

Table of Contents

<u>Subject</u>	<u>Page No.</u>
Object of Investigation	3
Personnel interrogated	3
Summary	3
General	3
Process 1	4
(a) Vogel Washer	4
(b) Froth flotation plant	4
(c) Froth de-watering	4
(d) Products	5
(e) Coking process	5
Process 2	5
(a) Electrostatic dry cleaner	5
(b) Froth Flotation, etc.	6
Outputs	6
Costs	6

Personnel of Team

H. F. Yancey (U.S.) T.I.I.C.

E. T. Wilkins (British) Ministry of Fuel and Power

Date of Visit

29th June, 1945.

The Preparation of Ultra Clean Coal at the Konigin

Elizabeth Colliery (Mannesmannrohren Werke A.G.) Essen.

Frillendorf

Object of Investigation: To obtain information on new developments in coal preparation, including the preparation of coal for carbon electrode manufacture.

Personnel interrogated: Most of the information contained in this report was obtained from Dr. H. Meyer and Dr. W. Vogel of the Bergbau Verein, Essen, during a visit to the Konigin Elizabeth Colliery. Some details were however provided by Dr. Wuster and Dr. Kuhlwein at the Bergbau Verein.

Summary: This colliery had been engaged in the preparation of about 12,000 tons/year of coal of about 0.5 per cent ash content. Additional plant which would have trebled this output was being erected when the colliery was damaged by aerial attack in March.

General: Two 2-stage processes have been developed for producing clean coal of the minimum ash content.

Process 1 treats coal sized about 10-1 m.m. The treatment consists of a preliminary cleaning in a specially designed heavy medium washer, followed by crushing and re-cleaning by froth flotation.

Process 2 was intended to treat coal sized 1.0-0.1 m.m. The treatment was a preliminary cleaning by means of a newly developed electrostatic dry cleaner, followed by crushing and re-cleaning by froth flotation.

Process 1 operated satisfactorily for about 1 year until March 1945, and a duplicate plant of this type was in course of erection. The plant for process 2 had not operated but was almost complete.

The colliery was bombed in March, 1945 and although the coal preparation plants were not seriously damaged they had not been put into working order again.

Process 1. The hand-picked coal containing about 12% ash was crushed to pass an 8 m.m. screen, dedusted at 0.1 m.m. and re-screened at 1 m.m. the 8-1 m.m. grade being treated in the Streamline flow washer (Laminarstromfahren) designed by Dr. Vogel. It was intended that when the duplicate plant was available there would be two grades, 10-5 m.m. and 5-1 m.m. treated in separate washers.

(a) Vogel Washer

Some details of this plant have been published by Schormüller (Gluckauf 1941, 77, 93, 109). It is of the heavy medium type in which the coal is floated on a magnetite suspension.

Provision is made for withdrawing products of different ash contents from six levels in the bath, but the following 3-product separation is typical of the results obtained at Konigin Elizabeth (Feb., 1944):-

	Yield (%)	Ash (%)
Clean Coal	76	1.5
Middlings	8	12
Dirt	10	65

The main difficulty is in rinsing the washed coal free from magnetite, and a large jiggging-screen with ample water sprays is necessary. The recovery of the magnetite from the rinsing water is carried out electro-magnetically.

(b) Froth flotation plant

The clean coal from the Vogel plant is crushed to 0.2 m.m. or less and re-cleaned in a Krupp Grusenburg froth-flotation machine of conventional type. This machine consisted of 15 double cells, each 4200 litres capacity, arranged in 3 banks of 5. The final product had an ash content of 0.5 - 0.7 per cent. The flotation agent was a tar-oil fraction of b.p. 270°- 320°C., and the amount used was 1.2 - 1.5 kilo/ton coal.

(c) Froth de-watering

There were three "Ter Meer" centrifuges erected, or in course of erection, for treating the froth. These were made by Escher Wyss Maschinenfabrik of Ravensburg, and were of the automatically intermittent type in which the coal builds up on the

non-perforated inner wall of the cylindrical rotor. The output of each machine was about 4 tons/hr.

It was said that a "disc filter" had also been used but this had been destroyed.

(d) Products

The following data is based on the performance of the plant during Feb., 1944.

Products	Analysis		Output	
	Ash %	Moisture %	Tons/hr.	%
Raw Coal	12	2	12.1	100.0
Lump refuse (hand picked)	-	-	0.3	2.3
Fine dust (-0.1 m.m.)	7	1	0.7	5.5
Coarse dust (1.0-0.1 m.m.) [#]	6	1	3.5	29.5
Vogel refuse (S.G. 1.9)	69	16	1.2	10.1
Vogel middlings (S.G. 1.35-1.9)	12-26	12	0.6	5.0
Froth flotation tailings	4.2	22.6	2.5	20.8
Froth flotation clean coal	0.69	22.5	3.3	26.8

[#]For treatment by Process 2.

(e) Coking Process

The clean coal containing about 18 per cent of moisture was mixed in a disintegrator with pitch of m.p. 133°C. in the proportion 2 parts of coal to 1 part of pitch. This mixture was transported by rail to the Konig Ludwig Coke-oven plant where it was coked.

Process 2.

(a) Electrostatic dry cleaner.

This plant had been developed by Lurgi Apparatebau of

Frankfurt and is probably the only commercial sized unit in existence working on this principle (with the possible exception of America).

The installation consists of six tall box-like units, each capable of cleaning 2 tons/hr. of coal sized 1.0 - 0.1 m.m. The feed is delivered as a layer 2-3 m.m. deep on a roll revolving at 160 r.p.m. A voltage of 30-50,000 is applied between the roll and an electrode to one side, and this causes falling particles of high ash content to be deflected towards the electrode, while the clean coal falls vertically. It was not possible to see much of the internal arrangement of the apparatus and no drawings were available, but each machine was said to contain six sets of rolls which progressively cleaned the coal as it passed from top to bottom of the apparatus.

The plants had not actually worked and so their performance was not known. Data obtained from a pilot plant at Osterfeld had indicated that a coal of 8-10 per cent ash content would be cleaned to between $1\frac{1}{2}$ and 4 per cent. The operating cost was said to be about 5 marks/ton.

(b) Froth flotation, etc.

The final cleaning and handling of the coal was to have been carried out as in Process 1.

Outputs The actual coal output of Process 1 during 1944, when the plants were working 8 hours a day, was about 12,000 tons. This would have been approximately doubled by the duplicate Process 1 plant, and trebled when Process 2 was operated.

The maximum potential output assuming 24 hour working of these plants would thus be about 70,000 tons a year.

