Mission. These officers opened one of the fractionating columns and examined the sizes of pipes and valves etc. Their finding will be incorporated in a detailed ALSOS report which will be circulated in due course.

Possible Existence of Similar Plants:

It is reported that the German technicians who installed the plant at Tillieur ivariably referred to it as Job No.33, and that they had previously been associated with the construction of thrity-two other new liquid oxygen plants operating a similar process. There is no evidence as to the size of the other 32 plants, but it seems fairly clear that most of them at least are in Germany and not in occupied territory. The German engineers left Tillieur for Paris where they were intending to start work on installation No. 34. It should be noted that these serial numbers did not include ammonia plants in Belgium converted for the production of liquid oxygen (e.g. the plant at Tertre). These installations were handled by a different group of German interests and were not numbered in the same series.

Rumours Current as to the Reasons for German Interest in Liquid Oxygen:

It was believed by the Belgians that the Germans had two reasons for requiring large quantities of liquid oxygen: First for the production of hydrogen peroxide by direct synthesis. The Belgians were strengthened in this view by increasing German interest in Belgian hydrogen peroxide production, particularly demands received in August 1944 for high concentration Hydrogen peroxide. Secondly, it was commonly believed that a considerable part of the liquid oxygen was to be used for some form of long range weapon. The most concrete rumour of this kind was obtained from a Belgian who had a friend who was an Italian working in Belgium. This Italian had met a second Italian (a former friend of his) in Brussels in April 1944. This second Italian was working on the construction of V.I. installations and after a few drinks revealed to his friend that in addition to the V.l. weapon the Germans were working on launching sites for a new type of "bomb" carrying a one ton explosive head and propelled by a mixture of liquid oxygen and "fuel".

4. Englebert Fils, Liege:

This plant was visited in company with Lt.Commander Bullard U.S.N. of the ALSOS Mission. Discussions were held with M. Englebert, Snr, M. Englebert, Jnr., M. Melles, director of the company, and several plant chemists and engineers.

History of the Factory during the Occupation Period:

The Englebert factory normally produces a variety of rubber goods, including automobile tyres, cycle tyres, belting, hose, rubber soles and heels, and other moulded articles. Before the German occupation the factory consumed on an average about 600 tons of natural rubber per month. In June 1940 they were left with a stock of approximately 600 tons of crude rubber. The Germans did not requisition this stock and work continued on a much reduced scale until April 1941 when supplies of natural rubber became virtually exhausted. During this period, and indeed throughout the occupation, the Englebert factory was almost entirely successful in avoiding producing rubber articles directly for German use. The Germans made several attempts to place orders but the company always succeeded in maintaining that they were fully occupied on Belgian civil requirements, although in point of fact the actual production during the period of the occupation was only about one-fifth of the normal pre-war output. In spite of this the company were successful in avoiding any considerable conscription of their workders for labour inside Germany.

Deliveries of Buna:

As supplies of natural rubber became exhausted it became essential for the Englebert factory to obtain buna. In April 1941 the Germans agreed that supplies of buna, together with small supplies of natural rubber, would be made available without special conditions as to the destination of the manufactured rubber goods, provided that the Englebert Company was sponsored by, and came under the control of, a German concern. In consultation with their subsidiary company at Aachen (who appear to have been consistently pro-Belgian rather than pro-German throughout the occupation period) Engleberts got over this difficulty in a most ingenious way by making an approach to the Austrian Semperit rubber combine. This concern was anything but Nazi in its views, and even in the early part of 1941 was anxious to ensure against an ultimate German defeat by making a gentleman's agreement with Englebert whereby they would go through the form of taking control of the Englebert Company but would at the same time delay the consummation of the amalgamation indefinitely on the understanding that in the event of an Allied occupation of Austria Englebert would exert their best efforts on behalf of Semperit. This device effectively fooled the Germans, and in point of fact no legal amalgamation with Semperit ever occurred, and the Englebert Company maintained its independence and even control of its subsidiary factory in Aachen.

On the basis of the supposed amalgamation with Semperit, deliveries of raw material from Germany started in June 1941 with a shipment of 30 tons of buna S from Schkoppay. At this time an approximately equivalent quantity of natural rubber was also delivered and rubber articles containing 50% of buna were manufactured. The proportion of automobile tyres in the total manufacture was very low at this time and remained so throughout the occupation period. It is perhaps significant that Englebert continued to receive small deliveries of natural rubber until as late as March 1944. These deliveries were in continually decreasing amounts and were alleged to have come in part from rubber obtained from Indo-China before June 1941 (presumably via Russia) and of rubber obtained subsequently by Blockade Running, and in part from a stock of rubber collected in a fort, or forts, on the Maginot Line which represents the loot of the French rubber industry.

Buna deliveries were promised at the rate of 30 to 50 tons per month, but were irregular. For a period of three to four months after the bombing of the buna factory at Huls no deliveries were received.

As supplies of natural rubber progressively declined, larger and larger proportions of buna had to be used in all the production. In the latter part of the occupation the average incorporation of buna was 95-98%.

In February 1944 the German authorities told Engleberts that it had become very urgent for the German Army to receive additional supplies of automobile and truck tyres, and demanded an output of at least 80 tons per month. After a prolonged negotiation in which the Englebert directors used every obstructive device, a compromise was reached demanding an output of 40 tons of tyres per month for the occupation authorities. Even this programme was never in fact achieved, the maximum monthly output being about 30 tons in one month only. During the whole period of this greatly reduced production only 23 of somewhat over 2,000 employees of the factory were deported for labour in Germany.

Technical Information Regarding the use of Buna:

The following types of buna were known to the Englebert management:-

Buna S: was the staple product for general use.

Buna SS: was used particularly for moulded articles. It had good moulding properties and was believed to contain more styrene than Buna S.

Buna SR: was intended particularly for the making of inner tubes. It had beeter cold resistance than other types of buna. Engleberts had no idea as to its composition. They thought it had been developed by the Germans as a result of experience in Russia in the winter of 1941/42.

Buna N: (or perbunan). An oil resisting buna designed particularly for the manufacture of gas capes etc. Only 50 kgs of this material were received during the occupation period.

Buna SSe: This product was intended to replace natural rubber in solutions. It polymerises very rapidly. Only 5 kgs of Buna SSe were received during the occupation.

Buna 32: This was a viscous product used as a plasticiser. Its composition is not known.

Buna Latex: This was used for impregmating artificial silk used in the manufacture of tyres.

Buna S.iii This was a new product on which the Germans placed great hopes. It was alleged by the Germans that buna S.iii would beat natural rubber. It was to be used specifically for the manufacture of tyre carcases but not for treads. Engleberts had only a small quantity of this material and did not know its composition. They believed that it contained more styrene and more acrylo-nitrile than buna S or Buna SS. In practice it was not very satisfactory since it was too sticky for convenient working.

Engleberts found that one of the greatest difficulties in handling buna was that successive samples of the same type of buna were not regular in physical properties. The Germans themselves plainly realised this, since each batch (in the case of buna S a 22 lb. roll) had a label attached giving importent physical data (e.g. plasticity number, etc.).

Sources of Buna Supplies:

Buna supplies were always received labelled "Despatched from I.G.Frankfurt". In point of fact, however, Engleberts had been able to deduce the origin of most of the parcels they had received. Huls and Schkoppau were their chief suppliers, but some samples had been received from Ludwigshafen, the first in March 1943.

Technical Processes:

1. Buna S: Buna S was received in 220 lb. rolls which were shredded and depolymerised in an oven with hot air at a temperature of 130/150°c under a pressure of about 4 atmospheres for 40 to 50 minutes. The conditions for depolymerising varied slightly from batch to batch owing to the irregular physical properties of the buna deliveries received. There was neither gain nor loss of weight in the polymerising treatment from which buna passes directly to mixers for compounding. Three typical mixes were as follows :-

25/436

Buna S - Plast 2,5	100,000
Sulfur	2,500
Vulkacit D.M. (Altax)	0,300
Vulkacit Az	0,600
Zinc Oxyde	5,000
Phenylbetanaphtylamine	1,000
Maftolene Z.D.	3,000
Kautschol	3,000
Black C.K.3.	9,000
Black L.T.	6,000
Rosin	2,000
Koresine	2,000
	134,400

for coating of fabric (adhesive compound without natural rubber)

CEMENT FROM ABOVE:

	Mixing 25.436 A	13,000 kg.
(essential)	Koresine	1,680 kg.
	Benzol	78,800 kg.
		93,480 kg.

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25533 - The most practical formula for skim and squegees of the carcass of tyre.

	Buna S III Depolymerised by heat	46,000
	Buna S III Not depolymerised	54,000
	ZnO	50,500
	Naftolene	27,000
	Cumar resin	1,000
	Resin	5,000
	Mercapto	1,730
	Vulkacit Az	0,430
Active CB	Black C.K.3	11,500
Thermax or P3	Black P.1250	11,500
	Sulfur	2,160
	Phenylbetanaphtylamine	0,460
		211,280

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25.006 Tread Mixing

Buna S III - depolymerised	100,000
Black C.K.3	32,000
Sulfur	1,800
Zno	10,000
Phenylbetanaphtylamine	1,000
Vulkacit Az	0,600
Vulkacit D.M.	0,150
Naftolene	2,500
Bu 32	2,500
Kautschol	2,000
Aktiplast	0,750
Black P. 1250 Soft Black	8,000
Rosin	1,000
Lamp Black	1,000
	163,300

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2. Accelerators:

The same accelerators could be used as for natural rubber but the most successful was a product known as Vulcacit Az which was prepared by I.G. Farben. Vulkacit is a syrupy liquid with an amine-like smell. A sample was obtained and has been submitted for analysis.

3. Softeners and Plasticisers:

Two products known as Kautoschol and Naftolene (Z.D. or N.V. grades) were used to soften and plasticise buna. Naftolene Z.D. was the most satisfactory product. This was said to be obtained from Rumanian oil residues. A sample of Naftolene was obtained and has been submitted for analysis.

4. Koresine:

Koresine is a black resin prepared by I.G. Farben at

Ludwigshafen. A sample was taken to ascertain whether it was identical with samples of Koresine which we had previously received. This has been sent for analysis.

5. **Stearic Acid:**

No supplies of stearic acid could be obtained in Belgium or Germany and a substitute known as antiplast was employed. This was said to be the zinc salt of a high fatty acid. It was not known whether the fatty acid was zinc.

6. **Carbon Black:**

Considerable difficulties were experienced in obtaining suitable carbon black for compounding with buna. American blacks were too hard for this purpose but latterly the Germans supplied very satisfactory synthetic carbon blacks know as CK.3 and CK.4. These synthetic blacks were originally made exclusively by DEGUSSA at Dortmund, but recently a second plant had been erected in an unknown place. A considerable part of the carbon black admixture was replaced by aluminium oxide, known by the Germans as Tonerde-gel, which was obtained from an aluminium plant near Coblens. Engleber were much pleased with this product and intended to continue to use it after the war.

Fabric for Tyres:

Supplies of natural fibre quickly became exhausted and carcases were made with artificial silk fabric. This yarn is supplied by Glanzstoff G.m.b.H. Wuppertal-Elberfeld and was woven by Belgian firms in Ghent.

Make-up of Buna Tyres:

As the quantities of natural rubber became less pure buna was used for the treads and any natural rubber available reserved for the carcase. Eventually both the tread side walls and carcase were 100% buna, while the "breaker" was done away with and replaced by a compound "breaker" containing cork etc. This was not very successful and was ultimately replaced by a small cushion of natural rubber. This cushion represents less than 5% of the total rubber in the tyre. The making of buna tyres in this way was considered very uneconomical and consumed about three times as many man-hours per tyre as for a corresponding article made of natural rubber.

Durability of Buna Tyres:

Buna tyres were defintely not as good as natural rubber tyres, and commonly failed owing to separation between the

plies before the tread was worn out. In this respect the Englebert technicians did not think that the Germans were any more successful than they themselves had been. It was believed that this separation between the plies was due to inclusion of air forming during vulcanisation, since crude buna is impervious to air. Somewhat better results were obtained using a pit heater instead of a single mould vulcanisation process, thus giving more time for air to defuse out and avoiding the immediate formation of an impervious skin of crude buna. This mixture was harder to work than 100% depolymerised buna but gave more durable results.

The I.G. ran an experimental rubber plant at Leverkusen and produced tyres under the Vewell trade mark which was said to incorporate the latest German technical ideas. In practice these tyres were generally conceded to be the worst buna tyres on the market.

Bomb Damage:

It was said that during the attack on the Englebert factory at Aachen on 31.7.41 seven high explosive bombs fell in the factory grounds and three struck buildings. The greatest damage, however, was due to incendiary bombs which not only caused the loss of a considerable stock of buna, but had a more serious effect in that they caused heavy fire damage to electric cables, and the factory was stopped for a time owing to lack of electric power. In the attack of May 1944 there were about 400 bomb craters within 100 yards of the factory boundaries, but no damage whatsoever to the plant itself. Work was, however, suspended as electricity and water supplies were cutt off. It is interesting that the damage of the raid of 31.7.41 was rapidly repaired by the Germans and compensation paid readily.

It was the opinion of the experts at Engleberts that our bombing of Huls had been very effective and that production had been virtually stopped for three to four months. They did not, however, consider that our bombing of Hanover had had any very great effect and they said that the one Continental plant which was hit was of comparatively small importance.

Personalities:

The Referat für Chemie in Belgium was originally Dr. Krafft who was shortly succeeded by Major Stresseman of the Luftwaffe who had no technical knowledge but was pleasant enough to deal with. Major Stressman was assisted by Dr. Eischner, who was reasonable enough and not noticeably

Nazi, and Dr. Hasse, who was described as a strong Nazi of the worst type, and who had been shot by the F.I. The Reich Controller für Kautschuk in 1940 was Herr Jehle who became General Assistant Commissioner for Civil Affairs in France. Herr Jehle was described as 100% Nazi. He was succeeded as Controller for Kautschuk by Herr Friedrich, who was not a politician but one of the managers of the Phoenix Rubber Co. Herr Friedrich was highly spoken of and was not apparently hard in forcing regulations on the Belgian factories.

The German Rubber Controller in Belgium from June 1940 to May 1942 was Herr Heugebauer, who was jailed for accepting bribes in May 1942 and was succeeded by Herr Schramm, who was an exceedingly unpleasant Nazi and distinctly slow in the uptake.

The Rubber Controller for France was Herr Berge, of whom nothing was known.

Maintenance of Personnel:

As stated above Engleberts had been very successful in maintaining their labour force despite very greatly decreased production and of something over 2,000 employees only 23 were deported for labour in Germany. The payment of workers was a most difficult problem since wages were theoretically frozen at very little above prewar levels while prices rose sharply. Engleberts maintained their workers by giving them tyres and other rubber goods which the workers sold on the Black Market. My general impression was that a considerable part of the gap between the German allocations of buna and the production of rubber goods was represented by articles disposed of in this way, and by tyres manufactured clandestinately for the use of the F.I.

Documents:

The Englebert Company placed at my disposal the following documents, copies of which are attached:-

Table I:	Comparative figures of the total output of all types of rubber goods during corresponding monthly periods in the year 1937-1944 inclusive.
Table Ia:	Similar comparative tables of the actual weights of rubber mixtures consumed at different times.
Table II:	Comparative tables of the actual nett output of a wide range of specified products in the years 1937-1944 with the mean war-time production expressed as a percentage of mean pre-war production.
Table III:	Actual consumption of natural and synthetic rubber in comparable periods before and during the war.
Table IV:	Programme and percentage realisation of programme and the percentage of buna incorporated in the tyres made from January 1942 to July 1944.

5. Soc. Belge de l'Azote, Liege:

A chemical factory belonging to this firm is situated in the suburbs of Liege. I held discussions with the following persons: M. Leroux, General Manager; M. Victor Huban, Technical Manager; M.F.Braconier, Chief Chemist; M.G. Deschamps, Research Director; M.L. Manograef, Sales Manager, on September 25th at their temporary offices. The offices at the factory had been severely damaged on 25th August by air attack. The Ougree factory of the Soc. Belge de l'Azote is complementary to their factory at Marly, near Brussels. Both plants produce ammonia and nitric acid, but whereas the Marly plant produces only inorganic chemicals, the Ougree factory also manufactures a limited range of organic products.

Ammonia Production:

The lay-out of the ammonia and nitric acid units at the Ougree factory is identical with that of the Marly plant. Coke oven gas is obtained from the adjacent steel plant at Ougree-Marihaye, the production of hydrogen, nitrogen and gaseous oxygen being so adjusted that the entire output of these gases is consumed in the production of ammonia and nitric acid respectively. The gaseous oxygen production averaged about 1,100 m^3 per hour, which was wholly consumed in nitric acid production throughout the war. No pressure appears to have been placed on the company to produce liquid oxygen.

Compressed Cases for Automobile Fuels:

During the occupation the Ougree plant did a considerable amount of work in preparing compressed methane and ethylene gases for use in place of petrol. Coke oven gas received from Ougree-Marihaye, as indicated above, was first freed from carbon dioxide and then cooled to remove carbon monoxide methane and ethylene. Carbon monoxide was removed from the liquefied gases by liquefaction, and the methane-ethylene compounds compressed into cylinders for use. This gas mixture has a calorific value of 8,000 cal/m^3. The Germans had no interest in this production until the last days of the occupation, when they made unsuccessful attempts to obtain supplies which they intended to use, no doubt, for evacuating personnel and stores in Belgian vehicles which had been fitted with gas cylinders.

Methyl Alcohol:

This was prepared by removing the carbon dioxide from coke oven gas and separating carbon monoxide, methane and ethylene by liquefaction as in the preparation of automotive fuel gas. The liquefied fraction was then re-evaporated and cracked in presence of a suitable catalyst and water vapour to give carbon monoxide and hydrogen was then catalytically reduced to methyl alcohol. A mixture of carbon monoxide and hydrogen was then catalytically reduced to methyl alcohol. Production averaged about 20,000 litres per day. To cover fluctuation in the supply of coke oven gas a new water gas plant had been installed at the factory. Almost all the methyl alcohol produced was converted to formaldehyde. The Germans made not attempt to take supplies of methyl alcohol from this plant.

Ethyl Alcohol:

This was manufactured from ethylene extracted from coal gas by absorption in sulphuric acid, followed by hydrolysis. Almost the entire production of ethyl alcohol was used in the manufacture of acetone. Frequently quantities of alcohol were purchased from outside sources to supplement the quantity produced on the spot from ethylene.

Acetone:

Acetone was manufactured by a patented process developed by the Soc.Belge de l'Azote. This method consisted essentially in reacting alcohol and water over a suitable catalyst and producing acetone in a single stage. Production during the occupation was about 3 tons per day, which was disposed of to the adjacent acetylene works belonging to the Air Liquide, and an artificial silk plant at Tubise.

Formaldehyde:

As mentioned above, this was made in considerable quantities from methanol produced in the works. The average production during the occupation was about 20 tons of 40% formaldehyde solution daily. Almost the whole of this was used for the production of plastics (See next page).

Solvents:

A number of organic solvents were made, but all of them quite small in amount, the chief products being methyl ether, ethyl ether, methyl and ethyl acetates, isobutyl alcohol and formaldehyde-dimethyl acetal.

Glycol:

The Soc. Belge de L'Azote operated a glycol plant of moderate size before the war but dismantled this before the arrival of the Germans, and no glycol whatever had been made during the occupation. The directors of the company alleged that they took this step fearing that glycol would be used by the Germans as a raw material for mustard gas manufacture.

Synthetic Carburants and Lubricants:

Before the war the company had a small pilot plant at Ougree hydrogenating coal tar oils producing 85-90 octane petrol. In the course of 1939 a total of about 600 tons of such petrol was delivered to the Belgian army. The plant was completely dismantled in 1940 and no synthetic carburant has been made since that date.

A synthetic lubricant of good quality was also made before the war by hydrogenating coal tar oils catalytically at 700 atmospheres pressure. This oil was tested by the Belgian forces in 1939 and found satisfactory for aircraft engines. It was said that the method had been published prior to 1940. The pilot plant had a capacity of 1 kg. per day. The Germans apparently did not learn of this development since they made no enquiries whatever concerning it.

Lubricants for Factory Use.

Throughout the occupation period the plant have suffered severely from lubricants for their compressors and other plant. Under German orders they used a staple emulsion of recovered lubricating oil in water. The emulsifying agent was supplied by the Germans and the emulsions were prepared by the German experts who visited the factory. The Soc. Belge de l'Azote chemists were unable to discover the nature of the emulsifying agent which the Germans used, as none of this was ever supplied to the Belgians for their own use. I took samples of oil and water emulsion prepared by the Germans and they have been sent to the Government Laboratories for analysis. I also took a sample of lubricant grease of German origin.

Plastics:

The Ougree factory manufactured several types of plastics during the occupation period. The largest production was of phenol formaldehyde resin, of which about 40 tons per month were produced. It is interesting that supplies of phenol for this purpose were obtained from Germany. The resin and moulding powders produced at Ougree were delivered to Belgian firms under the direction of the Office des Produits Chimiques, but since the Germans provided part of the raw material it seems likely that the Belgian moulders concerned were working for the enemy. Urea formaldehyde resins were also made to the extent of about 10 tons per month, and there was a considerable demand for partially polymerised urea formaldehyde resins which were water soluble and which were believed to have been used for plywood bending. This factory also made small amounts of resin from formaldehyde and para-tertiary-butyl alcohol, which is soluble in China wood oil and gives a high grade varnish of particular value in electrical work. There was also an intermittent production of resin made from formaldehyde and melamine. In some months about 30 tons of this type of resin were made, and at other times there was no production. This resin was particularly useful as an enticorrosion coating. Calcium cyanamide for the manufacture of melamine was supplied by the Soc. Belge d'Electrochemic at Langerbrugge.

The factory had small pilot plants for the production of vinyl and polystyrene resins, but there had been no commercial production during the war.

Special German Interests:

Apart from the inference mentioned above that the Germans were interested in obtaining plastics and plywood glues, the Germans specifically asked the Soc.Belge de l'Azote to manufacture iso-butyl alcohol, which was said to be for shipment to Japan. Negotiations were prolonged and no deliveries were actually made. The company was also asked to make calcium arsenide, but convinced the Germans that it was not possible to do this without a lot of additional plant. The directors had learnt that the Germans finally obtained calcium arsenide from the Nottoden plant in Norway.

During 1943 the Germans became very interested in supplies of phosphorus and phosphate and the Belgian deposits in Hainsult and in the Liege area were re-opened with the intention of supplying the Germans with 15,000 tons of low grade (15% P_2O_5) mineral oer month. Actual deliveries never approached this figure. A considerable amount of this phosphate was, however, made into compound fertiliser in Belgium at the Tessenderloo factory.

From time to time the Germans asked for deliveries of chloropicrin and calcium acetate, but did not press their demands for these materials very strongly. The former was presumably for chemical warfare purposes, but the German need for calcium acetate is rather hard to understand and the Belgians thought that it indicated a shortage of acetone in Germany. There was a greatly increased demand both from German and Belgian sources for trioxymethylene, which was used extensively for preserving potatoes.

Personalities:

In the opinion of the directors of the Soc. Belge de l'Azote, Major Stresseman, the Referat für Chemie in Belgium was normally connected with the DEGUSSA concern (other Belgian industrialists had told me that Major Stresseman had little chemical knowledge).

Dr. Kindt, of I.G. Farben, visited Ougree on several occasions and was believed to be a German delegate in the Belgian Office des Produits Chimiques. The Germans were apparently interested in organising the Belgian plastics industry, since the Soc. Belge de l'Azote was visited several times by representatives of Venditor Kunststoff (Plastics Section of Dynamit A.G.) who at first urged them to enter into a commercial agreement with Venditor. In May 1944 the Venditor representatives began to threaten Soc. Belge de l'Azote that they would be forced to co-operate, but nothing in fact came of this. The representative of Dynamit A.G. in Belgium was a Dr. Wengler, resident in Brussels, who was believed to have adopted Luxembourg nationality towards the end of the occupation.

6. Soc. Carbochimique, Tertre:

The normal business of this company is the manufacture of synthetic ammonia for fertilisers by the Casale (high pressure) process. The plant is up to date and very well equipped. In the Autumn of 1943 the Germans approached the directors of the Carbochimique asking them to release a part of the compressor capacity of their synthetic ammonia installation in order that it might be adapted for the production of liquid oxygen. The Germans informed the Belgian directors at the same time that this liquid oxygen was not required for any war purpose, but that it was needed to meet a greatly increased demand for oxygen for welding in Belgium. The Germans originally stated that the necessary fractionating equipment for purifying liquid oxygen would be supplied by the Linde Eisenmachinenfabrik free of charge. The directors of Carbochimique were very suspicious of the German intentions and temporized as far as possible. In January 1944 various pieces of equipment for the production of liquid oxygen began to arrive from Germany. The Belgians, however, took no active steps to erect this plant and by mid-March 1944 nothing had in fact been done. At this stage a German deputation served the directors with an ultimatum that the liquid oxygen plant must be installed forthwith, and further ordered that all the compressor capacity serving the synthetic ammonia plant must be adapted for the production of liquid oxygen, which would have cut the production of synthetic ammonia at Tertre almost to nothing. The directors protested at this and, the Germans being in no mood for further argument, the management of Carbochimique were forced to resign.

In the latter part of March 1944 German technical experts and workmen took over the Carbochimique plant and proceeded to alter the existing installation and to install new apparatus which would have had the effect of adapting the entire compressor capacity of the plant to the production of liquid oxygen. Three fractionating columns of Linde manufacture were erected. It was estimated that the likely capacity of these when finished would have been about 1 ton of liquid oxygen per hour at a purity of 99/99.5%.

The device which the Germans had adapted for the conversion of this plant to the production of liquid oxygen without the installation of any new compressor capacity was ingenious. The process followed the same course as that normally used in the production of synthetic ammonia up to the stage at which pure nitrogen is obtained under high pressure. This highly compressed nitrogen was then expanded and liquefied and the liquid nitrogen used to pre-cool the oxygen rich gas mixture (which itself is obtained as a by-product in the production of pure nitrogen) so that a comparitively modest degree of expansion of the gas mixture gave a "liquid aid" very rich in oxygen. This was then purified in the fractionating columns. In order to do this a very considerable amount of very well insulated piping had been installed to convey liquid nitrogen about the factory.

The work of installation was by no means complete. All the piping necessary to take liquid nitrogen from the compressors to the fractionating columns appeared to have been installed, but the columns themselves had not been completely lagged with insulation and no reservoirs for liquid oxygen had been installed. It was not quite certain in fact that reservoirs for liquid oxygen were going to be used at this plant, since a heavily lagged pipe about 8' above ground level led from the house containing the fractionating columns into a yard adjacent to a railway track, and it may have been the intention to transfer the liquid oxygen produced directly from the fractionating columns to rail tank wagons (presumably similar to those seen at Tillieur) and use these tank wagons as reservoirs.

It was the intention of the directors of Carbochimique to dismantle the German installations as rapidly as possible in order that they might restart the manufacture of synthetic ammonia. Their installations appear to be intact and there seemed no reason why they should not recommence their normal activity as soon as coke oven gas was available. At the time of my visit no coke ovens were operating in the Mons-Charleroi area and all the mines were idle. The Carbochimiques plant had apparently been attacked by the Allied Air Forces, but only one bomb had done material damage, and this was to a newly constructed storage building which was empty at the time of the attack.

I learnt that similar installations, all of approximately the same size, had been erected by the Germans in the Usines Chimiques Belge plants at Willebrook and Zandewoords, and in the factory at Houdeng belonging to the Soc. des Engrais Azotiques. None of thes liquid oxygen installations had been operated, but it was said that the Willebroek liquid oxygen plant was nearly finished at the time of the liberation.

It is perhaps significant that these converted plants were not apparently given serial numbers by the German technicians, and cannot therefore be included among the thirty-two unidentified plants in the series in which the liquid oxygen plant at Tillieur was No.33.

My chief informant regarding the Soc. Carbochimique was Mr.Delhaye, who was most helpful and co-operative.

7. Poudrerie Reunies Belge, Baelen:

Information which I had received from Belgium suggested that the national powder works at Caulille had not done anything significant during the occupation, but that the explosives factory of the Poudrerie Reunies Belge at Baelen had been entirely taken over by the Germans and had been active. I accordingly visited this plant on 29.9.44. I was cordially received by M. Albert Diels, engineur en chef, who told me the history of the factory during the occupation period and gave me some information regarding the German explosives position.

The Germans first took an interest in the Baelen factory early in 1941 when they ordered the plant to declare what explosives they could make for the Wehrmacht. The factory at that time was equipped to make a variety of explosives, of which the chief were dynamite and safety explosives, penthrite, nitroglycerine, nitroglycol, T.N.T. and R.D.X. The factory also had a fair sized shell filling plant which had been operating for the Belgian Government.

The first action of the Germans was to dismantle the shell filling plant and remove it. It was despatched by rail to Antwerp but M. Diels did not know where the plant had been finally re-erected. In the Autumn of 1941 the Germans placed the factory under the control of the firm of Meissner of Cologne. After reviewing the situation the Germans determined to concentrate on the production of T.N.T. at Baelen and enlarged and improved the T.N.T. plant. They did not appear interested in the production of penthrite, although the Baelen factory was equipped to make its own erythritol from formaldehyde and acetaldehyde, nor did they operate the R.D.X. plant. The R.D.X. plant was comparitively small (300 kgs per day) but the reason given by the Germans for their disinclination to use this unit was that it was adapted to use the English process for making R.D.X. from hexamine and strong nitric acid, while the Germans at that time apparently preferred to make R.D.X. from hexamine, ammonium nitrate and acetic anhydride.

Messners sent three directors to control the plant, led by a Dr. Höck, who was an active member of the Nazi party, but completely ignorant of chemistry and explosives practice, assisted by Herr Stutz, who was a retired bank clerk, and by a Dr. Tweer, whose knowledge of chemistry was described as that of the average drug store manager. These persons operated the T.N.T. plant in a most inept manner for about six months, during which time much of their products was rejected owing to impurities. At the end of this time there was a most serious explosion and the entire T.N.T. unit was wrecked. M.Diels was quite sure that this explosion was wholly due to the incompetence of Messrs. Höck, Stutz and Tweer, and that no assistance had been required from saboteurs.

After the explosion Höck, Stutz and Tweer disappeared from the scene and the plant was inactive for some months. The Wehrmacht authorities then proceeded to remove the wreckage of the T.N.T. nitrating units and to erect a very large T.N.T. washing and purifying plant. When this was done great quantities of captured French and British shell were brought to Baelen and broken down. The explosive fillings, which were mainly of amatol type, were washed and the T.N.T. content extracted and repurified, cast into slabs, and despatched to Germany. The maximum output of recovered T.N.T. was not known, but it was possible to establish that in the early months of 1944 T.N.T. was being sent away at the rate of about 300 tons per month, and it seems probable that at an earlier date there was a considerably greater output. The whole of this work was carried out by German workers under German control and the Belgian staff had little opportunity of discovering what was happening.

From the beginning of 1942 the factory was allowed, and even encouraged, by the Germans to make dynamite, the majority of which was believed to have been used in Belgian mines. Both nitroglycerine and nitroglycol were made, and it was found possible to produce a most satisfactory dynamite with a mixture of 40% of diglycoldinitrate with 60% of nitroglycerine. Glycerine came mainly from a large stock which the factory had at the time of the German invasion, but small quantities could still be purchased in Belgium from time to time. At the time of my visit the stock of glycerine had fallen to 3.2 tons. Nitric acid was supplied by the Soc. Belge de l'Azote, and strong sulphuric acid was obtained from the adjacent zinc works at Vielle Montagne, who have a contact plant. In the latter part of the occupation a certain amount of mining or demolition explosive was made with T.N.T. and ammonium nitrate; the T.N.T. originating from the processing of captured Allied ammunition referred to above.

The installations at the factory were said to be virtually intact, but it was not possible to examine them in detail at the time of my visit. The factory had a most up-to-date plant for making exploder pellets and for filling gaines. This plant had been comparatively little used by the Germans since they had not manufactured any great quantity of penthrite during the occupation.

It was not possible to visit the adjacent explosives factory at Arendonck as it was a scene of battle at the time, but I was informed that after a considerable period of inactivity the Germans had allowed this factory to make a limited amount of dynamite and safety explosives for mines since the latter part of 1942. It was not thought that the output of the Arendonck factory had gone to the Germans to any extent.

8. Interview with M. Dupont, Director of the Office des Produits Chimiques and the Belgian Ministry of Economic Affairs.

This gentleman does not appear in the C.I.P.C. Target-List, but since I was advised by several informants that he was the best source of information regarding the relations between the Belgian and German chemical industry, I obtained an interview with him. M. Dupont had represented the Belgian chemical industry in a number of discussions with the Germans. I found him most co-operative and he answered all my questions in the frankest possible manner.

German Shortages:

M. Dupont thought that the most serious German shortages were the following:-

1. Concentrated Sulphuric Acid:

The Germans were not thought to be seriously short of weak sulphuric acid, but for some unexplained reason there appeared to be a serious shortage of oleum. So far as Belgium was concerned there was practically no production of concentrated sulphuric acid except for a small quantity which was made for the manufacture of explosives in Belgium. The total production of sulphuric acid in Belgium during the occupation averaged about 6,000 tons per month, of which about one-third was requisitioned by the Germans. In the last year and a half of the occupation the German sulphuric acid position apparently became considerably worse. At the end of 1942 the Germans were particularly anxious to obtain 66°B acid from Belgium and also attempted to get acid of this strength made in Holland. Only the Lutterade plant in Holland was capable of producing acid of this strength at this time, and the Germans utilised this capacity not only for obtaining fresh acid at 66°B but also sent dilute acid to Lutterade for concentration.

M. Dupont was inclined to attribute the German sulphuric acid shortage to the difficulties in obtaining supplies of good quality pyrites. German domestic pyrites averaged only about 35% sulphur content and was inconvenient in use as it was obtained in large hard lumps. Some German pyrites was shipped to Belgium and decreasing deliveries were obtained from Norway and Finland until the end of 1943, but no deliveries of Spanish pyrites were obtained after the end of 1941. M. Dupont thought that the low grade German pyrites was fairly readily obtainable in Germany until the beginning of 1944 when even this product became very scarce. It is of interest that M. Dupont expressed the opinion that during most of the occupation period Germany was not particularly short of elemental sulphur. Some deficiency in this commodity became apparent in the latter months of the occupation.

2. Phosphorus:

The Germans were extremely short of every kind of phosphorus product. After the Allied capture of Tunisia the Germans made attempts to obtain 10,000 tons out of Belgium's total stock of 15,000 tons of Tunisian phosphate. The Belgians were, however, successful in resisting this demand. So far as M. Dupont was aware the only plant in Germany making elemental phosphorus was at Piesteritz.

An interesting development in the phosphate fertiliser position was the re-opening of the Belgian phosphate deposits referred to in the report on Soc. Belge de l'Azote. This Belgian phosphate was blended with basic slag and hitrogenous fertiliser in the reconstructed parts of the chemical factory at Tesenderloo which had been almost wholly wrecked by an explosion on 29.4.42. This explosion in M. Dupont's opinion was certainly caused by an attempt to break up a large dump of ammonium nitrate which had set into a solid mass. The dump of ammonium nitrate had been collected by the Germans presumably for the manufacture of explosives. No activities except making of mixed fertiliser had been undertaken at Tesenderloo since the explosion.

One interesting piece of information provided by M. Dupont gives a partial explanation of the apparent discrepancy in the German-Europe basic slag balance sheet. In the last three years Germany had rationed all farmers in German-controlled Europe to 30% of their 1938 consumption of phosphate fertilisers. In Belgium at least the practice was that the farmers were issued with their ration on a basis of 30% of 1938 requirements and subsequently received clandestinely an equal quantity for which the manufacturers collected payment by indirect channels. The toal consumption of basic slag for fertiliser was, therefore, upwards of 60% of pre-war.

3. Selenium:

The Germans were extremely short of selenium and seized the entire Belgian stock of selenium and selenium compounds and removed it to Germany.

4. Glycol:

The Germans seem to have been to some extent deficient in clycol since they made several unsuccessful attempts to get the chemical made in Belgium. The Belgian firms had anticipated this by dismantling their glycol plants at the beginning of the occupation. German interest was doubtless prompted by the greatly increased requirements of glycol for the manufacture of explosives as a substitute for glycerine, which is of course in extremely short supply, throughout Europe.

5. Toluol:

The Germans were apparently rather seriously short of toluol throughout the occupation period. M. Dupont thought that the Germans had not operated any hydroforming plants until the end of 1943 or the beginning of 1944, after which time he thought one plant was in operation which he suspected to be in Austria.

6. Other Coal Tar By-products:

In 1941 the Germans were apparently seriously short of naphthalene, phenol, cresol and anthracene, and during this year they requisitioned as much as they possibly could of these substances in Belgium. In 1942 and 1943 the position was apparently a little easier, not only were the requisitionings greatly reduced but small quantities of phenol were actually sent to Belgium; but after the beginning of June 1944 the Germans said that they had no further interest in requisitioning coal tar by-products but at the same time would be unable to supply any to Belgium. M. Dupont attributed this to bomb damage both to German coaltar distilleries and to the German factories utilising coal tar by-products.

7. Formaldehyde and Hexamine:

M. Dupont alleged that the Germans were very short of both formaldehyde and hexamine, particularly in the latter stages of the occupation. His only explanation of this was that German production of methyl alcohol must have been insufficient for industrial requirements, but in view of our own knowledge of changes in German explosives practice it seems likely that the greatly increased production of R.D.X. was the chief cause for these shortages.

8. Urea:

In 1941 and 1942 the Germans appeared to have plenty of urea. In 1943 and 1944 a very serious shortage of urea developed in Germany. M. Dupont could offer no explanation for this shortage.

9. Copper Sulphate:

Germany was very short of copper sulphate and the use of this chemical for agricultural purposes was forbidden in Belgium, and M. Dupont believed that latterly it was also forbidden in Germany. He called attention to the curious fact that the Germans were apparently more short of capacity to make copper sulphate even than of copper, since a total of 2,500 tons of copper were delivered to Belgium from Germany, in the course of the occupation for the production of copper sulphate in Belgium for industrial purposes.

10. Cobalt:

Cobalt compounds of all kinds were seriously deficient in Germany.

11. Nitrogen Industry:

The Belgians had succeeded in convincing the Germans that the largest possible production of fixed nitrogen should be achieved in Belgium in order to increase Belgium's domestic food supplies to the greatest possible extent, and thus reduce the amount of food which Belgium would have to obtain from Germany. In accordance with this policy the production of synthetic ammonia compounds in Belgium rose from 60,000 tons (N) per annum in 1938 to 92,000 tons in 1942. This was distributed mainly in the form of ammonium nitrate instead of ammonium sulphate in order to conserve supplies of sulphuric acid. In 1943 production still increased slightly and the Germans insisted that all production in excess of 92,000 tons (N) per annum should be delivered to Germany, and both anhydrous ammonia and ammonia liquor were requisitioned in comparatively small amounts. In point of fact the total requisitions were not delivered to Germany since the Germans themselves diverted a part of it to Northern France where there was a shortage of nitrogenous fertiliser.

General Observations:

M. Dupont's general view was that German chemical industry as a whole carried on reasonably well except for certain specific shortages (e.g. strong sulphuric acid) until the later summer of 1943, when there was a rapid worsening of the supply position for a great many industrial chemicals. This relatively sudden collapse was to be attributed in his view to a shortage of coal rather than to any direct effect of bombing. The coal situation became if anything worse in 1944 and the whole level of production of German chemical industry appeared to decline seriously.

Bomb Damage:

M. Dupont's knowledge of the state of particular factories in Germany was, I think, obtained largely by hearsay but was reasonably up-to-date to the end of July 1944.

He stated that the I.G. plant at Leuna was very seriously damaged indeed and that it would take a very long time to repair. The Ludwigshafen/Oppau plant was also much more seriously damaged than we had imagined and was almost completely stopped in all departments during July 1944. The I.G. plant at Hoechst had suffered some damage which had not seriously affected any vital installations, while the plant at Leverkusen could be regarded as virtually undamaged.

Removal of Plants:

M. Dupont confirmed that the synthetic ammonia plant at Sluiskil had been dismantled by the Germans with the original intention of sending it to Italy. In point of fact, however, the various components of the plant had been dispersed to several factories in Germany to replace worn out or bomb damaged machinery.

D. Detailed reports of information received from targets in France.

1. Distillerie de Deux Sevres (Usines de Melle)

I arranged a meeting with M. Guinot and M. Baayl of the Usines de Melle in their Paris office at 20 Rue de la Baume. They gave me a lot of information regarding the activities of their firm during the war and regarding the alcohol position in France generally.

The chief activity of the Usines de Melle might be described as research and development in the field of fermentation chemistry. They have developed and hold patents on processes for making anhydrous ethyl alcohol, and for the preparation of a number of other products, such as butyl alcohol, acetone, butyl acetate, glycerine, etc. both by special methods of fermentation and synthetically. The company's factory at Melle is equipped for the production of most of the products on which they hold patents on a comparatively modest scale, the chief interest of the company being to sell licences to operate their processes and patented types of apparatus to other concerns. This applies especially to the Melle process for making anhydrous methyl alcohol, which is operated under licence by a great number of distilleries throughout Europe.

During the occupation period the chief interest of the Usines de Melle (like that of so many French and Belgian concerns) was to avoid the deportation of their workers to Germany. With this object they maintained an appearance of activity in most sections of their works, and were successful to the extent that out of 360 employees at Melle only 80 were conscripted for work in Germany, and of these only 20 were actually deported owing to an ingenious piece of deception at which the directors connived.

Production during the occupation period averaged about 60,000 hectolitres of ethyl alcohol per annum; about 100 tons of butyl alcohol per month; and about 1 ton of acetone daily. There was also a small production of furfural and butyl acetate. No glycerine was produced during the occupation period.

Anhydrous ethyl alcohol was made at Melle by the formentation of molasses and by dehydration according to the patented Melle process. Butyl alcohol was made synthetically from ethyl alcohol as also were acetone and butyl acetate. Furural is obtained as a by-product of a special fermentation process and Melle also have a process for obtaining glycerine by fermentation, although they had not worked this during the occupation.

The Germans had not shown any very great interest in anhydrous alcohol in France, and had not made any requisitions of anhydrous alcohol from Melle. The Germans definitely did not use alcohol blends for carburant purposes in any military or air force vehicles. The directors of Melle thought that the Germans had given some consideration to this possibility and had tried it on a small scale, but since certain types of army vehicles had to be supplied with unblended petrol the inconvenience and confusion resulting from having at least two different types of carburant at all depots was too great to justify the use of alcohol blends. It was the opinion of the Melle directors that the Germans were surprisingly backward in their knowledge of the technique of making alcohol blend carburants. In such German experiments as the directors were aware of there had been considerable difficulty in obtaining stable blends, and the Germans were apparently ignorant of the use of normal bulyl alcohol as a co-solvent to stabilise alcohol petrol blends. Shortly after the French Armistice the Germans requisitioned between 150 and 200 tons of butyl alcohol, presumably for this purpose, but these requisitions soon fell off and the total German requisitions from Melle was less than 300 tons.

The greatest German interest in Melle was the production of glycerine. The Germans repeatedly urged the Usines de Melle to attempt to extract glycerine from the residues resulting from alcoholic fermentation, and advised the directors that the cost of the process was unimportant however great it might be. The Melle directors, however, successfully maintained that it was almost impossible to extract glycerine in this way and the Germans happily appeared to be ignorant of the fact that Melle had in fact solved this problem before the outbreak of the war. The Germans were also anxious to get supplies of furfural, and requisitioned about two-thirds of the very small production of the Melle factory. The greatest interest of the Germans in the French alcohol industry as a whole was in the supplies of copper to be obtained by taking down the old type copper-still installations, and the great majority of these were in fact requisitioned and taken away.

In French practice alcohol blended fuels were much used in the early part of the occupation for commercial vehicles. The percentage of alcohol in the blend was rapidly increased to 50% and more, and some vehicles were equipped to run on 100% alcohol with auxilliary petrol carburettors for starting. Latterly most of the vehicles that remained on the road were converted to run on gasogenes and by the middle of 1944 at least 90% of French vehicles remaining in operation relied on this type of fuel. The Usines de Melle operated a fleet of lorries in France. It was stated that the Germans brought no pressure to bear on the Usines de Melle to carry out any special researches on fermentation, or on the growth of moulds and yeasts, nor did the Germans ever suggest that the Usines de Melle might make penicillin.

On the advice of the directors of the Usines de Melle I visited M. Dubois, director of the French Government Service des Alcohols, who confirmed and amplified the information given by the Melle directors. M. Dubois, while confirming that at most only very small quantities of alcohol were requisitioned by the Germans for carburant, said that there had been considerable requisitioning of potable alcohol of 90/95% strength which the Germans used for fortified vin ordinaire up to about 20% ethyl alcohol which was issued to troops fighting on the Russian front.

II. Supplement to Report on Visit to the Huilleries de Congo Belge, Lever House, Rue Royale, Brussels.

A. ANALYSIS

The following report has been received from Unilever Ltd., regarding samples of synthetic detergents and synthetic fats obtained from the Huilleries de Congo Belge on 26th September 1944. The nature and use of these samples is described in a report on visit to Belgium and France September 21st to October 4th 1944 - Lt.Col. H.J. Phelps - Dated 6 October 1944.

Seven samples of products of enemy origin have been received for analysis from Brussels. They were labelled as follows:-

(i) Tylose
(ii) Alginate de Soude
(iii) Insaponifiable
(iv) Mersol.
(v) Mersolat 50%
(vi) A.G.Synthetiques Saponifies
(vii) A.G.Synthetiques

The products were examined and the following results were obtained:-

Tylose and Alginate de Soude

The Tylose consisted of white, soft, fibrous tufts of material which were easily broken down by gentle rubbing between the fingers.

The Alginate de Soude consisted of a thick greenish paste which had an objectionable smell.

The following analytical figures were obtained :-

	Tylose %	Alginate de Soude %
Loss at 110°C.	35.19	87.27
Total solids	64.81	12.73
Ash	30.96	4.00
Organic matter (by difference)	33.85	8.73
Alkalinity of ash (expressed as Na_2O)	12.04	1.96
Alkalinity of ash (expressed as Na_2CO_3)	20.58	3.34
Sodium chloride	10.78	0.09
Water insoluble ash		0.37

The Tylose gave a viscous solution in cold and warm water. Solid constituents were not precipitated from solution either by the addition of acetone or alcohol (distinction from solutions of gums). No precipitate was formed by the addition of dilute mineral acid (distinction from alginate). A precipitate was formed by the addition of ferric chloride methylated cellulose (tylose) does not give this reaction. The solution gave Molische's test for carbohydrates, and after hydrolysis with 15% hydrochloric acid at 100°C. for five minutes reduced Fehling's solution. The specific rotation of the hydrolysate was $^{20}_{D}$ = 23°. The specific rotation of the hydrolysate from a known sample of tylose (methylated cellulose) was $^{20}_{D}$ = 56°.

A microscopical examination of the product showed that it consisted of flat wavy fibres among which were dispersed some crystalline particles.

The above analytical data do not agree with the chemical composition of tylose which is described as methylated cellulose prepared by methylating cellulose fibre, but indicate that this enemy product is similar in composition to Cellofas W.F.Z. which is prepared by treating cellulose fibre with monochlor acetic acid. One molecule of $Cl.CH_2.CCOH$ condenses with each $C_6H_{10}O_5$ radicle to give a compound which has the general formula ($R.O.CH_2.COOH$). Cellofas W.F.Z. is the sodium salt.

The enemy product labelled Tylose, therefore, is the sodium salt of a cellulose carboxylic acid which corresponds in composition to Cellofas W.F.Z.

The Alginate de Soude gave an aqueous solution which coagulated on the addition of alcohol, acetone, and mineral acid, and gave a precipitate with ferric chloride. A hotaqueous solution did not gelatinise on cooling. The specific rotation was $^{20}_{D}$ = -129°.

The above data indicate that the Alginate de Soude consists of about 13% sodium alginate and 87% water.

Insaponifiable, Mersol, and Mersolat. 50%.

The Insaponifiable consisted of a clear yellow liquid which had a smell suggestive of petroleum products.

The Mersol consisted of a yellow turbid liquid which had a smell similar to that of the Insaponifiable sample -- suggestive of petroleum products.

The Mersolat 50% was a clear brown viscous liquid which had a smell a little different from those if Insaponifiable and Mersol but still suggestive of petroleum products.

An analysis of these three products gave the following figures :-

Insaponifiable

Ash	nil
Acid value (mg.KOH per g.)	0.6
Hydroxyl value (mg.KOH per g.)	11.2
Iodine value (after ½ hour)	1.0
Iodine value (after 20 hours)	2.2
Organic chlorine	5.21
Organic sulphur	nil
Specific gravity 20/20°C.	0.803
Refractive index $^{40}_{D}$	1.429

Qualitative tests indicated the absence of benzene ring structure.

95% of the liquid had a boiling range at 18 mm. pressure of 130° to 200°C. Both the original undistilled liquid and the distillate gave a strong fluorescence when they were exposed to ultra-violet light.

The above data indicate that the Insaponifiable sample consists of hydrocarbons, probably of natural origin, alkyl chlorides, and a small quantity of alcohols.

Mersol and Mersolat 50%

	Mersol %	Mersolat 50% %
Moisture	nil	29.81
Ash	nil	20.18
Unsaponifiable plus unsaponified oil	17.22	9.35
Soapless detergent (anhydrous)	nil	56.01
Total sulphur	8.87	5.50
Total chlorine	15.29	3.01
Saponification value (mg.KOH per g.)	398.0	

Unsaponifiable plus unsaponified oil

Hydroxyl value (mg.KOH per g.)	14.5	27.9
Chlorine	6.14%	6.35%
Iodine value	2.3	2.7

The sulphur in the Mersol was found to be *present as a sulphonyl chloride which formed the hydrolysable constituent of the product. On hydrolysis with alcoholic alkali and inorganic chloride and the alkali salt of an unhydrolysable sulphonic acid was obtained. The Alkali salt of this sulphonic acid was shown to be a soapless detergent. The amount of potassium sulphonate produced on hydrolysis was equivalent to 82.71% of sulphonyl chloride in the sample. Of the 15.29% chlorine present in the Mersol 9.83% was shown to be combined as an acid chloride, 1.06% was combined with the unsaponifiable plus unsaponified oil as an alkyl chloride, and the balance of 4.4% was in combination in the organic chain of the sulphonyl chloride.

The soapless detergent in the Mersolat 50% was shown to be the sodium salt of an unhydrolysable sulphonic acid of the alkyl sulphonic acid type.

From the above data the following compositions were calculated for Mersol and Mersolat 50%.

	Mersol %	Mersolat 50% %
Moisture	nil	29.81
Unsaponifiable plus unsaponified oil	17.22	9.35
Soapless detergent (anhydrous)		56.01
Alkyl sulphonyl chloride ($R.SO_2.Cl$)	82.71	
Sodium chloride		3.99
Undetermined	0.07	0.84
	100.00	100.00

The compositions of the Mersol and Mersolat suggest that Mersolat is manufactured from Mersol. The compositions, likewise, of the Insaponifiable sample and of the unsaponifiable plus unsaponified oils obtained from Mersol and Mersolat suggest that the former is similar to the two latter oils and has been removed from the Mersol or the Mersolat during some stage of manufacture.

In Chem. Abs. 1943, 2, 6370 in an abstract from a paper by M. Bauer in the Seifensieder - Ztg. 68, 524-6 (1941) it is stated that: "Mersol is a sulfonyl chloride of an aliphatic hydrocarbon of the formula $R.SO_2.Cl$ which is made by the action of $SO_2.Cl_2$ or chlorosulphonic acid on paraffin "gatsch". It smells strongly of HCl and SO_2 and contains about 17 to 20% of unsaponifiable residues of hydrocarbons. Its saponification number is approximately 390. The saponification to "Mersolate" is carried out by pouring Mersol into alkali which is not warmer than 60°C. The concentration of the alkali plays an important role in the formation of the final product. If the Mersolate glue is thick then a large part of the salt is pecipitated. If it is then then the unsaponifiable can be removed as thin oil a few days later. In practical operations a thick liquid is prepared first and after removal of the salt it is then diluted. Contrary to soap glue the Mersolate glue always remains fluid".

Mersolat 50% is therefore a soapless detergent of the sodium alkyl sulphonate type containing 56% of active matter. Mersol is an alkyl sulphonyl chloride containing 83% of active matter from which Mersolat is manufactured by treatment with alkali. The Insaponifiable sample is the oil which is removed from the Mersolat during the final stage of preparing Mersolat from Mersol.

A.G.Synthetiques Saponifies and A.G.Synthetiques.

The A.G. Synthetiques Saponifies consisted of cream coloured, irregular shaped, lumps, each of which was approximately the size of a pea. The sample had an odour suggestive of synthetic fatty acids.

The A.G. Synthetiques consisted of a brown liquid which contained a cream coloured flocculent deposit. The sample had a strong smell of synthetic fatty acids.

The following analytical figures were obtained:-

	A.G. Synthetiques Saponifies %	A.G. Synthetiques %
Loss at 110°C	10.77	
Ash	-	nil
Unsaponifiable fatty matter	2.63	3.1
Fatty acids	73.90	96.9
Total fatty matter	76.53	100.0
Total alkali (expressed as Na_2O)	11.2	nil
Alkali as soap (expressed as Na_2O)	10.67	nil

The A.G. Synthetiques Saponifies was found to contain the sodium salts of unhydrolysable sulphonic acids. There was not sufficient material available for a detailed examination of these acids.

Constants of the fatty acids	A.G. Synthetiques Saponifies	A.G. Synthetiques
Melting point (capillary tube)	31.5°C.	20.9°C.
Ratio	6.93	6.92
Iodine value (after ½ hr.)	12.6	15.6
Iodine value (after 24 hrs)	20.9	24.4
*Specific gravity 100/15.5°C.	0.858	
Unsaponifiable matter	3.56	3.1

* The specific gravity of the A.G.Synthetiques could not be accurately obtained at 100/15.5°C.owing to the volatility of the fatty acids.

The smell, the rise in iodine values (after twenty-four hours), the ratios and the specific gravity of the fatty acids from the A.G.Synthetiques saponifies indicate that the fatty acids of both these products are of synthetic origin. There was insufficient material available from the A.G. Synthetiques Saponifies for the examination of the fatty acids by the distillation of the their methyl esters, but there was sufficient of the A.G. Synthetiques for this examination. The methyl esters of the A.G. Synthetiques fatty acids were therefore prepared and distilled. The boiling point was plotted against volume of distillate and the curve obtained examined and compared with curves previously obtained by the distillation of the methyl esters of synthetic fatty acids of German origin. The examination indicated that the A.G.Synthetiques fatty acids were synthetic and included acids containing odd and even numbers of carbon atoms from C_9 to C_{18}.

A full description of the examination of these fatty acids by the distillation of their methyl esters is given in the appendix to this report.

Unfortunately, there were not sufficient fatty acids from the A.G. Synthetiques Saponifies available for a similar investigation. Their smell and their constants which except for the melting point are similar to those of the A.G. Synthetiques fatty acids, indicate that they are synthetic but a different fraction from the A.G. Synthetique fatty acids.

From the above data the following composition was calculated for the A.G.Synthetiques Saponifies :-

	%
Moisture	10.77
Unsaponifiable fatty matter	2.63
Anhydrous soap	81.50
Free alkali (calculated as Na_2CO_3)	0.90
Undetermined	4.20
Total	100.00

The undetermined consisted chiefly of the sodium salts of unhydrolysable alkyl sulphonic acids.

The A.G.Synthetiques Saponifies, therefore, consists of 10.8% moisture, 81.5% anhydrous soap together with unsaponifiable fatty matter, free alkali, and sodium salts of alkyl sulphonic acids.

The A.G.Synthetiques consists of 97% synthetic fatty acids and 3% unsaponifiable fatty matter.

APPENDIX

Fractional Distillation of Methyl Esters of A.G.Synthetiques.

The esters were fractionally distilled in a still fitted with an electrically heated column. The boiling point was plotted against the volume of distillate, so that a curve could be obtained for comparison with a curve which has been obtained previously with methyl esters of synthetic fatty acids from Germany. Fractions were also collected and analysed by means of the saponification value. It was observed that all the fractions had an iodine value and for the purposes of calculations it was assumed that it was due to the unsaturated acid of the mean molecular weight of the fraction.

Only the portion of the previous curve covering the range of boiling point of the present esters has been included, as it would appear from the analysis recorded later that the lower and higher boiling fractions are absent from the present esters. Comparison of the corresponding points of the curves indicates that while over a great deal of the boiling range the characteristics steps observed with normal fatty acid esters are absent from our new curve, there are steps at two points. The first of these, which is very well marked, is apparently due to a high concentration of C_{11} esters and possibly to the greater efficiency of the column which is now being used. There is no very satisfactory explanation of the second, which is not so well marked, possibly it is due to some constant boiling mixture.

Apart however from the type of curve being far more akin to that of the synthetic rather than that of the natural fatty acid esters, there are two other features which point to the acids being synthetic. These are:-

1.) The fractions except at the first step in the curve are all mixtures; with normal fatty acids most fractions are very rich in a single acid and there is only a single mixed fraction between each member of the series.

2.) There are peaks in concentration of the acids in the fractions, but these correspond to C_9, C_{10}, C_{11} etc., not just to the even numbered carbon atoms.

The quantitative analysis of the fractions is set out below with previous results and this shows the very broad distribution of the acids observed previously with synthetic fatty acids. As mentioned previously the unsaturated acids

have been considered as of the same molecular weight as the fraction in which they were obtained, on this basis 8 - 13% of the fractions up to C_{14} is unsaturated acid and as much as 46% in the last fraction.

APPENDIX (continued)

Fatty Acid.	Present results	Previous result.	Jantzen et alt.	Reunkamp
C_6	Nil	0.1)	7.35	Nil
C_7	Nil	2.9)		Nil
C_8	Nil	4.5	4.25	0.4
C_9	5.0	7.2	5.70	2.1
C_{10}	10.7	10.2	7.40	5.0
C_{11}	17.2	12.2	6.20	7,3
C_{12}	11.7	10.1	7.65	13.9
C_{13}	10.5	7.2	8.30	16.3
C_{14}	11.6	4.9	8.75	15.2
C_{15}	8.9	5.0	9.00	12.4
C_{16}	9.3	5.1	6.70	8.1
C_{17}	8.8	5.8	6.25	7.3
C_{18}	3.5	4.0	4.25	above C_{17} 12.0
above C_{18}	Nil	17.6	18.20	-
Nom-sap	2.8	3.2	-	-

<u>Note:</u> Our previous results are recorded in Ra 1087 Jantzen's in "Fette and Seifen" 1938 pp. 383-393 and Reunkamp's in Zts. physiolog.Chem." 1939, 235.

It is clear that the present sample of synthetic fatty acids represents only the middle boiling range, the lower and higher boiling fractions have been removed, presumably by fractional distillation.

TABLE No.1.

COMPARATIVE FIGURES OF TOTAL OUTPUT BEFORE AND DURING THE WAR

1. Pre-war figures 1.1.37 to 10.5.40.
2. Occupation figures 1.8.40 to 1.7.44.

Pre-war						
Years	Period of	Output Kgs	Years	Period of	Output Kgs.	Average output during occupation as percentage of pre-war.
1937	12 months	15.862.172^{k},760	1940	5 months	1.179.636^{k},640	
1938	12 "	14.185.896,500	1941	12 "	2.355.467,490	
1939	12 "	12.173.410,650	1942	12 "	3.176.251.060	
1940	4 "	4.232.376.260	1943	12 "	2.908.477.480	
			1944	6 "	1.341.881.760	
Total for	40 months	46.453.856,170	Total for	47 months	10.961.714,430	
Yearly average		13.936.136,800	Yearly average		2.798.734,200	20,0825%

TABLE NO. 1 a

TOTAL WEIGHT OF RUBBER MIXTURES USED

1. Pre-war figures 1.1.37 to 10.5.40.
2. Occupation figures 1.8.40 to 1.7.44.

Pre-war			Occupation			Average output during occupation as percentage of pre-war.
Years	Period of	Consumption kgs.	Years	Period of	Consumption kgs.	
1937	12 months	13.429.961,960	1940	5 months	927.449,590	
1938	12 months	11.185.566,450	1941	12 months	1.726.224,990	
1939	12 months	9.402.079,550	1942	12 months	1.991.350.150	
1940	4 months	3.104.501,420	1943	12 months	1.931.209.480	
			1944	6 months	872.898,960	
Total for	40 months	37.122.108,380	Total for	47 months	7.449.133,170	
Yearly average		19.336.632,760	Yearly average		1.901.906,280	20.3704 %

TABLE NO. 2

PRODUCTION OF VARIOUS RUBBER ARTICLES

1. Pre-war figures 1.1.37 to 10.5.40
2. Occupation figures 1.8.40 to 1.7.44

Type of Production	Pre-war						Occupation								Average output during occupation as percentage of pre-war.
	1937	1938	1939	1940 4 months	Total for 40 months	Yearly Average	1940	1941	1942	1943	1944 6 months	Total for 47 months	Yearly Average	
Auto tyres	10.765.292	9.455.641	7.547.876	2.013.426	29.782.235	8.934.672	5 months 455.910	625.865	485.000	350.937	159.587	2.077.299	530.374	5.936 %
Auto Inner tubes	1.022.309	825.653	593.634	170.097	2.611.693	783.504	44.622	56.308	43.383	26.702	15.307	186.322	47.572	6.072 %
Bicycle tyres	2.008.967	1.371.655	1.402.444	262.950	5.046.016	1.513.800	169.260	327.648	371.500	98.615	35.069	1.002.092	255.853	16.901 %
Bicycle inner tubes	496.199	294.576	283.415	69.413	1.143.603	343.080	34.717	94.787	44.765	9.585	11.528	195.382	49.885	14.540 %
Accessories A.M.V.	237.438	214.44	192.962	28.990	673.834	202.152	12.193	98.453	119.080	102.426	75.207	407.359	104.019	51.456 %
Tubing	192.807	225.797	187.115	75.920	681.639	204.492	4 months 76.820	192.613	186.966	110.155	32.653	46 months 599.207	156.315	76.441 %
Mouldings	252.654	162.908	165.844	41.707	623.113	186.936	70.959	301.303	115.641	50.468	17.463	555.834	145.000	77.567 %
Belting	268.565	140.091	249.735	387.624	1.046.015	313.800	93.540	172.904	205.635	280.922	119.104	872.105	227.506	72.500 %
Rubber soles	182.473	159.827	173.443	21.160	536.903	161.076	39.546	218.260	466.692	809.198	242.217	1.775.913	463.282	287.617 %
TOTAL	15.426.706	12.850.592	10.796.468	3.071.287	42.145.051	12.643.512	997.567	2.088.141	2.038.662	1.839.008	708.135	7.671.513	1.979.806	15.659 %

TABLE NO. 3

CONSUMPTION OF NATIONAL AND SYNTHETIC RUBBER

1. Pre-war figures 1.1.37 to 10.5.40
2. Occupation figures 1.8.40 to 1.7.44

Pre-war			Occupation			
Years	Period of	Consumption kgs.	Years	Period of	Consumption kgs.	
1937	12 months	8.289.998	1940	5 months	379.319	
1938	12 months	6.834.785	1941	12 months	601.734	
1939	12 months	5.656.384	1942	12 months	701.426	
1940	4 months	1.786.633	1943	12 months	608.809	
			1944	6 months	301.879	
Total for	40 months	22.567.800	Total for	47 months	2.593.167	
Yearly average		6.770.340	Yearly average		662.085	9.779 %

TABLE 4

AUTO TYRE PRODUCTION

Year	Month	Programm	% Realisation	Weight Tyres	% Buna in tyres
1942	Jan.	59.825 kgs.	60	18.086 kgs	72
"	Feb.	65.275	72	24.122	79
"	March	69.075	85,5	31,866	72
"	April	69.677	91,9	33.670	75
"	May	71.485	80,6	28.136	76
"	June	74.950	75,5	24.856	74,5
"	July	72.900	103,4	32.252	74,9
"	Aug.	75.700	82,5	30.022	74,2
"	Sept.	76.500	85,8	28.521	72,7
"	Oct.	75.600	81	28.394	74,5
"	Nov.	82.700	80,2	26.654	74,7
"	Dec.	89.300	53,8	17.458	78,1
1943	Jan.	96.330	75,7	35.999	74,8
"	Feb.	54.400	92,4	19.541	87,6
"	March	54.250	92,7	20.167	88
"	April	54.760	94,7	18.131	94,5
"	May	51.950	100,3	20.212	92,2
"	June	60.000	94,3	25.590	93
"	July	44.280	100	22.884	95,2
"	Aug.	44.505	92	20.541	96
"	Sept.	44.855	96	22.439	96
"	Oct.	46.867	96,4	22.067	96,5
"	Nov.	46.030	101	22.786	98,1
"	Dec.	47.061	87,6	17.612	97,5
1944	Jan.	50.045	92,2	19.144	97,9
"	Feb.	56.609	80,7	18.936	97,7
"	March	60.615	92,6	25.441	97,8
"	April	68.374	86,7	30.457	97,5
"	May	68.068	59,3	20.578	96,6
"	June	57.100	55,2	15.096	96,6
"	July	76.980	57,4	26.081	98

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RESTRICTED

LUBRICANTS MANUFACTURED AND USED BY ZEISS IN JENA

Rennekamp, Theodore J.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

V

RESTRICTED

LUBRICANTS MANUFACTURED AND USEDBY ZEISS IN JENA, GERMANY

28 August 1945

Reported by

Mr. THEODORE J. RENNEKAMP, U.S. ORD.

CIOS Target No. 9/1

Physical and Optical Instruments and Devices

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

RESTRICTED

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5 p. diagr.

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Personnel of Team

Mr. THEODORE J. RENNEKAMP, U.S. ORD.

LUBRICANTS MANUFACTURED AND USED BY ZEISS IN JENA, GERMANY

The Carl Zeiss firm in Jena manufactures and uses three greases of various viscosity. The nomenclatures used are E 10, E 75 and E 400. E 10 is the least viscous and E 400 the most viscous type.

All three are used on both military and civilian manufactured goods, such as optical instruments, directors and predictors. In recent years the plant made few, if any, civilian goods.

The compositions of the greases is as follows:

1. E 10 - 12% by weight Aluminiumstearat (Aluminium stearinicum der Firma E. Merck, Darmstadt)
   88% by weight "Spindelöl grün", obtained by the Luftwaffe from the manufacturer (Leipzig C 1, Rhenania Ossag, Herr Held, technischer Leiter). In most cases an uncolored variety of the Spindelöl grün was used.
   Viscosity at 20° C is app. 4.8 Englergrade
   Viscosity at 50° C is app. 1.9 Englergrade

2. E 75 - 18.33% by weight Aluminiumstearat, same as in No. 1.
   81.67% by weight Spindelöl grün, same as in No. 1.

3. E 400- 24% by weight Aluminiumstearat, same as in No. 1.
   76% by weight Syntheseöl Type 3400 der Firma Rhurchemie A.-G. Oberhausen - Holten - Westfalen. (No official permit was required for this oil).

The following is the composition of a special grease used for the protection against corrosion:

KKSF - 40% by weight Schutzöl 39; in accordance with the tech. Lieferbedingung 6018 (Rhenania Ossag, Mineralölwerke Leipzig).
60% by weight Schutzfett 40, in accordence with the tech. Lieferbedingung 6017 (Rhenania Ossag).

Each of the three "E" greases is prepared as follows:

Mix the ingredients at room temperature until they are thoroughly mixed. Fill metal container 3/4 full with this mixture and put in oven at 200°C. Oven may be at this temperature and should be held within 5° C below or above 200 degrees. After two hours, add the fungicide .001 to .01% Raschit by weight (see report on Tropicalization at Zeiss Plant in Jena by T. J. Rennekamp, X-017829) and stir well to obtain homogeneous mixture. It is said one or two minutes of stirring will be sufficient. The solution should also be stirred well at this time if no fungicide is added. After this the mixture remains in the oven at the same temperature for 8 more hours, making the total time 10 hours. At the end of the 10 hours, it is left to cool slowly to room temperature.

To insure a homogeneous mixture after cooling, one half the contents of the vessel are transferred to another clean vessel when the heat is turned off. Extreme care must be taken not to disturb the sediment in this process. After 5 hours the grease has cooled sufficiently to be used.

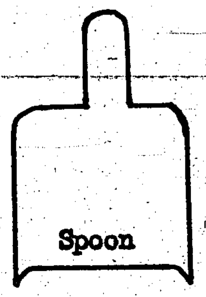

Fig. 1

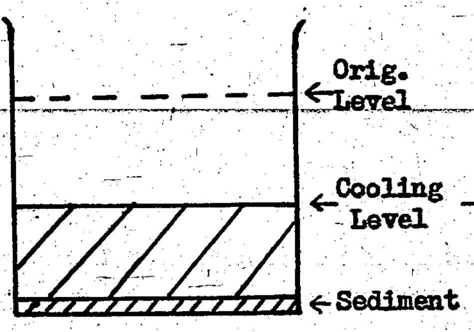

Fig. 2

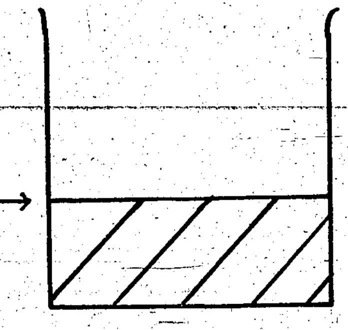

Fig. 3

If the foregoing procedure was carefully followed, all impurities remain in the original container and settle to the bottom during the preceding 8 hour heat treatment. A special spoon is used to remove the cooled grease from the original container. An illustration of such a spoon is given in Fig. 1. Fig. 2 shows the original container. It was said that the sediment is not over 1 mm thick and is usually analyzed. The impurities are caused by the Aluminiumstearat. It is of utmost importence to use a pure Aluminiumstearat which is neutral and dry. To insure dryness of this material, it is raised to a temperature of 80° C for 10 hours.

The vapor pressure of the spindle oil used in this process must be very low, not greater than .01 mm Hg. That is the distilling should be as sharp as possible. The chemical laboratory at Zeiss has no specifications on Spindle oil, but always tried to obtain the best quality.

In regard to the corrosion protecting grease KKSF, no details, that is specifications on the ingredients, had ever been known to Zeiss. It is known however where they were obtained and if possible more information will be gotten. The two ingredients are mixed either at room or a moderately raised temperature.

The three types of the Zeiss E greases are used for lubricating various mechanisms. E 10 is used on fine and more delicate parts where fits are close. E 75 is used on the somewhat larger parts and 400 in places where parts are fairly large and motions small. E 400 is also used to quite an extent for the sealing of optical instruments. More will be said about this in the following report on "Sealing Optical Instruments".

The technique of lubricating very small ball bearings with E 10 grease is as follows:

The grease is heated until it flows freely. The bearing is immersed and the excess allowed to drip off. When Zeiss people were asked if selsyn bearings were lubricated in this manner, it was stated they did not know since all selsyn assemblies arrive at this plant complete and ready to install.

As far as the usable temperature range of the three E greases is concerned, the Zeiss people claim satisfactory operation from -50°C to +70°C. At -50°C, the torque required to start any mechanism is quite high. During the first rotation however, it gets loose and again flows freely. The same was said about any mechanism which stood idle for long periods, as long as five years. Once it is started, the lubrication is perfect again.

The only difficulty which was pointed out was that these greases are not too well suited for high speeds. At high speeds they flow and leave the parts on which they were required. Dr. Smakula, who had done most here on the research of lubricants, stated he was working in that direction and expressed his hope to be permitted to continue it. This subject brought up the question of the drop point of the greases. They are as follows:

E 10 = 90° C, E 75 = 95° C, and E 400 = 105° C.

E 10 grease can be diluted with 10 parts of Benzin or Ether and is so used on fine mechanisms.

The information contained in this report was obtained by interrogating Dr. Smakula, Dr. Calsow and Herr Deutsch. All three were quite cooperative. The first two were being evacuated shortly after the interrogation and were in a slightly upset state of mind. Herr Deutsch was not on the list and will remain in the Jena plant. His services were extremely valuable after the others had left.

File XXVI-11
Item 22

Report No. 218

OFFICE OF THE PUBLICATION BOARD
DEPARTMENT OF COMMERCE
WASHINGTON, D. C.

I. G. FARBENINDUSTRIE A. G. HOCHST AM MAIN

Reported by

Major R. E. Richardson, CM, HQ.
J. G. Kern, CWS, HQ. ETOUSA
R. L. Murray, CWS, HQ, ETOUSA
R. W. Sudhoff, CWS, HQ, ETOUSA

[1945]

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

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

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R. W. Sudhoff	CWS, Hq ETOUSA

MISCELLANEOUS CHEMICALS

I.G. FARBENINDUSTRIE A.G.

HÖCHST am MAIN, GERMANY

1. INTRODUCTION.

The Hochst plant was visited on part or all of 7 days from May 7 to May 15 inclusive. Many different individuals were interrogated, the names of whom appear in the detailed reports which follow. The principal men interviewed were:

a. Dr. Lautenschlager, a Director of I.G. and general manager of all the I.G. plants in the Main area.

b. Dr. Lange, Manager of the Organic Division.

c. Dr. Winnaecker, Manager of the Inorganic Division.

d. Dr. Nusalein, Director of the application laboratories for colours and detergents.

All of the plant personnel who were interviewedwere very cooperative.

The plant suffered slight damage to a few buildings, but very little to the equipment. Operations were at a complete standstill due to lack of coal. The plant could be started up again very quickly if coal and transportation were available.

In normal times about 12,000 men were employed at Hochst. At the time of this investigation only a skeleton force was on the job.

At the request of the investigators, Dr. Lautenschlager presented the following list of products, dated 4 April 1945.

PRODUCTION OF I.G. HOCHST - 1944

Inorganic Chemicals

Nitric acid
Calcium nitrate
Sodium nitrate
Nitrous oxide
Amido sulfonic acid and salts
Sulfuric acid
Fuming Sulfuric acid

Chlorosulfonic acid
Sodium sulfite
Sodium sulfide (high grade)
Sodium pyrosulfite
Sodium disulfite liquor
Sodium bisulfate
Sodium hyposulfite

Sodium hydroxide solution
Solid sodium hydroxide
Flake sodium hydroxide
Sodium hypochlorite
Chlorine
Hydrochloric acid
Hydrogen
Acid resisting cements
Building insulation materials
Solvents for fire protection
Fluorescent pigments
Magnesium oxide

Organic Chemicals

Methyl chloride
Methylene chloride
Chloroform
Chloroacetic acid
Beta-naphthol
Resorcinol
Bromochloromethane
Organic tanning agents
Nitroaniline
Nitrobenzene
Dinitrobenzene
Aniline
Benzene sulfochloride
Dimethyl sulfate
Phenyl hydrazine
Pyrazolone
Amilide
Refrigerants
Beta naphthalene sulfochloride

Organic Chemicals Derived from Acetylene

Acetic acid
Other aliphatic carboxylic acids
Ethyl acetate
Methyl acetate
Butyl acetate
Acetic acid esters of various alcohols
Crotonaldehyde
Butanol
Methoxybutanol
Butyric aldehyde
Di-methyl ether
Sodium acetate
Ethyl ester of oxalic acid
Iso-propyl alcohol
Aceto-acetic ester

Artificial Products (Plastics)

Vinyl acetate and vinyl acetate polymerised to solid plastics and emulsions
Mixed polymerized products
Acetals (Mowital)
Chloroprene
Plasticizers for plastics and nitro-cellulose lacquers.
Hydrogenation of sugar to poly alcohols (glycerogen - glycerine substitute)
Methyl taurin
Sodium oxy-ethanesulfonate

Dye Group

Indanthrene Colors

Anthrimid dyes
Di-benzopyrenequinone dyes
Tetracarbonic acid dyes
Thio-indigo dyes

Helindone

Wool vat colors

Anthrasole

Sulfonic esters of vat leuco compounds

Triphenyl Methane Dyes

Sulfonic rosanilines
Bronze blues
Water blues
Ink blues
Acid wool dyes (patent blues)
Wool fast blues

Azo Colors

Pigment colors for lacquers, pigment printing and spinning colors
Vulcan colors
Food dyes
Acid dyes for textile purposes
Direct colors

Acid Wool and Chromium Dyes

Sirius light Dyes

Direct cotton dyes

Acid fuchsin
Basic colors (Methylene blue)
Fast new blue 3R
Safranin T
Nitro colors (amido yellow)

Initial Products for Photographic Dyestuffs and Sensitizers

Textile Auxiliaries and Raw Products for Washing Purposes

Products based upon fatty acids, i.e. Igepons, Alipons, Medialans, Seramins.
Fat free products, i.e. Igepals, Alipals, Emulphors, Servitals.

Auxiliaries for Treatment and Care of Leather

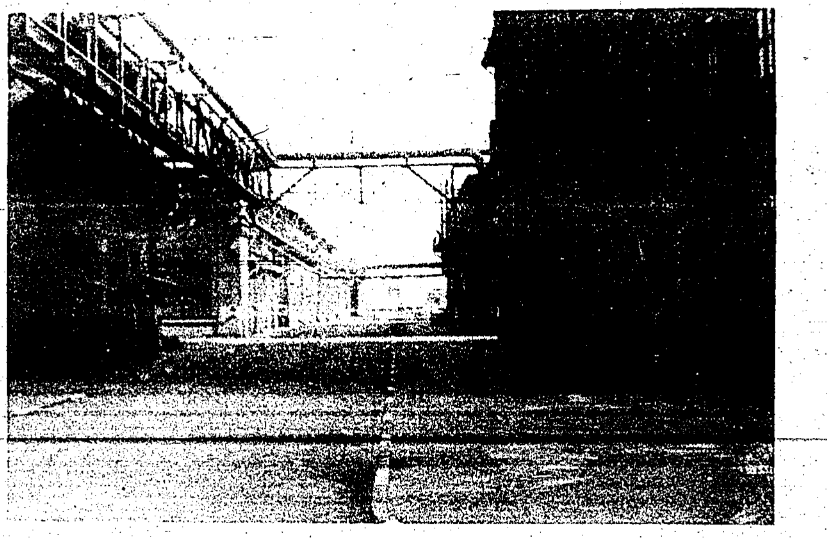
Leather oil, leather fat, leather liquor.

Products for Metal Treatment

Auxiliaries for metal drilling and emulsifier for cutting oils.

Many of these products and their processes of manufacture were discussed in detail and the plants visited.

A photograph down one of the many plant roads is shown below.



Höchst Plant Road

2. CHLORINE PLANT.

a. General.

This plant was inspected on 8 May. Dr. Winnacker, who was in charge of the Inorganic Chemicals Division, took the group through the plant. The entire chlorine plant was virtually undamaged by bombing but had been shut down since the occupation because of shortages of coal and power, although there was still sufficient salt and brine on hand for a week or so of operation.

The chlorine plant included 210 - 16,000 ampere I.G. mercury cells. The capacity was stated to be approximately 30,000 metric tons per year, equivalent to 82 tons per day. The highest daily production ever attained was about 93 tons per day. A 50% enlargement of the plant was about one-third completed when construction had to be discontinued because of shortages of materials. This enlargement included 42 - 28,000 ampere mercury cells, which are believed to be the largest capacity chlorine cells in the world. These were seen, in various stages of completion.

Dr. Winnacker stated that the first development work on the I.G. mercury cells was done at the Höchst plant. Included in the chlorine plant were several older types of I.G. mercury cells. An enlargement made in 1940 comprised their newest design and appeared to be a distinct improvement over the older types at least insofar as appearance and constructional details were concerned.

All of the chlorine was cooled, dried, and compressed, and part of it was liquefied. The compressed gaseous chlorine was used to make many products containing chlorine, including methylene chloride, chloroform, HCl, chlorsulfonic acid, bromochloromethane, chloroacetic acid and other chlorinated products.

Of these, methylene chloride used the most chlorine. Liquid chlorine was also used in the plant and some was shipped in containers and tank cars.

A very pure caustic soda solution was produced at 50% concentration by the cells and was also used in the plant or sold without further concentration or treatment.

Particular attention was given to the mercury cell installation including the treatment of the chlorinated depleted brine. Most of the remainder of the plant was inspected hastily as it appeared to be rather standard.

Some statistical information was obtained relative to I.G. chlorine production at its many plants, which is presented in paragraph 4.

b. Description of Chlorine Plant and Its Operation.

(1) Brine Department.

Mined and crushed rock salt was received from several sources by barge. It was unloaded at their Main river dock and transported by rail nearly half a mile through the plant to the chlorine department, where it was unloaded into huge concrete bins below ground level. The salt was dissolved ($NaCl$ concentration about 310 g/1) and pumped to four large outdoor storage tanks made of steel lined with sheets of Oppanol (poly-isobutylene), which was protected on the inside by a course of acid proof brick.

The raw brine was heated to about 70°C and then treated with sodium carbonate, caustic soda and barium chloride to precipitate the contained calcium and magnesium and to remove most of the sulfates. It was then filtered through filter presses and delivered to the cell feed storage tanks.

The anode brine flowed out of the cells along with the chlorine at about 250 g/1 $NaCl$ concentration. It was readily separated from the undissolved chlorine but underwent an elaborate treatment for removal of dissolved chlorine, in an extensive plant as follows: The hot chlorinated brine was first subjected to vacuum in large acid proof brick lined tanks, connected to special acid proof rotary vacuum pumps. Further chlorine was removed by air-blowing in a series of acid proof towers. Final traces of chlorine were then removed by chemical treatment (sodium sulfite) and the depleted brine was added to the raw brine prior to the chemical treatment describedabove. It was stated that almost no chlorine was lost in the treatment of the recycled brine. Purified brine at about 65°C and containing about 310 g/1 of NaCl was then fed to the mercury cells. The entire chlorinated brine treatment plant was in a large building and represented a substantial investment, although operating costs are probably fairly low. Salt consumption was stated to be 1.55 lbs NaCl per lb of NaOH.

(2) <u>Mercury Cell Installation.</u>

(a) The 240 mercury cells of several vintages were split up into two circuits, each rated at 16,000 amperes. From 200 to 205 cells were nomally in operation, the remainder being cut out for renewal.

The 1940 type mercury cell at Höchst (their latest except for their new 28,000 ampere cell) was about 32" wide by 28' long. It consisted of a built up steel member roughly in the form of a large I beam lying on its side. The top half of the flanges were lined on the inside with synthetic rubber. This rubber was poly-isobutylene having a Staudinger "K value" of 85. The catalyst used in making this rubber was sodium and the old Buna method was used. Styrene was avoided as it would be chlorinated. This rubber lining extended over the edges of the flanges and a short distance on to the web, which forms the bottom of the cell and was in direct contact with the mercury. The anode compartment was about 8 inches deep and was covered by steel cover sections which were lined with this same rubber. Great care was taken to have the cell bottom very true and with a definite but very slight slope toward the mercury discharge or "low" end of the cell. The cell body was designed for ready removal and repair of those rubber lined parts which are subjected to the greatest deterioration.

The cell contained 37 graphite anode blades each approximately 7" x 28" x 2½" thick. These were supported by 3" (approx) round graphite rods, extending through the cell covers, one rod to each blade. The 7" x 28" face of the blade was positioned a short distance from the top surface of the mercury, which flowed in a very thin sheet down the length of the cell body. The anodes could be adjusted vertically downward to compensate for graphite wear on the face exposed to the mercury. This adjustment was done every few months as necessary. The graphite blades had vertical holes drilled through them to facilitate removal of chlorine gas so as to lessen gas blanketing.

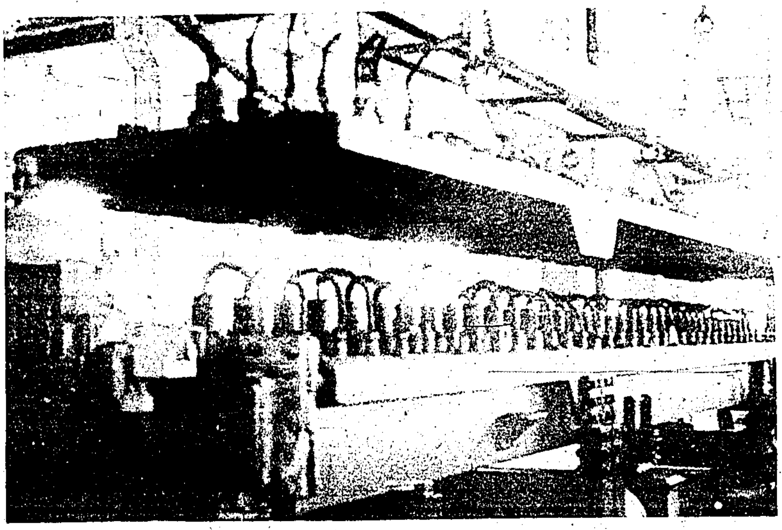
The decomposer or "peel", in which the sodium-mercury amalgam was decomposed into NaOH solution and hydrogen gas, was a rectangular steel tank approximately as long as the cell body and roughly 8" deep by 12" wide in cross section. This was located parallel with and adjacent to the cell itself but at a slightly lower level. It was fitted with graphite blades which were notched on the under side to expose a greater area to the amalgam and which were disposed horizontally over the decomposer a short distance from the bottom. These graphite blades were all tied together by steel bars. Their function was to facilitate the decomposition of the amalgam into NaOH and the release of the hydrogen gas.

The mercury flowed down the length of the cell body and then into the decomposer. It passed through the decomposer in the opposite direction from which it passed through the cell, and then flowed by gravity into the suction of a vertical-shaft direct connected centrifugal pump, which was located at the "high" end of the cell body. This pump picked up the mercury which had been reduced down to 0.01% Na in the decomposer and pumped it back into the "high" end of the cell. Each 16,000 ampere 1940 type cell was charged with about 700 kilos of mercury which was circulated through the cell body at such a rate that the sodium concentration at the "low" or discharge end of the cell was maintained at from 0.1 to 0.2% Na in the amalgam.

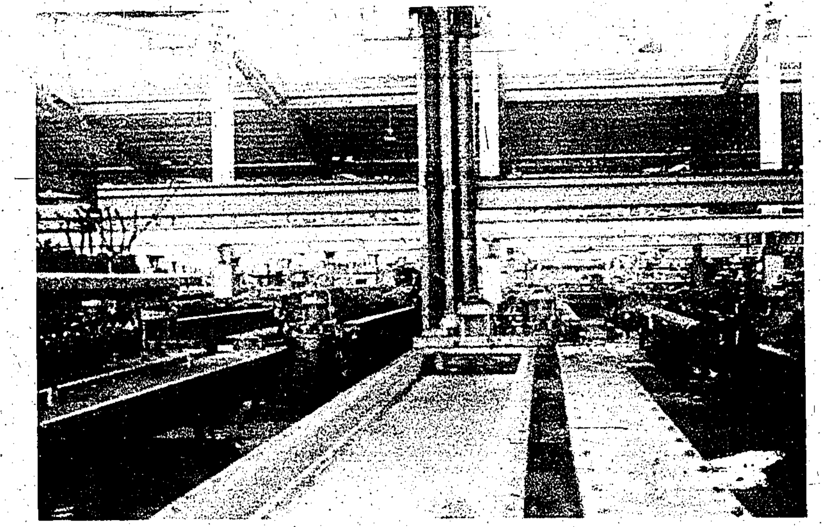
Saturated brine was also fed to the "high" end of the cell body at such a rate that its NaCl content was depleted from about 310 g/1 to about 250 g/1 by the time the brine reached the "low" end of the cell. Here the depleted brine overflowed through a rubber covered pipe which also conducted away the chlorine. After separation of the undissolved gaseous chlorine from the depleted chlorinated brine, it passed to the dechlorinating plant already described.