Costs. The price claimed for the finished coke product having an ash content of 0.7 - 1.0 per cent was 140 marks per ton, but this was not allowed, and a price of 125 marks was actually paid. (This information is contained in F.I.A.T. report on Target 30/7.06, C 30/73, "Fuel Research Activities of the A.G. der Kohlenwertstoff-Verbande, Bochum" reported by H. H. Lowry, H. J. Rose and E.T. Wilkins.)

Copy 1

FINAL REPORT No. 39
ITEM No. 30

**CONCEALED OIL TARGETS IN THE
BRILON - BREDELAR AREA**

Aston - Taylor, R. A., and Williams, J. A.

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**BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE**

R
ENCLOSURE NO. *XIXX4*

CONCEALED OIL PLANTS IN THE BRILON-BREDELAR AREA

Reported by

Major R.A. Acton-Taylor, British, Ministry of Fuel and Power

Major F.A. Williams, British, Ministry of Fuel and Power

on behalf of

British Ministry of Fuel and Power

Target No. C 30/273

Fuels and Lubricants

25th July, 1945

**BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE
32 Bryanston Square, London, W.1.**

During the assessment of the Wintershall A.G. works at Lützkendorf, Saxony, mention was made of part of the plant evacuated to the Erlon-Bredelar area. The implication was of five or six hidden oil plants, among which a Fischer-Tropsch plant seemed to be included. The lead was not for the moment pursued, but references to plants in the area were afterwards found in a Geilenberg document, and these plants bore the code names Ofen (distilling plant), Taube (cracking plant) and Lachs (of which the meaning was at that time unknown). It was thought that a short visit to this area would clarify the situation, and accordingly the district was investigated on 17th and 18th July.

It was found that the following plants were in the area:

Ofen 5/6	Messinghausen	} distillation of petroleum
" 7/8	Mühlenbein	
Taube 2	cracking of residues from Ofen 5-8.	
Lachs	plant for synthesizing alcohols and ethers (this seems to be the connotation of the code name "Lachs")	

OFEN 5/6 Messinghausen M.R. R.B. 6511, sheet L.52, Germany, 1:250,000.

The plant was operated by the Wintershall A.G., and was built of materials and plants from Rheine, near Osnabrück. It consisted of two units for the direct distillation of petroleum from Nienhagen, near Hanover. Each unit had a capacity of about 120 c.m. per day, which gives a monthly throughput of about 2,500 tons.

The process consisted in topping the petroleum for petrol (15%), and running off a middle fraction as diesel oil (25%). It was intended to crack the residue (60%) in Taube 2.

The plant was built in September and October, and started working in November, 1944. About 1,000 O.T. men were employed in building it.

The total of staff was at present about 35, which included a laboratory staff of about three.

OFEN 7/8. Mühlenbein, near Messinghausen (Mühlenbein is the name of a farm). M.R. R.B. 6612, sheet L.52, Germany 1:250,000.

The plant was also operated by the Wintershall A.G. and was built of material and plant from Lützkendorf. It was an exact duplicate of Ofen 5/6, but there was no laboratory. The staff had come from Lützkendorf.

Both plants were situated in disused quarries, and were covered with camouflage; they had good rail and road connexions.

Both plants were working on small reserves of crude oil for civilian and Military-Government use, but transport difficulties prevented the arrival of fresh supplies from the Hanover field. Difficulty would also arise in connection with the disposal of the residue.

TAUBE 2 Bredelar, on the north side of the road to Nieder Marsberg M.R. R.B. 7316, sheet L.52, Germany: 250,000.

The plant was due for completion in August, 1945, and at the moment of the visit part of the plant was being dismantled for emergency use elsewhere; it would have been finished quickly but for damage done by Displaced Persons. It took the form of Dubbs units for cracking the residues from Ofen 5/8 under a pressure of 50 atm., and was stated to give a 50 per cent. petrol yield.

The plant was built by the Deutsche Bergbau-u. Hüttenbaugesellschaft, Frankfurt. The capacity was estimated by the investigators to approach 100,000 tons a year. According to data collected from Ofens 5/8, it should have had to take 72,000 tons. No documents were available, but D.P.'s had burnt many in a hole in the ground, and fragments remaining were of drawings relating to cracking plant by Carl Still, Recklinghausen, and were dated 1937, although one of 21st February, 1945, related to a diesel-oil column, and to Taube II.

The plant was very cleverly concealed in a wood.

LACHS Bredelar, on the south side of the road to Nieder Marsberg, directly opposite Taube 2, M.R. R.B. 7316, sheet L.52, Germany: 1, 250,000.

This plant had been evacuated from Rheinpreussen, but little progress had been made in its erection. It had been in use at Rheinpreussen utilizing the unsaturated hydrocarbons from the Fischer-Tropsch plant. It was now proposed to use the cracking gases from Taube 2. These gases were said to be poor in ethylene. The propylene and butylene were to be liquefied by compression and converted by esterification with 70 to 80% sulphuric acid, followed by hydrolysis with superheated steam, to yield a mixture of isopropyl and isobutyl alcohols. The esterification was to be carried out in autoclaves working at 40 to 70°C. and 16 to 20 atmospheres. The yield of ethers as by-products increased at the higher temperature ranges. The mixed hydrolysed products were separated by fractional distillation. The total output of alcohols and by-product ethers was to be 200 to 250 tons per month.

The sulphuric acid from the hydrolysis stage had a strength of 20 to 25 per cent., and was reconcentrated up to 60 per cent. in lead-lined circulatory evaporators using a thermo-syphon, with a final concentration to 70 to 80 per cent. in 'through flow' evaporators of ferro-silicon.

Much of this information was obtained by interviewing Dr. Häusser from Rheinpreussen in the O.T. Barracks nearby. He was the production manager. Documents connected with the Lachs plant were said to have been destroyed by Italian displaced persons.

A short interview also took place with Dr. Schmidt, who was to be in charge of the evacuated research laboratory situated at Ludenscheidt. He had worked in the research laboratory at Rheinpreussen on the conversion of higher alcohols into ketones over catalysts, principally zinc oxide.

Both Dr. Häusser and Dr. Schmidt were subordinate at Rheinpreussen to a Dr. Grimme. Dr. Schmidt appeared to have no knowledge of Iso-Synthesis.

BIOS FINAL REPORT No. 444.
ITEM No. 19.27.31

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COMPRESSED AIR TURBINE DEVELOPED

BY THE

KARLSRUHE TECHNICAL HIGH SCHOOL

Anderson, E. F.

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LONDON—H.M. STATIONERY OFFICE

JUN 1946

COMPRESSED AIR TURBINE DEVELOPED BY
KARLSRUHE TECHNICAL HIGH SCHOOL.