Permutit treated water was fed to the "low" or discharge end of the decomposer and passed counter-currently to the sodium mercury amalgam, decomposing it into NaOH solution and hydrogen. The NaOH solution, together with the hydrogen, flowed out of the "high" end of the decomposer through an overflow pipe. The water feed to the decomposer was so regulated that the effluent caustic solution contained 50% NaOH by weight. The mercury discharge from the decomposer contained only about .01% Na.

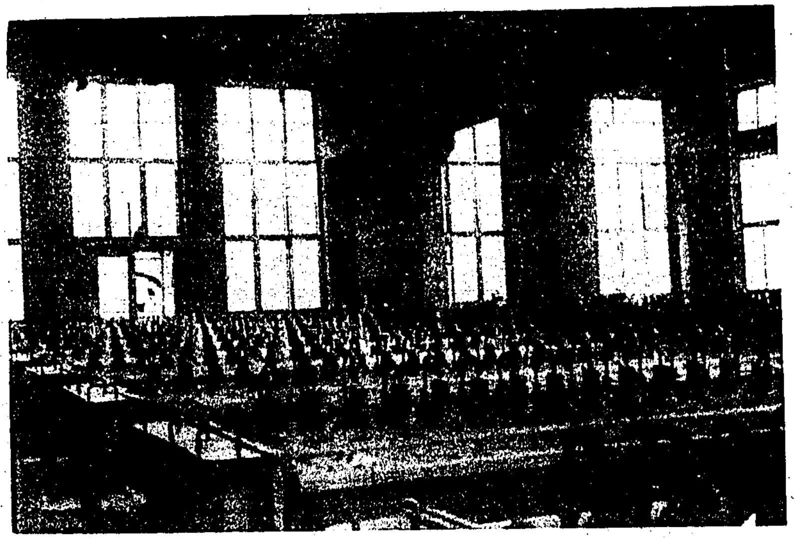
The following photos show the Höchst mercury cells.



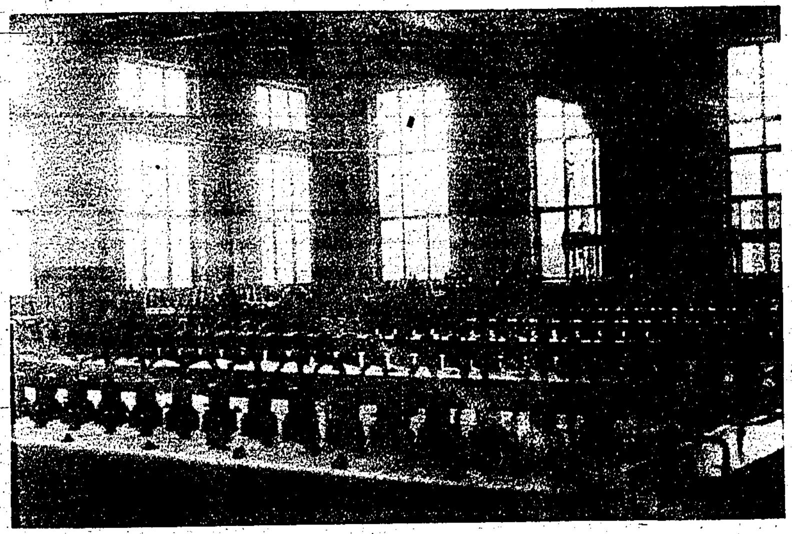
Höchst Mercury Cell. Assembled cell in background. Top section of another cell hanging from crane in foreground.



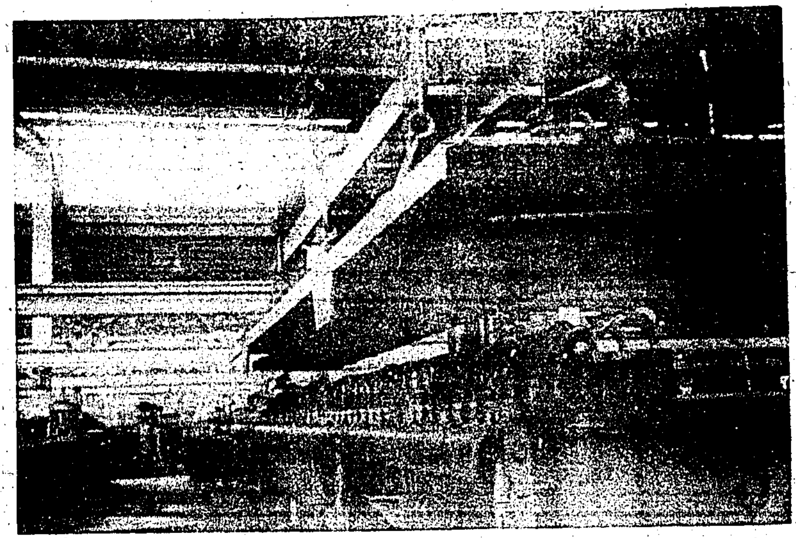
Höchst Mercury Cells showing electrolyzer with top removed in center and decomposer to right center.



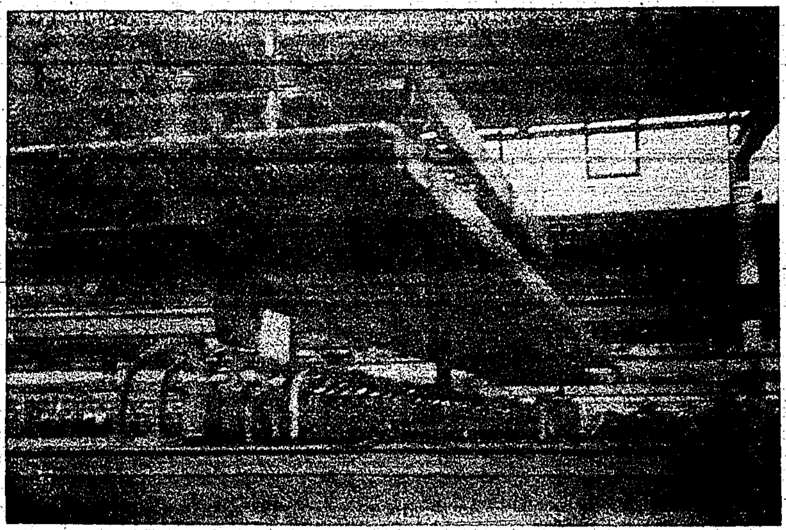
Höchst Mercury Cells. General view in Cell room.



Höchst Mercury Cells. General view in Cell room.



Höchst Mercury Cells. Underside of cell cover showing anodes.



Höchst Mercury Cells. Underside of cell cover showing anodes.

Höchst Mercury Cells.

(b) Cell Performanc

Dr. Winnacker
average voltage was 5.0 volts
about 95% and the graphite con
hangers) with Bitterfeld graph
ton of chlorine. With Acheson
Graphite anodes made by I.G. a
hours, whereas Acheson graphit
110,000 ampere hours.

Dr. Winnacker
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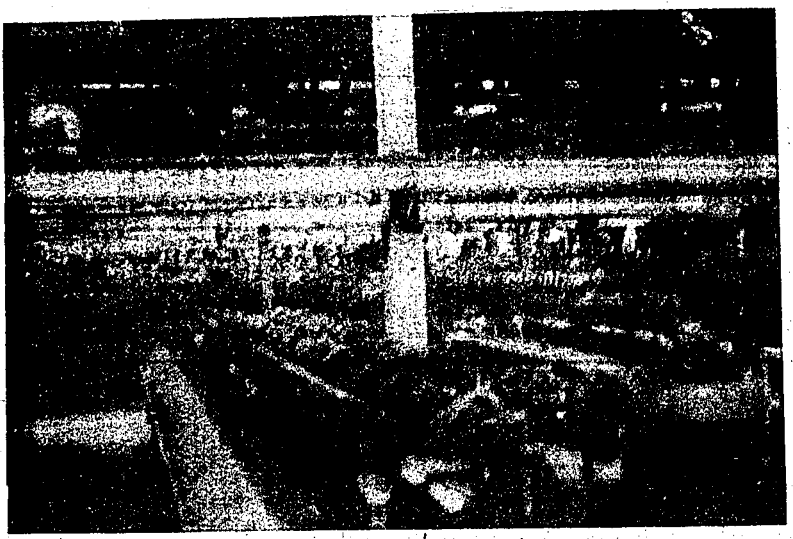
1% to a high of 8% a year. At
did not know if this accuratel
difficulty of inventorying acc

(c) New 28,000 Am

The new 28,00
up the 50% uncompleted enlarg
to, were seen in various stag
The cell was 13 meters (42 ft



Höchst Mercury Cells. General view in cell room.

(b) Cell Performance and Characteristics.

Dr. Winnacker stated that, at 16,000 amperes, the average voltage was 5.0 volts per cell, the ampere efficiency was about 95% and the graphite consumption (exclusive of the vertical hangers) with Bitterfeld graphite, approximately 7 to 9 lbs per short ton of chlorine. With Acheson graphite this was reduced about a third. Graphite anodes made by I.G. at Bitterfeld last about 70,000 ampere hours, whereas Acheson graphite anodes were said to last as long as 110,000 ampere hours.

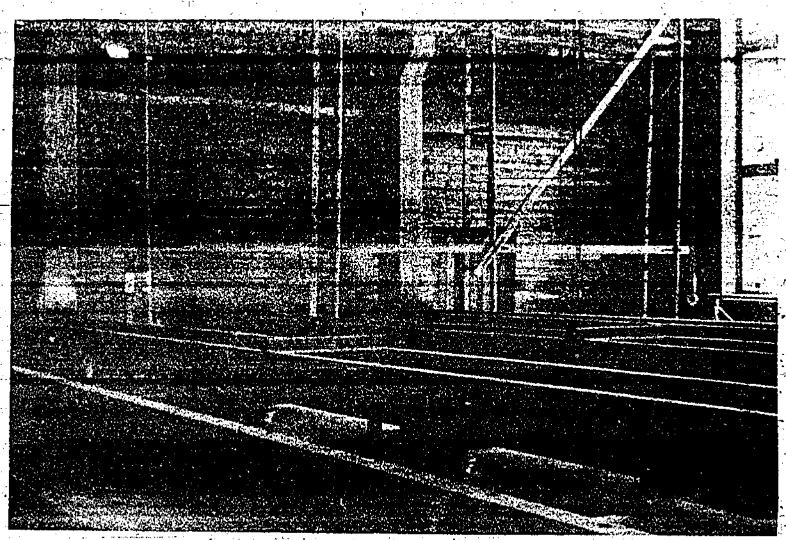
Dr. Winnacker stated that the mercury loss varies considerably in the different I.G. chlorine plants, running from a low of 1% to a high of 8% a year. At Höchst they charged off 2% a year but did not know if this accurately reflected their loss because of the difficulty of inventorying accurately.

(c) New 28,000 Ampere Mercury Cell.

The new 28,000 ampere mercury cells, 42 of which make up the 50% uncompleted enlargement of the plant, previously referred to, were seen in various stages of construction, none of them finished. The cell was 13 meters (42 ft) long by approximately 30" wide. The design and construction details were said to be almost identical with the 1940 Höchst mercury cell already described except for the added length (42" vs 28" approximately), and an increase in the number of anode blades from 37 to about 60. A few of these 28,000 ampere cells were said to have been experimentally operated at Leverkusen, and, according to Dr. Winnacker, they represented a distinct improvement over the shorter mercury cells, from the investment and operating cost standpoint.

It is recommended that performance data be obtained on the experimental 28,000 ampere cells which have already been in operation at Leverkusen.

A photo of the uncompleted electrolyser tank of one of these cells is shown below:



Höchst Mercury Cells. View showing electrolyser tank of 28,000 ampere cell.

(3) Chlorine Cooling, Drying, Compressing and Liquefaction.

The chlorine cell gas was cooled by river water in stoneware cooling pipes and was then dried with sulfuric acid in 3 steel towers lined with acid proof brick, the gas passing counter-currently to the flow of acid with individual circulation by pumps out of the bottom and into the top of each tower. The dried chlorine was compressed to 1.5

atmospheres in very large cumbersome looking reciprocating compressors, lubricated with sulfuric acid. Formerly, Höchst compressed their cell chlorine to 8 or 10 atmospheres but they later switched to a lower pressure plus lower temperature cooling. The compressed chlorine was piped around the plant and part of it was liquefied in equipment which was not seen. The liquid chlorine was stored in two large storage tanks which were protected against possible bombing by very heavy concrete shelters built over and around them.

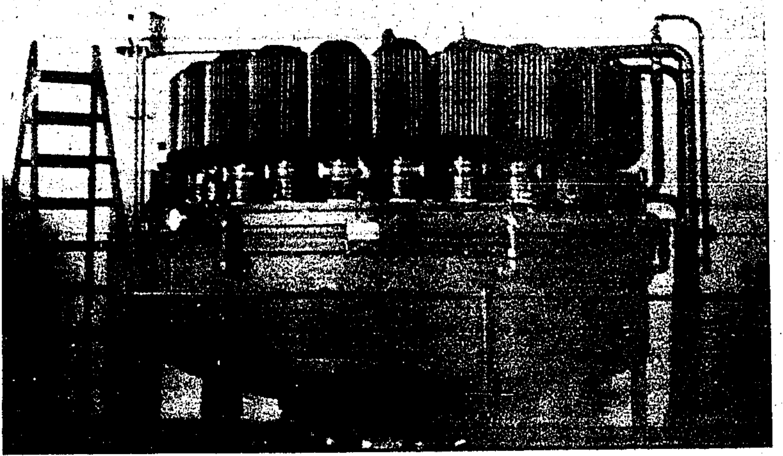
(4) Hydrogen Handling.

The hydrogen from the mercury cells was subjected to rather elaborate treatment to remove mercury which it had picked up. This treatment consisted of cooling to atmospheric temperature, washing with sulfuric acid in towers, cooling to -60°C with CO_2 refrigeration and then passing through activated carbon to remove the last traces of mercury. This treatment gave a hydrogen suitable for catalytic hydrogenation. If the mercury was not completely removed, it would come out in the hydrogen compressors.

c. A. C. Power Rectification.

All A.C. current was converted to D.C. by Brown-Boveri multi-tank rectifiers. Two new rectifiers were described by Dr. Winnacker as the largest he had ever heard of. They were 700 volt - 8,000 ampere capacity made by Brown-Boveri, apparently of the same general design as their three smaller ones. Dr. Winnacker said that they had proved to be very satisfactory in operation. The power station housing the five rectifier units was very spacious and excellently built.

A photo of one of the large rectifiers is shown below:



Höchst Mercury Cell Plant. 8,000 amp 700 volt rectifier.

d. Operating Costs and Data.

Dr. Winnacker presented numerous printed cost sheets showing detailed operating costs of all the I.G. chlorine plants, by months and years, arranged for ready detailed comparison of all costs for each plant. The following costs were obtained from these sheets and represent approximate averages of ranges:

	Cost in RM per 100 kilos of	++Equiv. cost in dollars per short ton of
Brine Dept. including salt, salt handling, dissolving, purification and treatment of recycled brine.	NaCl 2.5	NaCl 9.09
Mercury cost	NaOH 0.3	NaOH 1.09
All materials including power	NaOH 4.5-8.3	NaOH 16.36-30.18

	Cost in RM per 100 kilos of	++Equiv. cost in dollars per short ton of
Total works cost of chlorine including 40% added (by I.G.) for overhead expense.	Chlorine 6.0 to 10.0	Chlorine 21.82 to 36.36
Total works cost of NaOH (basis solid but as 50% solution) including 60% added (by I.G.) for overhead expense	NaOH 7.0 to 11.0	NaOH 25.45 to 40.00

++RM figured at 40 cents.

The D.C. power consumption varied from 3,100 to 3,650 KWH per metric ton of NaOH in the various I.G. chlorine plants. Ampere efficiency varied from 92 to 96.5%. Dr. Winnacker stated that they figure that one 16,000 ampere cell will produce about 500kgs of chlorine per day. At 95% efficiency, a 16,000 ampere cell should produce approximately 545 kgs of chlorine a day. Either the efficiency was lower than stated or the cells do not actually average 16,000 amperes, or shut down time was allowed for in the 500kg figure.

Power costs at Höchst were stated to be 0.1 RM per KWH or (.004 dollars) and steam costs (2.5 atmos pressure) 3.5 RM per 1,000kg (.63 dollars per 1,000 lbs).

The labor requirements in the Höchst chlorine plant (82 tons chlorine per day) was stated to be as follows:

Brine Dept.	9 men
Cell Oper. and Maint.	110 "
Power Conversion	6 "
Chlorine and Hydrogen Plants	25 "
Total	150 "

e. I.G. Chlorine Production.

Dr. Winnacker selected March, 1944, as a month representing the approximate peak of I.G. chlorine production and presented the following figures:

Production of Chlorine
Metric tons per month
March, 1944

Bitterfeld (North)	1,500
Bitterfeld (South)	4,300
Wolfen	1,120
Schkopau	4,150
Hydebreck	1,200
Rheinfelden	1,890
Gersthofen	2,050
Ludwigshafen	2,650
Höchst	2,600
Hüls	2,100
Gendorf	3,500
Dyhernfurth	4,500
Total I.G. (for March, 1944)	31,560
Equal to 12 months prodiction of	378,720

Dr. Winnacker stated that at the peak the I.G. chlorine plants were producing at the rate of approximately 400,000 metric tons per year. He estimated the total production of the "greater Reich" at 600,000 metric tons per year. Later he stated that the I.G. plants produced 70 to 75% of the chlorine produced in the "greater Reich" at its peak.

3. SODIUM SULFIDE.

A very pure sodium sulfide was made by Höchst in connection with their mercury chlorine cells. Some of the sodium mercury amalgam was withdrawn from the electrolyzing tanks of their cells prior to entrance into the decomposers. This amalgam (Na content 0.2% or possibly somewhat higher) was reacted with Na_2S_4 to give Na_2S and sulfur. One quarter of the Na_2S thus formed was reacted with sulfur to form Na_2S_4, which in turn was reacted with more sodium-mercury amalgam to form more Na_2S. The mercury was returned to the electrolytic cell system. The reactions follow:—

$$6Na(Hg) + Na_2S_4 = 4Na_2S + (Hg)$$

$$Na_2S + 3S = Na_2S_4$$

$$\frac{6Na(Hg) + Na_2S_4 = 4Na_2S + (Hg)}{12Na(Hg) + 3S + Na_2S_4 = 7Na_2S + (Hg)}$$

4. METHANE CHLORINATION PLANT.

a. Introduction.

Dr. Winnacker conducted the group through this plant and described the process, on 13 May 1945. Later he provided a written description with a flow chart which is included at the end of this section.

Coke oven gas, (called Leucht gas or Ferngas) was piped to the Höchst plant from the Ruhr. It was freed of CO_2, compressed to 15 atmos and fairly pure methane fractionated out by the Linde process. The small amount of ethylene present was removed by hydrogenation. The relatively pure methane was then chlorinated (methane to chlorine ratio 5:1) in cement lined cast iron chlorinators maintained at 370 to 390°C by external gas heating. The chlorinated products consisting of methyl chloride, methylene chloride, chloroform and higher chlorinated products including carbon tetrachloride and chlorinated ethane were condensed by low temperature refrigeration and separated from the unchlorinated methane which was recycled to the chlorinators. The mixture of chlorinated products was subjected to fractional distillation under moderate pressure and methyl chloride, methylene chloride and chloroform were fractionated out. The methyl chloride was recycled back to the chlorinators for conversion to methylene chloride. After stabilization, the methylene chloride and chloroform were ready for sale. The capacity of the plant was between 500 to 600 tons per month of methylene chloride and 100 to 150 tons per month of chloroform.

Methylene chloride was used extensively in cleaning metals and as a solvent in the manufacture of cellulose acetate, the use of which was widespread in Germany.

b. Preparation of Methane.

Stripped coke oven gas (illuminating gas) piped to the Höchst plant from the Ruhr was compressed to 15 atmospheres. The CO_2 (2.5%) was then scrubbed out by washing first with water and then with NaOH solution. The wet gas was then pre-cooled to -30°C in a counter-current gas cooler by means of low temperature gases from the Linde fractionating plant referred to below. A further cooling to -45°C in an ammonia refrigerated cooler reduces the moisture content to practically nil. The illuminating gas, pre-cooled and dried as described above, was fed to the gas liquefaction and fractionating apparatus which was of Linde design (Gesellschaft für Linde's Eismachinen A.G.). The gas was liquefied in steps and was fed countercurrently to, and refrigerated by, the outflowing liquefied products and also by means of liquid nitrogen distilled under vacuum. A methane cut boiling between -153° and -157°C and a hydrogen cut boiling between -208° and -209°C were taken off plus an uncondensed residual gas. At this point the methane cut contained about 0.6% of C_2H_4. This was removed by hydrogenation over a nickel catalyst supported on a contact mass.

The daily through-put of illuminating gas was about 1,130,000 cubic feet. 1,000 cubic meters of feed gas produced approximately:

195 cubic meters of CH_4
525 cubic meters of H_2
280 cubic meters of residual gas

The foregoing figures are the average of two sets of slightly different figures from different sources.

The analysis of the various gases at different stages in the process was as follows:

	H_2	CH_4	CO	CO_2	C_2H_6	C_2H_4	C_6H_6	O_2	N_2	Other hydrocarbons
1. Illuminating gas	54.0	24.0	6.5	2.5	1.3	2.4	0.4	0.5	7.8	
2. Above after washing	55.7	25.4	6.7	-	1.3	2.5	-	0.5	7.9	
3. Methane from Linde fractionation plant	-	98.4	0.2	-	0.4	0.6	-	-	0.4	
4. Methane after hydrogenation of the C_2H_4 fraction-now ready for chlorination	0.9	98.4	0.1	-	0.3	-	-	-	0.3	
5. Hydrogen from Linde plant	98.5	-	0.5	-	-	-	-	-	1.0	
6. Residual gas (used for fuel)	5.5	18.5	28.0	-	5.5	9.0	-	0.5	33.0	
7. Vent gas, after removal of the chlorinated hydrocarbons, which is fed back into the Linde plant.		73							15.0	10-12

The analysis of the methane produced for chlorination as outlined in the foregoing is shown on line 4 above. It is stored in a 175,000 cubic feet spheroid gas holder.

c. Chlorination of Methane.

The methane chlorination is shown on the attached flow chart. The plant consisted of 7 chlorinating furnaces, the approximate design and size of which are shown on the attached sketch. The chlorinators were steel reactors approximately 5' in diameter by 13' high. These were lined with a thin layer of Portland cement containing a low percentage of admixed sand. The lower 85% of each chlorinator was enclosed within a brick furnace fired by gas burners inserted near the bottom. The top of each reactor was filled with Raschig rings, supported on a grid, to a depth of about 3' from the top. The methane and chlorine in a ratio of five to one by volume were brought together outside the chlorinator into a single pipe which discharged the gases vertically downward at a point near the center of the chlorinator. The chlorine was said to be completely consumed. The temperature of the chlorinators was held at 370° to 390°C by external gas firing. The gases were distributed between the seven chlorinating ovens by hand regulators using manometers as a guide.

The hot chlorinated reaction products in vapor form passed out at the top of the chlorinators along with the excess methane and the HCl gas. These gases were cooled in cast iron coolers and the HCl removed by scrubbing with water which produced a 30% muriatic acid, which was stored in rubber lined tanks. The HCl absorption system was maintained at a temperature sufficiently high to avoid condensation of chlorinated hydrocarbons, which along with the excess methane were then scrubbed, first with sodium carbonate and then with caustic soda solution to remove all traces of CO_2 and HCl.

The gases were then drawn into blowers operating in two stages, which compressed them to about 13 lbs per sq in. The blowers had a capacity of 1,750 CFM at this pressure. After precooling, these gases entered a three-stage refrigeration system which condensed out the bulk of the chlorinated hydrocarbons. The first stage was cooled with refrigerated methylene chloride to +4°C. The intermediate cooler was cooled to -22°C also with methylene chloride. The gases were cooled in the third stage to -52°C by means of NH_3 expanding under vacuum. All of the condensate was accumulated in a refrigerated collection tank. The uncondensed gases, consisting of about 73% methane, 15% N_2 and 10 to 12% of other hydrocarbons were recycled back to the chlorinating ovens after bleeding off an amount necessary to maintain the nitrogen content at about this point. The bled gas was returned to the Linde plant for recovery of its methane content after removal of any chlorinated hydrocarbons by refrigeration and washing under pressure. Methyl chloride recovered in the fractionation plant was also added to the feed to the chlorinators, for further chlorination to methylene chloride, in spite of the fact that methyl chloride was made by the hydrochlorination of methyl alcohol elsewhere in the Höchst plant. This anomaly was explained by the fact that Höchst was short of illuminating gas from the Ruhr and wished to make as large an amount as possible of methylene chloride from the gas which they could get.

Make-up fresh methane from the methane gas-holder was added to the gas stream between the HCl absorbers and the soda ash and caustic scrubbing towers. Some methyl chloride overhead gas from their esterification plant, vent gas from the methyl chloride compression plant, methyl chloride from the recycled methane and waste gas from the pressure distillation plant were added to the gas stream at the same point and constitute part of the make-up.

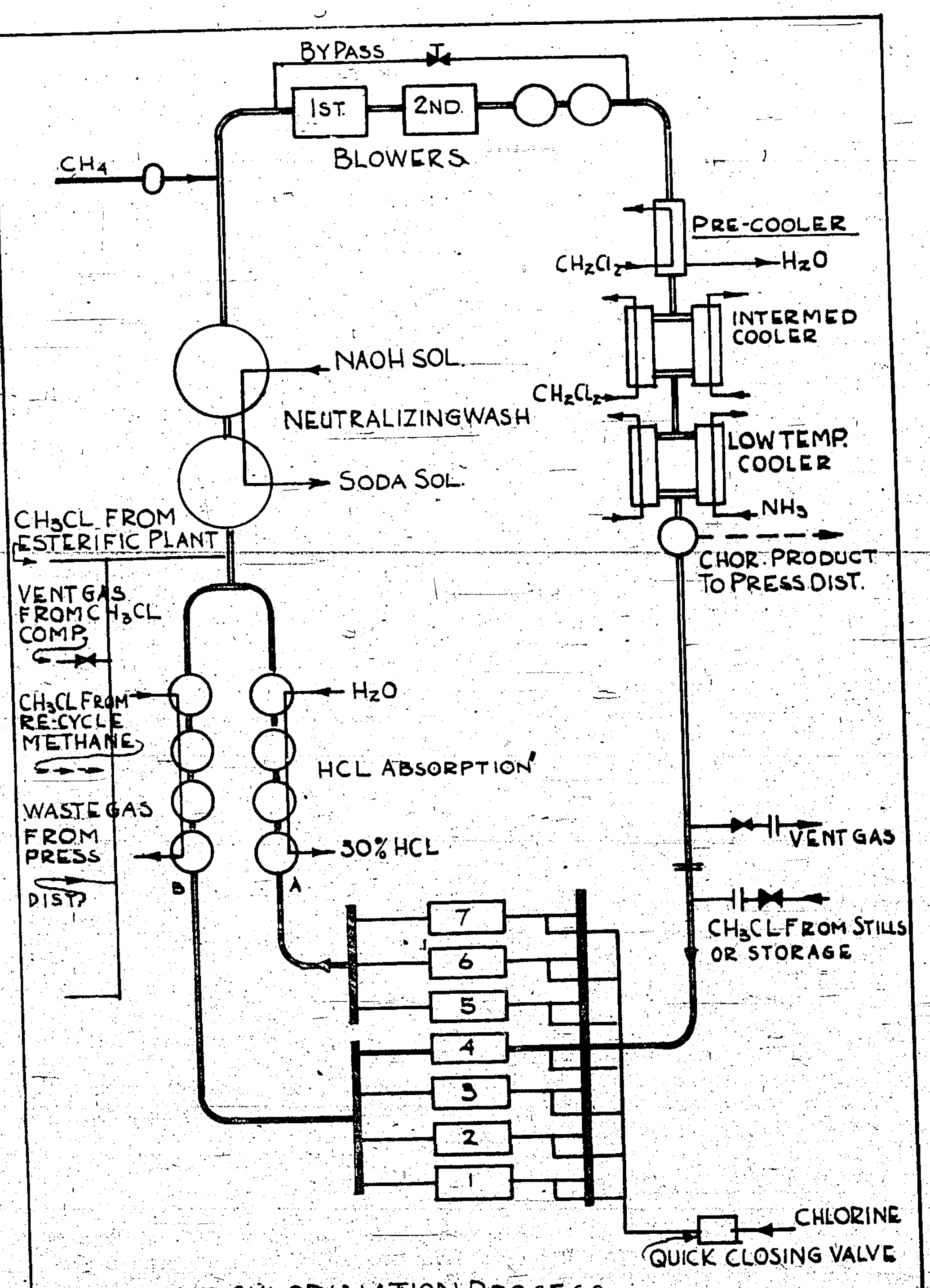
d. Fractionation and Treatment of the Chlorination Products.

The chlorination products consisting of two parts of methylene chloride to one part of methyl chloride plus much smaller amounts of chloroform, carbon tetrachloride and other higher chlorination products, were pumped continuously from the refrigeration plant previously described to the pressure distillation fractionation plant at 10 atmospheres pressure by means of a gas pressure pump operated by recycle methane. They first passed through a heat exchanger and then into a still equipped with a bubble cap column, which stripped off the methyl chloride from the methylene chloride, chloroform and higher boiling compounds. This still operated at about 8 atmospheres pressure. The methylene chloride was then stripped from the chloroform and high boiling compounds in a second still, also equipped with a bubble cap column, which operated at 4 atmospheres pressure. The residual chloroform and high boiling compounds, together with some remaining methylene chloride, was distilled in a batch still (capacity 6,600 gallons) equipped with a bubble cap column. This still produced some technical methylene chloride and chloroform (both technical and pharmaceutical grades). The still residue consisting of carbon tetrachloride and other higher chlorinated products were distilled as necessary to supply the demand for solvents.

The methyl chloride cut coming from the first distillation was returned to the chlorination plant to be chlorinated further as previously mentioned.

High grade methylene chloride was stabilized with 0.003% thymol and then stored in steel tanks. Technical methylene chloride was stabilized with an intermediate cut containing chloroform. Both grades of methylene chloride were shipped in steel drums or tank cars.

Technical chloroform was handled the same as technical methylene chloride. Pharmaceutical chloroform was stabilized in enamel lined tanks with 0.6 to 1.0% of ethyl alcohol and packed in glass bottles.



METHANE CHLORINATION PROCESS

5. MONOCHLOROACETIC ACID.

a. Summary.

Höchst operated a new process for the production of monochloroacetic acid. In contrast, the old process based on the chlorination of acetic acid, was operated at Gersthofen, an associate plant. Information on the new process was obtained from Dr. Thiel. The new process consisted in the reaction of trichloroethylene with sulfuric acid according to the following equation:

$$CHCl = CCl_2 + 2H_2O + (H_2SO_4) \longrightarrow CH_2ClCOOH + 2HCl + (H_2SO_4)$$

The sulfuric acid simply acted as a catalytic agent.

b. Description of the Process.

A cast iron reaction vessel of 1,800 gallons capacity was charged with equal weights of 98% sulfuric acid and chloroacetic acid and heated to 135 – 140°C. The reaction was thereafter carried out continuously by introducing into the stirred contents, through a pipe line extending to the bottom of the reactor, a mixture of trichloroethylene, 495 pounds per hour, and 74% sulfuric acid, 475 pounds per hour. The reaction mixture overflowed continuously into a receiver.

Monochloroacetic acid was recovered from the above reaction mixture by distillation at about 20mm absolute pressure using three cast iron boilers arranged in a series cascade system. The temperatures of the contents of these stills were 155°, 165°, and 180° to 190°C respectively. The heated liquor flowing from the final still was passed through an immersion seal to a receiver and then to a cast iron cooler from which it was pumped into one of two separators. The vapors from the distillation system, leaving the boilers at a temperature of about 110°- 120°C were cooled and condensed in a lead pipe condenser, which delivered the monochloracetic acid product at a temperature of about 65°C. The product was stored in a receiver and subsequently flaked to produce the finished product.

The residual sulfuric acid above was allowed to separate in a total of four receivers having a combined capacity of about 11,000 lbs. A small amount of resinous material separated out and was discarded. Acid losses were replaced with fresh sulfuric acid. The sulfuric acid (approximately 98%) overflowed from the separators to a dilution tank where it was cut to a concentration of 74% sulfuric acid and was then recycled.

c. General Information.

The yield, based on trichloroethylene, was 92 to 93% of theory. Losses comprised the resin separated from the sulfuric acid plus some vapor loss of trichloroethylene carried in the HCl off-gas. The monochloroacetic acid product was stated to be quite pure. A total of 5 reactors, installed in the Höchst plant, have a rated capacity of 300 tons of monochloroacetic acid per month.

The outstanding difficulty with the process was the high corrosion rate on the cast iron equipment used. The Höchst chemists were of the opinion that the process now shows about the same production cost as the process involving chlorination of acetic acid.

6. SULFURIC ACID AND CHLOROSULFONIC ACID.

Dr. Winnacker provided the following information:

a. Sulfuric Acid.

Höchst manufactured sulfuric acid by the standard contact process using tray type converters employing vanadium catalyst deposited on approximately 1/8" diameter by 1/8" high silica pellets.

The total plant capacity (6 converters) was 350 tons of sulfuric (100%) acid per day.

Höchst's practice followed the standard sulfuric acid practice as used in the U.S.A.

One interesting feature was that pyrites were used exclusively as the source of sulfur; the typical Spanish pyrite used normally contained 42% sulfur. Höchst's rotary kiln pyrite burner, 14' in diameter by 370' long, was about the largest size known. This kiln had a capacity of 120 tons of sulfuric acid per day.

b. Chlorosulfonic Acid.

The chlorosulfonic acid plant was erected fairly recently. Exit gas from the sulfuric acid contact plant converters, containing 8% sulfur trioxide by volume, was mixed in a jet with dry, 90 – 92% hydrogen chloride gas at room temperature. The mixture was then passed in series through two packed towers to permit the addition reaction to occur essentially adiabatically with a contact time of 10 to 20 seconds. Two Raschig ring packed towers about 12' in diameter by 12' high were used for an 80 ton per day plant. The tower exit gas at approximately 200°C was passed to an aluminum cooler, the gases passing in a vertical plane at right angles to water flowing through vertically arranged tubes. The liquid chlorsulfonic acid was condensed and collected. Exit gases were scrubbed with 98% sulfuric acid to remove traces of acid mist.

The single unit produced 2,500 tons chlorosulfonic acid per month. Of this quantity, approximately 500 tons were used at Höchst and the balance was available for the preparation of smoke mixture for war purposes.

An older unit having a capacity of approximately 300 tons per month employed a process based on the addition of HCl gas to highly concentrated oleum followed by subsequent removal of the chlorosulfonic acid by distillation.

Two views of the Höchst pyrite kiln, said to be the largest in the world, are shown below:

Pyrites Burning Kiln.

Bottom view Pyrites Burning Kiln.

7. ACID PROOF CEMENTS.

The Höchst plant was the chief I.G. producer of acid proof cements for use in the erection of chemical and other industrial equipment. The properties of these cements, their methods of application, and industrial uses are well known. However, the specific composition of such cements is not generally known.

Two types were manufactured; first, the acid proof type composed essentially of fluosilicates mixed with sodium silicate solution and second, an organic type termed "Asplit", which was based on a phenol formaldehyde resin. The latter type presumably is similar to a material made in the U.S.A.

Tables showing the properties, compositions, etc of the various cements are below. The use of Asplit EL for lining cement gasoline storage tanks is worth special note.

These data are based on information furnished by Dr. Diets of the Höchst staff.

TABLE I

ACID PROOF CEMENTS - HÖCHST

Name	Application	Resistant to	Composition		
			Powder		Liquid
SW 10 & 20	Acid proof brick linings. Cements are not liquid tight.	All acids except sulfuric and hydrofluoric.	Na_2SiF_6 Clay Quartz powder	4.0% 2.0 94.0	Sodium silicate solution containing 8% Na_2O and 26% SiO_2
SWK	Masonry work, linings, joints.	Sulfuric acid, all concentrations; salts, etc.	K_2SiF_6 Soluble silicic acid Clay Quartz powder	6.0 3.0 2.0 89.0	Potassium silicate solution containing 10% K_2O and 23.5% SiO_2
SWD	Brick work, tile linings, etc.	All acids except sulfuric and hydrofluoric.	Na_2SiF_6 K_2SiF_6 $CaSiF_6$ Clay Soluble silicic acid Gypsum Quartz powder	3.0 3.0 1.0 6.5 2.0 0.3 84.2	Sodium silicate solution containing 11.6% Na_2O and 31.5% SiO_2

Name	Application	Resistant to	Composition		
			Powder		Liquid
SWD-Z	Ceramic linings for pressure vessels; e.g. cellulose digesters.	Especially resistant to sulfurous acid	Na_2SiF_6 K_2SiF_6 $CaSiF_6$ Clay Soluble silicic acid Gypsum Slag wool powder Quartz-sand & powder	4.0% 2.0 0.8 5.2 3.2 1.5 20.0 63.3	Sodium silicate solution containing 11.6% Na_2O and 31.5% SiO_2
Z-Acid Proof mortar	Masonry work, tile linings, jointing of brick work	All acids except sulfuric and hydrofluoric	Na_2O SiO_2 H_2O	20.0 53.0 27.0	Water mixed in ratio of 79 pts per 21 pts of powder
K-Refractory cement	Acidproof and fireproof masonry work; e.g., drying kilns.	All acids except hydrofluoric	K_2SiF_6 $BaSO_4$ Soluble silicic acid Fire brick powder Quartz powder	3.0 12.0 3.0 50.0 32.0	Potassium silicate solution containing 10.5% K_2O and 23.5% SiO_2

TABLE II

SYNTHETIC RESIN CEMENTS - ASPLIT

Name	Application	Resistant to	Composition			
			Powder		Liquid	
Asplit	Jointing of tile and brick work	All acids except oxidizing acids; also resistant to sodium carbonate	p-toluene sulfone chloride Silica Quartz powder	10.0% 20.0 70.0	Condensation product of phenol and formaldehyde Benzyl alcohol	90% 10
Asplit A	Jointing of tile and brick work	All acids except oxidizing acids; also resistant to caustic soda	p-toluene sulfone chloride Barium sulfate Quartz powder	10.0 70.0 20.0	Condensation product of phenol and formaldehyde Benzyl alcohol ++Triethyl phosphate	75 5 20
Asplit El	Coating of larger tanks especially thick walled concrete reservoirs for gasoline in submarine stations.	Gasoline and all common solvents.	p-toluene sulfone chloride Polymer of vinyl chloride and maleic anhydride Kieselguhr Silica Quartz sand Quartz powder	6.5 1.5 1.0 10.0 41.0 40.0	Condensation product of phenol and formaldehyde Benzyl alcohol ++Triethyl phosphate	75 5 20

++Can substitute dichloropropanol or chlorobenzaldehyde.

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8. SYNTHETIC TANNING AGENTS.

Synthetic tanning agents have been prepared at Höchst since about 1913. Information was obtained from Dr. Pense and Dr. Asch. Initially these materials were used to supplement natural agents in order to improve the overall results. Later on, these synthetics began to replace the natural tanning agents. In the early war years roughly equal mixtures of synthetic and natural agents (such as hemlock, oak and quebracho) were used. Finally 100% synthetic tanning agents were employed quite successfully.

Höchst had a very complete testing and development laboratory. Small scale equipment was available for carrying out all of the processing steps in leather manufacture. The capacity of the plant was 300 to 400 tons of synthetic tanning agents (100% basis) per month. The first tanning agents were essentially naphthalene sulfonic acids. Later naphthalene sulfonic acids plus a condensation product of phenol and formaldehyde were prepared. The present Tanigans which contain additional phenol formaldehyde resins were developed in about 1934.

The steps in the preparation of a typical synthetic tanning agent, Tanigan SK-7, is given in detail as follows:

a. Preparation of naphthalene sulfonic acid mixture.

b. Preparation of phenol-formaldehyde condensation product - "alcohol".

c. Preparation of a second phenol-formaldehyde condensation product - "resin".

d. Mixing of the alcohol "b" and the "resin" "c".

e. Mixing of Item "d" with "a", followed by neutralization, etc., to prepare the finished Tanigan.

The preparation of the naphthalene sulfonic acid mixture was carried out as follows: 1,440 pounds of hot pressed naphthalene are melted and run into a 500 gallon reactor. The material, at 60° - 80°C, was treated first with 720 pounds of 96% sulfuric acid and then with a mixture of 995 pounds of concentrated sulfuric acid plus 716 pounds of 20% oleum. The reaction mass was finally heated to 125°C to complete the sulfonation. The sulfonated mass was transferred to the condensation vessel, an 800 gallon lead lined tank, cooled to 45-50°C and then reacted with 132 pounds of 30% formaldehyde.

The phenol-formaldehyde condensation product - termed "alcohol" was prepared by charging 609 pounds of phenol oil, SR-1, and 609 pounds of cresol-DAB 4 to a 500 gallon reactor. 818 pounds of 30% formaldehyde were added, followed finally by 4.5 pounds of dry soda ash. The mixture was heated slowly with stirring to 75°C during a period of four hours and then held at this temperature for an additional two hours. Finally the mixture was cooled to 60°C and 187 pounds of solid sodium chloride added in order to salt out the "alcohol." After standing for some time the bulk of the salt water layer was discharged to the sewer. The "alcohol" residue was then transferred to a second conical shaped separator where the mixture was settled further to separate the balance of the "alcohol" product. 1,450 pounds of water were added to the "alcohol" product and the mixture was then transferred from the condensation vessel to a 1,600 gallon lead lined tank. Here 117 pounds of urea were added followed by 220 pounds of water and then by a mixture of 264 pounds of 30% formaldehyde diluted with 77 pounds of water. Finally an additional 209 pounds of water were added.

A second condensation product termed "resin" was prepared by running 825 pounds of phenol oil SR-1 and 660 pounds of formaldehyde solution into a 250 gallon enamelled vessel equipped with a stirrer and an air condenser; then 506 pounds of crystal sodium sulfite were added. The entire mixture was then heated to 80°C during a period of one hour and then, in a second hour, to the boiling point. Finally boiling was continued, for a period of 6 to 8 hours until the finished resin was completely soluble in 1% sulfuric acid.

The first resin product termed "alcohol" was mixed with the second product, termed "resin." This mixture was then added to the naphthalene sulfonic acid. Finally the entire mixture was neutralized with about 2,015 pounds of aqueous ammonia. The batch was standardized by the addition of approximately 660 pounds of glacial acetic acid so that the acidity of the finished Tanigan was equivalent to 9-9.5cc of normal sodium hydroxide per 10 grams of tanning agent.

The yield was 12,540 pounds of Tanigan SK-7 product containing 37% of the synthetic tanning agent.

It is obvious from the process description that innumerable variations in the composition of the Tanigans can be made. The following list of the principal products produced by Höchst illustrates this.

Tanigan SK - 7	As described above, is corrected to about pH = 3.5
" SK	Is the same as SK-7 but acidified further with acetic acid to a pH below 3.
" HN) " HZ)	These two products are similar to SK with the exception that benzyl naphthalene is substituted for naphthalene. Benzyl naphthalene is made by reacting naphthalene with benzyl chloride.
" G	This product is prepared from resorcinol.
" GB	Prepared from catechol.
Extra F	This is a special product prepared by using resin and cresol.

9. ACETALDEHYDE DIVISION.

a. Introduction.

Höchst has large operations in processes based on acetaldehyde. Information on them was obtained from Dr. Möller. The general scheme of production is shown on the attached chart at the end of this section. The plant, which was erected in 1935 following the almost complete destruction of the original plant by a very serious explosion, is quite new and modern.

b. Acetaldehyde.

Acetaldehyde was received by barge from the Knapsack plant of Dr. Alexander Wacker, G.m.b.H. Höchst consumed about 35% of Wacker's production. The acetaldehyde was stored, uninhibited, in approximately 20,000 gallon steel tanks located along the Main river bank in a well camouflaged location. All of the acetaldehyde was redistilled continuously to raise the purity to 99.95%. A photo of the acetaldehyde storage tanks, showing remains of camouflage follows.

Höchst acetaldehyde storage tanks showing camouflage

c. Acetic Acid.

Acetic acid was prepared batchwise by the liquid phase oxidation of acetaldehyde according to the following equation:

$$CH_3CHO + \frac{1}{2}O_2 \longrightarrow CH_3COOH$$

To a heel of acetic acid was added the required acetaldehyde plus manganese acetate catalyst. The reactor consisted of an aluminum clad steel tank fitted with a stirrer. Oxygen (95 to 99%) was introduced at 60°C until the reaction mixture contained about 98% acetic acid. The reaction mixture was then batch distilled to yield acetic acid 99.5%, separating traces of such materials as acetaldehyde, crotonaldehyde, and ethylidene diacetate. The overall yield based on acetaldehyde was 97%.

The use of pure oxygen rather than air greatly simplified the absorption system. Oxygen was obtained from an adjoining Linde type plant.

The current acetic acid plant had a capacity of 1,500 tons per month. A new plant, under construction, based upon the same process, was designed for continuous operation. This unit was to have a capacity of 1,000 tons per month.

d. Aldol.

Aldol was formed continuously by the condensation of acetaldehyde in the presence of alkali at 20 to 30°C according to the following equation:

$$2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO$$

The conversion was 60%. The equipment, of steel construction, consisted of a water cooled tubular reactor, a circulating pump, feeding devices for acetaldehyde and caustic potash, and a finishing tank plus receiver, etc.

The equipment was filled initially with acetaldehyde and adjusted to equilibrium. Fresh acetaldehyde was then fed to the system continuously, together with a stream of 10% potassium hydroxide adjusted so that the KOH content of the mixture was equivalent to 1.1 to 1.5cc of normal hydrochloric acid per 100cc of aldol. The exothermic reaction was controlled carefully to maintain a reaction temperature of 20°C. This was accomplished by rapid circulation of the reaction mixture through the heat exchanger unit. Higher reaction temperatures resulted in the formation of longer chain condensation products. The reactor was equipped with devices for injecting phosphoric acid quickly in order to quench the reaction if the temperature

rose too rapidly.

Under summer conditions it was necessary to operate at 30°C, in which case the KOH content was lowered.

A quantity of reaction mixture, 60% aldol and 40% acetaldehyde, equivalent to the fresh acetaldehyde fed, overflowed to a finishing tank where it was maintained at 30°C maximum. The inventory time in the reactor was ½-1 hours; in the finishing tank 5 to 6 hours.

The reaction mixture leaving the finishing tank was acidified with acetic acid in order to stop the condensation reaction. The product was then ready for the next step - conversion to crotonaldehyde. Aldol as such was not separated.

Pertinent details on the capacity of the Höchst reactor are: acetaldehyde feed rate, 7,000 pounds per hour; circulating pump rate, 1,800 gallons per minute; velocity of the reaction mixture through the cooled tubes of the reactor, 4.5' per second.

e. Crotonaldehyde.

Crotonaldehyde was prepared by the dehydration of aldol according to the following reaction, with an overall yield of 90%:

$$CH_3CHOHCH_2CHO \longrightarrow CH_3CH = CHCHO + H_2O$$

The equipment consists of copper bubble-cap columns equipped with feeding devices, heaters, condensers and other accessories.

The mixture of 60% aldol plus 40% acetaldehyde was acidified with acetic acid to an equivalent acidity of 3 to 4cc of normal sodium hydroxide per 100cc of aldol. 10% water was added and the mixture fed into the first bubble-cap column where it was distilled to remove acetaldehyde, as an overhead product, which is recycled to the aldol process. The free bottoms were fed to the center of a second column. The overhead from this column consists of a mixture of crotonaldehyde plus water which on condensation and cooling separated into two phases. The upper crotonaldehyde phase passed forward and the lower water phase was returned to the column. The bottoms from the column consisting of higher boiling condensates plus water were discarded.

f. Ethyl Acetate.

Ethyl acetate was prepared by the condensation of two molecules of acetyldehyde in the presence of aluminum ethylate catalyst, which was prepared in the following manner:

2,000 pounds of dry ethyl acetate were charged to a 1,200 gallon steel vessel equipped with a stirrer and a reflux condenser. 175 to 200 pounds of aluminum borings and 45 to 55 pounds of aluminum chloride were then added. Some evolution of hydrogen began immediately due to reaction with traces of ethanol. As soon as the evolution of hydrogen slowed down, an additional 5,200 pounds of ethyl acetate were added and the mixture heated. When the temperature reached the boiling point, 950 pounds of absolute alcohol were added slowly over an 8 to 10 hour period. After 24 hours of boiling, all of the aluminum was dissolved to form the aluminum ethylate catalyst mixture. The mixture was then cooled to 25°C and transferred to the catalyst measuring tank. Instead of the absolute alcohol in ethyl acetate they could have used an azeotropic mixture recovered from the distillation operations.

The ethyl acetate reaction was carried out in the following manner: Water free ethyl acetate was prepared by distillation and charged continuously to a brine-cooled stirred vessel of about 1,000 gallons capacity, together with an equal weight of the aluminum ethylate in ethyl acetate solution. The reaction temperature was controlled at 0 to 5°C. A siphon overflow delivered the reaction mixture to a second final reaction kettle. The reaction time in the first reaction kettle was about 20 minutes, and the conversion of the acetaldehyde about 90 - 95%. In the finishing tank, the temperature was raised to about 12°C to complete the reaction of the remaining acetaldehyde.

After a 24 hour period the product was delivered to a Frederking vessel and the ethyl acetate removed by distillation. The residual catalyst mass was reacted with water to form an aluminum oxide residual and ethyl alcohol. The alcohol recovered was used for the preparation of further batches of catalyst. The dry aluminum oxide, obtained on heating the residue to dryness, was discarded.

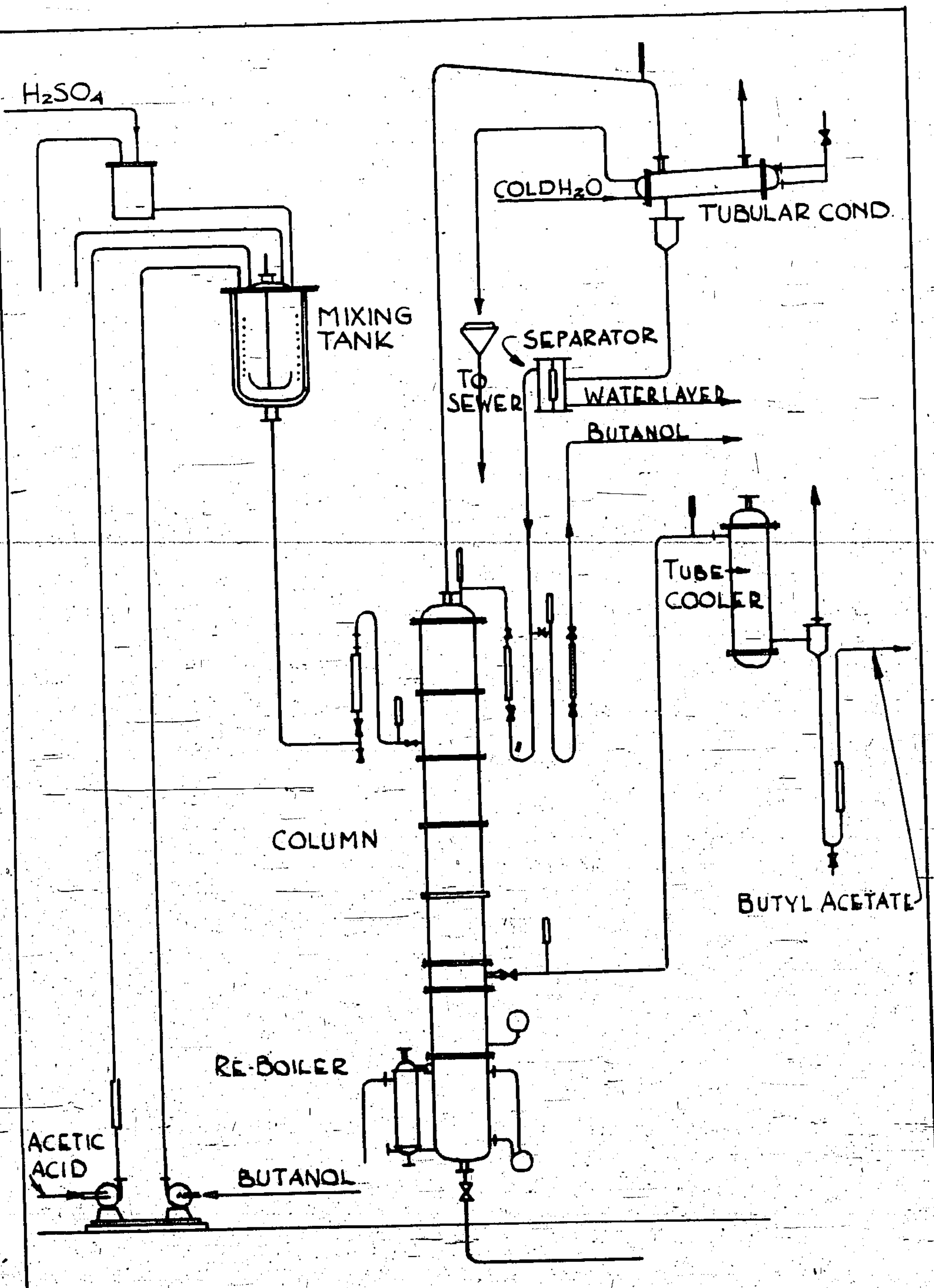
The ethyl acetate was purified by continuous distillation. The first was a ternary mixture of ethyl acetate water and alcohol plus a little acetaldehyde. The second fraction was a binary mixture of ethyl acetate and alcohol and was used for the decomposition of alumimum ethylate catalyst. The third fraction was the pure ethyl acetate product; the residue from this operation contained water plus a small emount of crotonaldehyde and diethylacetal by-products.

g. Butanol.

Butanol was prepared by hydrogenation of crotonaldehyde in the vapor phase at 180 - 250°C using copper on pumice as a catalyst.

h. Butyraldehyde.

Butyraldehyde was prepared by the low pressure liquid-phase hydrogenation of crotonaldehyde at 20 to 30°C using nickel on pumice as a catalyst.



BUTYL ACETATE FLOW CHART

6/8/45 MH

i. Methoxybutanol.

Methoxybutanol was prepared from crotonaldehyde. The product was esterified with acetic acid to produce a solvent, methoxy butylacetate.

j. Butylglycollate.

The sodium salt of monochloracetic acid was heated with butanol at 150°C to split off sodium chloride. Additional butanol was then added to esterify the glycollic acid to form butylglycollate, which ester was known as Polysolvan O.

k. Miscellaneous Esters.

A series of esters was made mostly for solvent uses. The most important of these was butyl acetate which was prepared continuously using sulfuric acid catalyst. A schematic diagram for this process is attached.

Among the other important esters prepared were:

Methyl acetate
Propyl acetate
Isobutyl acetate
Isohexyl acetate
Isoheptyl acetate

These were made by standard methods using in the three latter cases alcohols obtained from the Leuna works of I.G. It was stated that Höchst produced over 80% of the German output of acetate esters in recent years.

l. Miscellaneous.

Acetic anhydride was not made by Höchst; however, in our discussions it was learned that the Knapsack plant produces acetic anhydride from acetaldehyde by the oxidation method. Wacker dehydrated acetic acid to ketene, which was hydrated to acetic anhydride. In this process acetic acid vapor was heated to about 700°C to yield ketene with approximately 95% yields with a 60% conversion per pass. Triethylphosphate catalyst was added to the vapor to the extent of 0.2% of the acetic anhydride formed.

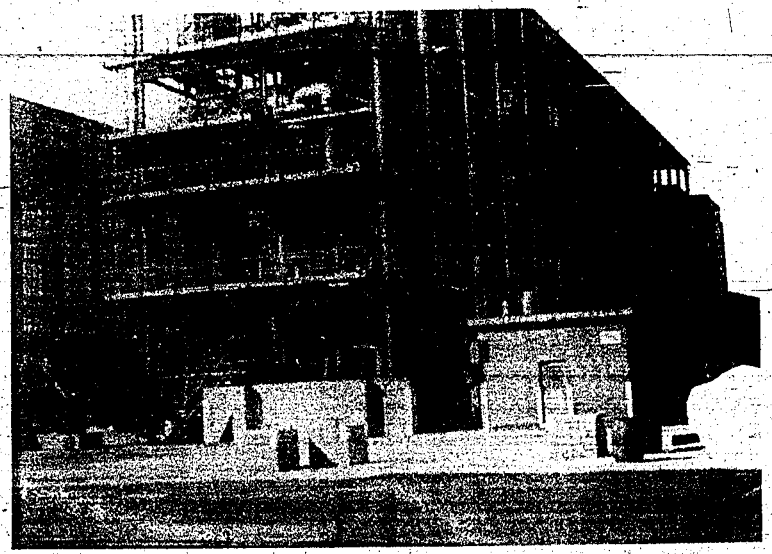
m. Production Data.

The production capacity of the various operations in Höchst was given in the following table:

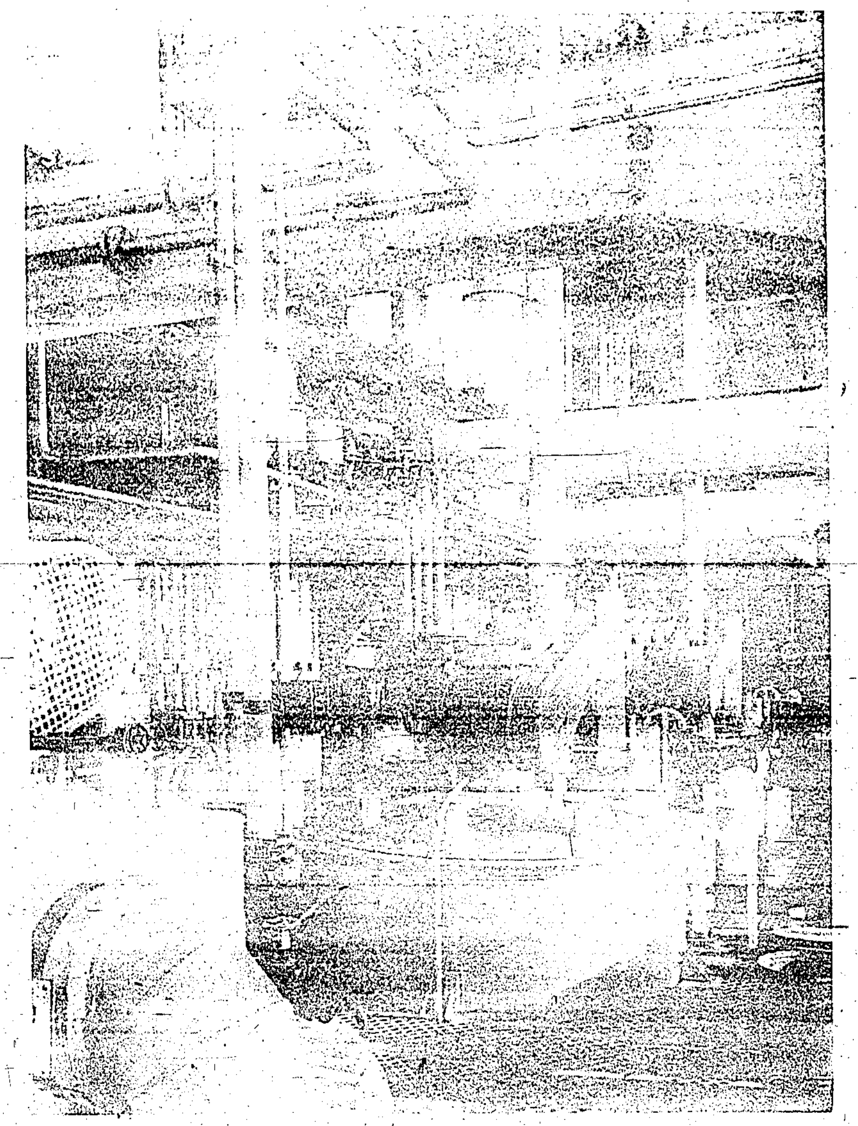
Item	Capacity-metric tons per month
Acetic Acid	1,500+
Crotonaldehyde	2,000
Butanol	700
Esters-Butyl and Isobutyl acetate	1,200
Ethyl acetate	1,300
Methyl acetate	1,200
Higher esters	300

+An additional 1,000 tons capacity was under construction.

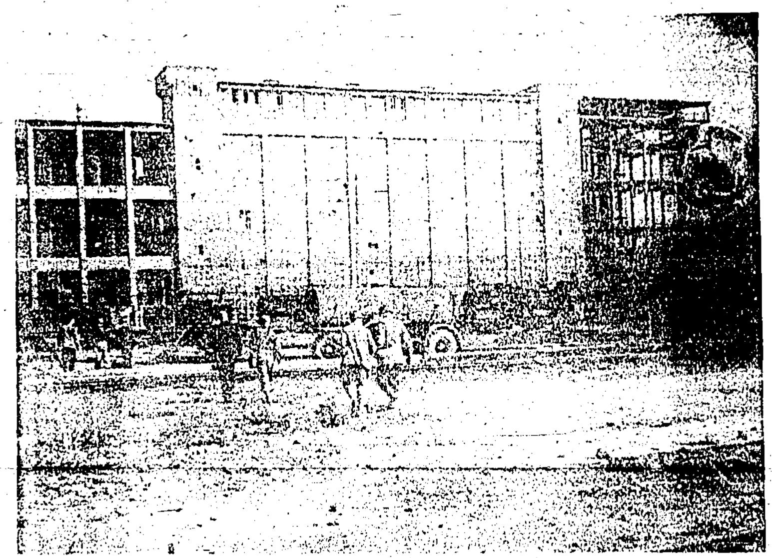
The following photos show several views of the Höchst acetaldehyde products plant.



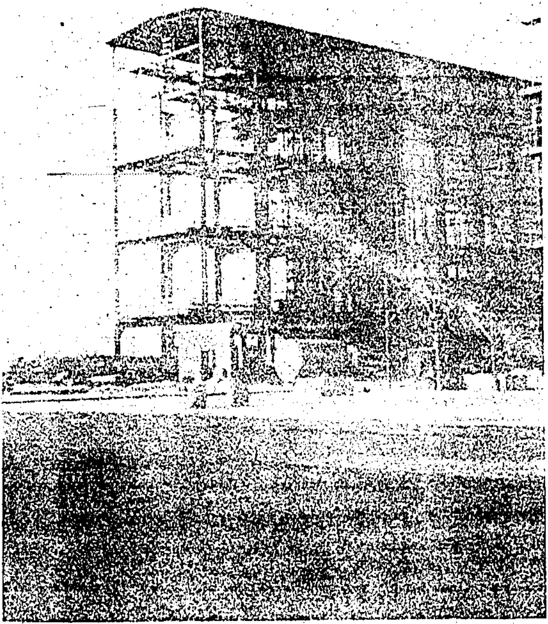
Höchst Acetaldehyde Products Plant



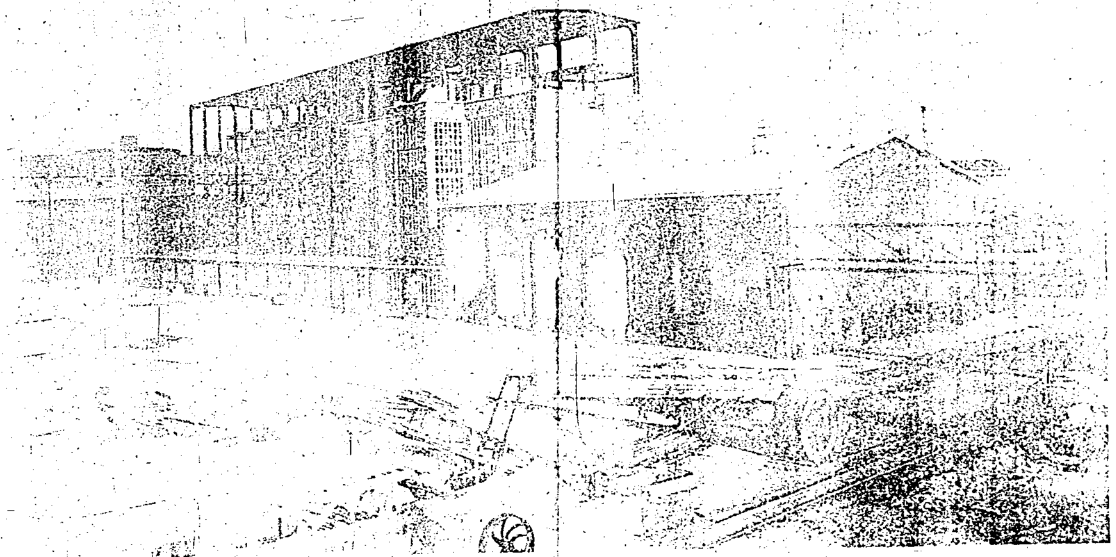
Höchst Ethyl Acetate Reactors



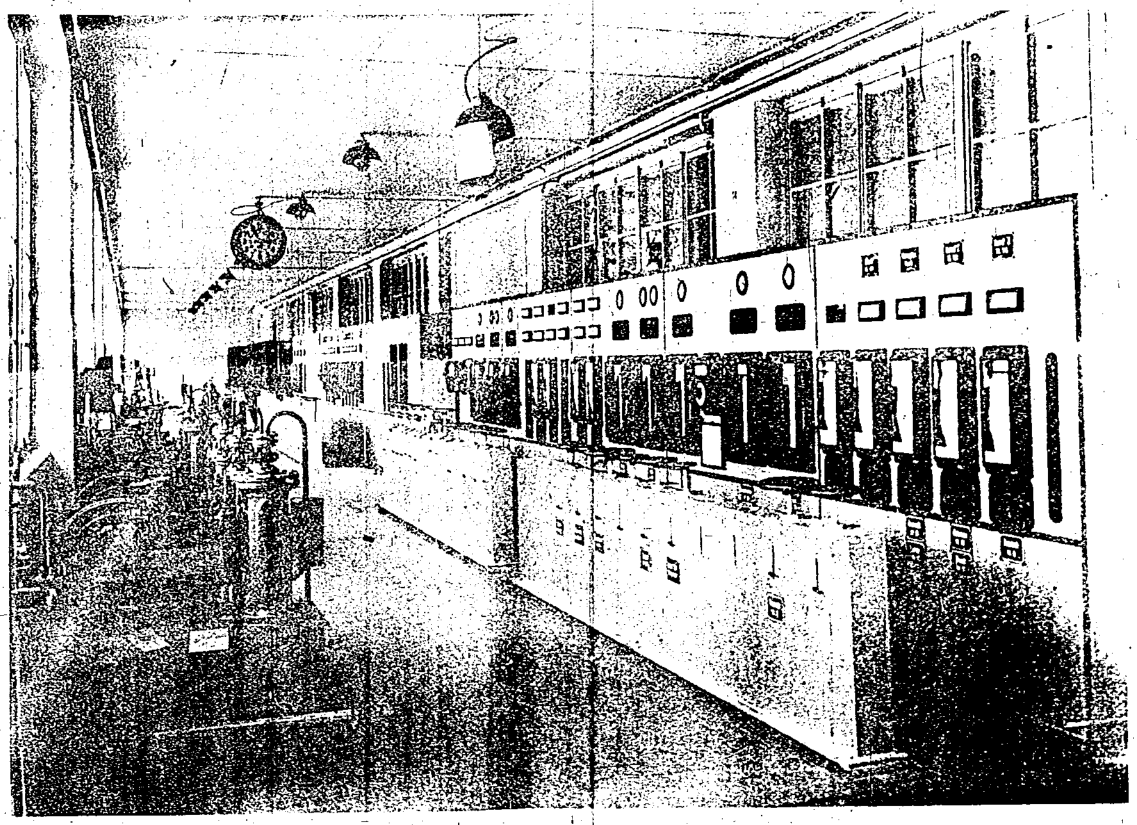
Höchst Acetaldehyde Products Plant



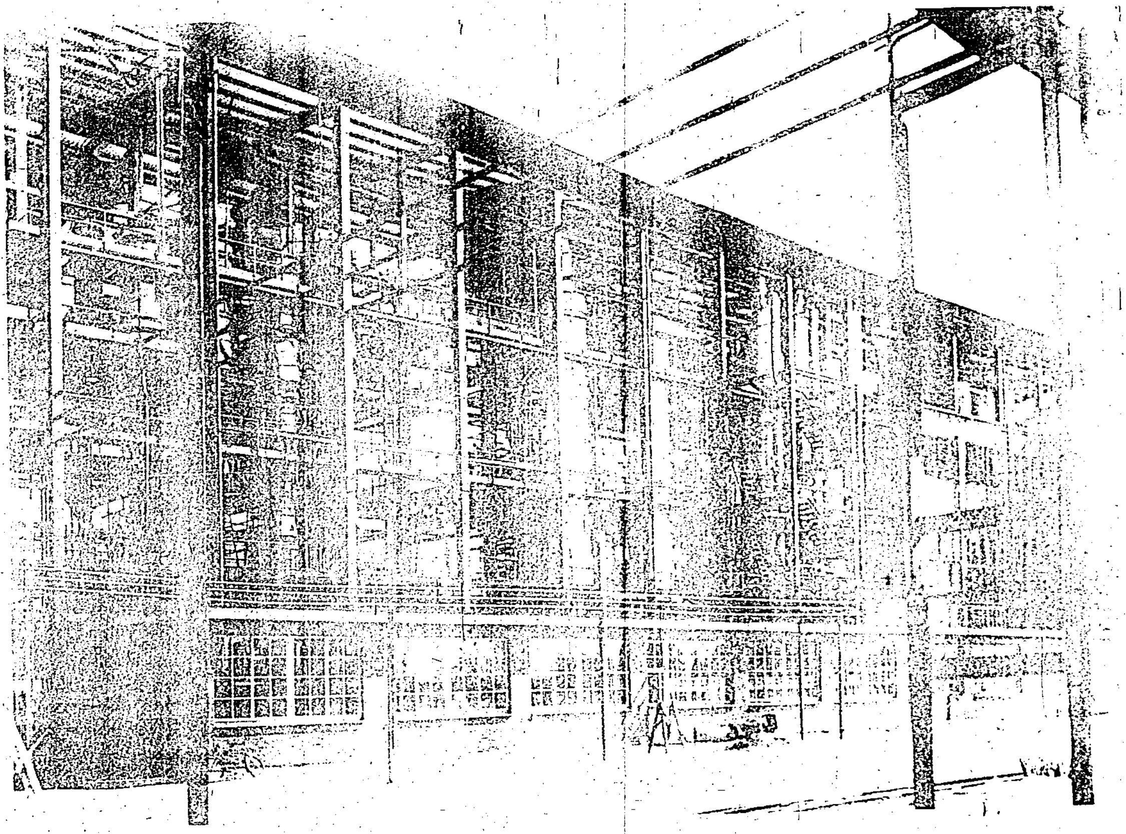
Höchst Acetaldehyde Products Plant



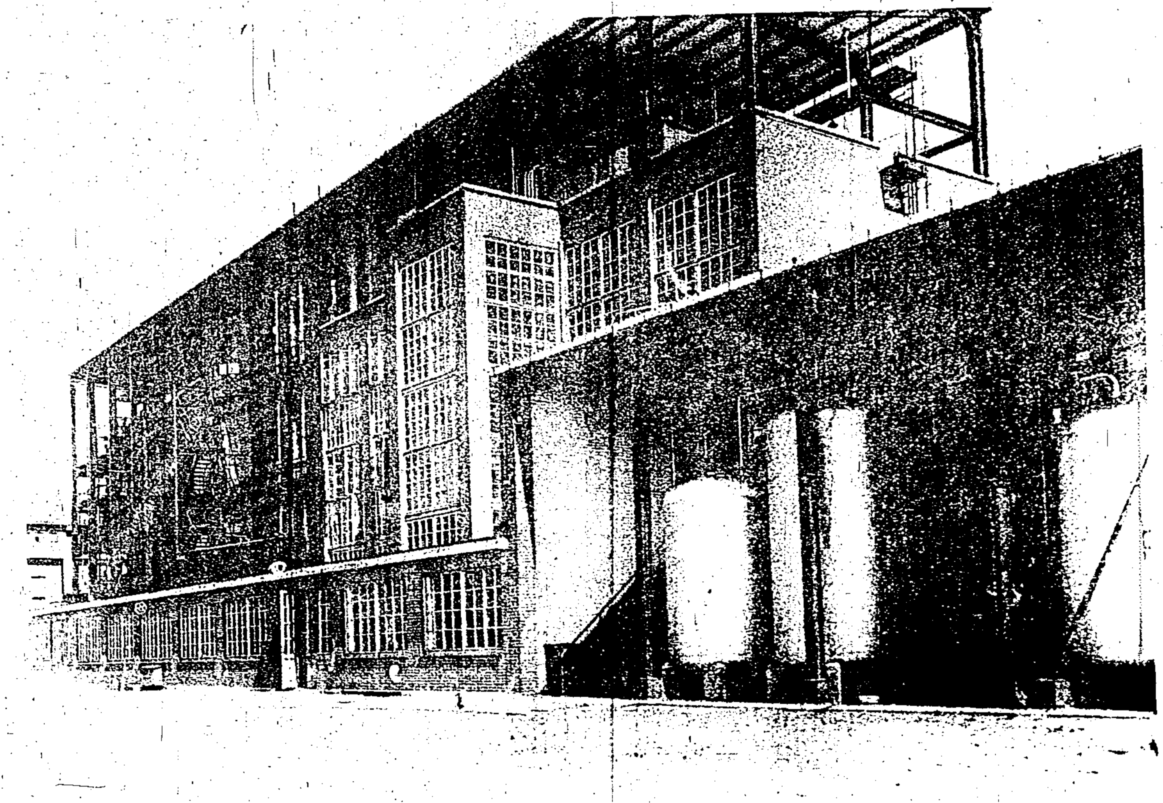
Höchst Acetaldehyde Plant



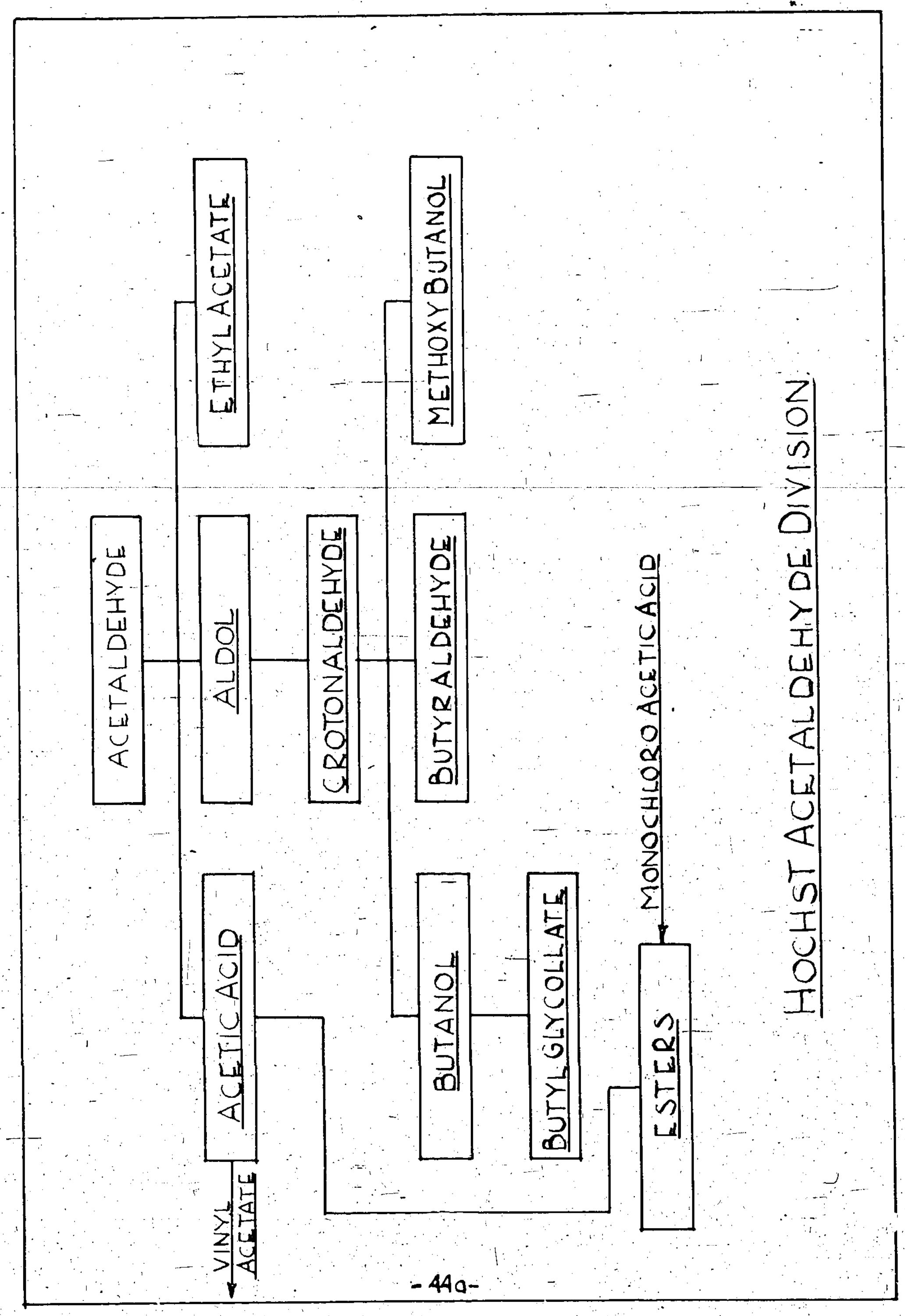
Höchst Acetaldehyde Products Plant



Höchst Acetaldehyde Plant.



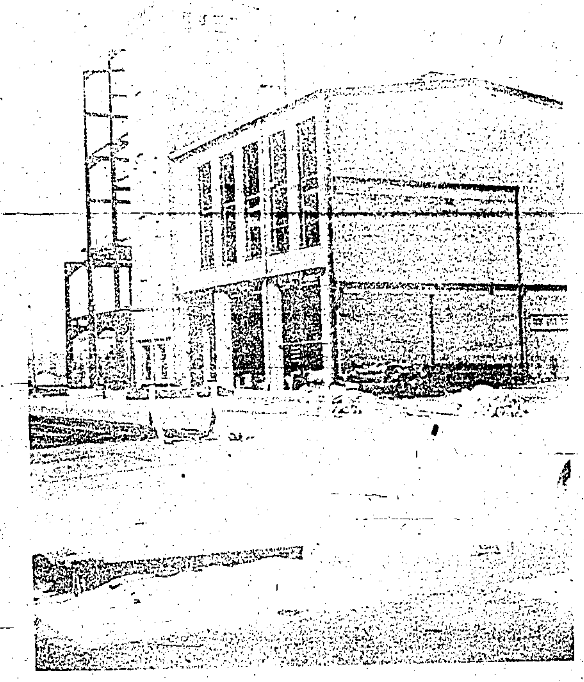
Höchst Acetaldehyde Products Plant.



HOCHST ACETALDEHYDE DIVISION

10. VINYL ACETATE MONOMER.

Höchst prepared vinyl acetate monomer as the basis for their production of polyvinyl acetate, polyvinyl alcohol and the acetals. The vinyl acetate plant was the largest in Germany. Present production capacity was 1,000 tons per month. A new unit, of 1,000 tons per month capacity, was under construction; the building, and a small portion of the equipment had already been installed.



Höchst New Vinyl Acetate Unit

The old Wacker process employing a mercury catalyst in the liquid phase was stated to be still in use in plants in France and Italy. The catalytic vapor phase process used at Höchst was developed originally by Wacker for use in one of their plants and was subsequently expanded and improved by Höchst. A description of the process follows:

Acetylene was generated from calcium carbide in "wet" type units. The resulting gas was purified by scrubbing with 80% sulfuric acid followed by passage over a mixture of potassium bichromate and kieselguhr placed in 2" deep layers on a tray type unit. In vinyl acetate manufacture, it was essential to remove all traces of hydrogen sulfide and phosphine.

A portion of the process for the production of vinyl acetate is illustrated in the attached flow sheet.

Fresh acetylene plus recycled gas was blown through acetic acid maintained at approximately 60°C to yield a vapor containing 23 weight percent acetic acid. The vapors were heat exchanged and then superheated with steam to a temperature of 170°C prior to entering the catalyst unit. The electrically heated oven shown in the sketch had recently been replaced by a high pressure steam heated unit. The converter entrance temperature varied. Initially, with fresh catalyst, operation was at 170°C. This temperature was increased gradually to a maximum of 210°C at the completion of the catalyst life cycle. The converters, further details of which are given later, were charged with 3 to 5mm granules of activated carbon impregnated with zinc acetate solution so as to contain 100 parts of carbon and 15 parts metallic zinc equivalent. No promoters were used. Cadmium, mentioned in the literature, showed no advantages. Traces of copper were particularly harmful since copper tends to produce cuprene. The converter exit gases were heat interchanged, passed through a separator to remove carbon dust and cooled initially with water to 40°C, then to 10°C with cold water and finally to 0°C by the use of brine. The resulting gases in part were bled to waste to remove the inert gases, the balance being reheated and recycled to the system by means of a blower.

The liquid product collected contained approximately 60% vinyl acetate and 40% acetic acid. This mixture was distilled continuously in a series of three columns to obtain:

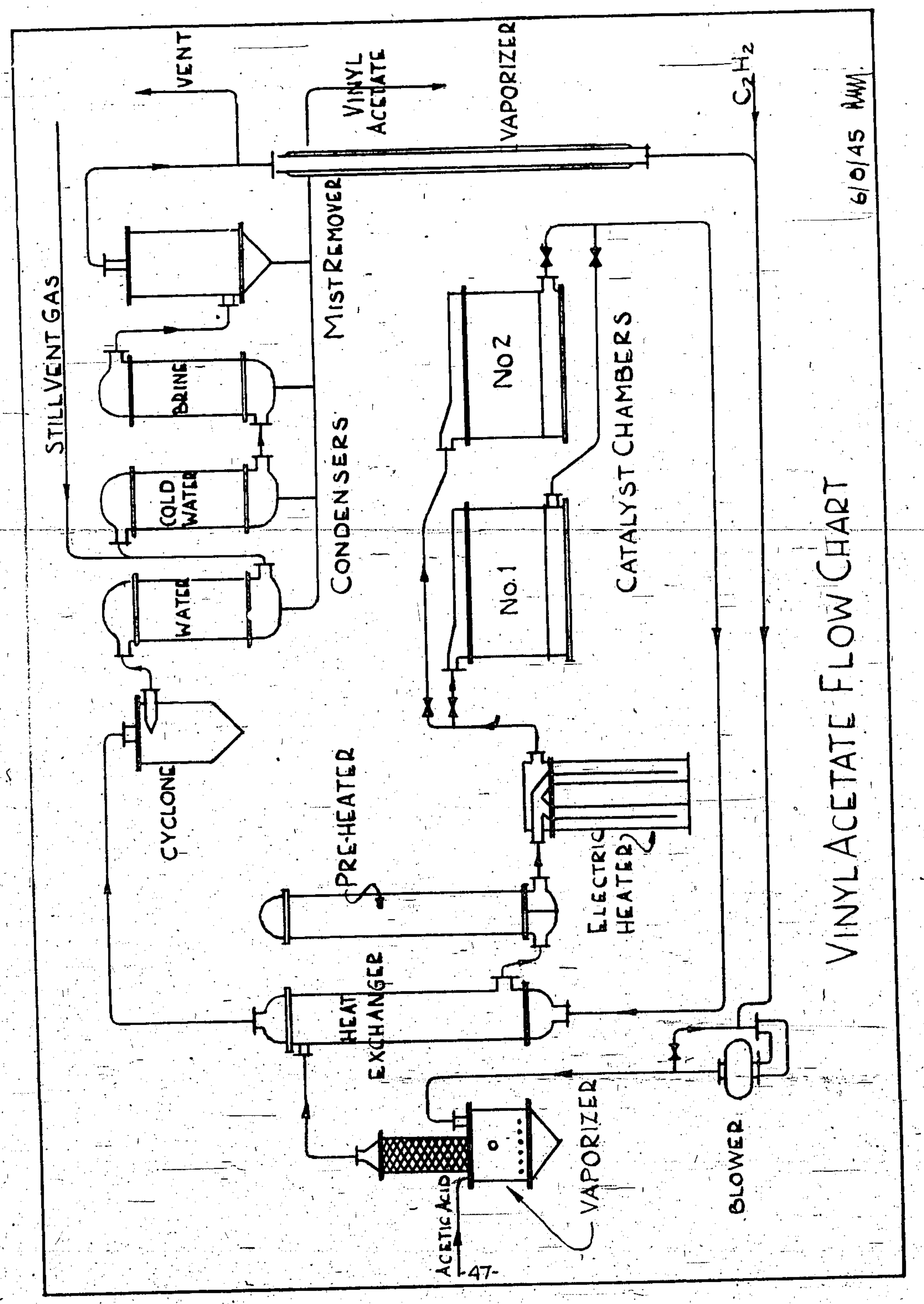
a. A low boiling overhead consisting essentially of acetaldehyde and acetone,

b. The vinyl acetate monomer product, and

c. Acetic acid for recycling.

In these distillation operations thiodiphenylamine was added as a stabiliser to avoid resin formation. The pure vinyl acetate monomer could be stored without the addition of stabilizers.

The yield of vinyl acetate on acetylene was 92 to 95% and on acetic acid 97 to 99%.



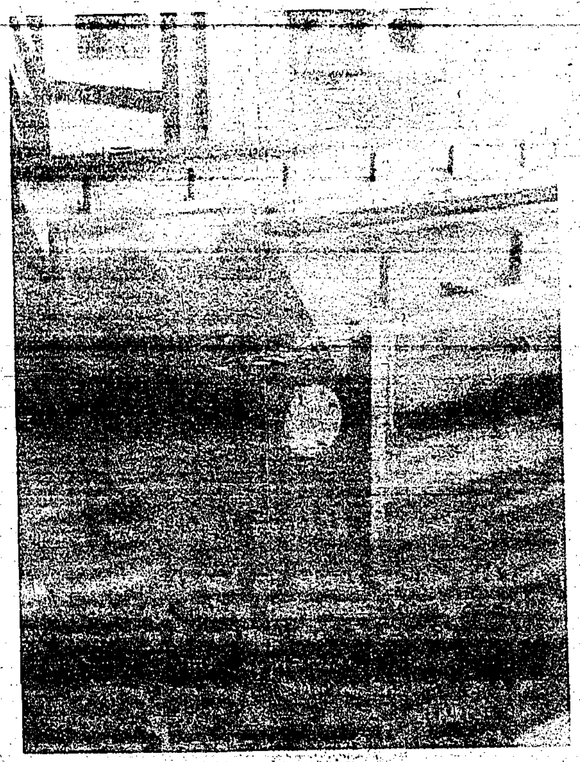
VINYL ACETATE FLOW CHART

6/1/45 RWM

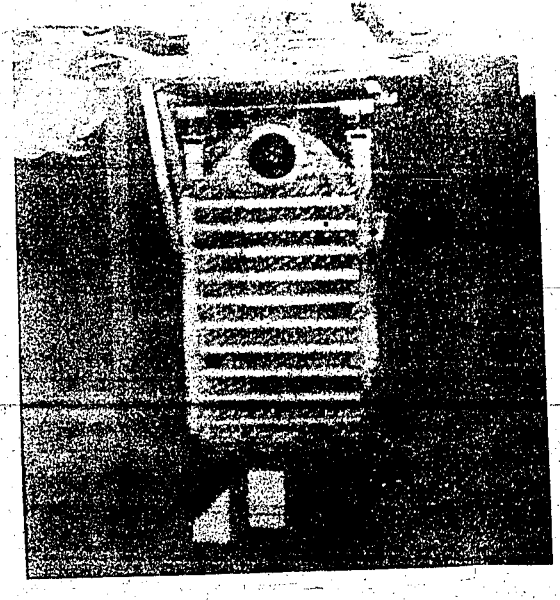
The following additional details were of interest:

The converters consisted of steel units filled with a number of 2" diameter water cooled tubes arranged horizontally. The converter was box-shaped, roughly 6' wide, 10' high and 20' long. Gases entered through a top header, flowed downward through the catalyst bed and entered a lower bottom header. The catalyst was contained between a series of approximately 1/8" thick steel plates set vertically 1" apart. Each converter contained about 490 cu ft of catalyst.