Reported by:

H. F. ANDERSON, M.A.P.

B.I.O.S. Target No. 19/50(a).
C31/2114, C27/424.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE
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(1944)

6 p.

TABLE OF CONTENTS

<u>Subject.</u>	<u>Page No.</u>
Object of Visit	3
Summary	3
Interview with Herr E. Weizenfels.	3
Visit to Langenberg Power Station	4
Description of Turbine	4
Comments on Turbine	5
Action with regard to Turbine	5

Personnel of Team

MR. E. F. ANDERSON, M.A.P.

MR. D. BAGLEY, Donald Bagley Ltd.

1. Object of Visit.

The visit was made to inspect a small compressed air turbine which has been developed by Prof. Wilhelm Spannake at the Karlsruhe Technical High School, as it was thought that it might have been designed for use as an expansion engine in a plant producing liquid air or oxygen. Turbines have been used for this purpose in the U.S.S.R. (under the direction of Kapitza) and are now being developed in U.S.A. and U.K.

2. Summary.

The Turbine design is not considered as good as that of turbines recently constructed in U.S.A. and in U.K. for use in oxygen producing plants. The turbine did not appear to have been tested under low temperature conditions.

3. Interview with Herr E. Weizenfels.

Herr E. Weizenfels was interviewed in German by Mr. Bagley at the Gasthaus zur Krone, Langenberg an der Jagst on the 27th July 1945. He said that Prof. Spannake had left on a visit to Karlsruhe a few days previously. He had been assisting Prof. Spannake at the Karlsruhe Technical High School in the development of a high speed compressed air turbine for use in an oxygen producing plant. The turbine had been slightly damaged in an air raid which had destroyed the K.T.H.S. and had been removed to an outbuilding adjoining the Langenberg water power electricity station. One of the rooms of the Gasthaus had been taken for a drawing office in which new types of compressed air turbine were being designed.

While it appeared that Herr Weizenfels answered all questions quite readily, he refrained from disclosing the professor's principles. This, with the secretion of the turbine rotor (see para.4), inevitably leads to some conjecture on our part.

/Herr

Herr Weizenfels said that the turbine was not being made for use in any particular oxygen producing plant but on the 5th November 1945, Herr A. Christensen, T.L.R. E.5 Berlin, said that this project had probably been sponsored by Messer A.G. of Frankfurt-am-Main who had been manufacturing fixed and mobile oxygen producing plants for the G.A.F.

4. Visit to Langenberg Power Station.

Accompanied by Herr Weizenfels we visited the Langenberg Electricity Works on the Rover-Jagst about a mile from the town. The turbine was unearthed from its protective covering in an outbuilding. It was in a slightly rusty condition and the rotor was missing. We were informed by Herr Weizenfels that the rotor was kept by the Professor in his flat as a "safety measure".

In a room in the electricity station work had been in progress up till the time when the Allied Armies overran the neighbourhood to instal the turbine and its associated motor-driven air compressor.

5. Description of Turbine.

The principle appears to be based on Kapitza's work in so far as the stabilising of the rotating parts is concerned. The turbine rotor and an air compressor rotor are mounted on a common vertical spindle with a single plain bearing between the two rotors. The compressor is on top and acts as a brake for the turbine. An oil cup, situated above the independent of the compressor, supplies oil to the centre bearing through a hole bored axially in the spindle. The turbine is supplied with compressed air at 60 p.s.i. gauge and attains a speed of 70,000 r.p.m. The rotor diameter was stated to be 50 m.m. but is considered to be probably somewhat larger than this in which case it would be similar to the Kapitza unit. We were informed that the turbine had not been tested at low temperatures.

6. Comments on Turbine.

Assuming the opposed thrusts of turbine and compressor to be balanced and not susceptible to variation, the conception is reasonable correct, for lateral instability is correctable by oil cushioning, which should automatically re-centre the spindle. However, in Mr. Bagley's experience these thrusts are variable, the disparity increasing with decreasing temperatures. Mr. Bagley, after experimenting with a turbine of this type, found that a complete change of design was necessary to prevent the lubricating oil from being gradually squeezed out of one end of the bearing with subsequent seizure. What precautions Prof. Spannake had adopted are unknown in the absence of the rotor and of the drawings. Possibly this difficulty had not been discovered, especially if the turbine had not been operated at low temperatures.

At first sight the use of spindle oil (Engler 3-8) stated to have been used seems open to serious objection, as this type of oil will congeal at low temperatures. Herr Weizenfels, in a somewhat vague statement, referred to the compressor merely as a means of compressing air from room temperatures. In this case a limiting temperature interval of 220°C would be established between the turbine and compressor rotors and this might serve to preserve the fluidity of a special lubricant by conduction.

7. Action with regard to turbine.

We discussed whether

- (i) We should visit the Professor's flat to search for the rotor;
- (ii) We should arrange for the turbine to be transferred to the U.K. and tested under the auspices of Mr. Bagley.

/we

We finally decided against both of these courses, having regard to the similarity between this turbine and Mr. Bagley's original model (now abandoned). Mr. Bagley's later models, which have been in operation at low temperatures for long periods, are considered to be much superior to Prof. Spannake's turbine, judging the latter on the information available.

Copy 1

FINAL REPORT No. 367

ITEM No. 22

MANUFACTURE OF 1:4 BUTINEDIOL AT I.G. LUDWIGSHAFEN

*Appleyard, B. J. S., and
Bartshore, J. F. B.*

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MANUFACTURE OF 1:4 BUTYNE-2-DIOL

AT I.G. LUDWIGSHAFEN

Including manufacture of 1:4 butanediol and
tetrahydrofuran, precautions in handling acetylene,
and semi-technical preparation of 1:4 butenediol.

Reported by:-

C. J. S. Appleyard M. O. S.
J. F. C. Gartshore M. O. S.

BIOS Target Number
C22/82(a)

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

32, Bryanston Square, W.1.

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TABLE OF CONTENTS

	<u>Page</u>
<u>Summary</u>	1
<u>Part I. Introduction</u>	
Development of the 1:4 butinediol process	1
Layout of the Ludwigshafen Buna Plant	3
Table 1 - Block Materials Flowsheet for Buna LU	6
Raw materials list	7
<u>Part II. Handling of Acetylene under pressure</u>	
1. Summary of precautions observed on the Ludwigshafen Butinediol plant	8
2. Experimental work leading to the formulation of this code of precautions	9
Manner of acetylene decomposition	10
Effect of sources of initiation	10
Effect of gas composition	11
Effect of temperature	12
Effect of presence of catalyst	12
Effect of shape and size of containing vessel	13
Form of test apparatus	13
Measurement of impact pressures	14
Experiments in narrow tubes	15
Effect of bends in narrow tubes	16
Effect of cooling narrow tubes	16
Packing of wide pipes with bundles of narrow tubes	16
Deposition of soot upon the tube walls	16
Protection of medium diameter pipes	17
Interference of tube bundles with orifice-plate installations.	17
Extension of the tube bundle to higher working pressures	17
Non-return valves	17
Effect of ring-packing of empty spaces	18
Effect of wire-gauze filters	18
Working pressure of plant	20
Conclusion	20

	<u>Page</u>
5. Authors' comments	21
Tables 2-6. Experimental results on acetylene decomposition	23-28
<u>Part III. Butinediol stage</u>	
1. Outline of Process	29
2. Description of process	
General layout of plant	29
Liquid circulation	32
Gas circulations	33
Distillation	34
Filtration of butinediol solution	36
Charging and development of catalyst	36
Discharging catalyst	37
3. Notes on process	
Control of converters	37
Acetylene recovery	39
Distillation	39
Neutralisation and filtration of "pure butinediol" solution	42
Precautions in using the catalyst	44
Deposition of copper acetylide in pipe lines	45
Alternative productions of the butinediol plant	
propargyl alcohol	45
3-hexine 2:5 diol, etc.	46
Authors' comments	46
4. Summary of materials flows and yield data	46
Converter volume, etc.	48
5. Notes on plant construction	
Corrosion-resisting steels	48
Electrical equipment	49
Valves and pipe-lines	50
Cranes	50
Compressors for acetylene	51
Converters	52
Protection against acetylene detonations	53
3-Pass evaporator ("durchlaufverdampfer")	53
Condensers	54
Construction and efficiency of bubble-plate columns	54

	<u>Page</u>
Instrumentation and automatic controls	55
6. Summary of experience on pilot plant	57
2nd report	58
3rd "	59
4th "	60
5th "	61
6th "	62
7th "	63
8th "	66
Tables 7-9 accompanying 8th report	71-74
<u>Part IV. Butanediol stage</u>	
1. Outline of process	75
2. Description of process	
General layout of plant	75
Normal running process	76
Starting hydrogenation plant	77
Hydrogen purification	78
Instrumentation and control on hydrogenation	79
Distillation	79
3. Yield and output data	82
4. Notes on constructional details	
Joints for copper-lined high-pressure pipes	82
Cranes	82
Motor operated high-pressure valves	82
Electric preheaters	82
Instrumentation	83

Part V. Tetrahydrofuran stage

1. Outline of process	85
2. Description of process	
General layout of plant	85
Normal running process	85
3. Yield and output data	87

<u>Part VI. Catalyst plant</u>	<u>Page</u>
1. Manufacture of the butinediol catalyst	88
2. Treatment of the spent catalyst from the butinediol plant	91
3. Manufacture of the butanediol catalyst	91
4. Output of catalyst plant	92
5. Experimental development of a porous stoneware support for the butinediol catalyst	93

Part VII. Capital and operating cost estimates

Overall operating costs for Reppe process	96
Services estimates for Ludwigshafen plant	97
Capital cost estimates for Ludwigshafen plant	98
Staffing and labour requirements	101

Appendix I. Partial hydrogenation of butinediol to butenediol

List of Figures

1. Site layout
2. Acetylene explosions, experimental apparatus
3. Butinediol, simplified flowsheet
4. " , converter details
5. " , converter and pump room flowsheet
6. " , distillation flowsheet
7. " , tank farm flowsheet
8. " , filtration flowsheet
9. Flash evaporator, diagram
10. Liquid distributor for 2000 litre pilot converter
11. Rotary water-ring compressor, diagram
12. Butanediol, hydrogenation flowsheet
13. " , distillation flowsheet
14. Tetrahydrofuran, flowsheet
15. Catalyst manufacture, flowsheet 15a and 15b
16. Butenediol preparation, flowsheet (Appendix I)

Personnel of team

* J.D. Rose, Team Leader	M.O.S.
* C.J.S. Appleyard	"
* J.W. Fisher	"
* J.F.C. Gartshore	"
P.W. Blaylock	Can. Dept. Reconstruction
A.H. Andersen	" " "

* Only those marked thus took part in this investigation.

SUMMARY

This report records an examination of certain sections of the Ludwigshafen Buna plant made in November, 1945. The precautions taken in handling acetylene under 5 atmos. pressure, with the experimental work leading up to their formulation; and the manufacture of 1:4 butinediol from formaldehyde and acetylene, with a summary of the experience gained by I.G. in their operation of the pilot plant, have been described in some detail as showing the most outstanding new advances in technique in this plant. The preparation of the butinediol catalyst has also been treated fairly thoroughly. The butanediol and tetrahydrofuran stages appear to be quite straightforward, and have been described generally. The other parts of the Buna plant, acetylene generation, butadiene manufacture and polymerisation, were not within the remit of the investigation.

PART I. INTRODUCTION

Development of the 1:4 butinediol process for butadiene

Before the war, butadiene for synthetic rubbers was made in Germany from acetylene via acetaldehyde, acetaldol and 1:3-butylene glycol. From patent literature however it is clear that since about 1935 the I.G. Research Department at Ludwigshafen had a team of chemists directed by Dr. W. Reppe working on an alternative process based on butinediol, prepared from acetylene and formaldehyde at super-atmospheric pressure using a copper catalyst. In this process, one molecule of acetylene adds two molecules of formaldehyde yielding 2-butene 1:4-diol (referred to generally throughout this report as "butinediol"), which is hydrogenated to 1:4-butanediol, catalytic dehydrogenation of which yields successively tetrahydrofuran and butadiene.

All the stage yields were good, and the route was encouraged on several grounds;

(a) Preliminary costings indicated that butadiene via butinediol would be as cheap, and possibly cheaper, than butadiene via acetaldol and 1:3-butylene glycol, and

(b) butenediol was a versatile raw material from which intermediates for other chemical products (adiponitrile, adipic acid, hexamethylene diamine, etc.) could be obtained. 1:3-Butylene glycol, on the other hand, had no uses other than as an intermediate for butadiene.

There appears to be little doubt that this versatility of butenediol as an intermediate for other syntheses was a factor of importance in guiding the decision to adopt the route for large scale production of butadiene. In conversations which the authors held with Dr. Reppe it became clear that one important objective he had in mind was the synthesis of intermediates for polyamides, particularly nylon, on a basis of acetylene rather than benzene. Benzene was a more expensive source of carbon than acetylene, and this urge to dispense with benzene whenever possible is well illustrated by the fact that late in the war, Dr. Reppe's team were endeavouring to synthesise styrene (the second component of Buna S) by tetramerisation of acetylene, in an effort to produce this synthetic rubber by a route entirely independent of benzene.