The "on stream time" of a converter was about 2 months, during which time 700 to 900 tons of vinyl acetate were produced at a monthly rate of 400 - 500 tons. At the end of this period the catalyst was removed by blowing it out with a current of air and discarded. In order to provide continuous operations, three converters were piped so that two units in parallel could be "on stream" at any one time. The linear velocity of the gas flowing through the catalyst bed, based on the free space in the catalyst mass, was 2.0' per second. Two views of converters under construction are shown below:



Höchst Vinyl Acetate Converter Under Construction



Höchst Vinyl Acetate Converter Under Construction

The original converter unit developed by Wacker employed a solid bed of catalyst with no means for internal cooling. This was found impractical not only because of the low conversion (below 20%) and short catalyst life but because of fusion of the catalyst. Fusion likely resulted from the exothermic decomposition of C_2H_2 which was appreciable above 220°C.

The conversion could be varied from as low as 20% vinyl acetate used in initial operations to as high as 90% or even 98% in laboratory tests. Catalyst life and yield decreased as conversion increased, hence the best economic balance appeared to be at 60%. Increasing the gas velocity or decreasing the temperature lowers the conversion.

The materials of construction of the plant were as follows

Heat exchangers and preheaters	steel
Converters	steel
Condensers	stainless steel (V4A)
Recycled Blower	steel
Still	stainless steel (V4A)
Boiler	" " "

Aluminum rather than stainless steel was used originally in the vinyl acetate plant, but it showed a life of only 10 to 18 months. It was found that while aluminum was suitable for pure acetic acid, or pure acetic anhydride the presence of as little as 1 to 2% of acetic acid in anhydride or of anhydride in acetic acid, increased the corrosion rate markedly.

11. POLYMERS FROM VINYL ACETATE.

a. Introduction.

Vinyl acetate monomer was the basis for a large production of polymer products at Höchst, specifically, polyvinyl acetate, polyvinyl alcohol, and the acetals. This section of the report deals only with the preparation of the polymers. Data on the industrial uses of the polymers are given below. The attached chart shows schematically the products manufactured.

b. Polyvinyl acetate - Solids.

(1) Introduction.

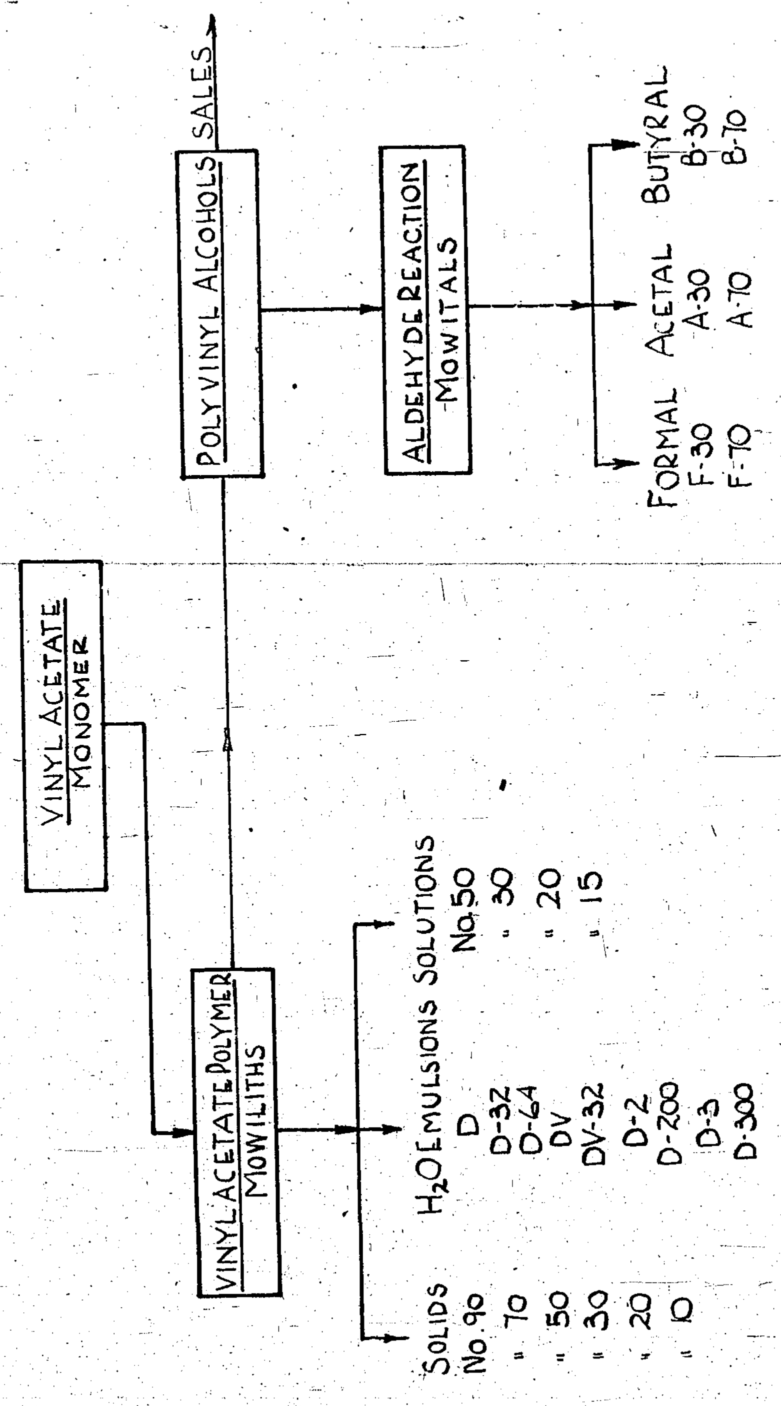
A series of solid polyvinyl acetates (Mowilith) were made differing in molecular weight as shown in the following table:

Mowilith No.	Apparent mol. weight
20	3,500
30	7,500
50	40,000
70	50,000
90	70,000

The above molecular weights were based on the old Staudinger method. Because of the wide difference in the viscosity of the products, their methods of manufacture differed.

(2) Mowilith 20.

Mowilith 20 was polymerized in an enameled kettle fitted with a conventional stirrer. Accessory equipment consisted of a



HÖCHST POLYMERS FROM VINYL ACETATE

6-9-35 Wm.

reflux condenser, measuring tanks and piping, all of aluminum construction. Vinyl acetate plus a small amount of benzoyl peroxide catalyst and acetaldehyde regulator was charged to the reactor using about 10% of the total batch. The mixture was stirred and heated slowly. As soon as polymerization began, the balance of the vinyl acetate (90%) mixed with the regulator and catalyst was added slowly. After about 15 hours, the polymerization was finished. Finally the batch was heated to about 100°C and placed under slight vacuum in order to draw off the excess monomer (1 to 3%). The polymer was drained hot to the final shipping containers.

(3) Mowilith 30.

Mowilith 30, being quite viscous, could not be made in mass in a kettle. Instead, a unit of special design was employed. This unit consisted of a stainless steel tank, roughly 2' in diameter by 10' high enclosed in a second vessel so as to leave an annular space about 4" wide between the two vessels. The inner vessel was equipped for cooling. The outer vessel was fitted around the outer circumference with a series of 5 annular rings equipped either for steam heating or for cooling. Vinyl acetate was charged to the annular space and polymerised therein. A reflux condenser was also attached to this chamber to permit removal of heat through refluxing of the monomer. The working capacity was 1,000 pounds, which was only 60% of the total available volume since considerable frothing occurred. Vinyl acetate, plus the necessary amount of catalyst and regulator, was pumped into the polymerizing unit. The temperature was regulated to 80°C. As soon as the material in the bottom of the chamber was essentially polymerised, the finished product was drawn from the bottom of the unit at a continuous rate while fresh monomer was fed at the top at a like rate. Reaction time in the polymeriser was 8 hours. The polymer drawn from the bottom was dropped to an endless band approximately 3' wide by 10' long, which permitted air cooling of the polymer. The solid polymer leaving the far end of the band was broken into pieces approximately 1/4" thick by 2" square.

After about 8 to 10 weeks operation, quantities of polymer began to build up on the walls of the vessel, interfering with proper heat exchange and a polymer which shows a turbid solution was produced. Therefore, at the end of this time it was necessary to empty the apparatus, boil out with ethyl acetate and then repeat the polymerization cycle.

The capacity of the unit described was 40 tons per month. Recently the operation had been altered by pre-polymerizing to 20% in a separate vessel before charging to the special polymeriser. In this manner a unit capacity of 50 tons per month could be obtained.

(4) Mowilith 50 - 70 - 90.

These three grades of polymers were made in the same type unit. Initially, the operation was carried out in bulk containers, following the process developed at Ludwigshafen for polystyrene. A cylindrical aluminum container of 220 pounds capacity was lined with paper and charged with the vinyl acetate. The lid of the vessel, to which were attached a reflux condenser and a vertical handle located in the center of the lid, was then put in place. The entire unit was next charged to an oven and heated to induce polymerization. After completion of the polymerization, vacuum was applied to assist in the removal of the excess monomer. Then the unit was dipped into hot water and the lid with the block of polymer adhering to the central handle, was removed. After removal of the paper lining from the outside of the block, it was broken up and the polymer cut to size.

More recently this method had been replaced by a process which produces the polymer in a water suspension as beads of approximately 1mm in diameter. The reactor consisted of an 800 gallon enameled vessel equipped with a stirrer, a heating jacket, and an aluminum reflux condenser.

The vessel was charged with water containing about 0.1% of dispersing agent, a copolymer of equal mols of styrene and maleic anhydride. This solution was then heated to about 60°C and to it was added vinyl acetate monomer containing a small amount of benzoyl peroxide catalyst. The monomer mixture was added slowly as the polymerization progressed; the heat of reaction was removed by refluxing the monomer. After about 2 hours, the polymerization was finished, about $\frac{1}{2}$-1% free monomer remaining. The vessel was then vented to the atmosphere and the contents heated to 90°C so that the excess monomer distilled, leaving a polymer containing about 0.5% unpolymerized vinyl acetate. The batch was then cooled to 0 - 5°C in order to harden the product, charged to a centrifuge, and washed with water at 5°C in order to remove the excess dispersing agent. The amount of emulsified polyvinyl acetate removed in the filtrate was negligible - less than 1% of the total product.

The polyvinyl acetate had been dried in a number of ways:

(a) A continuous multi-tray rotary drier operating somewhat like a Herreshoff type furnace.

(b) On aluminum trays, and

(c) On a belt or sieve type dryer similar to a Proctor and Schwarz type unit.

c. Polyvinyl Acetate Emulsions.

The general scheme for the preparation of all the polyvinyl acetate emulsions listed in the table was the same. In general, it is customary to add the plasticizer prior to polymerization.

The equipment consisted of an 800 gallon enameled vessel with a stirrer, heating jacket, aluminum charge tank, and a reflux condenser. 2,310 pounds of a 5% water solution of polyvinyl alcohol (Grade 50), 2.3 pounds of formic acid and 7.3 pounds of 40% H_2O_2 were charged to the vessel. 330 pounds of vinyl acetate monomer were added and the mixture slowly heated to about 70°C at which temperature polymerization began. As soon as a temperature of 72°C was reached, the additional vinyl acetate monomer was added slowly as the reaction progressed until a total of 2,310 pounds had been charged. The reaction was completed at the end of about two hours. During this time the temperature rose as the monomer was polymerized until at the end of the reaction a temperature of 90 - 93°C was reached, indicating that the reaction was complete. At the end of the reaction, vacuum was applied carefully in order to remove the excess monomer by distillation - 1 - 1½%. Thereafter, the mixture was cooled to 50°C and delivered to a 2,500 gallon storage tank.

Specifications for the finished product were as follows:

Monomer content	0.5% maximum
Acid No.	2.0% maximum
Polymer	48 - 52.0% by weight
Viscosity of the latex at 20°C	varies

As measured on a Höppler viscometer, it ranged from 50 - 500 centipoises. The high viscosity material was used for paints and surface coatings, and the low viscosity material was used for artificial leather materials.

d. Polyvinyl Acetate Solutions.

Polyvinyl acetate, grades 15, 20 and 30, was made in a 60% solution in ethyl acetate. Grade 50 could be made but it was amost too viscous to handle. The equipment consisted of 2 towers, each roughly 200 gallon capacity. The first tower only was equipped with a stirrer. The ethyl acetate solvent was mixed with the required amount of catalyst and the vinyl acetate was mixed with the required amount of acetaldshyde regulator. The required quantitites of each mixture were then pumped into the first tower so that a 70% solution of vinyl acetate was produced. The temperature was maintained at 70-85°C, and the feed rate was controlled so that the product flowing from the bottom of the first tower and entering the bottom of the second tower had a monomer content of about 5%. The finishing reaction occurred in the second tower to deliver a product containing 2% monomer. Total time was 12 to 15 hours. The product leaving the second tower was cut with additional ethyl acetate to yield a 60% polymer solution, which was then filtered through a silk cloth and charged into a finished product container. Occasionally, particularly when producing Mowilith 30, quantities of solid polymer (showing poor solution properties) built on the walls of the vessel and it was necessary to clean the equipment at regular periods.

e. Polyvinyl Alcohol.

Polyvinyl alcohol was made by the hydrolysis of polyvinyl acetate (Grade 70 was usually employed) using either sodium hydroxide or sulfuric acid as a catalyst. Where the polyvinyl alcohol was to be used for emulsions sulfuric acid was employed. For the production of acetals for safety glass, caustic was employed since the use of sulfuric acid tended to produce a brown colored product.

In the acid hydrolysis, 100 mols of polyvinyl acetate were dissolved to form a 15% by weight solution in a mixture of 60% methanol and 40% methyl acetate. The mixture was then treated with 0.5 mols of sulfuric acid. Hydrolysis was carried practically to completion by boiling the mixture at reflux temperature for 24 hours. The mixture was then cooled, centrifuged, washed with methanol, neutralized with dilute sodium carbonate solution, washed and finally vacuum dried to produce polyvinyl alcohol as a very fine powder. Excess solvent was recovered by distillation and returned to the system.

For the production of emulsions, polyvinyl alcohol was mixed with an equal weight of water containing the emulsifying agents. The emulsifying agent most commonly used was polyacrylic acid; 0.2, 0.5 or 1.0% based on the polyvinyl alcohol. The plasticizers most commonly used were tricresyl phosphate and dibutyl phthalate.

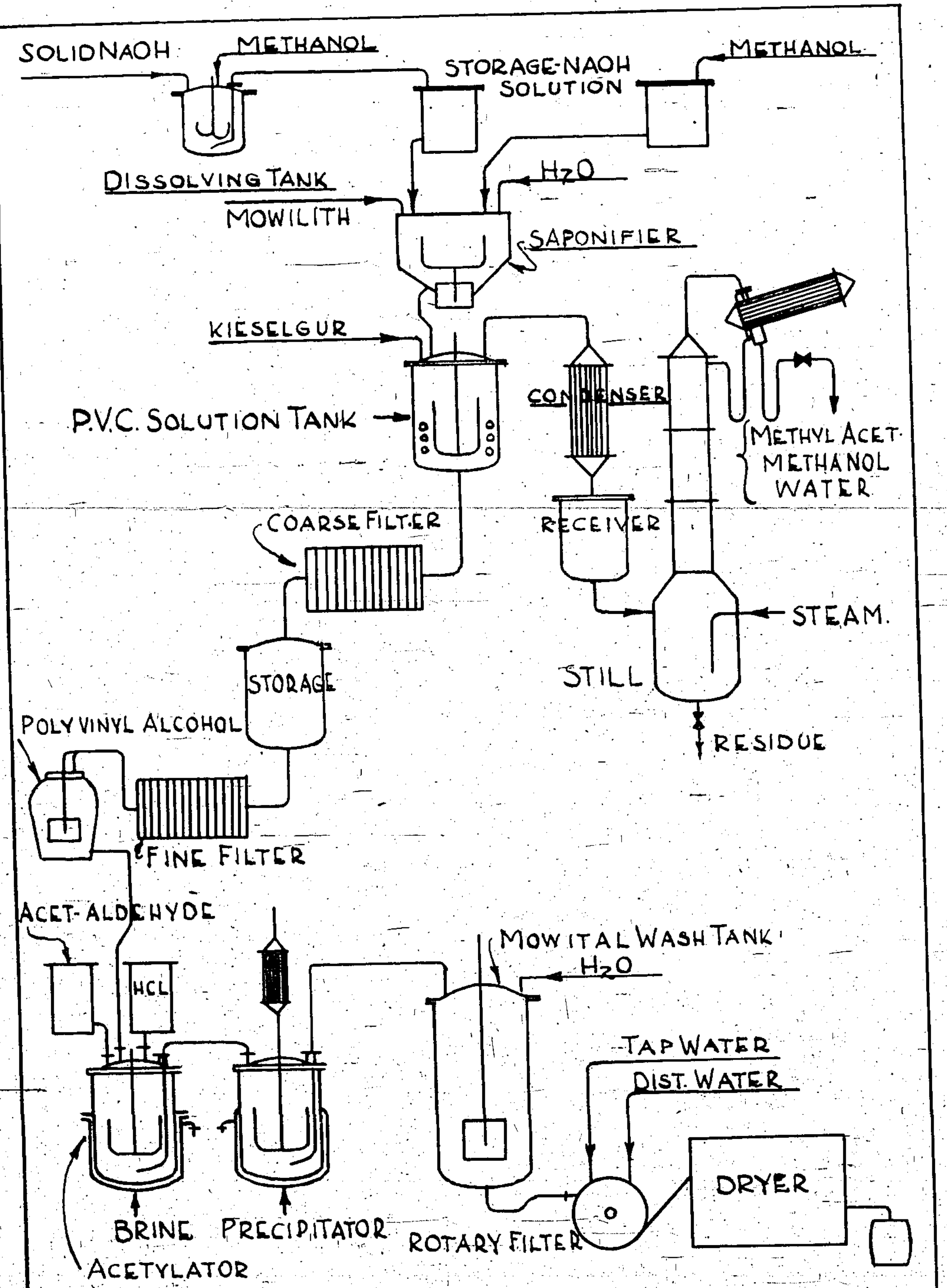
f. Polyvinyl Alcohol and Acetals (Mowitals).

The attached flow chart shows the equipment for the caustic process for polyvinyl alcohol and for the subsequent production of acetals.

Solid caustic was added to methanol to prepare the catalyst solution. 100 mols of polyvinyl acetate were dissolved in the boiling solvent (60% methanol, 40% methyl acetate) to obtain a 40% by weight solution of polyvinyl acetate. 1 to 2 mols of NaOH in methanol are then added. The hydrolysis reaction was carried out by boiling the mixture for 10 to 15 minutes, during which time a practically complete hydrolysis occurs. Because of the viscous nature of the batch, this reaction was carried out in a W-P type mixer made by the Petzold Company of Dresden.

The hydrolyzed batch was mixed with water to form an equivalent 8% polyvinyl alcohol mixture which was then distilled to remove the solvent. Kieselguhr was added to the 8% PVOH solution and the mixture subjected to coarse filtration before storing. Prior to the acetylization reaction the mixture was filtered a second time on a Seitz filter to remove all traces of foreign matter.

To the 8% solution in an acetylization kettle, acetaldehyde was added, 130% of theory, together with a trace of HCl catalyst. The mixture was stirred at 20°C and finally heated to complete the



MOWITAL 070 FLOW CHART

RMM 6-7-45

reaction. It was then cooled and diluted with water. The finished acetal was obtained by filtration on a continuous rotary filter washing first with considerable quantities of "city" water and finally with distilled water.

The dry powder was shipped to Landsberg where the necessary films and sheets for safety glass were prepared. The material had been used for the production of artificial leather but not for the production of raincoats.

g. Miscellaneous.

In general, all the equipment in the polymer plant consisted of glass or stainless steel vessels. Aluminum was widely used for the pipes, measuring tanks, receivers, etc. Höchst claimed that stainless steel would serve equally well for the polymerising unit, glass being used only because of the shortage of stainless material.

Detailed production figures were not obtained. It is worth noting, however, that the capacity for polyvinyl emulsions was 700 tons per month; the capacity for solid polyvinyl acetates, 300 tons per month.

12. COMMERCIAL APPLICATIONS OF VINYL POLYMERS.

a. Introduction.

This information was secured mainly from Dr. Schulz in conference and by examining samples in his laboratory. It should be kept in mind, however, that Höchst were primarily producers of the raw polymers and that the practical applications in general took place in fabricating establishments not directly connected with the I.G. The information obtained, therefore, presents an overall picture of the uses of the polymers but does not include manufacturing details. There were some discrepancies between the information obtained from Dr. Möller and Dr. Schulz who were interviewed separately.

The Höchst plant of the I.G. made polyvinyl acetate, polyvinyl alcohol, and the vinyl acetals of formaldehyde, acetaldehyde and butyraldehyde. They were sold as solids, solutions, or emulsions. In the preceding section of this report a table was given showing the chemical relationships between the various vinyl chemicals made at Höchst. The figures (such as D32, F30, etc.) used in this table will be frequently referred to in this discussion as a means of indicating the raw materials used in each product. These figures (D32) were I.G. "Intraplant" designations. The products were sold to the trade under various trade names.

Polyvinyl alcohol was generally sold as a dry powder and was used for blending in glues, lubricants, and sizes.

Polyvinyl acetates were classed under the name of "Mowiliths". Polyvinyl acetals were known as "Mowitals". Polyvinyl acetates were often used where an acetal would have been technically preferred due to their lower cost.

The vinyl polymers were used for glues, paints, food preserving, safety glass, cloth impregnation, artificial leather, and extruded tubing.

Before discussing these uses individually the following table is presented to indicate more fully the range of polyvinyl acetate emulsions made and used.

Polyvinyl Acetate Water Emulsions

Polymers	Code	Plasticizers
Polyvinylacetate	D	None
	D32	3 dibutylphthalate 2 tricresylphosphate 10 parts polyvinyl acetate
	D64	6 dibutylphthalate 4 tricresylphosphate 10 parts polyvinyl acetate
Polyvinylacetate very finely emulsified	DW	None
	DW32	3 dibutylphthalate 2 tricresylphosphate 10 parts polyvinyl acetate
Vinyl benzoate copolymer added	D2	None
	D200	Plastisized
Vinyl chloride copolymer added	D3	None
	D300	Plasticized

Miscellaneous acrylate mixed emulsions. Crotonic acid (5) plus vinyl acetate (100). Vinyl benzoate and vinyl crotonate plus vinyl acetate. Termed A.B.C.

Note: All emulsions contained about fifty parts water to fifty parts of polymers. Tricresylphosphate was scarce or it would have been more liberally used. These emulsions were opaque white, with a stiff whipped-cream like appearance. They were very smooth, stable, uniform, not gummy, and yet very adherent.

The solutions of the vinyls were generally made in ethyl acetate.

b. Glues.

The polyvinyl materials of various molecular weights, etc, were sold direct to furniture manufacturers, etc, who blended them to suit. D was a very popular material. 50 was also very popular and was generally sold as the solid and put into solution by the manufacturer. For normal work, these glues were stated to be much more convenient than phenol or urea glues since heating and frequent mixing were not required. They were not suitable for aircraft use. For this use Dr. Schulz preferred phenol-formaldehyde, placing it superior even to urea stating that in his experience it was less affected by water.

c. Paints.

Two general types were made. There were organic solvent paints and water emulsion type paints. The organic solvent types made use of polyvinyl acetates 50, 30, and 20 but mostly 50 and 30. They were used as cellulose lacquer extenders and opacifiers. F30 and B30 aldehydes were also used to add elasticity. F30 was used with phenol formaldehyde to insulate wire (formex equivalent presumably). B30 was used to coat cans. They made one paint called ABC. The A stood for vinyl acetate, the B for vinyl benzoate, and the C for vinyl crotonate. B was said to add water resistance. The "Mowitals" gave added elasticity but were considered to be poor in water resistance, hence they were rarely used alone.

Water emulsion type paints generally were based on D32. $CaCO_3$, talc, $ZnSO_4$, Fe_2O_3, carbon black, and other pigments were used in these paints. Adding D to D32 hardened the paint. DW added penetrating powers. D200 was the most resistant to water and was used in outside paint formulae. Many German box cars were painted with D200 base water emulsion paints. These had stood up well in service. Light colors were found impractical for outside paints but were very practical for inside paints. It was stated that light colors would have soon been available for outside paints if research had not been stopped by the invasion.

d. Food Preserving.

The basic idea was to coat foodstuffs with a polyvinyl acetate layer. The "Mowilith" used was D32. Various proportions of chalk, talc, and lithopone were added and the coated article had more or less the appearance of a plaster cast. Bread in particular was preserved by this coating as a war measure. Properly treated bread showed only a slight interior mold growth after eight months. Fresh bread was dipped immediately in the vinyl emulsion. The coating was dried and the bread was re-dipped. The bread was then sterilized by heating to 140°C for one-half hour. The temperature in the center during this treatment probably only reached 70°C. Dr. Schulz felt that if the 140°C had been uniform to include the center that the first mold growth (center) would have been even further postponed.

Cheese was preserved by dipping in "Mowilith" emulsions. If the cheese was of a fully fermented type a polyvinyl chloride copolymer water emulsion with a little plasticizer (D3) was used. If the cheese was of an only partially fermented type, "Mowilith" D32 was used. The partially fermented types were presumed to give off water during storage much the same as the bread and to require the same coating.

Sausages were preserved, but only in the laboratory. It was stated that not much raw material was available for these experiments.

e. Safety Glass.

A70 was used with sixty parts of triglycoldiisobutyl ester plasticizer. Polyvinyl butyraldehyde was not used as they did not know how to make it so that it would not discolor. They had less trouble with discoloration with polyvinyl acetaldehyde. The raw material was sold direct to companies at Wolfen and Landsberg who dissolved it in a benzol-methanol mixture and sheeted it on a nickel steel plate, stripped it off, and dusted it with sodium carbonate for storage. These firms sold the material in turn again to the actual laminator. The washing off of the carbonate and the laminating did not involve novel procedures. No spray or glue was used to promote a bond. Edge separation in service was apparently bad and bitumen edge paints were used. Dr. Möller claims that alkali (rapid) saponification of the polyvinyl acetate to polyvinyl alcohol prevented discoloration and that acid (slow) saponification during manufacture resulted in a material that discolored. Dr. Schulz said that acid saponification was satisfactory if all the acid was removed, and that it must be if polymerization was not to go too far. Dr. Schulz frankly admitted lack of knowledge about discoloring and would not credit Dr. Möller with knowing. Dr. Schulz was sure no special material was made for bullet resisting panzerglas. A five layer, symmetrically constructed, 5.5cm thick panel was tested with two shots from a U.S. 30 caliber carbine at twenty yards. Both shots were well stopped. The plastic sheets looked very thin. They were stated to be successfully made 0.5mm thick with unsuccessful attempts to make them 0.3mm. It was concluded that safety glass construction in Germany was not superior to that used by Allied manufacturers.

f. Cloth Impregnation.

This provided an outlet for a fair amount of polyvinyl acetate. The products used were similar to those used for the making of artificial leather of the fabric base types. (See next section). If the coating was translucent to any extent and permitted the fabric to be seen, the product was denoted as an impregnated cloth and came under Dr. Guteman's supervision. If the film was sufficiently opaque to obscure the fabric base, the product was considered to be a leather and remained under Dr. Schulz.

g. Artificial Leather.

Höchst sold vinyls for the fabrication of three types of artificial leather. Each type was developed for a specific class of goods so no comparison as to the serviceablility of the various types could be drawn.

One type was a resinous coating on a textile base suitable for making raincoats and also for the uppers of ladies and childrens shoes. The Germans had no substitute for men's upper shoe leather. A textile base was coated first with an adhesive layer of "Mowilith 50" in solution. Five or more layers were overlaid on this initial tacky layer. These overlayers were composed of methacrylate ester 90% and Mowilith 10% plus pigments and plasticizers as desired. A final layer of clear methacrylate resin (hard resin containing no Mowilith) left a hard glossy non-sticky finish. This type was also made by using D32 water emulsions of Mowilith. The water emulsions were less expensive to make chemically but the drying of each successive film was very slow and required quite a bit of heat. The methacrylate esters came from Ludwigshafen.

The second type of artificial leather (Faserleder - fibrous leather) was a substitute for sole leather. It was made from ground up leather scrap. This scrap was mixed with D32 and beaten in a paper mill beater for ten minutes. This was then precipitated with $Al_2(SO_4)_3$ while beating for a further thirty minutes. Some wood fiber was sometimes added but cotton fibers were not. It was found that the nature of the precipitate varied with the type of tanning of the original scrap leather. Naphthalene, formaldehyde, sulfates, and tannic acid were sometimes added in small amounts. The mixture was turned out on a screen and pressed very slowly to remove the retained moisture. When nearly dry the temperature was increased very slowly to 60 to 70°C and an overnight cure made. The heat was required to melt the Mowilith but not to hurt the leather scrap.

The third type of artificial leather (Fliesleder - fleece leather) was intended to compete with the second type but was not successful for any purpose. DW and DW32 were used to penetrate into cotton and blotting paper scrap. The mixture was then treated like the second type.

None of the actual fabrication took place at Höchst. Various leather goods manufacturers throughout the country made their own brands and had their own formulae.

A partial list of such firms follows:

Faserloder

Freudenberg	at	Weinheim
Salamander	"	Turkheim
Moeller	"	Bopfingen

Fliesleder

Kotitzenlederbachwerks	at	Kotitz
Carl Lissmann	"	Munich

h. Extruded Tubing.

Dr. Schulz had several very presentable samples in his laboratory but stated that they had not as yet had much success in extruding the vinyls.

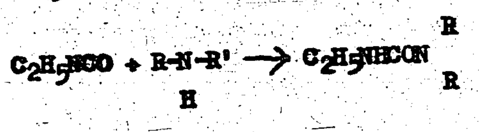
13. POLYURETHANE.

a. Introduction.

The "Polyurethanes" were also known by the name of "Superpolyamides" and also (debatably) as "Nylons". It was known to the investigators that the polyurethanes would be the subject of several investigations and that the main source of information would likely be the Leverkusen plant of I.G. Farbenindustrie A.G. where Dr. O. Bayer developed these compounds. Accordingly no attempt was made to study this subject exhaustively. The following information, however, was considered to merit reporting since it might add some details to the phases studied by other groups. Information was obtained from discussions with Dr. Lange and from papers written by Dr. Bayer which were provided by Dr. Lange. These papers date from 1941 to 1943.

I.G. Farbenindustrie immediately realized the importance of the American development of Nylon. They wanted to have an equally good or better product. Dr. Bayer of the I.G. at Leverkusen began the task of developing Nylon-like substances and examined the reactions between isocyanates, diisocyanates, diamines, secondary amines, alcohols, and glycols. The simplest of these reactions were:

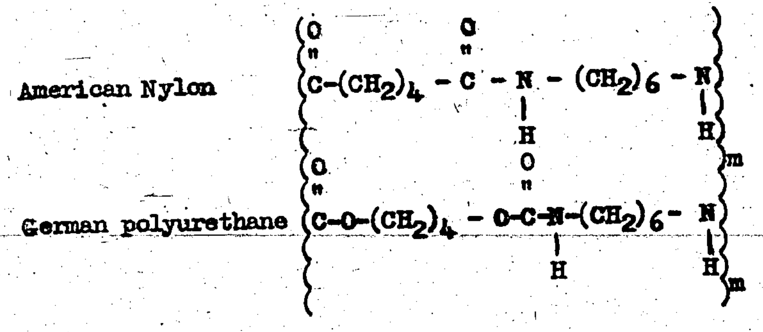
$$C_2H_5NCO + C_2H_5OH \rightarrow C_2H_5NHCOOC_2H_5$$



$$C_2H_5NCO + R-\underset{H}{N}-R' \rightarrow C_2H_5NHCON\genfrac{}{}{0pt}{}{R}{R}$$

Longer chains were tried, particularly long chain aliphatic diamines and long chain diisocyanates. The products were resinous but hydrophylic and therefore useless for Nylon like bristle material where hydrophobic qualities were desired.

The I.G. ambition or desire for a Nylon substitute finally crystallized on the reaction products of straight chain diisocyanates and glycols for the first commercial exploitation. Later more complex structures were also used. The basic diisocyanate and diol reacting groups were generally retained. The analogy to the simplest American Nylon reactions between diamines (substitute diisocyanates) and diacids (substitute diols) is very close. The final products would appear to differ in basic chain structure as follows:



American Nylon $\left\{ \overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}} \right\}_m$

German polyurethane $\left\{ \overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}} \right\}_m$

In conversation the Germans referred to their product often as Nylon but in writing they always used the terms polyurethane or superpolyamide.

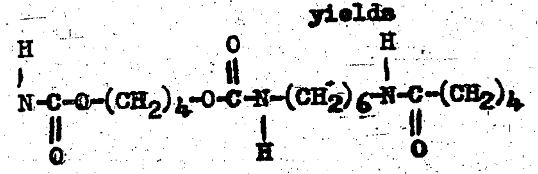
The first part of this section on polyurethane is devoted to notes from a report dated 1941; the second part to a report dated 1943.

b. Data from 1941 Report.

Technically the easiest superpolyamide polymer to make was the polyurethane from 1, 6, hexanediisocyanate and 1, 4, butylene glycol. The NCO and OH groups reacted progressively to form a long chain,

$$-N=C=O + HO-(CH_2)_4-OH + O=C=N-(CH_2)_6-N=C=O=HO(CH_2)_4$$

yields



$$\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_4$$

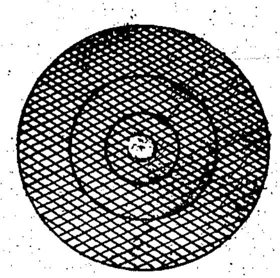
This simple polyurethane proved very useful for the preparation of artificial silk and artificial bristles.

It was prepared by the addition of one mol of 1,6, hexane diisocyanate and one mol of 1,4, butyleneglycol in a solvent such as monochlorobenzene. The heat of polymerization is fifty-two calories per mol. After one hour polymerization, almost quantitative yield was obtained. The chain length could be altered by using other solvents such as dichlorobenzene. Quite a number of specific products were given code names such as "Igamid". The following table lists some physical properties for three "Igamids".

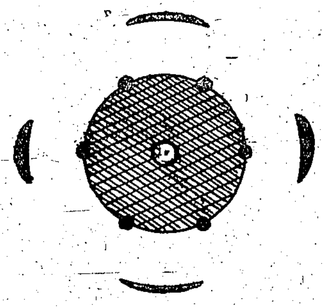
	Igamid U	Igamid A	Igamid B
Specific gravity..................	1.21	1.41	1.15
Melting point, °C..................	183	255	210
Injection molded Material			
Brinnell..........................	750	1,000	600
Impact............................	100	100+	
Compression molded material			
Tensile strength, kilograms/cm²..	620	cannot mold	380
Cold test (no details)..........	+8		+13
Oriented material			
Tensile, as above................	1,874		1,050
Cold test.........................	-30		-30

The tensile strength of the drawn fibers was very good. 7.5 grams per denier compared well with the normal value of 3.5 for natural silk. The water absorption of Igamid U was 0.5% after being immersed for ten days at 20°C. The water absorption after immersion for ten days at 80°C was only 2.4%. Igamid U was fairly resistant to HCl. The Igamids dyed as well as acetates and in this respect were said to be superior to the American product.

The X-ray diagram of 400% stretched material showed good orientation.

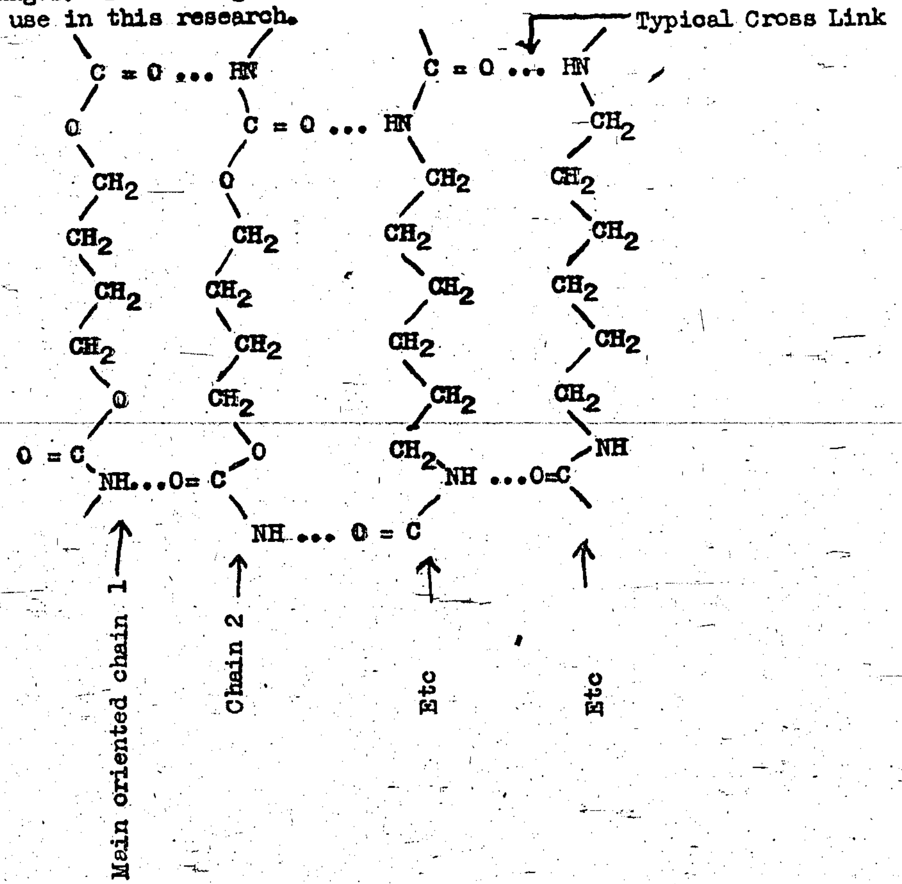


Unstretched



Stretched

A diagramatical formula for the complex polymer had been worked out. The diagram given below shows principal oriented chains with weak cross linkages. This diagram shows only two dimensions whereas the polymer structure actually existed in three. The unoriented material consisted of twisted chains with irregular or absent cross linkages. These diagrams were extensively developed and models made for use in this research.



In the following table the melting points of several polyurethanes are shown related to the number of carbon atoms in the diisocyanates and glycols used to prepare them.

Diisocyanate	Glycols	Polyurethane Melt. Pt.
4 carbons	4 carbons	193°C
4	6	180
4	10	171
6	3	167
6	5	153
6	9	147
12	12	128

Polyurethane (Perlon U) from 1,4, butanediisocyanate and 1,4, butyleneglycol was made like Igamid U. It was cheaper since 1,4, diaminobutane could be made from C_2H_2 and HCN independent of phenol. Polyurethane was soluble in 90 parts of phenol and 10 parts of water and is insoluble in all other common solvents except carbon tetrachloride. It could be plasticized for use as a molding powder with ten mol percent of butylene glycol.

For making a leather substitute a mixed polymer Igamid UL was used. It was prepared from;

1/2 mol 1,4, diisocyanate
1/2 mol 1,6, diisocyanate
0.8 mol 1,4, butyleneglycol
0.2 mol methylhexanediol

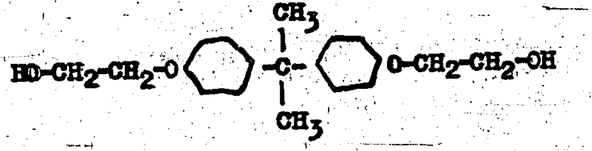
This was a soft material, soluble in a chloroform ethanol solution.

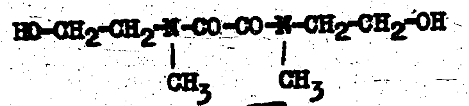
Because of its elastic properties a mixture of;

1 mol 1,6, diisocyanate
1/2 mol 1,4, butyleneglycol
1/2 mol 2,2 dimethyl 1,3 propanediol

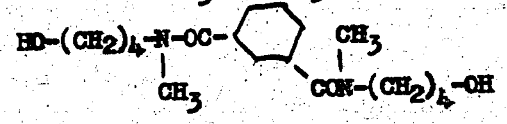
was especially good for impregnation.

Other glycols useful in syntheses were;





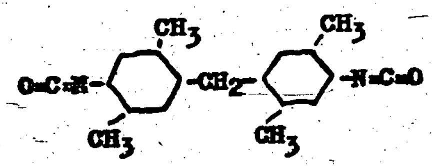
$HO{-}CH_2{-}CH_2{-}\underset{CH_3}{\underset{|}{N}}{-}CO{-}CO{-}\underset{CH_3}{\underset{|}{N}}{-}CH_2{-}CH_2{-}OH$



If molecules with more than two reactive hydrogen atoms were used a three dimensional polymer was obtained, for example, by using glycerine, acetyl cellulose, or polyvinyl alcohol.

Other diisocyanates useful in syntheses were;

1, chlorophenyl 2,4, diisocyanate
1,6 hexanediisocyanate



1,4, butylene glycol was made from formaldehyde and acetylene.

Methylhexanediol was made by hydrogenation of the ester of crude methyl adipate such as resulted at Leuna from the oxidation of cyclohexanol-methylhexanol mixture.

2,2 Dimethyl 1,3, propanediol was made by reacting isobutyraldehyde and formaldehyde followed by hydrogenation.

Usually diisocyanates were made from aliphatic or aromatic diamines by the following type reaction:

$$COCl_2 + H_2N{-}R{-}NH_2 + COCl_2 \longrightarrow OCN{-}R{-}NCO + 4HCl$$

The yield of pure diisocyanate in a dichlorobenzene suspension was said to be 80% of theory.

The preparation of the diamines required in the type reaction shown above was illustrated by the preparation of 1,4, diaminobutane from acetylene,

$$HCN + C_2H_2 \longrightarrow CH = CHCN$$

This took place in the presence of copper chloride catalyst. In the presence of alkaline catalysts another mol of HCN was added giving;

$$NC{-}CH_2{-}CH_2{-}CN$$

On gentle hydrogenation the diamine was formed;

$$H_2N{-}(CH_2)_4{-}NH_2$$

1,6, hexamethylenediamine was formed by the hydrogenation of adiponitrile.

c. Data from 1943 Report.

In 1941 the basic polyurethane (Igamid) reaction between 1,6, hexanediisocyanate and 1,4, butyleneglycol was conducted in monochlorobenzene. In 1943 it was reported that a new method not involving monochlorobenzene had been in use for several months at Dormagen and was reported to have been better. In this reaction the 1,4, butyleneglycol was charged to a kettle and the 1,6, hexanediisocyanate was slowly added. Atmospheric oxygen was prevented from coming on contact with the reaction mixture.

Another Igamid denoted as Igamid UM was stated to contain ten percent of methyl 1,6, hexanediol.

There were references to the use of polyurethanes in electrical equipment for war purposes and it was also spoken of as a silk substitute.

Igamid UL was still spoken of as the polyurethane most suitable as a leather substitute but its chemical constitution had evidently been slightly changed. It was now given as;

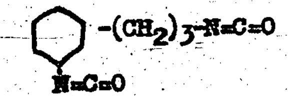
1/2 mol 1,4, butyleneglycol
1/2 mol methyladipol
1 mol hexanediisocyanate

This was made by charging the mixed glycols to a kneading machine. The diisocyanate was then slowly added to obtain a product with a "K-Wert" of about 100.