The dehydration of butenediol either through tetrahydrofuran as a separate stage, or directly, is sufficiently similar to the dehydration of 1:3-butylene glycol to be approached with confidence. The hydrogenation of butenediol to butenediol is also quite straightforward, though of course a hydrogenation at 300 atmos. upon the scale of synthetic rubber production must be regarded as a major enterprise. - But the manufacture of butenediol presented certain novel problems; firstly the methods of handling acetylene at around 5 atmos. pressure upon a large scale, and secondly the operation of a process using a copper acetylide catalyst which, by the deposition upon it of cuprene (or so-called acetylenic resins), tended to be short-lived.

The handling of acetylene under pressure was already being investigated jointly by I.G. and the Chemische Technische Reichsanstalt, which, as the Government Department concerned with safety precautions, would eventually have to sanction the methods; and this investigation was considerably extended.

The stages in the development of the butenediol process were:-

Laboratory work, done in semi-technical plant, with a converter of 2-3 inches diameter.

The first pilot plant, which had a 700 litre converter; this shortly became part of the second pilot, which had a 2000 litre converter and made about 50 tons of butenediol per month. This plant was built in Bau 606 at Ludwigshafen, and when that place was rendered unusable by air-attack, it was dismantled and sent to Gendorf. Some of the parts arrived, but it was never re-erected.

A third pilot, with a capacity of 300 tons/month, was built at Schkopau.

The main plants were erected at Ludwigshafen and at Schkopau. The Ludwigshafen plant has a design capacity of 2500 tons/month, 30,000 tons/year, but the highest output attained was 1,800 tons/month. It has 8 converters each 24 cbm. in size.

In addition to the effort upon the running and development of these pilot plants (each of which, it should be noted, had hydrogenation and butadiene plants of appropriate scale), numerous side-investigations dealing with the manufacture of catalysts upon silica supports, distillation of the products, etc., were carried out: only occasional traces of these are now obvious.

Although the yields eventually reached in the route as a whole were such that its advantage over the 1:3-butylene glycol route was problematical, the development of the novel processes in the route in a few years - the main Ludwigshafen plant went into production at about the beginning of 1944 - makes an impressive and interesting achievement.

Layout of the Ludwigshafen Buna Plant

The Ludwigshafen Buna Plant (Buna Lu, Buna III) is a practically self contained plant built on the area between the Ludwigshafen and Oppau factories. In the

centre of the area is a roughly square site carrying the butinediol, butanediol, tetrahydrofuran, butadiene, polymerisation and milling plants. On the outskirts of the area are the carbide, acetylene generation and acetylene purification plants, and the power station (these are in the direction of Oppau and lie along the Rhine bank), the catalyst plant, the formaldehyde plant which takes methanol from Oppau, and the engineering workshops. This report is concerned only with the butinediol, butanediol and tetrahydrofuran units, and the catalyst plant: Figure 1 shows the site layout of these and indicates the position of the other parts of the plant.

The butinediol plant is housed in four buildings: converter house, pump room, still house and tank farm. The pump room contains the compressors and gas circulating pumps which supply acetylene to the converters. The liquid feed to the converters is made up in the tank farm from fresh formaldehyde and various recycle liquors. The output from the converters goes to the still house, where 35% butinediol is separated (the distillates are partly used to make up the converter feed) and sent to the tank farm for filtration: it is then stored as feed for the butanediol plant. The butanediol plant has two main buildings, the compressor house and the converter house, and a separate central control room. The compressor house feeds butinediol solution from the tank farm and circulated hydrogen (supplied at 300 atmos. from Oppau) to the converters. The crude butanediol solution is worked up in the still house, and pure butanediol solution stored in the tank farm to supply the tetrahydrofuran plant. Tetrahydrofuran is sent direct to the butadiene plant. Alternatively 100% butanediol may be isolated by distillation for other uses such as polyurethanes. These three plants are thus grouped as: converters and pumps for butinediol, converters and pumps for butanediol, a tank farm and a still house serving both plants, and a self-contained tetrahydrofuran plant. This grouping of similar operations allows the various plants to be operated with a minimum of skilled staff.

The butinediol and butanediol converter buildings are tall structures more or less skeleton in general appearance; except that on the lower floors each converter and its ancillary plant is contained in a cubicle open on

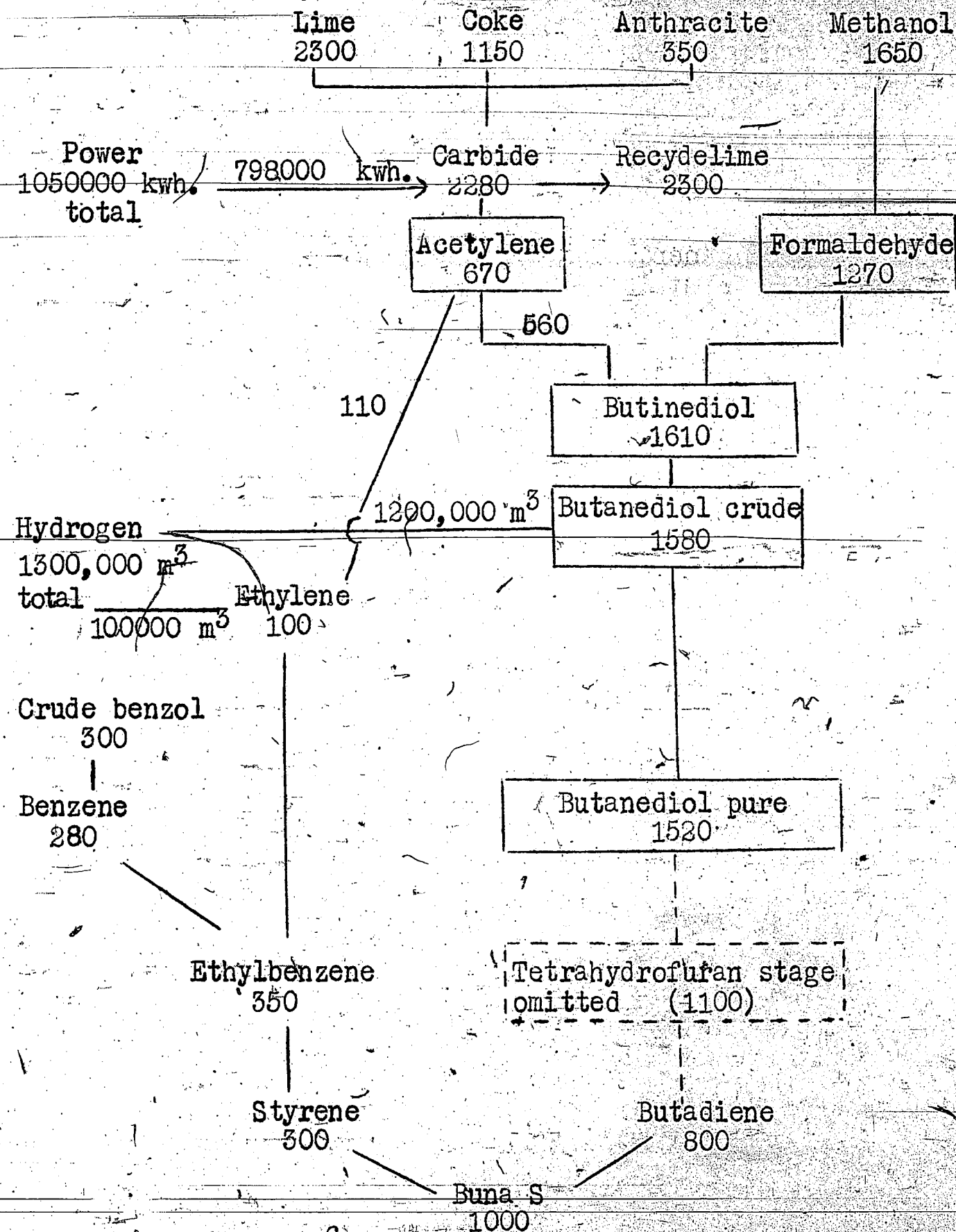
one side and closed on the other three by blast walls of 9-inch reinforced concrete. This is essentially a protection against the hazards of the processes. These two structures are in line, and a Goliath crane straddles both. In contrast, the other buildings are of abnormally heavy construction, especially at the roof, and some (the butinediol pump house, the still house, and the tank farm) are sunk deep below ground level: this was done as a precaution against air attack. The taller columns of the still house come through the roof: reflux is pumped.

A general idea of the material flows in the whole Buna plant is given in Table 1. This is taken from a schedule prepared in November, 1945, for the French Military Government; it is pointed out that this is an abnormal schedule, as the plant had been badly damaged and could not be run in the normal way or at normal yields.

The acetylene plant was not inspected, but a brief outline of its operation was obtained as background. Dry generators are used and the gas is washed with water and dilute hydrochloric acid to cool it and remove dust. Residual traces of ammonia are washed out with dilute sulphuric acid; sulphur and phosphorus compounds with dilute sodium hypochlorite followed by caustic soda. There is then a coke-filled tower to stop mist, and the acetylene is finally purified through active carbon adsorbers. The gas as sent to the butinediol section contains about 20 mg./cbm. of sulphur and phosphorus. The presence of chlorine is undesirable.

TABLE 1. BLOCK MATERIALS FLOWSHEET FOR BUNA LU

Figures are tonnes per month
for 1000 tonnes of Buna S



The raw materials list accompanying this flowsheet is:-

Main	Tonnes/1000	Tonnes
Lime	2300	2300
Coke	1150	1150
Anthracite	350	350
Methanol	1650	1650
coke equivalent	4300	
Benzene	300	300
Hydrogen 1.3 M cbm.		
coke equivalent	1300	1300
Electric power 10.5 M kwh.		
coal equivalent	4700	4700
Steam raising, coal		
(1 Kg. coal = 2.14 kwh.)		4000
Coal equivalent of total coke		9500
(6750)		18900
Total coal		

Auxiliaries

Diperoxide	1.7
Emulgator 1000	75
Acetic acid	10
Potassium persulphate	9
Phenyl β	28
Linseed oil fatty acids PS 14	8
Talc	15
Calcium chloride brine 20°Be	120
Rocksalt or brine, as 100%	100
Aluminium chloride	8
Electrodes	40

Catalysts

Coke catalyst Lu 603 for butadiene	96
Hydrogenation catalyst 13340	6
Butenediol catalyst 526	16
Styrene catalyst	0.5
A-H catalyst	0.2

PART II. HANDLING OF ACETYLENE UNDER PRESSURE

1. Summary of precautions observed on the Ludwigshafen Butinediol Plant

In this plant acetylene is compressed to and circulated at pressures up to 5.5 atmos. (1). The acetylene is plant gas of about 96% acetylene content, and is normally saturated with water vapour at the prevailing temperature.

Firstly, conditions which might lead to the initiation of an acetylene decomposition are avoided. The compressors are of the rotary type and are water-sealed, that is, all the moving parts are flooded with water, which prevents sparking or local overheating from the contact or friction of metal parts. Valves have metal-to-Klingerite seats: spring-loaded safety valves have been removed or rubber-lined. The development of local hot-spots in the catalyst mass is regarded as a potential source of initiation, and is thought to be avoided by the high liquid rate and good liquid distribution over the catalyst.

Secondly, large volumes of free gas are avoided. The whole volume of a converter is filled either with granular catalyst or with raschig rings: the whole volume of liquid-gas separators is similarly filled with raschig rings. Wide-bore pipes (say 100 mm.) are packed throughout their length with a bundle of narrow thin-walled tubes: the maximum length of pipe left unpacked (at bends, valves, and flowmeters) is 300 mm. for a 100 mm. bore pipe.

Thirdly, the plant is designed for a working pressure of 100 atmos. The second set of precautions is believed to prevent an acetylene "explosion" (maximum pressure say 10-12 times the initial absolute pressure, i.e. 65-78 ata) developing into a "detonation", with a far higher final pressure, but "explosions" may still occur.

(1) The conventions used throughout this report are: "atmos" signifies "atmospheres gauge pressure", "ata" (the German convention) signifies "atmospheres absolute pressure", i.e. atmos + 1.

The true proof of these precautions is that the plant has been run and no disaster has occurred.

2. Experimental work leading to the formulation of this code of precautions

It is convenient to start this account, a little out of chronological order, with a meeting held between the I.G. and the Chemische Technische Reichsanstalt (C.T.R.) at Ludwigshafen on 10th December, 1940. The I.G. asked for a Government ruling on two questions: to what pressure could acetylene be safely compressed, and how could acetylene be piped at 3000 c.b.m. per hour over a distance of 83 km. from Gogolin to Radwitz. The official answers, supported by experimental work at Griesheim in which the C.T.R. had collaborated with the I.G., were that the maximum pressure tolerated by international custom for pure acetylene in even narrow pipes was 1.5 atmos, and that in a wide long-distance pipe-line the maximum pressure for pure acetylene was 0.3 atmos, or for a 50% acetylene-50% nitrogen mixture 3.0 atmos. The I.G. pointed out that rulings such as these would completely hamstring the development of acetylene processes in Germany, particularly the butinediol route to Buna S, and claimed that acetylene could be safely handled - with proper precautions - even at 20 atmos. It was agreed that a comprehensive programme of tests should be planned and executed jointly.