Igamid ULW 15 and ULW 25 indicate the addition of 15 to 25% softening agents (Dillatol).

For films and foils Igamid UF was reported suitable but it was stated that its handling must be studied. It was a mixed polyurethane made from:

0.8 mol hexanediisocyanate
0.2 mol



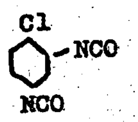
0.5 mol 1,4, butyleneglycol
0.5 mol methyl 1,6, hexanediol

The method of preparation of 1,6, hexanediisocyanate from the diamine intermediate had evidently been improved by the addition of a carbon dioxide stage. This process was called the "carbamic process" and at least 15 tons were produced by this method. A solution of hexamethylene diamine was placed in a lead lined kettle and carbon dioxide led in. At 90°C a jelly like mass was formed.

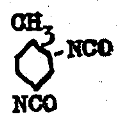
This was transferred to a second vessel and cooled to 0°C with brine. Two mols of $COCl_2$ were then lead in. Carbon dioxide was generated. The mass was then heated to 150°C in a third kettle and $COCl_2$ slowly added. HCl was evolved and diisocyanate was formed. The reaction was complete in 20 hours. The 1,6, hexanediisocyanate was pumped off and distilled. The yield was 88% in the laboratory and 70% in the plant. With experience they hoped to make it 85%. Five to seven percent was 1-chloro 6-hexyl isocyanate. The $COCl_2$ used was 130% of theory.

The following polyisocyanates were developed and used in the later stages of the superpolyamide projects and it was believed the term Desmodur was used in the code designations for superpolyamides made from these molecules. Various Desmodur types are shown below:

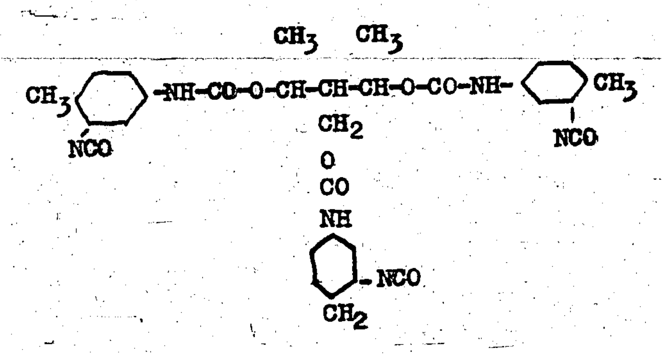
Type C



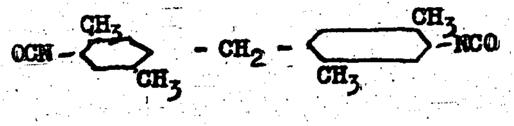
Type I



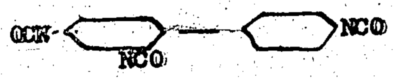
Type TH



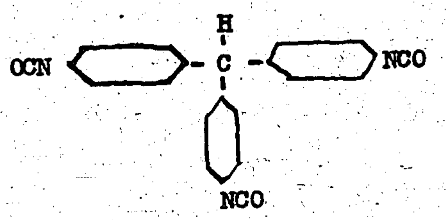
Type X



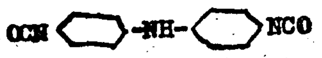
Type DR



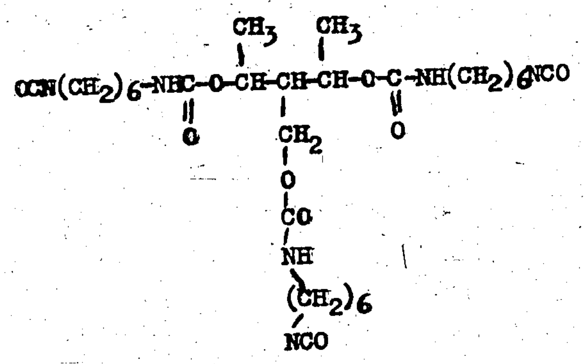
Type R



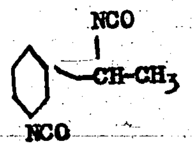
Type M



Type HH



Type A



In the later stages of this research, variations on the diol side of the diisocyanate-diol superpolyamide reaction were also tried. These complex diols were in general polyesters based on the reactions of adipic acid with diols and triols. As a class they were, therefore, moderately well known polymers themselves. The name Desmophen was used in designating these polymers.

Desmophen 900's were made from 3 mols of adipic acid and 4 mols of a triol such as glycerol, hexanetriol or trimethylol propane. Desmophen 1200's were polyesters made from 3 mols of adipic acid, 3 mols of 1,4, butyleneglycol and 1 mol of a triol.

A Desmophen polyester with an acid number of 30 was made having a honeylike consistency. This was stirred with diisocyanates, then poured into forms and baked.

The Desmophens were useful in making lacquers. It was possible to vary the drying times at will by the use of the Desmophens. The practical applications were airplane wood lacquers, surface coatings for oil bunkers, acid proofing wood, and impregnating papers. Some of them would withstand water, alcohol, oil, and a mixture of phenol and chlorobenzene.

The Leverkusen plant planned a production of 150 tons per month of polyisocyanates with an additional planned production of 300 tons per month at the Wolfen plant. These plans were not fully consumated but the polymers reached large scale commercial production before the occupation.

14. SYNTHETIC CARBAZOLE.

a. Introduction.

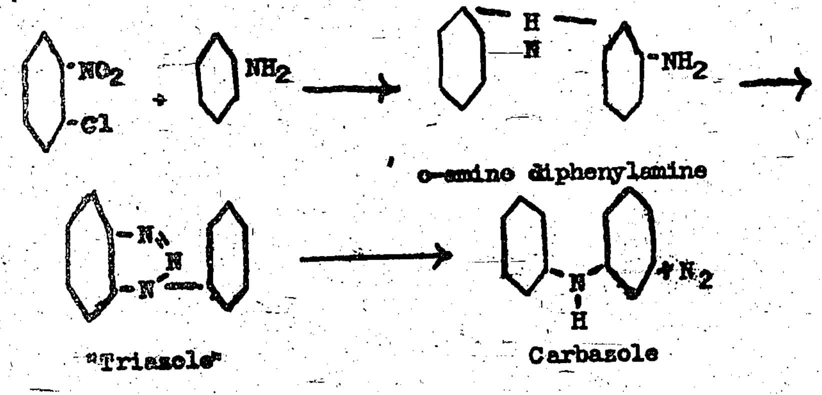
According to Dr. Greune, Höchst's development of dyes and insecticides based upon carbazole prompted their interest in its synthesis since natural supplies, particularly during the war, were restricted. Specifically, carbazole was used for tetra nitro carbazole, a new insecticide and for such dyes as Hydron Blue.

In Germany natural carbazole was recovered from anthracene oil which was available at a rate of 50,000 tons per year. The anthracene oil averaged only 10% carbazole, the content being dependent upon the nitrogen content of the coal used in coking. Some anthracene oils might contain as much as 25% carbazole. A further difficulty during the war was the fact that carbon black, which was badly needed for rubber, was made from anthracene oil. The normal price of natural carbazole was 60 pfennigs per kilo.

b. Synthetic Carbazole Syntheses.

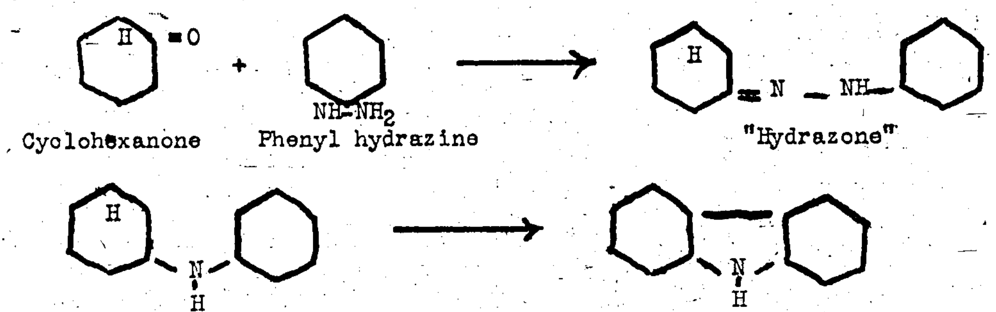
Höchst's work on the synthesis of carbazole, as explained by Dr. Greune, was carried out along the following lines:

(1)

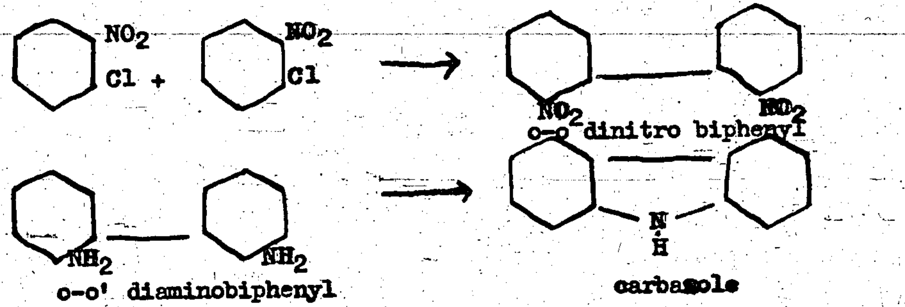


Ortho-nitrochlorobenzene was condensed with aniline to yield o-amino diphenylamine. This was diazotised in methanol solution to the triazole which on heating to 350°C yielded nitrogen plus carbazole.

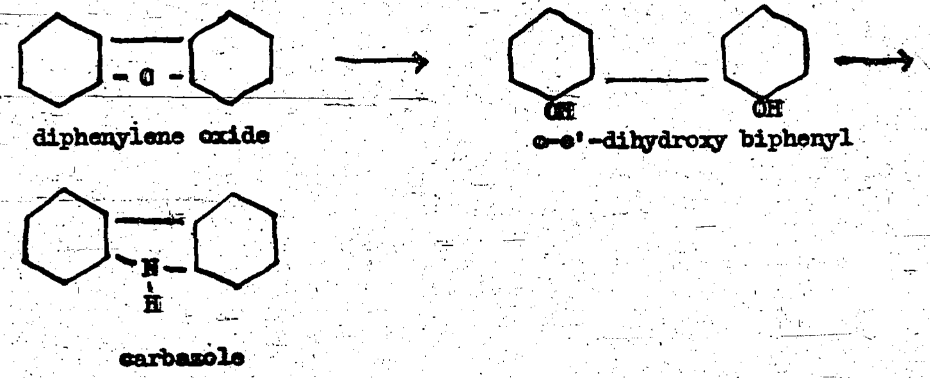
(2) A synthesis developed by Prof. Bücherer involved the reaction of cyclohexanone with phenyl hydrazine to form hydrazone, which on heating with boiling 20% sulfuric acid yielded tetrahydro carbazole. The latter compound was heated in naphthalene solution in the presence of nickel at 150°C to yield carbazole.



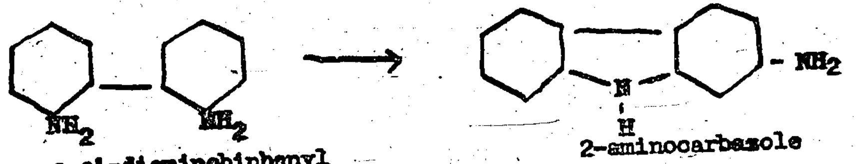
(3) The Tauber synthesis consisted first in the reaction of two mols of o-nitrochlorobenzene in the presence of metallic copper powder to yield o,o'-dinitrobiphenyl. This was reduced, with nickel in alcohol solution, to the corresponding diamine. The diamine on heating with 63% phosphoric acid gave practically quantitative yields of carbazole.



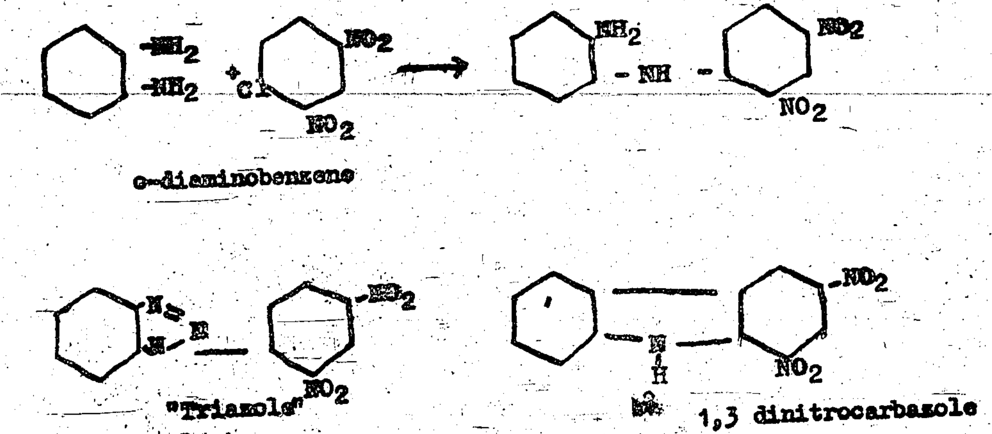
(4) Diphenylene oxide was available in Germany as a by-product from coal tar distillation. Its cost was 80 pfennigs per kilo. Reaction with molten caustic soda yielded, o,o'-dihydroxybiphenyl which on treating with ammonia under pressure at 180°C yielded carbazole but only in 25% yield maximum.



(5) o,o'-diaminobiphenyl resulted in about 15% yield as a by-product in the manufacture of benzidine and was available within the I.G. Farbenindustrie companies to the extent of 200 tons per year. Heating with lime yielded 2-aminocarbazole. However, this compound could not be converted readily to carbazole nor to carbazole derivatives suitable for dyestuff or insecticidal uses.



(6) 1,3-dinitro carbazole was prepared in good yields from o-diaminobenzene. However, nitration to the desired tetranitrocarbazole was not practicable. Mononitrocarbazole could be synthesized fairly readily but it too proved to be undesirable as such or for nitration to the tetra compound.



c. Conclusion.

Höchst's conclusions were that the best method for the preparation of synthetic carbazole was that based on the Tauber synthesis. However, production by this method was impossible during the war due to an extreme shortage both of copper and of phosphoric acid. It was estimated that the cost of synthetic carbazole by this method was 4RM per kilo (about 3RM for materials and 1RM for conversion costs). On this basis the synthesis of carbazole did not look promising and no further work was contemplated.

15. INSECTICIDES.

The following insecticidal compositions were made at the Höchst plant according to lists presented by Dr. Lautenschläger.

a. Calcium Arsenate Spray.

Use - for the control of the Colorado beetle
Composition:

Calcium arsenate[+] (As_2O_5 content 42%)	93.9%
Powdered sulfite "oyl"	6.0%
"Alkali echtgrün B.BF" (green acid dyestuff)	0.1%
Application strength	0.4% in water

[+] Raw material - As_2O_5

b. Calcium Arsenate - Green Colored (100%).

Sold for export.
As_2O_5 content = 40.0 to 42.5%

c. Calcium Arsenate Dust ("Gralit").

Use - for control of Blitophaga opaca.
Composition:

Calcium arsenate (fatted)	29.3%
Alkaliechtgrün (dye)	0.1%
Tallow	70.6%

d. Nosprasit.

Use - for control of pests in fruit growing.
Composition:

Calcium arsenate (As_2O_5 content 42%)	27.50%
Basic copper chloride (7.5% Cu)	13.00%
Calcium naphthol pitch sulfo acid	20.00%
Spreader of basic poly ethylene oxide iso-octyl phenol (a wetting agent of the Igepol series)	.25%
Alkaliechtgrün BBF (dye)	.10%
Powdered sulfite "oyl"	3.30%
Precipitated chalk	35.85%
Application strength	1.00% in water

e. Vitigran.

Use - Spray for control of fungi (downy mildew of the vine, downy mildew of the hop, potato blight).

Composition:

Basic copper chloride	26.0%
Powdered sulfite "oyl"	6.6%
Sticker of basic hydroxy ethyl methyl cellulose	3.0%
Precipitated chalk	64.4%
Application strength	1.0% in water

f. Nirosan.

Use - Non-poisonous spray for control of the first and second generation of the vine moth.
Composition:

Tetranitrocarbazole	25.00%
Powdered sulfite "oyl"	10.00%
Spreader of basic poly-ethylene oxide iso-octyl phenol	0.25%
Precipitated chalk	20.00%
China clay	44.75%
Application strength	1.00% in water

g. Nirosan dust.

Use - Non-poisonous dust for control of the first and second generation of vine moth.
Composition:

Tetranitrocarbazole	10.00%
Tallow (fatted)	90.00%

h. Copper-Nirosan.

Use - Spray for the contemporary control of insects and fungi in vine culture.
Composition: (Copper content - 15%)

Titranitro carbazole	25.00%
Basic copper chloride	26.00%
Powdered sulfite "oyl"	8.00%
Spreader of basic polyethylene oxide iso-octyl phenol	0.25%
Precipitated chalk	40.75%

i. Copper-Nirosan Dust.

Use - Not specified.
Composition (Copper content - 8%.

Tetranitrocarbazole	10.0%
Basic copper chloride	14.0%
Powdered sulfite "oyl"	3.5%
Diatomite-fatted	14.5%
Tallow-fatted	58.0%

j. **Spray 2317W.**

Use - Control of the downy mildew of vine and hops and potato blight.

Composition: (Copper content - 2.5%)

1-sulfocyano-2,4-dinitrobenzene	15.0%
Basic copper chloride	4.5%
Powdered sulfite "cyl"	11.0%
Sticker-basic hydroxy ethyl methyl cellulose	1.5%
China clay	15.0%
Precipitated chalk	53.0%

k. **Nikopren.**

Use - Spray for the control of insects in vine culture.

Composition:

Nicotine (95-98%)	28.0%
Spreader - polyethylene oxide, iso-octyl phenol	32.0%
Water	40.0%
Application - Water Solution	0.15%

l. **Venetan.**

Use - Spray for the control of lice in horticulture.

Composition:

Nicotine (95-98%)	3.0%
Spreader - as above	4.0%
Water	93.0%

Application - 1% water solution

m. **Brassikol.**

Use - Soil disinfectant for the control of "damping-off".

Composition:

Pentachloronitrobenzene	20.0%
Tallow	80.0%

n. **Brassisan.**

Use - Soil disinfectant for the control of club-root.

Composition:

1,2,4-trichloro-3,5-dinitrobenzene	20.0%
Engine oil	3.0%
Tallow-fatted	77.0%

o. **Bulbosan.**

Use - Dust for the control of tomato leaf mold.

Composition:

1,3,5-trichloro-2,4,6-trinitrobenzene	7.5%
Tallow-fatted	92.5%

p. **Tritisan.**

Use - Seed disinfectant for the dry treatment of wheat.

Composition:

Pentachloronitrobenzene	20.0%
Tallow	80.0%

q. **Dizan.**

Use - Dust for the control of cockroaches.

Composition:

Phenyl-diazopynolidin (piperidin)	2.5%
Tallow	97.5%

r. **Grodyl.**

Use - Oil spray for the control of weevils.

Composition:

Mineral oil - b.pt. 225-360 C	98.0%
Emulsifier-basic poly ethylene oxide diisoheptylphenol	2.0%

Application - 10% in water.

s. **Synthetic Raupenleim.**

Use - An adhesive material to catch winter moth and mottled Umber moth on fruit trees.

Composition:

Kogasin-chlorinated to 52% Cl	80.7%
Phenoxypropylene oxide	0.8%
Oxycresylcamphane - a condensation product of cresol and camphane	15.0%
I.G. Wax S	3.5%

t. **Gix.**

Use - Spray for the control of flies, mosquitoes, etc in rooms.

Composition:

Di-p-fluorophenyl-trichloroethane	60.0%
Gas oil from Lobau	20.0%
Emulsifier - polyethyleneoxide-iso-octylphenol	20.0%

Application - 3% solution in water.

16. PHARMACEUTICALS AND MEDICINALS.

a. On 10 May 1945, Dr. Lautenschläger supplied a list of 127 pharmaceuticals and medicinals made at Höchst, together with 3 copies of recent German pharmacopeias each of different issue dates. The list was made up almost entirely of trade names.

The following statements were made by Dr. Lautenschläger:

b. I.G.'s sulfa-drugs, aspirin and anti-malarials are mostly made at Elberfeld. Salvarsan, vitamins, hormones and other medicinals are made at Höchst, which is well equipped for testing them.

c. Dr. Lautenschläger expressed the opinion that in general chemotherapeutic agents were not very successful against virus diseases. Nitro-acridine had been tested with some success as a preventative for influenza. Penicillin was a good drug for syphilis, but its cost and the many years probably necessary for clinical testing led to the belief that it will not soon, if ever, replace 606.

d. Phenothiazine was used for animals (worms). Its use for mosquitoes (learned of at Casella-Mainkur) was still under test. This drug had not yet been used on human beings.

e. Carbon tetrachloride had been used for hookworm but was somewhat poisonous. Hexachloroethane was also used in the treatment of liver flukes in cattle. It was, strangely enough, more toxic to fat than lean cattle. 50% of the cattle slaughtered in Frankfurt had liver ailments. Hexachloroethane was used as an emulsion in water. It was packed into capsules and also used as a powder.

f. Höchst had no new anti-malarials. Atabrine and plasmochin were both made at Elberfeld. Dr. Hörlein had done a lot of work on these.

g. Höchst had made a good many tons of fluor DDT. It made a much better emulsion than the chlor compound. The process for making fluor DDT was analogous to the chlorine DDT process except that the monofluorobenzene was made by diazotization of aniline in the presence of HF to make benzene diazonium fluoride which was then decomposed into fluorobenzene and nitrogen.

17. GLYCEROGEN - A SUBSTITUTE FOR GLYCERINE.

a. Summary.

(1) Information concerning this important substitute for glycerine was obtained at the Höchst plant 12 April 1945, from Dr. Lange.

(2) This glycerine substitute has not as yet been successfully applied to nitro-glycerine manufacture because of the presence of excessive amounts of by-products. It had, however, acquired great importance in the preparation of vat dye pastes of the suprafix type, e.g. Indanthrene Druck Oliv GW Suprafix Teig, a Chemical Warfare item used in camouflage dyeing and printing, which is reported separately. It was also used in the preparation of other vat dye printing compositions where its consumption was quite large. Glycerogen also proved valuable when added to tobacco as a mold-proofing and humidifying agent. It was used in a variety of glycerine applications, where the presence of the by-products was considered unimportant or secondary. Its main use was as a textile assistant.

(3) The Glycerogen process was based on the inversion of sugar (cane or beet) to hexose in the presence of oxalic acid. The acid was then neutralized with chalk, followed by a liquid phase reduction with hydrogen (nickel catalyst fixed on pumice) under 300 atm pressure at temperatures from 80°C (initial) to 200°C (final). The crude solution was then filtered, clarified, and freed from H_2O under vacuum.

The final product had the following composition:

40% glycerine
40% propylene glycol
20% hexyl alcohols

In 1944 the total production reached 1,530 tons, produced by the continuous process described below.

b. Description of Process.

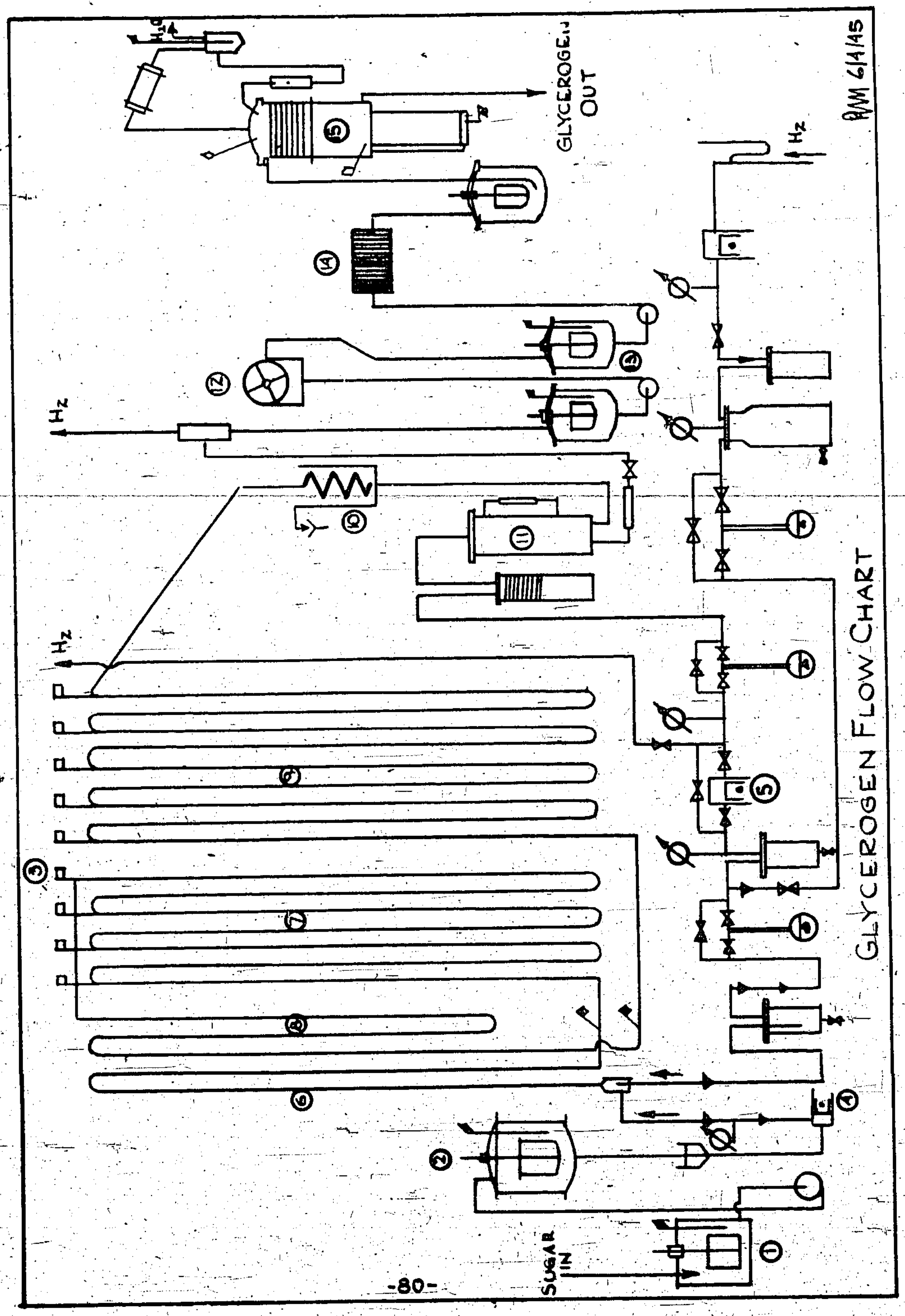
(1) Equipment.

The plant equipment included wooden vats for the solution and inversion of the sugar, a mixing tank for the mixing of the sugar solution with the nickel catalyst, high-pressure pumps for liquids, high pressure recycle gas compressors, a system of high pressure hydrogenation tubes, high pressure coolers and expansion vessels, storage tanks, filter press for the separation of the catalyst, clarification vats and filters to eliminate charcoal (Norite) and vacuum distillation apparatus.

(2) Process.

Reference is made to the attached flow chart.

18 tons of beet sugar were dissolved by agitation in 8 cbm water in a wooden tank (1) and 18 kg oxalic acid added thereto. The



GLYCEROGEN FLOW CHART

temperature was then raised to 75°C and kept at this level for about 20 hours. At this stage inversion had proceeded to a degree sufficient to leave about 1-5% beet sugar in the inverted sugar solution which had a concentration of 70-75% and a sp gr of 1.64 20/4.

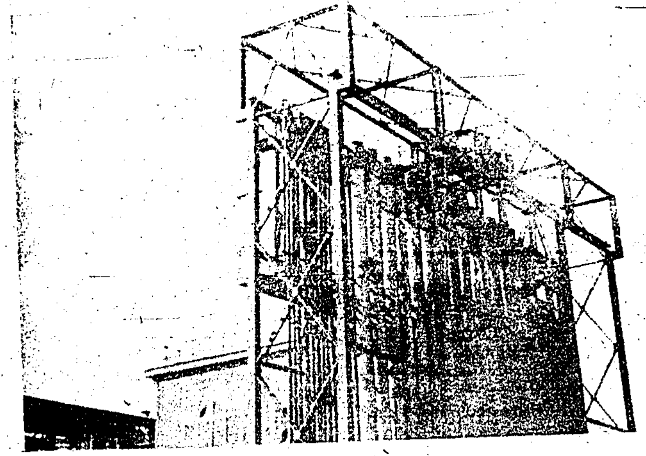
3,000 liters = 3,000 kg of inverted sugar were then pumped into tank (2), diluted with 1,000 liters of water, treated with 2kg chalk, and the nickel catalyst added. The nickel catalyst was composed of Ni powder, fine pumice and an amount was added to give 5% of Ni metal based on the original weight of sugar, made up of 10% fresh catalyst and 90% used catalyst. The solution was buffered with an additional amount of chalk slurried with water in order to maintain the proper pH and the total solution made up to 42-44% sugar content.

The inverted sugar solution containing the catalyst and chalk in highly dispersed form was then recycled continuously through the high pressure system (3), by means of Balcke high pressure pumps (4) under pressures varying from 270-300 atmospheres. Similarly, hydrogen gas was recycled through the apparatus by means of high pressure recycling gas compressors (5). The solution was first heated to 75°C in a preheater (6) and circulated through the first set of hydrogenation tubes (7), the temperature slowly rising from 75°C to 135°C. Reduction of the inverted sugars into the C_6 alcohols occurred in these tubes at the exit of which the solution was passed through a second pre-heater (8), which raised the temperature to 180°C. In the second set of hydrogenation tubes (9) following the second preheater the C_6 chains were partially split into C_3 chains at a temperature which was slowly raised from 180°C to 210°C. At the end of the cycle a product with the composition given above was obtained.

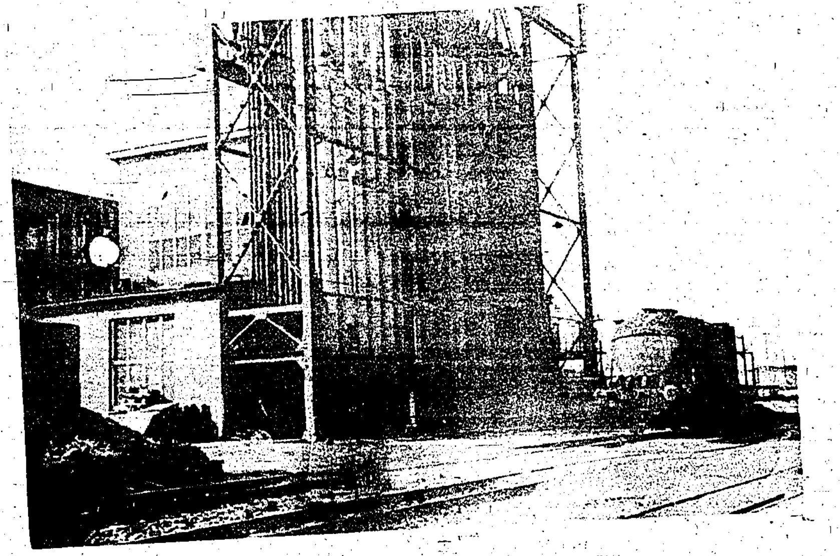
From the last hydrogenation tube the solution was pumped through a cooler (10) where the temperature was lowered to 30°C, and through an expansion chamber (11) from which the hydrogen gas was recycled into the system. The solution was then filtered in a plate and frame filter press (12) to recover catalyst for re-use. The solution was then clarified with charcoal (Norite) in (13), filtered in (14), and freed from H_2O by vacuum distillation in (15).

c. Product Specifications.

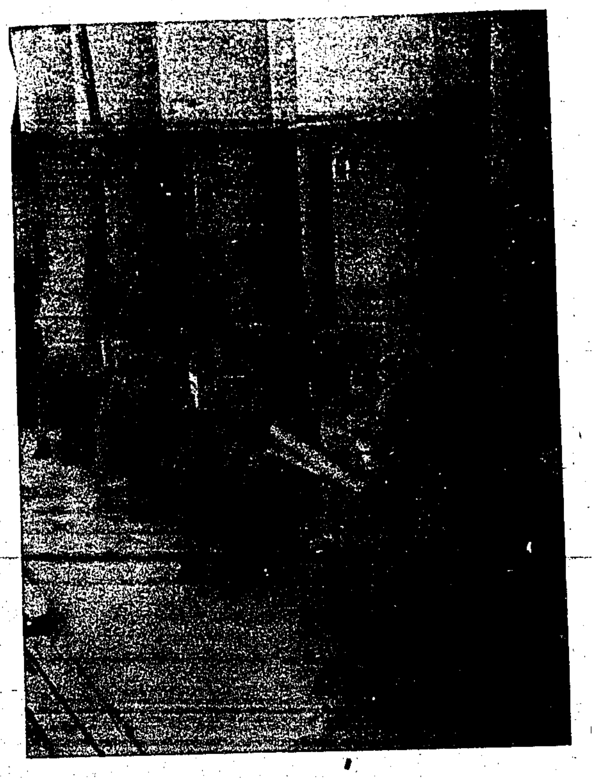
The product was required to be water clear and free from reducing impurities. Specific gravity D4 20 = 1.200 - 1.230 20/4.



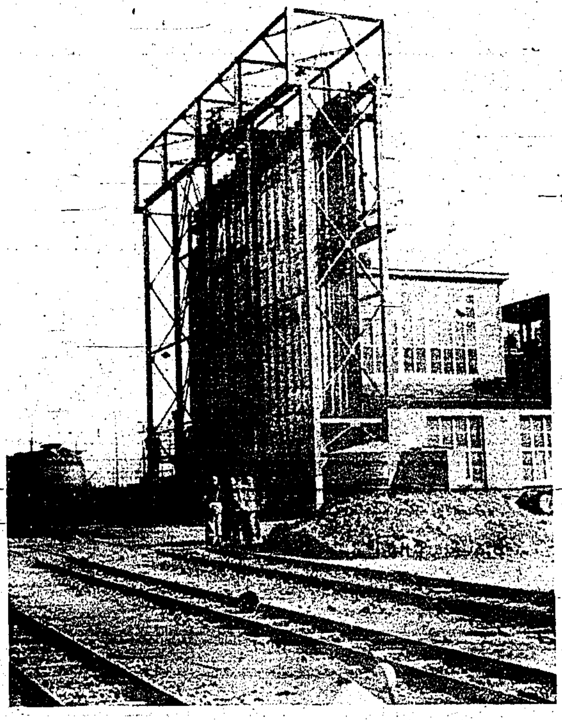
Höchst Glycerogen Unit



Höchst Glycerogen Unit



Höchst Glycerogen Plant. Bottom of Hydrogenators.



Höchst Glycerogen Plant Hydrogenators

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SYNTHETIC EMULSIFYING AGENTS, WETTING AGENTS, DETERGENTS AND SOAP SUBSTITUTES

I.G. FARBENINDUSTRIE A.G., HÖCHST/MAIN

Richardson...

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

SYNTHETIC EMULSIFYING AGENTS, WETTING AGENTS, DETERGENTS, AND SOAP SUBSTITUTES

I.G. FARBENINDUSTRIE A.G.

HÖCHST/MAIN, GERMANY

7 - 15 May 1945

Reported By

Major R. E. RICHARDSON, C.M. HQ
J. G. KERN, CWS, HQ ETOUSA
R. L. MURRAY, CWS, HQ ETOUSA
R.W. SUDHOFF, CWS, HQ ETOUSA

25 June 1945

CIOS Target No. 22/1(G)
Miscellaneous Chemicals

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

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39 p. diags.

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

SYNTHETIC EMULSIFYING AGENTS, WETTING AGENTS DETERGENTS, AND SOAP SUBSTITUTES

I.G. FARBENINDUSTRIE A.G.

HÖCHST/MAIN, GERMANY

1. INTRODUCTION

Information on synthetics for use as cutting and drawing lubricants, emulsifying agents, finishing oils, wetting agents, detergents, and soap substitutes for textile and household needs was discussed with various personnel of the Höchst plant of the I.G. Farbenindustrie A.G. during the period 7-15 May, 1945. Prominent in these discussions were Dr. Nusslein, head of the Höchst Application Laboratory; Dr. Lange, Director of the Organic Division; and Dr. Pensel, an authority on the development of synthetics from Fischer-Tropsch materials.

During war years the entire development was influenced considerably by the availability of raw materials. Particular emphasis was placed on the replacement of all oils and fats of vegetable or animal origin with synthetics built from carbon chain compounds available within the Reich. The problem was to develop, from such materials, products which would be acceptable for industrial and household use. Research on this program which was started soon after the 1925 merger of the IG finally culminated in manufacturing activities of large magnitude. Höchst with its prewar developments of Igepons, Igepals, and the Alipals was the principal factor in this new field. During the war this list was augmented with additional emulsifying and wetting agents which were known under the generic trade names of Emulphors and Servitals. At least 200 to 300 important compounds were developed, although only 25 to 30 of these have attained any considerable commercial importance.

The total annual sales of synthetic detergents and emulsifying agents by IG during the war period reached the astounding figure of 75,000,000 pounds, equivalent to 60 million RM sales value.

2. PREWAR DEVELOPMENTS

The chief organic detergents and emulsifying agents made at the Höchst plant were as follows:

a. Igepons

(1) The following commercial types were important:

Igepon A.P. extra conc.
Igepon T Powder, extra conc.
Medialan A Powder.

These materials were derived by the reaction of oleyl chloride with hydroxy ethane sodium sulfonate, the sodium salt of methyltaurin and the sodium salt of sarcosine, respectively.

(2) Raw Materials

The above products, made from oleic acid, represent the type of product. Because of continuously changing economic conditions brought on by the war affecting the availability of oleic acid, other fatty acids and raw materials were used as substitutes. In this case the final product was tested by appropriate use tests and standardized to the proper strength.

The following table lists the various types of raw materials and uses for the finished products therefrom:

Animal Origin	Use and Application
Train oil fatty acid (fish oils as whale, etc.)	Leather assistants
Stearic acid, "Schlammfettsäure"	Washing and softening agent. Better grade washing agents.
Vegetable Origin	
Palm-Kernel oil fatty acid	Better grade washing agents for textiles and household use.
Coconut-oil " "	
Babassu oil " "	
Sunflower oil " "	
Peanut oil " "	
Tall oil acids - from Swedish tall oil	Detergent for Sweden.

Synthetic

Fatty acids from oxidation of hydrocarbons (M.W. about 216)	A Type - better grade) B Type - Industrial grade) (Detergents)

(3) Manufacturing Processes.

Detailed information on processes for the manufacture of the Igepons are as follows:

(a) Manufacturing Process for Chloroil A.u.T. Oleyl Chloride.

Chloroil A.u.T., an intermediate for the Igepons, is essentially oleyl chloride:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COCl$$

Equipment

8,000 gallon aluminum tanks for oleic acid storage.
3,000 gallon steel, homogeneous lead lined tank, for phosphorus trichloride storage.
250 gallon steel, homogeneous lead lined tank, for measuring $POCl_3$.
2,000 gallon stirred reactor with conical bottom, and heating jacket. Reactor is homogeneous lead lined steel.
Rubber lined steel ventilating lines and stoneware fan.
Ring packed rubber lined tower for HCl absorption.
1,200 gallon product receiver, homogeneous lead lined steel.

Charge

Oleic acid	3,000 kg
Phosphorus oxychloride	782 kg

The oleic acid is a blend of 50% regular oleic acid and 50% sperm. Oil acids or various fatty acids or mixtures may be used; for example, stearic acid or acids from palm, peanut and other oils as discussed in the Section "Products and Raw Materials."

Procedure

3,000 kg of the oleic acid mixture are charged to the reactor and warmed to 50°C. During the course of an hour 782 kg of phosphorus trichloride are added from the measuring tank, under the surface of the mixture and with slow stirring. The temperature during the reaction rises to 55°C. After the addition is complete, stirring is continued for 5 minutes following which the mixture is allowed to stand overnight. The lower phosphoric acid layer is separated and drawn off through a closed lead line where it is flushed with water and discharged to waste. After repeated stirring, the mixture is allowed to stand again for one hour and the balance of the phosphoric acid settled and withdrawn. Finally the acid chloride product is drained to the receiver.

Yield

The yield is 3,315 kg of a product containing about 3,182 kg of the pure material, (95.4%). Yield is better than 99%. The product is a clear brown liquid having a strong odor. It fumes on exposure to air due to evolution of HCl. Specific gravity is about 0.93.

(b) Manufacturing Process for Igepon AP High Concentrated.

Igepon AP High Concentrated is essentially the sodium salt of the oleyl ester of hydroxyethane sulfonic acid as shown by the following formula:

$$C_{17}H_{33}COOCH_2CH_2SO_3Na$$

Equipment

500 gallon condensation vessel of homogeneous lead lined construction with low pressure heating and cooling jacket. Stirrer of heavy construction. Bottom discharge.
1,200 gallon Chloroil measuring tank of homogeneous lead lined steel construction.
Weigh tank on scales.
Absorption equipment for HCl off-gas.

Charge

Chloroil A-95% mol wt. 300.5	316 kg
Ethane salt W; 98-99% Mol wt. 14.8 The sodium salt of hydroxy-ethane sulfonic acid......................	185 kg
Sodium carbonate - approx	10 kg

Process

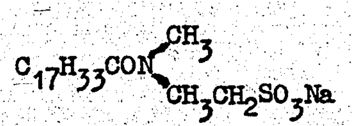
185 kg of the ethane salt are shoveled into the reactor and full pressure steam, at three atmospheres, is applied to the jacket. The manhole cover is closed and 316 kg of Chloroil A is run in from a measuring tank. The mixture is heated to 100°C. After about 15 minutes the reaction becomes quite vigorous and hydrogen chloride gas is evolved. Stirring is continued and the temperature rises to about 110°C. The reaction product, which originally is a thick liquid mass, passes first to a crumbly solid and then disintegrates into waxy lenticular flakes. The product is cooled to 90-100°C with continued stirring whereupon a gritty powder results. Finally, solid sodium carbonate is added to the product to adjust the pH and the product is discharged through the bottom outlet of the reactor directly into containers. The above product, known as Igepon A High Concentrated, is allowed to cool and then milled; the powdered material is also known as Igepon AP High Concentrated.

Yield

The above batch yields 460 kg of the product as a yellowish powder which is completely soluble to a clear solution in hot water. The 5% solution shows pH 7.2 - 7.5. Approximate bulk density is 0.5.

(c) Manufacturing Process for Igepon T High Concentrated Powder.

Igepon T is essentially the sodium salt of oleyl methyl tauride:



$C_{17}H_{33}CON\begin{cases}CH_3\\ CH_3CH_2SO_3Na\end{cases}$

The technical product has a purity of about 64%.

Equipment

4,000 gallon steel reactor, brick lined, and cemented with Asplit and equipped with a wooden stirrer rotating at 28 rpm, a heating-cooling coil of stainless steel (V2A) construction, and a vertical line of aluminum.

Measuring tanks as follows:

500 - gallon homogeneous lead lined steel - for $POCl_3$.

650 - gallon steel tank for methyl taurin solution.

400 - gallon steel tank for sodium hydroxide solution.

Double drum drier of 26 square meters surface, heated with high pressure steam.

Grinding mill - (Alpine - "Perplexmuhle.")

Mixing machine - 350 cu ft capacity (Tiedke Mixer).