The description of the experimental work which follows here has been compiled from a series of reports by Dr. Weissweiler (now reported dead), headed generally "Versuche über dem Acetylenzerfall", and dated 5.2.40, 10.6.41 and 24.9.42, and an interrogation of Dr. Buche, research engineer at Ludwigshafen, on 19.11.45.

All the experimental results tabulated in these reports have been quoted, except that certain columns irrelevant to this account have been excised, and that peak pressures measured by admittedly inaccurate methods have not been shown in their original detail. Some of the results were shown graphically in the originals, by plotting ratio of peak pressure to initial pressure against initial pressure, etc.

Manner of acetylene decomposition

The decomposition of acetylene into hydrogen and carbon, which is deposited as soot, is exothermic with a heat liberation of 56 K.cal./g.mol. Small amounts of methane and benzene are usually formed. Depending on the conditions, such as initial pressure, purity of gas, volume and shape of container, etc., (and also upon an acknowledged arbitrariness of behaviour), the decomposition may proceed:-

quite slowly, that is in a time of the order of 1 second or longer; in some cases the decomposition may be quenched while some acetylene still remains undecomposed;

as an "explosion", with a speed of propagation arbitrarily characterised as of the order of 1000 m./sec.; this produces a noise ranging from a dull thud to a sharp crack, and a peak pressure roughly up to 20 times the initial pressure;

as a "detonation", with a speed of propagation arbitrarily characterised as of the order of 10000 m./sec.; this produces exceedingly high peak pressures, roughly speaking 100 times the initial pressure and over, and almost inevitably leads to the rupturing of the containing vessel (usually at the end towards which the detonation wave is travelling, suggesting that the principal stress is due to reflection of the pressure wave from the end-plate).

(It is worth emphasising that these decompositions are decompositions of acetylene per se, and are not combustions of acetylene with oxygen).

Effect of sources of initiation

Any hot area may act as an initiating source for a decomposition, and the violence of the decomposition depends on the temperature of the source. The following figures were obtained by fusing short lengths (about 0.3 mm.)

of fine wire in a chamber of 15.5 litres volume filled with cylinder acetylene:-

<u>Metal of wire</u>	<u>Melting point of metal °C.</u>	<u>Initial pressure required to produce decomposition</u> <u>atmos</u>
Molybdenum	2550	1.40
Platinum	1773	1.40
Iron	1550	1.74
Copper	1083	1.84
Aluminium	658	2.65
Lead	327	7.50

The fusing of three parallel platinum wires (0.3 mm. long and 0.15 mm. dia.) in a special holder was adopted as standard in all the work, as giving a source more vigorous than any likely to be encountered under plant conditions. It was regarded also as roughly equivalent to the sources likely to occur when welding with oxy-acetylene. Initiation of decomposition by fusing platinum wire is referred to hereafter as "sparking".

Effect of gas composition

The decomposition of acetylene is not very sensitive to impurities in the gas: it requires very substantial dilution with an inert gas to suppress explosions. The following figures for the effect of nitrogen were obtained by sparking various gas mixtures in a vessel of 6.4 litres capacity, at an initial total pressure of 6 atmos.

<u>% nitrogen in gas mixture</u>	<u>peak pressure, atmos.</u>
0	62
10	61
20	58
30	53
47	49
48	43
49	no decomposition

The limit between a fairly severe explosion and no decomposition at all is very narrow, but the effect of the diluent at lesser concentrations is to slow the rate of pressure rise quite noticeably.

Carbon dioxide is a more effective diluent than nitrogen, since only 42% in the gas is required to suppress decomposition completely. Water vapour is also regarded as a useful diluent.

Cylinder acetylene ("dissous gas"), containing 99-99.2% acetylene, was used for the earlier experiments at Griesheim; and plant gas, containing 96% acetylene, 2% hydrogen, 1% carbon monoxide and 1% carbon dioxide, for most of the Ludwigshafen experiments.

Effect of temperature

It is argued that the violence of decompositions, depending as it does on gas pressure, will likewise depend on gas density as influenced by temperature; a vessel full of acetylene at 130°C. will contain at any given pressure less weight of gas than a vessel held at 30°C., in the ratio 303/403. This appears to be upheld by the several pairs of results quoted in Table 2, where under conditions otherwise similar, the higher temperature shows a lower peak pressure and a slower decomposition than the lower temperature. But most of these experiments were conducted in presence of excess water, so that the partial pressure of the acetylene would be depressed by the saturation vapour pressure of the water, which is for example 3.25 atmos. at 130°C. The water vapour would thus have an appreciable effect as a diluent.

Effect of presence of catalyst

The catalyst for butinediol production is essentially copper acetylide, a substance which (whether deposited on an inert carrier or not) might be regarded as an undesirable concomitant of rapidly decomposing acetylene. Table 2 shows that whereas the "normal" peak pressure of acetylene decomposing in a vessel of this size is some 8-10 times the initial pressure, when "dry" gas (i.e. the catalyst is wet with water or butinediol solution,

but the temperature is 30-40°C., where the vapour pressure of water is comparatively low) is present the peak pressure is 12-14 times the initial pressure and the decomposition is roughly ten times more rapid. But with "wet" gas (i.e. the catalyst is wet with water or butinediol solution at 130°C.) the peak pressure is only 3-6 times the initial pressure, and the decomposition is again slow. This demonstrates at least that the presence of the copper acetylide catalyst does not increase the hazards under reaction conditions.

Similar results to those in Table 2 were obtained with a tube 5.5 m. long and 120 mm. bore. (Details were not found).

Effect of size and shape of containing vessel

The early experiments were all carried out in fairly small vessels and suggested the encouraging conclusion that even an "explosion" would produce a peak pressure of only 10-12 times the initial pressure. But when longer pipes were tried, it became apparent that with large gas volumes "detonations" occurred very readily, and it was at one time doubted whether detonations could be avoided even in quite narrow tubes (say 12.5 mm. bore) if they were very long. The searching investigation which followed dispelled these doubts and showed that reasonable safety could be ensured even in large vessels. The general conditions of these tests (appropriate parts of which apply to the experiments of Table 2) will be described now.