Charge

Methyl Taurin W - mol wt 139 - as a 25% solution containing 556 kg pure compound	2,224 kg
Sodium chloride	320 kg
Water	3,416 kg
Chloroil T-96% basis	1,252 kg
Sodium hydroxide - 33%	800 kg
Hydrochloric acid - 20° Bé approx.	125 kg

Procedure

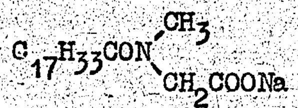
2,224 kg of sodium methyl taurin solution are charged to the reactor and 320 kg of sodium chloride plus 3,416 kg of condensate are added so that the solution has a concentration of about 10%. 500 kg of 33% sodium hydroxide are added and the mixture is stirred and cooled to 24-30°C. 1,252 kg of Chloroil T are then added together with 400 kg of 33% NaOH during a period of 2-3 hours, maintaining the NaOH addition so that the mixture is always alkaline to triazene paper. Finally, the mixture is stirred an additional one-half hour to insure that the alkaline reaction test is permanent. Then in the course of one hour the mixture is warmed to 50°C and neutralized with 125 kg of 20° Bé hydrochloric acid to a pH of 7.2-7.5. Then the mixture is diluted with condensate to a dry solids content of 35% and transferred to a vessel, mounted to permit gravity feed direct to the drum drier. The product, dried on the drum drier at about 13 atmospheres steam pressure is a yellow-white powder. After milling and blending, the finished Igepon T Powder is shipped in steel drums.

Yield

The finished product totals 2,440 kg. It is a yellowish white powder soluble in water to form a clear 5% solution of pH = 7.2-7.5. Bulk density is about 0.6.

(d) Manufacturing Process for Medialan A Powder.

Medialan A is essentially the sodium salt of the condensation product of oleyl chloride with sarcosine:



$C_{17}H_{33}CON\begin{cases}CH_3\\ CH_2COONa\end{cases}$

Specifications of the Product are as follows:

Equivalent mol wt (pure product)........ 375
Purity 32.6%
Total fatty acid equivalent 24.5%
pH of solution - approx 7.5

Procedure

89 kg of pure sarcosine equivalent in the form of a 15% solution of the sodium salt is mixed with 100 kg of sodium chloride at 25-30°C. 200 kg of 33% caustic soda are then added followed by 313 kg of the oleyl chloride mixture, approximately 97% purity. During the reaction, it is necessary to make certain that the mixture continues to show an alkaline reaction to triazene paper. After stirring for a half hour at 50°C the mixture is neutralized with about 40 kg of 20° Be hydrochloric acid. Sufficient technical anhydrous iron-free sodium sulfate is then added (about 570 kg) so that the mixture yields a total dry product weight of 1,150 kg.

The pasty mass, having an average water content of 70%, is dried on a drum drier operating at about 6 atmospheres steam pressure. The dried product is cooled and milled in a pulverizer set with 0.75 mm wide slits.

b. Igepals

(1) General Description

The introduction of Igepons AP and T represented considerable progress, particularly in the field of scouring agents in wool processing. However, apart from a few special cases, the Igepons are inferior to soap for the processing of cellulose fabrics and are reported to be inferior to Medialan A. This substance is said to be a considerably better cleansing agent than soap, since in the Medialan A molecule the drawbacks of soap have been largely removed but the carboxyl group is retained. Both in fulling properties on wool and in leveling properties in the direct dyeing of cotton and rayon, this compound surpasses soap and is even superior as a softener. Also, it is exceedingly free-rinsing. However, its resistance to hard water is limited being about half way between that of soap and the Igepons. In this respect, it is definitely inferior to the Igepals.

In 1937, Höchst introduced new substances synthesized from organic and low molecular weight compounds which could be produced cheaply, in bulk. These new surface active agents differ from soap in character and are allegedly superior in properties. The behavior and characteristics of these new scouring and finishing agents are influenced fundamentally by the fact that they contain neither the carboxyl group characteristic of soap nor the sulfonic acid group of the Igepons or the synthetic detergents of the alkyl-aryl-sulfonate type. Actually they contain no ionogene groups. Solubility was obtained primarily by the presence of polyether radicals and in some instances by an additional SO_3Na group. As a result these products do not form insoluble salts with heavy metals.

(2) The Igepals produced commercially by IG are listed in the following table giving the trade name, chemical composition, and use:

Trade Name	Chemical Composition	Use
Alipal Cl 35%	Dodecyl (Propylene polymerisate)-phenyl poly (3)[**]glycolether sodium sulfonate.	Industrial soap substitute
Alipal D 35%	Di-(isohexyl/isoheptyl)phenyl poly (4)[**]glycolether sodium sulfonate.	Industrial soap substitute
Igepal B Conc.	Di-(isohexyl/isoheptyl)-phenyl poly (5)[**] glycolether sodium sulfonate 50%.	For the washing and soaping of vegetable fibres
Igepal C extra conc	Dodecyl (Propylene polymerisate) phenyl (Phenol oil SRI)-poly (12)[**] glycolether 100%	Dyeing assistant (wetting-out, dyeine, printing, etc) Washing agent for Cellulose fibres.
Igepal C Conc.	59.5 parts Igepal C extra conc. 30.0 " Detergent Höchst 153 do/SR[x] 10.5 parts distilled water 100.0 cut 70% [xx]	Dyeing assistant (wetting out, dyeing, printing, etc)
Igepal W extra conc.	Dodecyl (forerun of crude decylene 130-180°C from Uerdingen) phenyl-poly (6)[**] glycolether 100%	Detergent for wool, emulsifying and fulling agent.
Igepal W conc.	59.5 pt Igepal W extra conc. 30.0 pt Detergent Höchst 153 Do/SR 10.5 pt Distilled water 100.0 cut 70% [xx]	Detergent for wool, emulsifying and fulling agent.

[**] Numbers after the word poly indicate number of molecules of ethylene oxide used.

[x] Detergent Höchst 153 do/SR = dodecyl phenyl (phenol oil SRL)-poly (5) glycolether sodium sulfonate, 35%

[xx] Adjusted to a strength of indicated % with water.

Igepal L conc.	37.5 pt Igepal W extra conc 16.5 " Höchst 155 intermediate do/SR* 11.0 " Detergent Höchst 153 Do/SR 3.0 " Polysolvan HS 32.0 " Distilled water 100.0 cut 60.8%	Washing, fulling, cleaning, desizing.
Igepal F extra conc	Iso-octyl phenyl poly (9)** glycol ether 100%	Washing of feathers
Igepal ~~F~~ conc.	59.5 pt Igepal F extra conc 30.0 " Detergent Höchst 153 Do/SR 10.5 " Distilled water 100.0 reduced to 70% conc xx	Washing of feathers
Igepal M	71 pt Mesapon N 24 " Detergent Höchst 153 do/SR 5 " Water 100 " reduced to 75% conc.xx	Textile assistant for washing, wetting out and fulling (etc.)
Diglycol ether	Di(isohexyl/isoheptyl) phenyl poly (2)** glycolether 100%	Emulsifying and/or dispersing agent for Monilith emulsions
Dismulgan III	Dodecylphenyl (Phenol oil SRI) poly (30)** glycolether, 100%	Emulsion breaker for petroleum industry
Emulphor MW	Di(isohexyl/isoheptyl) phenyl poly (7.5-8)** glycolether, 100%	Emulsifying agent for mineral oil for the preparation of textile lubricating oils (spinning, weaving) and softening oils
Emulphor A extra	Di(isohexyl/isoheptyl)phenyl*** poly (6.5)** glycolether	Oil-emulsifier, softener and leather assistant (under the trade name of Remolgan A)

*Höchst 155 intermediate do/SR = dodecyl phenyl (Phenol oil SRI) (7) glycolether 100%.

***A 10-12% forerun from the alkyl phenol mixture.

Emulphor ELN	85 pts di(isohexyl/isoheptyl) phenyl poly (20)** glycolether. 100% 15 pts distilled water 100 reduced to 85% conc.	Emulsifier for olein (Textile Oil) and as a softening agent.
Servital OL conc.	66.6 pts Emulphor MW (free from low boiling fatty acids) 33.3 pts mineral oil 3.5°E .5 pts low boilers (C_6-C_9) from fatty acid fractionation.	Textile lubricating oil.
Servital AC conc.	93.5 pts Servital OL conc 6.5 material DOMB (Ludwigshafen)****	Lubricant for acetate silk yarn.
Wetting Agent 2406	Tri-isobutyl-beta-naphthyl poly (10) glycolether 100%	Wetting agent for insecticides and fungicides.
Soromine SG	Stearyl-poly (6) glycolether.	Finishing oil for staple rayon and artificial silk (imparts "scroop")

(3) Raw Materials

(a) Ethylene oxide, the principal raw material, was obtained from I.G. Farbenindustrie A.G., Gendorf (Bavaria). It was produced from acetylene generated from calcium carbide. First, acetylene was hydrogenated to ethylene and converted to ethylene monochlorohydrin which was converted to ethylene oxide by reaction with boiling hydroxide solution.

(b) The various alkyl-hydroxy-aryl compounds required for the Igepals were produced at the Höchst plant from phenols, cresols, and xylols, by reaction with olefinic hydrocarbons. In most cases the raw materials were obtained from various I.G. subsidiaries as shown in the following:

Phenol was obtained from coal tar distillation companies in the Ruhr or as synthetic phenol from Ludwigshafen or Lever-

****Material DOMB is dioctadecylethanol amine +15 Aeo.

kusen. Cresols (phenol oil SRI) and xylols were procured from the same sources, mainly from Meiderich (Gesellschaft für Teerverwertung A.G.)

Olefins were obtained from Uerdingen. Propylene polymerisate, also termed P-12, is a propylene polymer having an average chain length of 12 carbon atoms. Dodecylene, used in the preparation of Igepal W extra conc, is a forerun cut, 130-180°C range obtained in P12 manufacture.

Isohexylene and Isoheptylene were obtained as a mixture of these two olefins. Presumably this was obtained from Uerdingen.

The di(isohexyl-isoheptyl) phenol used in the manufacture of Emulphor A extra was a 10-12% low cut fractionated from crude alkyl phenols.

Alkyl phenol has been referred to by Höchst as "Phenol Oil", the product of P-12 and phenol.

Isoctane used for the preparation of isooctyl phenol and Igepal F extra conc. was prepared at Leuna by the hydrogenation of diisobutylene.

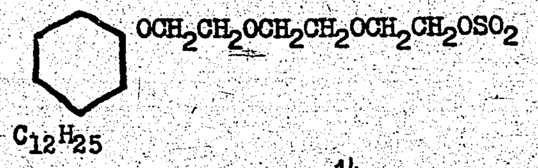
Low boiling aliphatic acids in C_6 to C_9 required for the manufacture of Servitol OL conc. were produced by the fractionation of fatty acids obtained by catalytic oxidation of Fischer-Tropsch hydrocarbons at Ludwigshafen. The dioctadecyl ethanol amine, termed "preparations mittel" DOMB in above list also came from the same source. The triisobutylene required for the manufacture of triisobutylnaphthol came from an unknown source, possibly Leuna.

(4) <u>Process Manufacture of Igepals is given in the following:</u>

The Igepals process may be divided into four distinct operations:

(a) Preparation of P-Oil; an alkyl phenol.
(b) Preparation of alkyl phenol polyglycol ether; by the condensation of P-oil with ethylene oxide.
(c) Preparation of the sulfonate and mixing with additives.
(d) Preparation of Igepal in Powder Form.

The chemical composition of a typical Igepal is illustrated by the following formula:



$C_{12}H_{25}C_6H_4OCH_2CH_2OCH_2CH_2OCH_2CH_2OSO_2$

The alkyl side chain and the number of ethylene oxide chains may be varied over a considerable range as described in detail in the text.

(a) <u>Preparation of Alkylphenol (P-oil)</u>

<u>Equipment</u>

2,500 gallon steel vessel coated with a phenolic resin lining and equipped with a blade type stirrer rotating at 30 rpm; a heating jacket and a phenolic resin coated cooling coil.
Steel coil reflux condenser.
A calcium chloride drying tower for the olefin.
300 gallon steel measuring tank for the olefin.
2,000 gallon phenolic resin lined steel weigh tank for the alkyl phenol product.

<u>Charge</u>

Phenol..................	1,880	kg
Boron trifluoride.......	37.6	kg
Propylene polymer (P-12).	3,000	kg

<u>Procedure</u>

The phenol charge is dried batchwise heating to 130°C under an absolute pressure of 600 mm. Dried phenol is stored in an aluminum tank maintained at 50°C by a coil through which warm water is circulated. The olefin is dried by passing it over calcium chloride in the drying tower, stored and transferred using nitrogen pressure to insure against access to water.

The phenol is charged to the reactor, boron trifluoride added from a scale tank and the mixture heated to 45-50°C. The olefin is then added with stirring, maintaining the temperature at 50°C maximum. After the addition of the olefin has been completed the mixture is stirred for an additional hour or more. Next, water is added and the mixture heated to 70-80°C at which time the stirring is stopped and the mixture allowed to separate for one-half hour. The lower layer, water, is separated and discarded. The upper layer, the product, is washed several times with water until it is neutral to Delta paper. Usually four washes are required. The ease of separation and washing depend greatly on the water ratio which at the minimum should be equal to the weight of the oil layer. After washing, the reactor is closed, the stirrer started again and the mixture heated slowly up to 130°C during which time small amounts of unreacted olefin and phenol steam distill. The overhead is separated and the water layer discarded. After reaching 130°C the reaction mixture is cooled to 90°C, vacuum applied by means of a water jet (400-450mm absolute pressure) and heating continued up to 130°C in order to

TABLE OF TYPICAL ALKYL PHENOLS

ALKYL PHENOL (WEIGHTS ARE IN KILOGRAMS)

MATERIAL	MOL WT.										
Phenol	94	94	94		94	94	94			94	94
Phenol oil SR	106			106				106		106	
Boron trifluoride		1.7	1.9	1.9	2.8	2.8	1.9	1.9	2.8	2.8	1.9
Diisobutylene	112	112									
Mixed polymer diisohexylene, diisoheptylene	185		185	185							
Isohexylene-Isoheptylene mix	90				90	180					
Raw polymer R-12	150						150	150			
Low raw polymer 130-180°C	121								121	121	
Triisobutylene	147										147
Temp. for olifin addition °C	-	45	45	45	45	45	65	65	65	65	65
Final stirring period hrs.	-	2	6	6	4	4	6	6	4	4	4
Final reaction temperature	-	45	45	45	45	45	65	65	65	65	65
Yield - kilogram		195.7	262.3	273.5	173.0	257.6	217.2	238.1	195.7	206.6	224.1
Essentially mixed cresols											

remove the last traces of water. Finally the mixture is cooled to 90°C and transferred to storage.

The types and quantities of materials required for preparation of various alkyl phenols are shown in the attached table.

Yield

Theoretical yield is 4,880 kg, actual yield is 4,343 kg for 89%.

(b) Preparation of Alkyl Phenol Polyglycol Ether

Equipment

A 1,200 gallon steel reactor, equipped with a blade type stirrer rotating at 480 rpm, two coils for steam heating or for water cooling, and a safety disc set for 2 atmospheres and connected to a vent line.

Steel measuring tank, 700 gallon capacity, 10 atmospheres working pressure, for the storage of ethylene oxide.

Steel measuring and storage tank for the product, 2,000 gallon capacity.

Charge

The following charge is based on a ratio of 7 mols ethylene oxide to 4 mols phenol:

Phenol oil	976	kg
Sodium acetate flakes........	4.9	kg
Ethylene oxide - 5% excess...	1,292	kg
Nitrogen ....(about)	300	CF

Procedure

The alkyl phenol is treated with about 0.5% sodium acetate flakes so as to yield a reaction mixture of pH 6 and heated with stirring to 150°C. With the stirrer off, the kettle is vented with nitrogen to remove air and with ethylene oxide, to displace the nitrogen. Next, the required amount of ethylene oxide liquid is run in with rapid stirring. The temperature rises and is held at 185-210° C. If the cooling is not sufficient the flow of ethylene oxide is throttled. Normally, 400-450 kg ethylene oxide are absorbed. The pressure is maintained at 0.8-1.2 atmospheres. After the addition of the ethylene oxide is complete the batch is cooled to 100°C. The vacuum generated thereby is relieved with nitrogen. Then the reactor is opened and vented with a current of nitrogen and the mixture transferred to a weigh tank receiver. The venting is necessary to prevent the formation of an explosive mixture of ethylene oxide with air.

Ethylene oxide is stored in 8,000 gallon steel tanks equipped with cooling coils containing circulating brine in order to maintain the contents of the tank at 0°C. It is transferred to a 600 gallon weigh tank and from there to the reaction vessel by means of nitrogen pressure. Vented nitrogen ethylene oxide gases are passed first through an empty vessel (trap) and then through a solution of sodium bisulfite at 50°-60°C. This absorbs the ethylene oxide to form hydroxy ethane sulfonic acid. The bisulfite is made by mixing two parts of 40°Bé $NaHSO_3$ liquor with 1 part of water.

Yield

The yield of 2,208 kgs is theoretical, since the entire product is used.

The product is a thick oily liquid which with increasing ethylene oxide content becomes pasty to waxy. The water solubility increases with an increasing ratio of ethylene oxide.

(c) Preparation of Finished Igepal (Igepal B)

Igepal B, as described here, is a 35% solution of alkyl phenol-poly (5) glycol ether sodium sulfonate plus inorganic salts in water. In this particular case the phenol is the di-isohexyl-isoheptyl compound.

Equipment

1,800 gallon enamelled reactor with an enamelled stirrer, steam heating jacket, and water jacketed vent line.

5,000 gallon brick lined vessel with a wooden stirrer and a stainless steel (V2A) heating or cooling coil.

Charge

Intermediate product - alkylphenyl-polyglycol ether ...	1,500 kg
Amido sulfuric acid	375
Sodium hydroxide solution - 33%	180
Muriatic acid - 20°Bé, about	35
Sodium chloride	500

Procedure

The intermediate is charged to the reactor and warmed to 90°C. Then, during a period of about one-half hour the finely ground amino-sulfuric acid is added. The temperature rises to 125°C or even to 130°C and is maintained at this point until a test sample shows a complete solution in water. Further, this solution should not become turbid on standing. During about an hour it is important to maintain the temperature by addition of the acid as quickly as possible. If the temperature is not maintained, as for example because of the use of wet acid, then it is necessary to supply external heat in which case the resulting product is not typical but shows a poor water solubility. The further working of the product is carried out by one of two methods.

First, after the product shows an acceptably clear solution, the mixture is cooled to 50-60°C, the stirrer is stopped and 2,500 liters of water are added followed by 180 kg of 33% sodium hydroxide solution. Finally, the mixture is stirred to obtain complete mixing and yield the finished product as a paste.

Second, the water and the caustic soda are charged to the brick-lined reactor and the sulfonated mass, cooled to 100°C, is then run into the mixture. The operation is based on the fact that the sulfo group is split off in acid solution particularly at high temperatures. As soon as the batch is completely mixed, it is heated to 70-80°C and held at this temperature for about 12 hours until all the ammonia has been removed. It is tested with turmeric paper and additional caustic added as necessary. The batch is then cooled to 50-60°C and treated with 35 kg of 20°Bé muriatic acid to about pH 7.5 followed by the addition of 500 kg of sodium chloride. After stirring for three hours, the finished batch is diluted with water to a 35% equivalent detergent and stored in beechwood barrels or in glass containers.

Yield

The yield is theoretical, since no by-product is withdrawn from the reaction vessel.

For Igepal B, water is added to the above mixture to yield a total weight of 5,151 kg. For Igepal B-Concentrated, water is added only to a total weight of 3,605 kg.

The product is a brown paste varying in consistency from a flowable paste to a gelatinous mass.

Igepal B Concentrated

The method here is identical with that for Igepal B with the exception that the quantity of water is changed. 1,800 liters of salt solution containing 350 kg of salt are added and the mixture diluted with water to a 50% product which is stored in beechwood barrels.

(d) Manufacturing Process for Igepal in Powder Form.

The composition of the mixture is as follows:

Material	Wt. %	Actual Charge		
Alipal C. I.	35	292 kg of	60%	material
Sodium carbonate	35	175 "	100%	"
Sodium sulfate	18.2	91 "	91%	"
Tamol NNO	10	50 "	100%	"
Tylose HBR	1.8	27 "	33%	"

Alipal C.I. is dodecyl phenyl poly (3) glycol ether sodium sulfate. Tamol NNO is a condensation product of naphthalene sodium sulfonate with formaldehyde. Tylose HBR is the reaction product of sodium cellulose with monochloracetic acid.

The processing is carried out as follows:

1,250 liters of water are charged to a 750 gallon jacketed, glasslined vessel and heated to 80°C. The batch is stirred and the shredded Tylose then sprinkled in during the course of 10 minutes, after which the mixture is held at 80-85°C for one and one-half hours. The Tamol and the Alipal are then added and the mixture stirred for one hour. Finally the sodium carbonate and sodium sulfate are added, stirring is continued for one hour at 85°C and the mixture then transferred to the prewarmed storage tank.

The mixture is dried on a 12 square meters double drum drier, rotating at 6 rpm and heated with steam at 8 atmospheres pressure. The hourly throughput is 65 kg of dry powder. Yield from the above charge is about 500 kg.

The resulting powder is hygroscopic and cannot be milled. The use of Tamol permits the high content of Igepal in the mixture; up to 40% is possible. In the absence of Tamol the maximum permissible concentration of Igepal is 20%.

3. WARTIME DEVELOPMENTS

a. Detergents of the Alkyl-Aryl-Sulfonate Type

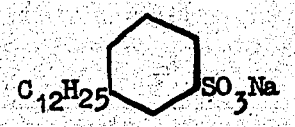
Discovery of this type of detergent was made by Höchst in about 1932. These products represented very specific alkyl-aryl-sodium sulfonates the 12 to 15 carbon chain alkyl portion of which was derived from special petroleum fractions from Western European oils of paraffinic nature. Since these compounds were based on petroleum, their commercial development was handicapped. Therefore, investigational work was begun logically on the utilization of alkyl derivatives obtainable for example from the Fischer-Tropsch synthesis, in particular, the polymerizates of low alkenes, such as propylene, which were available in quantity.

It was further anticipated that the supply of ethylene oxide in war times would be limited thus restricting the manufacture of the Igepals. Moreover, Höchst anticipated a war need for emulsifiers of diverse nature required for example in the cutting and drawing of metals where products of the above type were found suitable.

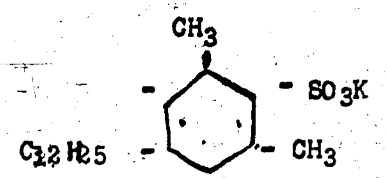
(1) Commercial Types

Höchst developed two products of industrial importance on a large scale. Specifically these are:

Detergent HÖ No. 1/181. Substantially the sodium salt of dodecylbenzene sulfonic acid:



Emulphor STX. HÖ No. 1/184. This emulsifying agent is substantially the potassium salt of dodecyl-xylene sulfonic acid.



(2) The raw materials used in the preparation of these compounds are benzene and commercial xylene and a propylene-polymer fraction. obtained from the IG Uerdingen plant and described previously under the Section 2b on Igepals.

(3) Manufacturing Process

The manufacturing processes for these detergents are given below:

(a) Preparation of Detergent Höchst No. 1/181 (Alkyl Benzene Sodium Sulfonate.

The process comprises the preparation of alkyl benzene, sulfonation and neutralization to the finished detergent.

Preparation of Alkyl Benzene

1,076 kg of pure benzene cooled to 10°C are charged to an iron vessel and 547 kg of anhydrous hydrofluoric acid are added. Then with stirring 1,472 kg of propylene polymer (P-12) are added at such rate that the temperature does not exceed 10°C. Then the mixture is stirred for two to three hours at 5-10°C, to complete the reaction. The excess of benzene and hydrofluoric acid are removed by distillation at atmospheric pressure recovering normally 304 kg of benzene and 492 kg of anhydrous HF. The residual alkylbenzene is treated with 9 kg of sodium carbonate, stirred for one-half hour and clarified by filtration.

Yield - 1,940 kg of alkyl benzene.

The P-12 polymerizate is stated to be prepared by the polymerization of propylene. This operation was carried out at the Uerdingen plant of IG. Details of the operation were not available at Höchst.

Sulfonation

4,642 kg of alkyl benzene are charged to an iron reactor at 20-30°C and 3,476 kg of sulfuric acid monohydrate (84.5% H_2SO_4) are added. Next 5,324 kg of 20% oleum are added and the mixture stirred at 20°C until sulfonation is complete as indicated by complete solubility of a test sample in water. The sulfonation mixture is then transferred to a brick lined kettle

charged previously with 5,808 kg of water. The residual sulfuric acid is separated and 2,450 kg of water added to the residue. 4,400 kg of 33% NaOH are then added to neutralize and 1,430 kg of sodium sulfate stirred into the mixture. The solution is dried on a drum drier to yield 8,230 kg of raw sulfonate.

Preparation of Detergent

2,280 kg of raw sodium sulfonate from the drum drying operation above are mixed with 1,720 kg of sodium sulfate and ground and mixed in a drum mixer. The product, about 4,000 kg is the finished detergent Höchst 1/181.

(b) Preparation of Emulsifying Agent for Mineral Oil - Höchst No. 1/184

The mineral oil emulsifying agent Höchst 1/184 is similar to the 1/181 material, alkyl benzene sodium sulfonate, with the exception that it is prepared from xylol instead of benzene.

Preparation of Alkyl Xylene

1,008 kg of purified xylol, commercial xylenes, are cooled to 0°C in an iron reactor and 531 kg of anhydrous hydrofluoric acid are added. Then with stirring, 1296 kg of propylene polymer (P-12) are added maintaining the temperature at 2°C or lower. After the addition of the polymer, the mixture is stirred for one hour at 0-2°C and then the hydrofluoric acid is removed by distillation, recovering in this manner 495 kg of HF which is recycled to the next reaction. The resulting alkyl xylol is neutralized with 21 kg of sodium carbonate and 11 kg of Tonsil AC added. Stirring is continued for one-half hour after which the mixture is clarified by filtration.

Yield - 2,124 kg of alkyl (P-12) xylol.

Sulfonation

5,000 kg of the above alkyl xylol are charged to an iron vessel at 15-20°C. 1,950 kg of sulfuric acid monohydrate are added and finally 5,550 kg of 20% oleum. The reaction is stirred for 5-6 hours at 40-45°C and then is transferred to a brick-lined vessel containing 4,100 kg of water. The resulting excess sulfuric acid is separated to yield 7,050 kg of the sulfonate of about 70% purity.

Preparation of Emulsifying Agent

6,518 kg of the sulfonate mixture above are charged to a brick-lined vessel, 548 kg of water added, and the mixture neutralized with 2,820 kg of 48.3% KOH solution. Finally 509 kg of white mineral oil are stirred into the mixture.

Yield - 10,000 kg of the finished emulsifier.

b. Emulsifying Agents and Detergents from Fischer-Tropsch Oils.

The large scale development of the Fischer-Tropsch synthesis provided a source of special hydrocarbon cuts which found an immediate war time use in the manufacture of cutting oils and detergents. Leuna took the lead in this development when it introduced the important soap substitute or soap extender known as Mersolat. This compound was made from a special Fischer-Tropsch fraction, known as Kogasin II, having a distillation range of 220-330°C and an average chain length of 15 carbon atoms. This Fischer-Tropsch cut was hydrogenated over nickel tungstate catalyst and then redistilled in order to remove olefinic and oxygenated compounds. The resulting product, termed Mepasin, was then converted into the sulfone chloride derivative by reaction with SO_2 and chlorine in the presence of light according to the Reed process. The resulting product, Mersol, was sold directly to soap manufacturers for conversion to the sodium salt known as Mersolat. It was primarily a soap extender and when mixed to the extent of 60-70% of the finished product, it found extensive use as an excellent washing compound.

Detailed information on the Mersol process is given in a report dated 18 May 1945, on I.G. Farbenindustrie, A.G., Leuna, Germany, by W. S. Calcott, CWS, Hq ETOUSA.

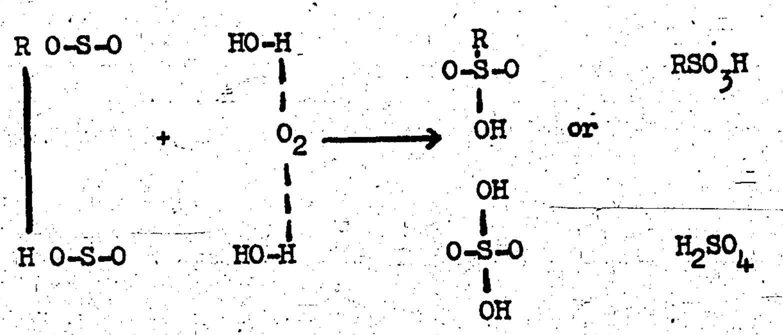
(1) Mepasin as a Höchst Raw Material

Höchst was interested in Mepasin as a raw material for the production of Mersol type materials through the use of sulfur dioxide and oxygen eliminating the chlorine used in the Leuna process. The Mepasin for their use was prepared by Leuna in a manner similar to that described above excepting that the cut used was likely more carefully fractionated. The product actually used by Höchst in their pilot plant work had a boiling range of 220-240°C, equivalent to an average chain length of 13-14 carbon atoms.

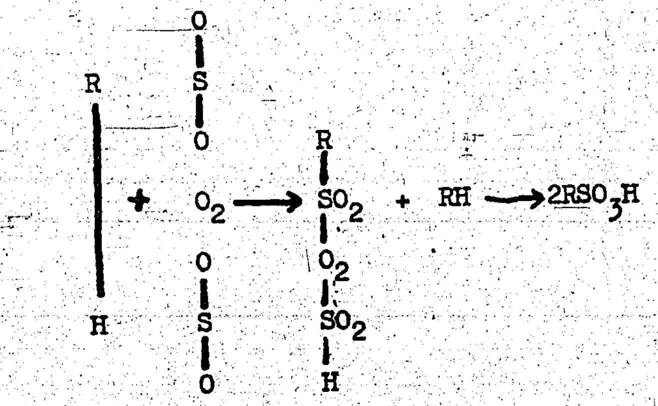
(2) New Syntheses of Mepasin Sulfonic Acid

Höchst's development work on the synthesis of the sulfonic acid from Mepasin without the use of chlorine followed three different methods. For this purpose it was necessary to have a Mepasin hydrocarbon which was entirely **paraffinic**; that is, free of aromatics, olefins, and oxygenated hydrocarbons. The Mepasin preparation has been described previously.

(a) The first synthetic method consisted in the reaction of Mepasin with sulfur dioxide and oxygen in the presence of water and activated by light or ozone. The mechanism of this reaction is illustrated in the following:

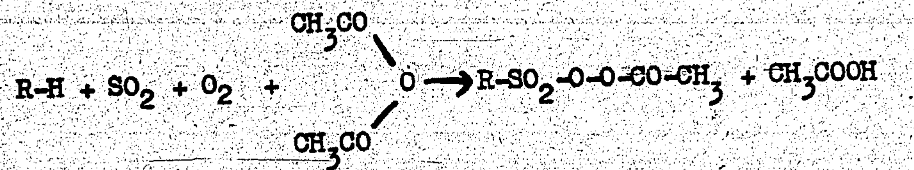


(b) In the peracid process the sulfur dioxide and oxygen were reacted in the absence of water. The reaction is presumed to proceed through the persulfate as illustrated by the following reactions:

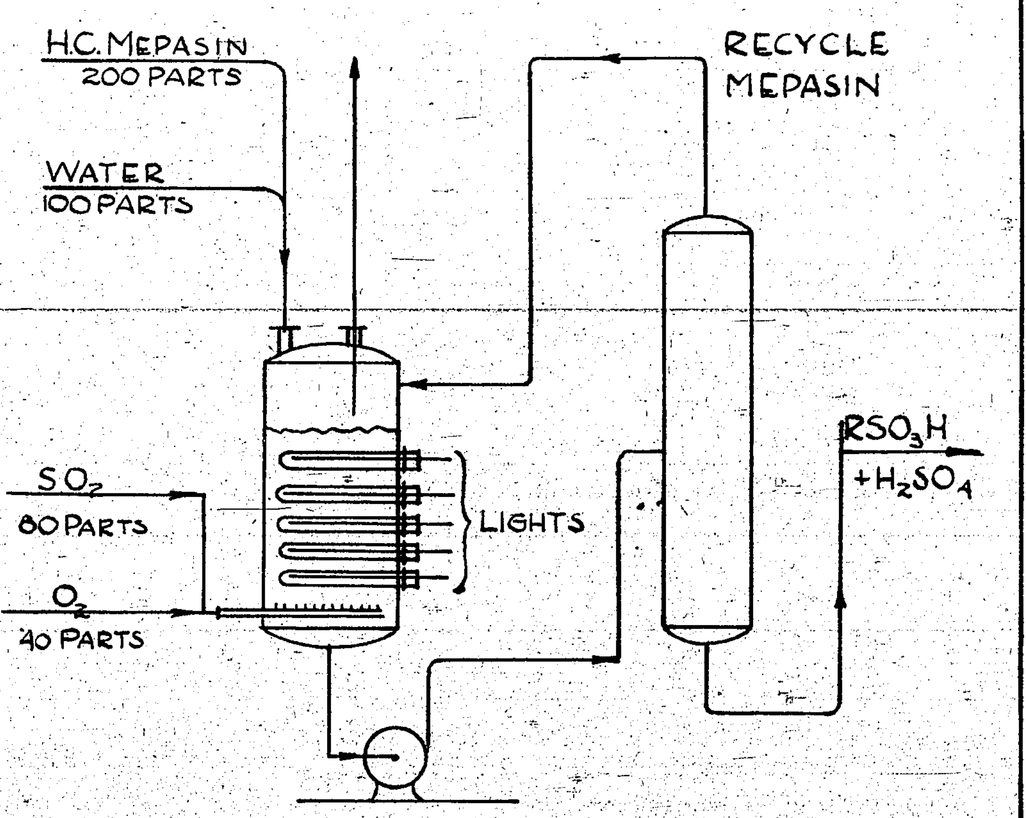


Persulfate has actually been isolated from the reaction mixture. However, the operation of this process was rather difficult and yields were poor and certain operating hazards with the peroxides were involved. Although it is assumed that a catalyst was not used, this is not known definitely since full process details were not obtained.

(c) The third process, also a peracid method, involves the use of SO_2, oxygen and acetic anhydride. The reaction was assumed to proceed in two steps. First, the per compound is formed; this, when reacted with water, or rather with dilute acetic acid yields the required sulfonic acid:



$$R\text{-}H + SO_2 + O_2 + (CH_3CO)_2O \longrightarrow R\text{-}SO_2\text{-}O\text{-}O\text{-}CO\text{-}CH_3 + CH_3COOH$$



MEPASIN SULFONIC ACID-PILOT PLANT

LIGHT ACTIVATION METHOD

6/10/45 AM.

and

$$R\text{-}SO_2\text{-}O\text{-}O\text{-}CO\text{-}CH_3 + H_2O \longrightarrow R\text{-}SO_3H + CH_3COOH + \tfrac{1}{2}O_2$$

(3) Pilot Plant Manufacture of Mepasin Sulfonic Acid

(a) Activation Using Light

Mepasin was reacted with oxygen, from a Linde plant, sulphur dioxide and water as shown in the attached sketch. The reactor was leadlined and provided with eight vertically arranged quartz lights (Hanovia Manufacturing Company), each of 2,000 watts. 200 parts by weight of Mepasin were reacted with 100 parts of water, 80 parts of sulphur dioxide, and 40 parts of oxygen, maintaining the mixture at 40-50°C and stirring by means of a centrifugal pump which cycled the reaction mixture through the system. The reaction product was then separated into two layers; an upper layer of Mepasin which was recycled to the reactor and a lower product layer which was passed to a second separator where it was mixed with the required quantity of hot water and heated to 120°C. Under these conditions the mixture yields an upper layer of Mepasin sulfonic acid plus sulfuric acid, termed "Hostaphen" and a lower layer of 50% sulfuric acid, which is removed. Some Mepasin steam distills from the separator. The "Hostaphen" layer was used as such or it was further concentrated by high vacuum distillation.

"Hostaphen" was the raw material for the preparation of cutting oils and detergents, in particular Emulphor STH which will be discussed later. A 15,000 ton per year plant was designed from the 2' diameter by 6' high pilot plant reactor. This would produce sufficient Mepasin sulfonic acid to replace the Mersol purchases from Leuna. Because of the unusually high requirement of 840 quartz lamps each of 2,000 to 4,000 watt capacity, the process was considered impracticable.

(b) Per-Acid Process

The per-acid synthesis involved the use of acetic anhydride; this was also in the pilot plant stage.

The reaction of Mepasin with acetic anhydride, sulfur dioxide and oxygen in the absence of water was carried out in a tower similar to that just described. In this case, however, it was necessary to use two towers operated in series. The first tower was about the same relative size as the tower used for the light catalyzed synthesis while the second tower was about twice as large. The flow of sulfur dioxide and oxygen was split about equally between the two towers and as indicated previously, activation with light was not required. Also the reaction, which was carried out in the dark at 40°C, is more strongly exothermic then in the light catalyzed process.

The product leaving the second tower and containing the per-acid $R-SO_2-O_2COCH_3$ was passed to a third tower operated at 55-60°C where it was mixed with recovered dilute acetic acid to furnish the water necessary for hydrolysis. Separation took place in the tower. The lower layer of dilute acetic acid containing also some by-product sulfuric acid was separated by distillation into a dilute acetic acid (about 35%) which was circulated, in part, back to the system to furnish the water of dilution. The acetic free residue was discarded. The dilute acetic acid not recycled was recovered. About 374 lbs of Mepasin sulfonic acid resulted per 80 pounds of anhydride used.

The upper layer containing the finished product, RSO_2OH, plus some unreacted Mepasin, was ready for further processing.

All of these processes were in the early development stage and hence accurate detailed operating data were not available. The data are not sufficiently conclusive to show whether or not this process would replace the present SO_2 plus Cl_2 Reed Process.

(4) Emulsifiers from Mersol

(a) General

Originally Mersol, RSO_2Cl, was intended as the key raw material in the preparation of low cost softening, wetting, and detergent agents. However, because of the inferior quality of the compounds obtained from Mersol as compared with the Igepons and Igepals other applications were sought. As a result, industrial applications were developed for emulsifiers based on Mersol, particularly emulsifiers for metal drawing and cutting oils.

(b) Emulphors STH and STX

In the preparation of these emulsifying agents, the Mersol was first condensed with ammonia and the resulting product reacted with monochloroacetic acid according to the following reactions:

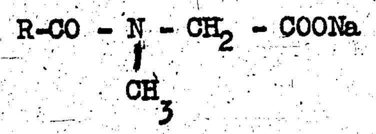
$$R-SO_2Cl + NH_3 \longrightarrow R-SO_2NH_2 + HCl$$

$$R-SO_2NH_2 + ClCH_2COONa \longrightarrow R-SO_2-NH-CH_2COOH + NaCl$$

In the commercial product the pH was adjusted by the addition of caustic soda to yield a product slightly above the neutral point (pH-7) when the emulsifier was added to water. The commercial product contained from 30-50% of the sodium salt with 70-50% of mineral oil, Mepasin ($C_{15}H_{32}$). These compounds were marketed under the generic term "Emulgatoren" and more specifically as Emulphor STH and STX containing 50 and 30% mineral oil, respectively.

(c) Uses and Applications

Although these two products were used primarily as cutting and drawing oils, they also found some uses as detergents because of the shortage of ethylene oxide, the principal raw material for the Igepals. It is of interest in this connection to note the resemblance between Medialan A and Emulphor STX.

Medialan A 

$$R-CO-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2-COONa$$

Emulphor STX $R-SO_2-NH-CH_2-COONa$

However, the washing efficiency of these Emulphors did not equal that of the Igepons and Igepals. To further complicate the story, another new detergent appearing under the same trade name, Emulphor STX, was marketed during recent years. This material was a C_{12} (propylene) polymer condensed with xylol and sulfonated. This material which has been described in detail in Section 3a (1) above as emulsifier Höchst 1/184 was produced because of the shortage of Mersols. It is inferior to the original products, insofar as oil emulsification is concerned; but it is superior in detergent properties.

(d) Properties

The emulsifiers of the type:

$$R-SO_2-NH-CH_2-COONa$$

showed interesting properties as was indicated by an exhibit. A dilute solution of Emulphor STH was poured over steel borings on a Buchner funnel. The borings so washed did not rust for a matter of hours; it was stated that they would remain rust free for at least several days. On the other hand chips washed in a similar manner with distilled water only showed definite signs of rusting within 15 minutes.

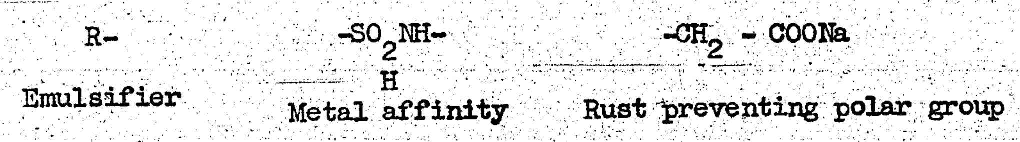
These emulsifiers were valuable in war use for the drawing of metals; e.g., shell casings. Sample 88 mm steel shell casings drawn with the use of Emulphor STH solution showed a perfectly smooth finish with no striations, a result of the adherence of the film of the emulsified oil-water phase during the drawing operation. It was stated that the use of these emulsifiers eliminated some of the intermediate heat treating operations and that the Parkerizing process now regularly employed in metal working can in many cases be eliminated.

(e) Theoretical Considerations

The theory behind the extraordinary behavior of these emulsifying agents is interesting. In the usual type detergent or emulsifying agent containing SO_4Na or SO_3Na polar groups, the acidic OH group resulting from partial ionization in the water-oil phase possesses a metal affinity and attaches itself to the surface of the treated article with the hydrophobic radical R extending vertically from the surface to form a protective film and to supply the emulsifying properties. However, the film so formed has little stability with the result that the oil-water dispersion coalesces into large drops thereby disrupting the protective film. As a result, during drawing, some portions of the metal are not properly lubricated and surface striations result. In practice this means an extra finishing step or an increased number of drawing operations.

Also a number of industrial applications exist where the fabricated material must be degreased and Parkerized to minimize rusting. It is believed that the free SO_2-OH radical promotes the formation of rust.

In the case of this new emulsifier the entire molecule consisting of the hydrophobic group, R, and the complex polar group, $SO_2 - NH - CH_2 - COONa$ possesses three distinct advantages which may be illustrated by the following picture:



$$R- \qquad -SO_2\underset{H}{N}H- \qquad -CH_2 - COONa$$

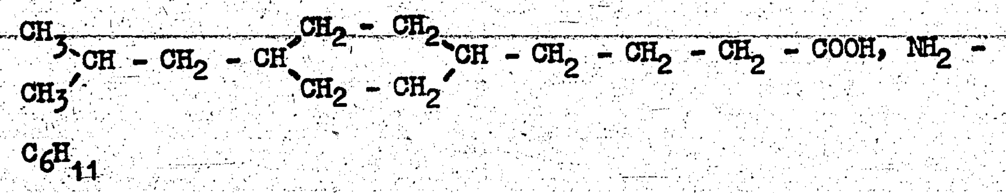
The protective film is produced by the radical R extending vertically from the metal surface in the same manner as most emulsifiers. The carboxyl group similarly adhere to the metal surface. The acidic hydrogen atom attached to the nitrogen exerts primarily a similar action and has a tendency to close the contact with the metal surface. In addition, this acidic hydrogen is also attracted by the negative carbonyl group of the polar group of the adjacent molecule. In this manner the two "metal affinity" bonds form a lattice-like structure attached to the metal, yielding an extremely adherent and uniform film. In addition neither radical promotes rusting.

(5) New Developments

A recent development under study concerns the use of compounds of the Emulphor STX type as gasoline additives. It has been known generally that the injection of small amounts of water into the cylinder of an internal combustion engine improves the performance. Such a device has been used on airplane engines. However, difficulty lies in the fact that the wear on valves, valve seats,

and cylinder walls at the high temperature conditions is so great that the continued use of water injection is not possible. It was theorized that emulsifiers carried in the gasoline might form a protective film within the engine which would be replenished continuously and thus permit regular operation. Obviously, in this case the presence of any sulfur or sodium atoms should result in the formation of a deposit on the working parts of the engine, thereby offsetting any expected advantages gained from the film-forming properties of the emulsifier. Therefore, the initial problem was the development of products in which the inorganic radicals were eliminated. Among some 200 products tested for this purpose, two proved most promising. These are represented by the following formula:

$$C_{12}H_{25} - C_6H_4 - CH_2 - CO - NH - CH_2 - COOH,\ NH_2 - C_6H_{11}$$



The first compound was obtained by the condensation of dodecylphenyl acetylchloride with glycerine then neutralizing with cyclohexylamine to form a neutral salt. The second compound was formed by neutralizing iso-butyl-cyclohexyl-n-butyric acid with cyclohexylamine to form a neutral salt.

According to Dr. Lange, the latter compound appeared to be the more promising. It was contemplated to add about 0.1 - 0.2% of the additive to the gasoline. These compounds were rather new developments and details on their manufacture and particularly on field trials are not yet available.

(6) Improvements in Detergent Compositions

(a) Summary of Höchst Wartime Research

From a chemical point of view, Höchst's war-time research in this important field did not result in any improvement involving structural changes in the detergent molecule. Whereas in the field of emulsifying agents, definite improvements were achieved with the introduction of the $-SO_2$,-NH,-COONa groups into the hydrocarbon molecule, research on long chain radicals (the detergent active aliphatic radical of the soap) looking towards increased efficiency in washing (especially cotton) appeared to have remained stagnant.

The source of raw materials only was changed as necessitated by war-time economics. These raw material changes did not improve the products and frequently affected the quality adversely to such an extent that new application methods with the help of special assistants had to be developed to make the products usable. This angle was pursued by Höchst in a most skillful manner, the substance of which was outlined by Dr. Nüsslein in a series of statements and illustrations which are incorporated as a matter of the utmost interest to the Detergent industry into the following part of this report.

(b) Development and Use of Tylose

The great majority of synthetic detergents of the sulfonate type, while often and erroneously considered as colloidal substances in view of their high molecular weight and their resemblance to soap, yield solutions which are analytical rather than colloidal, according to type. As compared to soap solutions, especially concentrated ones, they have less detergent and dispersing efficiency but possess inferior colloidal properties. The Höchst laboratories determined that the degree of detergency was intimately connected with the colloidal properties of the detergent, and thus discovered that most synthetic detergents could be improved in respect to colloidal properties by an appropriate increase in the electric charge of the **negative** ion radical. This in itself may not have been entirely novel, because the addition of protective colloids to synthetic detergent solutions of the sulfonate type had been emphasized long ago for the purpose of increasing their washing efficiency, primarily on soiled cotton. Not much, if any, improvement was gained by doing this, and in general the results were frequently negative because of the wrong choice of the protective colloid. With the development of tylose, the sodium salt of cellulose-oxyacetic acid, also known in the textile printing trade as Coloresin (cellulose - O-CH_2COONa) Höchst found a compound which resulted in the much desired effect when used in aqueous solution. Its addition to a polar synthetic detergent of the sulfate, sulfonate or carboxylate type, resulted in a compound action which was considered to be the equal of a concentrated soap solution. The improvements gained are best illustrated in the following **simple** table:

	Washing	Dispersing	Colloidal Property
Soap-low conc.	+	±	-
Soap - high conc.	++	+	+
Synth. Detergent - low conc.	+	±	-
Synth. Detergent - high conc.	+	±	-
Tylose	-	-	+
Synthetic Detergent plus Tylose	++	+	+

A demonstration of the washing of soiled cotton piece goods illustrating this point was made, in which various Höchst detergents and one synthetic detergent of the alkyl-aryl sulfonate type of American manufacture were tested with and without the addition of Tylose. Castile (olive oil) soap was taken as a standard and the detergents were tested alone and also with the addition of soda ash. A test was also run with Castile soap and soda ash. The detergent solutions were run with 0.5 g/l, 2.0 g/l and 5.0 g/l concentrations; the soap solution in 2.0 g/l and 5.0 g/l concentrations. The detergent Tylose solution contained 1.0 g/l of Tylose in one test and 0.5 g/l of Tylose plus 1.0 g/l of soda ash in another test solution. In each case the detergent solutions containing the Tylose displayed improved detergent action, equal to that of 5.0 g/l soap solution. This is one improvement which should not be disregarded, for it is well known that as yet there is no effective synthetic washing agent for cotton. Addition of Tylose to soap solutions does not materially affect the efficiency of the lather.

On the basis of tests made by Höchst, a good washing compound should contain:

10-15%	Detergent (Igepon, Igepal powder, Mersolat, etc. types)
1-2%	Tylose.
4%	Sodium tri-silicate.
20-30%	Calcined soda ash.
Balance	Sodium sulfate crystals.
100%	

These quantities are illustrative and were adjusted to more desirable concentrations in other mixtures. The above formulation is typical of a cheap washing agent giving excellent results. In addition, Höchst made numerous washing compounds using appropriate mixtures of detergent and Tylose. In view of the rather low solubility of Tylose, a dispersing agent of the Tamol type (a condensation product of naphthalene sodium sulfonate with formaldehyde) was used to advantage. In this connection it was also noted that Tylose imparted detergent properties to aryl sulfonates containing alkyl chains as low as 3 carbon atoms.

Tylose was manufactured by I.G. Farbenindustrie A.G. in Biebrich/Main-Kalle & Co., from where Höchst procured it as a raw material.

(c) Future of Tylose

Höchst had made plans to erect a plant to produce 30,000 tons of Tylose annually. On the basis of 1 part of Tylose to 4 parts of finished detergent, this program would correspond to a total yearly output of 120,000 tons of synthetic detergents of all types. Höchst's recent output was not learned but the overall annual sales value of all IG detergent compounds was stated to be about 60,000,000 RM or about 60 to 80 million pounds per year on a 100% organic content basis.

The use of Tylose would therefore boost the total I.G. output of all brands of detergents to 240 million pounds a year which would appear to be a three or four-fold increase.

4. DISMULGANS

a. Discussion

Dismulgans were produced at the Mainkur works of I.G., a unit of the Main-Gau Betriebs group of which Höchst is the key plant. Although these materials belong to the class of emulsion breakers, they are included in this report on Höchst in view of their close relation to emulsifying and dispersing agents discussed therein.

The series includes five members known respectively as Dismulgan III, IV, V, VI, and VII. The first item, Dismulgan III, was produced at Höchst, the balance at Mainkur. These materials were useful as emulsion breakers for crude oils. Types IV and VI were stated to be used for oils from the Vienna district, Type V from Alsace (Pecheltronn) oils and Type VII for oils from Hamburg district. In addition Type V, also known as Humectol CX, was of specific value in the textile industry where it was used as a wetting and leveling agent. Data on the composition and method of manufacture follow. These data were translated from Mainkur documents.

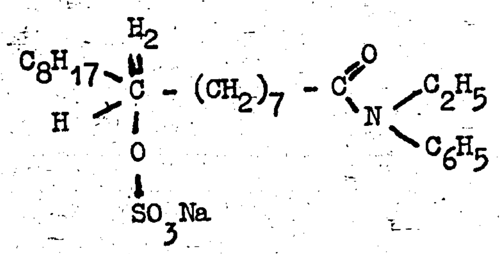
b. Manufacturing Processes

(1) Dismulgan III

This product is dodecylphenol (Phenol oil SR 1) poly (30) glycol ether. Its manufacture has been outlined in the general process discussion on Igepals.

(2) Dismulgan IV

This product is essentially a sodium sulfate ester of oleic acid ethyl anilide of the following formula:



Equipment

Reaction vessel of 250 gallon capacity, acid proof brick lined with a homogeneous lead covered stirrer 30 rpm.
Separation tank for oleic acid ethylanilide. Capacity 750 gallons. Homogeneous lead lined with anchor type stirrer, 36 rpm.
Sulfonation reactor 850 gallon lead lined cast iron, with anchor stirrer rotating at 60 rpm. Jacketed for heating or cooling.
Separator for acid-sulfate separation lead lined with gate type stirrer.
Still cast iron 1,000 gallon vessel with cement lining. Wooden stirrer.
Copper heating coil and cover of lead lined steel. Foam separator. Copper condenser.
Miscellaneous receivers, measuring tanks, etc.

Charge

Oleic acid - mol wt 282	500 kg
Phosphorus trichloride (56 kg/mol oleic)	100
Monoethylaniline	214
Sodium hydroxide - 33°Be	300
Sulfuric acid - 85% (monohydrate)	550
Trichloroethylene	660
Sulfuric acid - 66° Bé basis diluted to 50%	300
Sodium hydroxide, 33°Be	280

(540 kg of the trichloroethylene above is recovered by distillation)

Procedure

500 kg of oleic acid are charged to the reactor, heated to 50°C and 100 kg of phosphorus trichloride are added below the surface of the mixture. The mixture is then brought to 55°C and held at this point for three hours in order to complete the reaction.

Next, the reaction mixture is transferred to the separator where, after 12 hours, the phosphoric acid is removed as a lower layer and discharged to the sewer.

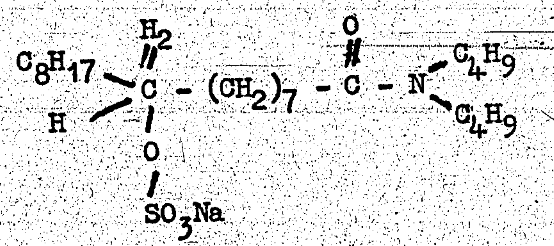
The second step is carried out by charging the 300 kg of NaOH solution, 200 kg of water and 214 kg of monoethylaniline. The oleylchloride is added to this stirred mixture and the reaction continued for 8-10 hours cooling to 20°C by means of brine. After all of the oleylchloride has been added the mixture is heated to 50°C, maintained at this temperature for one hour, next at 60°C for one hour and then warmed to 70-80°C. The mixture is finally transferred to a 750 gallon tank and the anilide washed with 50% sulfuric acid at 75°C and allowed to stand at this temperature for three hours. The lower acid layer is discharged to the sewer. Following this the operation is repeated washing with an additional 250 litres of 50% sulfuric acid. The lower acid layer is again wasted and the upper anilide layer transferred to the sulfonation vessel to which 660 kg of trichlorethylene have been charged. The above mixture is cooled to 0°C and maintained at this temperature during a 10-12 hour period during which time 550 kg of 85% sulfuric acid are added. The mixture is then added slowly to 3,000 kg of water containing 350 kg of ice, cooling so that a temperature of 5°C is not exceeded. After standing overnight the lower layer of the sulfatetrichloroethylene mixture is withdrawn and passed to the still. 200 litres of 33°Be NaOH solution plus some water are added to the still to make the mixture faintly alkaline to phenolphthalein. The batch is then heated slowly to remove the trichloroethylene which starts to distill at 85°C and finished when the temperature reaches 98-100°C. During the distillation the product is tested and adjusted continuously so that it is alkaline to litmus but neutral or very slightly alkaline to phenolphthalein. Foaming during the distillation is particularly bad between 70 and 80°C. The stripped product is diluted with water to about 1,800 kg to yield a light brown liquor of 1,055 sp gr and a fatty acid content of 35% .

Yield

The above materials yield a 1,800 kg of finished, Dismulgan IV, product.

(3) Dismulgan V

The formula of this material is essentially:



The commercial product contains some sulfo ester of oleic acid as well as some sodium oleate.

Equipment

The equipment required and the manufacturing procedure is essentially the same as that given in detail under the discussion of Dismulgan IV.

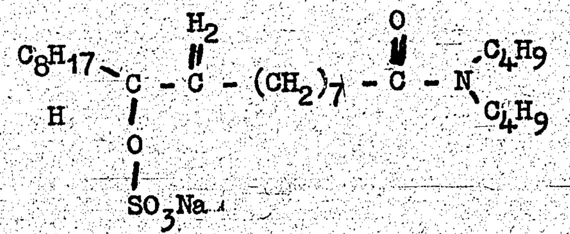
A typical bill of materials is:

Oleic acid - mol wt 282	500 kg
Phosphorus trichloride	100
Sodium hydroxide - 33°Be	344
Diisobutylamine mol wt 129	208
Sulfuric acid -95% basis (Dilute to 50%)	500
Trichloroethylene	730
Oleic acid**	180
Sulfuric acid monohydrate (theory - 236)	748
Trichloroethylene	176
Ice	1,600
Sodium hydroxide 33°Be (128 kg of 100%)	432
Oleic acid**	50

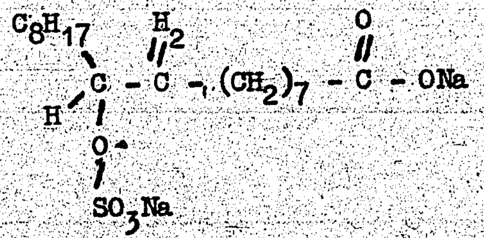
The yield from the above reactants is 2,678 kg of finished product.

(4) Dismulgan VI

This material is similar to Dismulgan V except that it contains a small amount of the sodium salt. In other words, it is a mixture of :



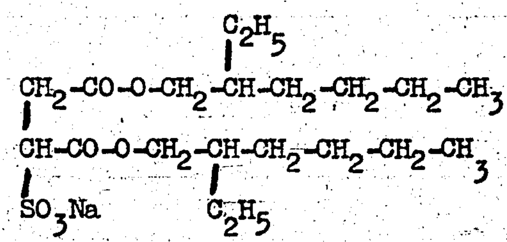
and



*The extra oleic acid is added first to the sulfonated mass (180 kg) and finally (50 kg) to the still residue product in order to adjust the oleic acid content.

(5) Dismulgan VII

This material has the following formula:



$$\begin{array}{l} \qquad\qquad\quad C_2H_5 \\ \qquad\qquad\quad | \\ CH_2-CO-O-CH_2-CH-CH_2-CH_2-CH_2-CH_3 \\ | \\ CH-CO-O-CH_2-CH-CH_2-CH_2-CH_2-CH_3 \\ | \qquad\qquad\qquad\;\; | \\ SO_3Na \qquad\quad\;\; C_2H_5 \end{array}$$

Equipment

Reactor, a 2,000 gallon jacketed, homogeneous lead-lined vessel with anchor type stirrer. Lead lined reflux condenser and copper coil condenser for product. Enamelled, jacketed vessel of 1,000 gallon capacity. Stirred tank, about 1,000 gallon capacity, brick-lined.

Charge

Alpha ethyl hexanol	4,307 kg
Maleic acid	1,830
p-toluene sulfonic acid as 50% paste.	75
95% ethanol..........................	4,330
Sodium bisulfite powder - 100% basis.	2,194
Sodium hydroxide - 33°Bé	190

Procedure

4,307 kg of ethylhexanol are charged to the lead-lined reactor and with stirring 1,830 kg of maleic acid and 75 kg of p-toluene sulfonic acid are added. The ethyl hexanol purity is based on the hydroxyl value. An excess of 5% above theory is used. The temperature is raised to 101°C during the course of an hour and then slowly heated up to 145°C during an additional 7 hour period. Water begins to distill as soon as the temperature reaches 101°C. Any ethylhexanol distilling over with the water is separated and returned to the reactor. After the bulk of the water has distilled, heating is continued overnight until the temperature reaches 152°C. Finally distillation is continued under a slight vacuum and without returning the alcohol water distillate until at the end of 5 hours at 152°C the water removal is complete. The vessel is then cooled to room temperature, leaving about 1,750 gallons of ester product, of 0.94 gravity.

The ester product above is charged to the enamelled reactor, and the ethanol is added. NaOH is then added until the mixture is weakly alkaline to litmus. Meanwhile the sodium bisulfite solution (22.5% $NaHSO_3$) is prepared in a brick-lined tank and added to

the neutralized ester mixture. Then the reaction mixture is heated slowly to 100°C and held at this temperature for 12 hours; the pressure showing 1.6 atmospheres. Next the mixture is cooled to 60°C to reduce the pressure and is then heated to 80°C at which temperature ethanol begins to distill. Heating and distillation of the ethanol is continued until a **temperature** of 91°C is attained, after about 7 hours and most of the ethanol has distilled. The mixture is then cooled to room temperature. The resulting finished product is transferred directly to plywood containers.

The alcohol distillate is purified by rectification. About 75% of the charge is recovered in this manner. The balance of the ethanol remains in the Dismulgan product.

Yield

The yield is 560 kg of the Dismulgan VII product per 100 kg of maleic acid or 10,250 kg for the above batch.

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

PREPARATION OF "ALKAZID" M AND DIK

Roberts, J. H.

RESTRICTED.

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

PREPARATION OF "ALKAZID" M AND DIK

Reported by:

Mr. F.H. ROBERTS
NavTecMisEu

June 1945

CIOS Target No. 22/1f
Miscellaneous Chemicals

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

RESTRICTED

7 p.

TABLE OF CONTENTS

SUMMARY

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

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

Appendix - Operating Instructions,
15 March 1944, preparation of potassium salt of Methyl alanin.

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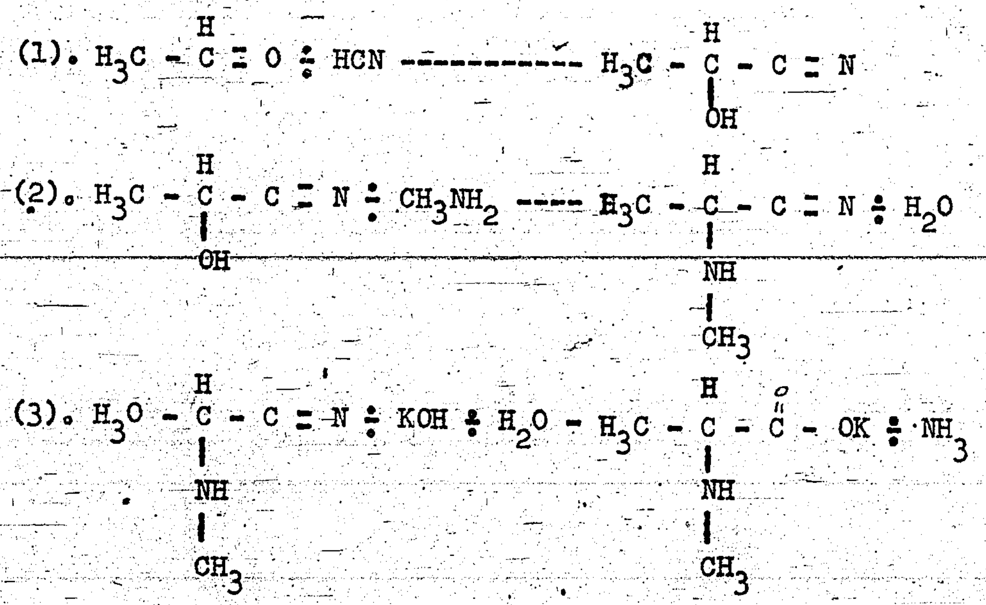
1. Details

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

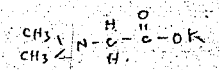


(1). $H_3C-\overset{H}{C}=O + HCN \longrightarrow H_3C-\underset{OH}{\overset{H}{C}}-C\equiv N$

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

(3). $H_3O-\underset{\underset{CH_3}{|}}{\underset{NH}{\overset{H}{C}}}-C\equiv N + KOH + H_2O - H_3C-\underset{\underset{CH_3}{|}}{\underset{NH}{\overset{H}{C}}}-\overset{O}{\overset{\|}{C}}-OK + NH_3$

ALKAZID - M



$\begin{matrix}CH_3\\CH_3\end{matrix}\rangle N-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OK$

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

(b) An iron autoclave equipped with an agitator and brine cooled coil and jacket is charged with a thirty-five (35) percent aqueous solution of the amine. The temperature is adjusted to fifteen (15) to eighteen (18) degrees centigrade and maintained there during the slow simultaneous addition of hydrogen cyanide and the aldehyde. The completion of the reaction is determined by titration with aqueous silver nitrate solution for free hydrogen cyanide. The nitril thus formed in equations (1) and (2) above is hydrolyzed by the addition of potassium hydroide solution and heating to one hundred and ten (110) degrees centigrade.

The concentration of the product is adjusted by distillation under vacuum to remove water and adjust the specific gravity to 1.18 to 1.20 which corresponds to approximately a thirty (30) percent solution.

* See Appendix

APPENDIX

Betriebsvorschrift
15.3.44 As./Str.

Herstellung von Alkazid M (Methylalanin - Kalium).

1. **Anlagerung.**

In einem eisernen Ruhrkessel von 1 500 Ltr. Inhalt mit Kublschlange und Kuhlmantel, Ruhrerdrehzahl 60 Um/-Minute, werden zu 200 kg Methylamin in ca. 35 %iger waBriger Losung bei 15-18° pro Stunde 27,5 kg Blausaure (aus 50 kg NaCN in 30-35 Vol.%iger Losung entwickelt) eindestilliert und 2 kg Kalk in 4 kg H_2O vorgelegt. 20 Minuten nach Beginn der HCN-Destillation last man bei 15-18° gleichzeitig 27,5 kg Blausaure und 50 kg Acelaldehyd pro Stunde zulaufen. Nach 4 Stunden fugt man nochmals 2 kg Kalk zu. In etwa 7 Stunden laufen so die auf Methylamin berechnete Theoretische Menge Blausaure (316 kg NaCn in 30-35 %iger Losung) und die ebenso auf einen Gehalt von 92 % berechnete Menge Acetaldehyd (390 kg). Die Endtemperatur soll 15° betragen, nachdem der Acetaldehyd-Einlauf 20 Minuten gestoppt wurde. Zur Kuhlung dient Sole aus einer Kalteanlage von ca. 15 000 WE/St. von + 5° Temperatur. Nach Baendigung des Acetaldehyd-Einlaufs wird noch 1 Stunde bei 20-25° geruhrt, wobei zu beachten ist, dab die Temperatur nicht durchgegt. Der Ansatz soll zum Schlub einen Blausauregehalt entsprechend 3,0 - 3,2 n/20 Ag fur 5 ccm IUsung (salpetersauer titriert) aufweisen, wenn er hoher ist, wird die entsprechende Menge Acetaldehyd zugesetzt. Fahler entstehen, wenn die Temperatur nicht genau eingehalten wird.

2. **Verseifung.**

Sie schliesst sich unmittelbar an die Anlagerung an. In einem Ruhrkessel von 2 - 3 cbm Inhalt mit Heizmantel oder Heizschlange werden 80 % der Theorie KOH, berechnet auf das angewandte Methylamin, in Form von 30 %iger chemisch reiner Kalilauge unter Zumatz von 6 % CaO vorgelegt, mit dem Ansatz nach 1. bei 20--25° vermischt und3 Stunden bei dieser Temperatur geruhrt. Daun wird langsam unter Vermeidung des Uberschaumens auf 105° hochgeheizt und 1 Stunde bei dieser Temperatur gehalten.

3. **Eindampfung.**

3 Ansatze nach 2 werden zusammen in einer Ruhrkanone

mit Dampfmantel von ca. 7 cbm Inhalt im Vakuum auf ein spezifisches Gewicht von 1,2 eingedampft. (Ausbeute an Methylalanin 70-73 % d.Th.).

4. Ausdampfen.

2 Ansatze von 3. werden nach Zusatz von 15 kg CaO in einem Ruhrbehalter von 10 cbm Inhalt mit Heizschlange auf 105-110° erhizt.Dann werden 3-4 Stunden bei 110° Dampf oder N_2 durchgeleitet. Durch haufige Probenahme ist festzustellen, dass kein Eisen in Losung geht, in welchem Falle das Ausdampfen sofort zu unterbrechen ist.

Analyse:

Nach 3-4 Stunden Abdampfwert. Es werden aus einer filtrierten Probe von 1 kg im Glaskolben 350 ccm abdestilliert, die Losung dann auf 1 Ltr. aufgefullt und mit $^{n}/1$ HCl gegen Methylorange titriert. Der Verbrauch soll nicht uber 20-30 ccm $^{n}/1$ HCl pro kg betragen.

5. Aufarbeitung.

Aus der nach 3. anfallenden, auf 25° abgekuhlten ca. 8,5 cbm Losung wird der Kalk durch Einleiten von ca. 90 kg CO_2 ausgefullt, eine Losung von 35 kg Kaliwasserglas von spez.Gew. 1,362 in 70 kg Wasser und anschliessend 35 kg vorbenutztes Carboraffin zugesetz.+) Anschliessend wird 3 Stunden bei 50-60° geruhrt, in einen gummierten Ruhrkessel filtriert, ca.180 kg CO_2 eingelentet bis zur sodaalkaalkalischen Reaktion gegen Triazenpapier, dann mit 35 kg frischem Carboraffin bei 35-40° 14 Stunden geruhrt, auf ein spez.Gew. von 1,2 eingestellt und filtriert. (Der Filterruckstand wird wie oben beschrieben einer folgenden Partie als vorbenutztes Carboraffin zugesetzt.)

Fehler: Lauge schaumt. Dann nochmala mit Carboraffin behandel

6. Produktion

betragt 3,5 - 4,5 tato:

7. Analysen

werden wie bei Dik - Lange D ausgefuhrt. Absorptonswert: 70 - 72 ccm CO_2 / 1 ccm Lauge von d = 1,18. Bei graphischer Darstellung entsteht eine steile Kurve gegen CO_2

Der Korrosionswert soll konstante Werte oder eine geringe Gewich zunahme ergeben.

Der Abdampfwert betragt 20-30 ccm $^{n}/1$ HCl pro kg.

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

+) Carboraffin absorbiert die schaumenden Bestandteile.

ITEM No. 22
FILE No. XXX—2

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SYNTHESIS OF ACETONE

Roberts, F. H.

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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SYNTHESIS OF ACETONE

Reported by

Mr. F. H. Roberts, NavTecMisEu

June 1945

CIOS Target No. 22/1f

Miscellaneous Chemicals

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

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4 p.

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SYNTHESIS OF ACETONE

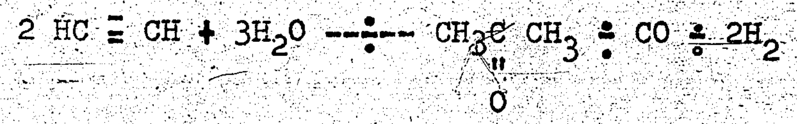
1. Summary.

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

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

2. Details.

(a) Acetone and water react according to the following scheme:



$$2\ HC \equiv CH + 3H_2O \;{-}{-}\div{-}{-}\; CH_3\underset{\overset{\|}{O}}{C}\,CH_3 \div CO \div 2H_2$$

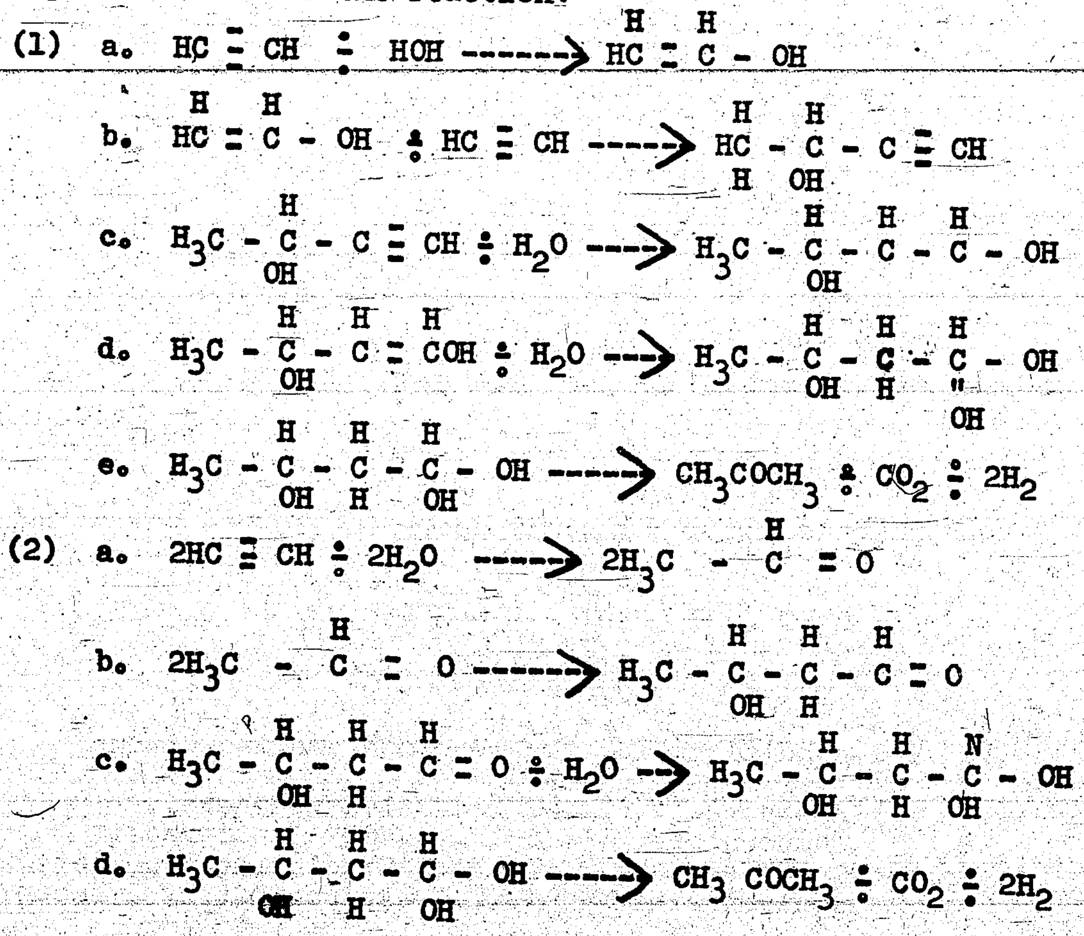
(b) The conditions for the reaction are as follows:

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

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

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

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



(1) a. $HC \equiv CH + HOH \longrightarrow \overset{H}{HC} = \overset{H}{C} - OH$

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

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

d. $H_3C - \underset{OH}{\overset{H}{C}} - \overset{H}{C} = \overset{H}{C}OH + H_2O \longrightarrow H_3C - \underset{OH}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - \underset{\substack{\| \\ OH}}{\overset{H}{C}} - OH$

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

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

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

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

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

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ITEM NO. 22.
FILE NO. XXX - 5.

Classification Cancelled,
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SYNTHETIC LUBRICATING OILS

Roberts, J. H.

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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

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SYNTHETIC LUBRICATING OILS

Reported by:

Mr. F.H. ROBERTS
NavTecMisEu

[1945]

CIOS Target No. 22/124
Miscellaneous Chemicals

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

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3 p

SYNTHETIC LUBRICATING OILS

1. Summary.

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

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

2. Conclusions and Recommendations.

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

3. Details

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

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

ITEM NO. 22.
FILE NO. XXX - 4.

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

Roberts, F. H.

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

Reported by:

Mr. F.H. ROBERTS
NavTecMisEu

June 1945

CIOS Target Nos. 22/1f & 22/1h
Miscellaneous Chemicals

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

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3 p.

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

1. Summary

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

2. Details

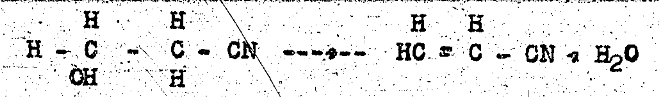
(a) Methyl formate is produced at Ludwigshafen by the addition of carbon monoxide to methanol. A solution of one percent sodium methylate in methanol is used as catalyst. $CH_3CH + CO\ CH_3ONa;\ HC = O - OCH_3$. To this solution, contained in a pressure autoclave, of steel resistant to carbon monoxide attack, carbon monoxide is slowly added. The heat of reaction is large and cooling by means of a brine jacket is used. Carbon monoxide is added up to an ultimate pressure of 200 atmospheres. The temperature is allowed to rise slowly from 30 degrees to 110 degrees centigrade. The reaction is terminated when there is no further absorption of carbon monoxide as indicated by a drop in the pressure on the autoclave. The operation is entirely batch wise. It is imperative that the entering carbon monoxide be dry and free of carbon dioxide. Either of these impurities would attack the catalyst by hydrolysis in the case of water or neutralization to form sodium carbonate in the case of carbon dioxide, thus precluding a further reaction. The crude reaction mixture from this step is subjected to distillation to separate the methyl formate and methanol from the sodium methylate. No attempt is made to separate the alcohol and ester. The yield in this step is approximately 70 percent.

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

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

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

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



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

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

(e) Acrylonitril is produced on a very small scale at the Hüls plant by the direct addition of hydrogen cyanide to acetylene. This reaction takes place in aqueous medium in the presence of a monovalent copper salt catalyst described by Nieuland in the United States for general reactions of acetylene, especially the dimerization of acetylene to vinylacetylene. The acrylonitril is isolated continuously from the aqueous reaction medium by distillation.

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~~CONFIDENTIAL~~

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

Roberts, F H

~~CONFIDENTIAL~~

COMBINED INTELLIGENCE OBJECTIVES
SUB - COMMITTEE

~~CONFIDENTIAL~~

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

Reported by

Mr. F.H. ROBERTS,
NavTecMisEu

August 1945

CIOS Target No. 30/257
Fuels and Lubricants

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

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SUMMARY

The information given here was obtained from Dr. Delfts of the I. G. Farbenindustrie during an interview at the Leverkusen Plant on May 26, 1945. It has been found that, by a complicated procedure, tetrahydrofuran will polymerize, in the presence of a catalyst, to compounds having properties desirable in a lubricant. Among these are a high flash point, a high viscosity index and extremely low pour point. The nature of the polymeric complex can be changed by the addition of co-polymerizing substances such as ethylene oxide and its derivations. The nature of the polymer ranges from liquid to a relatively tough solid melting about 60 degrees Centigrade. The physical state for a particular use depends upon the catalyst used, the temperature of operation and the molecule ratio of tetrahydrofuran to other co-polymerizing components. From a long research it has been shown that the best catalyst is a complex of ferric chloride and thionyl chloride. Special materials of construction are needed because of the corrosive nature of the reaction medium. A simple polymer of tetrahydrofuran has been made which is identical with polybutylene glycol. This glycol and its esters have also been used as lubricants. Compounds have been made for crankcase lubrication of internal combustion engines and for high temperature steam lubrication applications by the co-reaction of tetrahydrofuran with 50 parts by weight of ethylene oxide and 25 parts by weight of ethylene oxide respectively. The involved process of manufacture, the limited availability of the necessary raw materials and the cost would preclude any large scale production of these lubricants in competition with refined natural hydrocarbons.

The production in Germany is illustrated in the following figures:

		1942	1943
Crankcase lubricant	(M620	7.0 Tons	10.7 Tons
High temperature steam lubricant	(M586)	2.4 Tons	5.4 Tons

No operating or performance data are available for these synthetic oils. The basis for their lubricating value to date is dependent on their physical properties. A synthesis is also described for the production of the tetrahydrofuran monomer from formaldehyde and acetylene by liquid phase condensation.

Enclosed with the original copy of Letter Report 123-45, Reference L, are short reports. Reference A to K, covering in detail the theoretical chemistry involved in the synthesis and the detailed production procedure. It is suggested that reference be made to these if such information is wanted.

References:

(a) Scientific Paper "Polymerization of Tetrahydrofuran; No. 38; Dr. Morschel; 1 October 1940.
(b) Scientific Report "Polymerization of Tetrahydrofuran" Dr. Delfts, Leverkusen, 13 October 1941.
(c) Scientific Paper "Polymerization of Tetrahydrofuran"; No. 165; Dr. Morschel, 17 July 1942.
(d) "Esters of Polymeric Butylene glycol", No. 208; Dr. Schulte, Leverkusen, 2 September 1943.
(e) Scientific Paper "Esterified Tetrahydrofuran Polymers"; No. 213; Dr. Morschel, 20 September 1943.
(f) Scientific Paper "Brake Fluids"; No. 185; Dr. Morschel, 12 January 1943.
(g) Scientific Paper "Polymerization of Tetrahydrofuran"; No. 186; Dr. Morschel, 12 January 1943.
(h) Scientific Paper "Polymerization of Tetrahydrofuran"; No. 189; Dr. Morschel, 12 January 1943.
(i) "Polymerization of Tetrahydrofuran"; No. 227; Dr. Morschel, 31 December 1943.
(j) "Preparation of Polymeric glycols"; No. 232; Dr. Schulte, 10 January 1944.
(k) Four (4) Laboratory Data Sheets - Physical Properties of Tetrahydrofuran Polymer Exp. No. 2555, 3241, 5202.
(l) Letter Report No. 123-45(S)

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

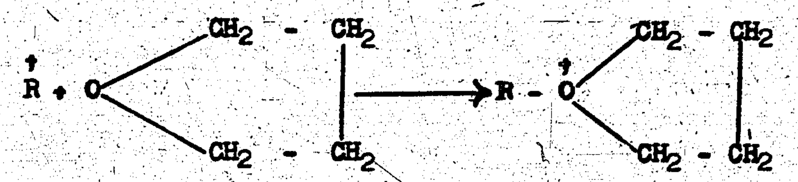
During a research which apparently covered about four years, a series of catalysts, as follows, was developed for the polymerization of tetrahydrofuran:

(1) Tertiaryoxionium salts of acid boron fluoride compounds.
(2) Boron trifluoride - ethylene oxide complex.
(3) Antimony pentachloride.
(4) Aluminum trichloride.
(5) Ferric chloride and thionyl chloride.
(6) Stannic chloride.
(7) Perchloric acid.
(8) Chlorsulfonic acid.

Subsequent work has demonstrated that the best of these, for large scale production, is the ferric chloride-thionyl chloride complex. The basis for this choice is:

(1) Safety in operation.
(2) Ability to give a high degree of polymerization.
(3) Ease of hydrolsis of the terminal groups.
(4) Speed of reaction.

Tetrahydrofuran polymerizes by a free radical or ionic chain mechanism as follows:

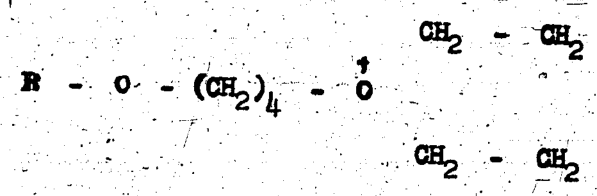


(I)

An opening of the furan ring follows with the production of an alkyl-cation.

$$\left[R - O - CH_2 - CH_2 - CH_2 - \overset{+}{CH_2} \right] \qquad (II)$$

The assumption for further reaction is that the ionic state is maintained and that the complex Ion (II) is a reaction initiator capable of further reaction with tetrahydrofuran to give:



$$R - O - (CH_2)_4 - \overset{+}{O}\begin{matrix} CH_2 - CH_2 \\ \\ CH_2 - CH_2 \end{matrix} \qquad (III)$$

This radical (III) in turn undergoes ring fixation to give:

$$R - O\ (CH_2)_4 - O - (CH_2)_3\ \overset{+}{C}H_2 -$$

By this means a chain mechanism is perpetuated until reaction with an Ion og negative charge meets the propagating Ion and removes it from further reaction.

It follows from the above mechanism that chain length is dependent upon catalyst concentration since the greater the amount of catalyst the greater the number of chain molecules present in any preparation.

The polymers range from liquids at room temperature to crystalline solids with a melting point about 60 degrees Centigrade.

The products are soluble in aromatic hydrocarbons, in chlorinated aliphatic hydrocarbons, and in many ethers, esters and ketones. The solubility decreases with increase in molecular weight as is usually the case with macromolecules.

The consistency of the polymeric products may be roughly grouped as follows:

up to 16 carbon atoms per molecule - liquid at room temperature.
16 " 25 " " " " - vaselinelike.
25 " 50 " " " " - waxy.
50 "100 " " " " - tough wax to brittle.

These polymers are unstable to oxidation, the attack taking place at the carbon atom adjacent to the ether oxygen. Esters and acids are the products of this oxidation. Apparently this sensitivity to oxygen is so pronounced that atmospheric oxygen is sufficient to cause a breakdown. Stability in operation is achieved by the addition to small amounts 1.0 to 3.0 percent of phenyl B-naphthylamine.

In practice for lubricant production tetrahydrofuran is always copolymerized with ethylene oxide or one of its derivatives such as propylene oxide or epichlorhydrin. These copolymerizing monomers tend to keep the polymeric product liquid over wider temperature differences. The more branched the chain of the oxide additive the broader is the liquid range of the polymer.

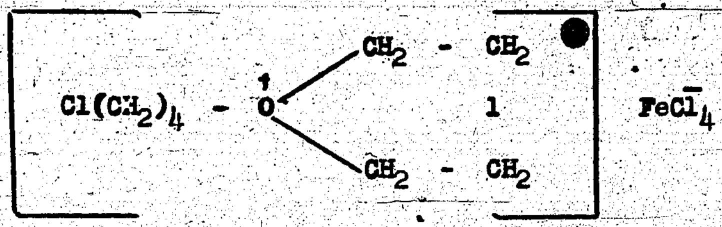
These polymers have also been tried in applications other than lubricants. These uses are briefly noted as follows: Products containing 18 to 71 carbon atoms per chain are compatible with Buna S and cause a softening which accelerates sheeting in the processing of this synthetic rubber. Polymers containing less than 30 carbon atoms per molecule give no decrease in the strength of the compound Buna S, above 30 there is a decided lowering in the strength of the rubber. Tetrahydrofuran polymers have also been used as a substitute for wool-fat as an aid in spraying Buna S compositions for certain applications. These same polymers have also been used as substitutes for whale-pol for treating leather and as lubricatns for synthetic fibers in spinning operations.

It is essential in this process that all reagents be carefully dried before use. This is mandatory for control of the reaction and for best yields. The presence of water hydrolyzes the catalyst give rise to acidic components.

A typical preparation is briefly outlined. The catalyst is prepared previous to its utilization in the process by mixing the following:

12 liters tetrahydrofuran
5 Kg. ferric chloride
3 Kg. thionyl chloride

During reaction of these sulfur dioxide is lost and the product, a crystalline mass is thought to have the following structure:



This material is isolated and charged back to the reaction so that the concentration of the catalyst based on the total product is as follows:

Component	Engine Lubricant M 620 Molecules	Steam Lubricant M 586 Molecules
Tetrahydrofuran	100	100
Ethylene Oxide	50	25
Thonylchloride	8	3
Ferric Chloride	0.3	0.3

The apparatus used is an iron kettle, equipped with an agitator and open to the atmosphere through a reflux condenser. The kettle is jacketed for cooling. The tetrahydrofuran and ethylene oxide are mixed and fed to the catalyst at such a rate as to maintain a temperature of 28 to 30 degrees Centigrade. Approximately 90 to 95 percent of the tetrahydrofuran enters into the polymer during reaction. The crude oil is washed free of iron salts or corrosion by treatment with awueous sodium bisulfite, the washed oil is then treated with sodium methylate under reflux to replace the terminal chlorine groups with methoxy groups, then neutralized and stripped of any remaining tetrahydrofuran, water and low boiling compounds by a vacuum distillation.

Typical physical properties of an M 620 oil are as follows:

Solidification point - -270° C.
Flow point - - 18° C.

Viscosity ° Engler

-20° C.	-	-
0	-	-
20	-	370
50	-	10.2
100	-	2.0
Polhöle (a)	-	1.0

(a) Polhöle is value which corresponds to viscosity index used in American oil industry and has been described in detail in U.S. Naval Technical Mission in Europe Technical Report Number 73, of March 1945.

The tetrahydrofuran used in this lubricant is synthesized by I.G. at Ludwigshafen by a liquid phase reaction described in detail in U.S. Naval Technical Mission in Europe Technical Report No. 105-45 of June 1945.

Prepared by:

F. H. ROBERTS,
Technician

U. S. GOVERNMENT TECHNICAL OIL MISSION
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JONES, J. P. Edeleanu G.m.b.H., Altenburg, Germany. 1945. 73 p. diagrs. Drawings added: Chain Type Cellular Filter (AS-12450)(10-10690); and Scheme of Chain Type Filter (50-11825).	XXXI-85	30
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RICHARDSON, R. E.; KERN, J. G.; MURRAY, R. L.; SUDHOFF, R. W. Synthetic emulsifying agents, wetting agents, detergents, and soap substitutes, I. G. Farbenindustrie A. G., Hochst/Main, Germany. 1945. 39 p. diagr.	XXVI-2	22
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