Form of test apparatus

The general form of the test apparatus is shown in Fig. 2. It consists of a forechamber, usually 100-200 mm. bore and 60-300 mm. long, provided with gas charging pipe and pressure gauge for measuring the initial pressure, vacuum connection for evacuating the apparatus before admitting the acetylene, the sparking device and several appliances for measuring the peak or impact pressure of the decomposition. Then comes the pipe length which is the true subject of the test: this may be 10-400 mm. diameter and up to 60 m. long, and may contain various protective devices. Finally there is an empty chamber similar to the

forechamber, referred to as the "end", carrying pressure measuring appliances. The test apparatus was very heavily built (300 atmos. or higher working pressure) and was set up in open ground away from buildings: sometimes the pipe was buried.

The purpose of these experiments was this. It was recognised that decompositions of acetylene would probably occur in the butynediol plant (and they did): the problem was to demonstrate conditions under which a decomposition would not develop into a detonation, but would be retarded sufficiently to be classed as an explosion at the worst. If this could be guaranteed, the maximum pressure reached would be 10-12 times the initial pressure in ata, i.e. 60-72 ata for an initial pressure of 6 ata, and the explosion would be contained by a plant designed for 100 atmos working pressure. If a detonation occurred, no plant could be built to contain it. A successful protective device was thus one by which the decomposition initiated by the spark in the forechamber was damped out along the length of the pipe, and did not reach the "end" as a detonation: if an explosion occurred in the pipe the test length was said to be "penetrated" ("durchschlag", "P" in Tables), but the experiment was still successful in demonstrating the suppression of a detonation.

Measurement of impact pressures

Three appliances were used: in two of them a steel ball was driven into a copper block by the force of the explosion, and the size of the impression measured. One appliance was made by the I.G. and is referred to variously as "Kupferverstaechzylinder" or "Druckmesser"; the other form was made by Krupps, and is referred to as "Messeier" or "Kugeldruckapparat". A sketch is given in Fig. 2 of the Krupps instrument. The third was a quartz piezo element coupled to a cathode ray oscillograph (Zeiss Ikon A.G. Dresden); the initiating spark was registered also, so that both the peak pressure and the speed of the decomposition could be measured. After a good deal of experience it was agreed that the oscillograph method was reliable and reasonably accurate, and that the two impression devices gave figures accurate enough at

pressures up to 100 atmos but becoming increasingly inaccurate at higher pressures: they read roughly twice too high at 200-300 atmos. In the tables of results quoted in this account the readings of the impression devices, given in detail in the original reports, are accordingly mentioned only as ranges under the heading "Impact pressure".

Experiments in narrow tubes

The results quoted in Table 3 establish several important points.

(a) A detonation is not likely to develop in narrow straight horizontal or vertical tubes, even of considerable length. Thus in a $\frac{1}{2}$ inch (sic in original, presumably equivalent to 12.5 mm.) bore horizontal tube at an initial pressure of 8.0 atmos there was penetration but not even an explosion. In vertical tubes sparked at the lower end much the same applies, but the violence of the decomposition seems to be slightly greater. In a vertical tube sparked at the top the tendency towards decomposition was very much less; this behaviour is similar to that of explosively-burning gas mixtures.

Even although peak pressures of 15-25 times the initial pressure were recorded in some of these experiments, the decomposition was still to be classed as an explosion, and not as a detonation. The rate of pressure rise was comparatively slow, the noise was only a rustling sound detectable by placing the ear against the tube, and the tube became only hand-warm.

(b) The violence of decomposition increases with the bore of the tube. For example, for 10 atmos initial pressures in 10, 12.5 and 16 mm. tubes the peak pressures were 160, 173 or 199, and 277 atmos respectively.

(c) The violence of the decomposition increases with the size of the forechamber. For example, for 10 atmos initial pressure in a 10 mm. tube, the peak pressure was 160 atmos with a 300 mm. forechamber and 275 atmos with a 500 mm. forechamber.

Effect of bends in narrow tubes

Experiments 52-57 in Table 3 indicate that bending the narrow tube into a zig-zag coil (Fig. 2) does not produce any significant decrease in the violence of decomposition.

Effect of cooling narrow tubes

The explanation given for the efficacy of a narrow tube in suppressing explosions is that the rate of heat loss from the reaction is so rapid that either it is completely extinguished, or at least so much energy is lost that a detonation wave cannot develop.

Cooling the pipe by immersing it in a water bath (Table 3, Expts. 58, 59) showed nothing to suggest that this would be useful.

Packing of wide pipes with bundles of narrow tubes

Following up the lead from the comparative safety from detonations shown by a single narrow tube, wide pipes (up to 400 mm. bore) were packed throughout their length with a longitudinal bundle of narrow (10-12.5 mm. bore) thin-walled steel tubes. This proved the most effective convenient treatment of wide pipes; Table 4 shows the results of one series of tests, in which detonations did not develop at initial pressures of even 6 atmos. "Penetrations" did occur: that is the acetylene did decompose throughout the whole length of the pipe, and the peak pressures were fairly high, demonstrating that an "explosion" took place, but within the terms of reference the tube bundle gave complete protection.

Deposition of soot upon the tube walls

The results of Table 4 are claimed to show the gradual fall in efficacy of a tube bundle packing as the soot deposited by successive acetylene decompositions builds up on the tube walls, and the recovery of efficacy after the soot has been removed (presumably by taking out the tubes and cleaning them separately: it is stated that

even the most vigorous air-blast was not sufficient to blow off the soot). In the authors' view the evidence presented is insufficient to support this, but considerable emphasis is placed upon the point in the text accompanying the table, and the experimenters' opinions are not to be underestimated.

Protection of medium diameter pipes

The tube bundle idea was applied also to pipes which were too narrow to pack with tubes, but too wide to be safe as they stood. Pipes of about 25 mm. bore on the experimental plants were fitted with a tin-plate septum dividing the pipe longitudinally into two semi-circular ducts: 30 mm. bore pipes had 2 such divisions and 40 mm. pipes had a Y-shaped baffle (Fig. 2). Decomposition experiments do not appear to have been carried out to prove these precautions, but the experience on the pilot plants was that they were satisfactory.

Interference of tube bundles with orifice-plate installations

The maximum unpacked length of 100 mm. pipe tolerated was 300 mm. It was established that if the tube bundle stopped 300 mm. upstream from the orifice plate, and started again 60 mm. downstream, there was no interference with the normal calibration of the orifice. (Flange taps are standard).

Extension of the tube bundle to higher working pressures

The standard diameter of packing tubes for a working pressure of around 5 atmos of acetylene is 10 mm. It is stated that for 10 atmos working pressure 5 mm. tubes should be used, but no evidence from experimental results was discovered.

Non-return valves

When acetylene is being piped under pressure in narrow lines over a fair distance (say to service a laboratory or in an experimental plant) rubber non-return valves of the Bunsen type as in Fig. 2 are interposed every

5-6 metres. In the main plant spring-loaded non-return valves were fitted in many positions, such as would be suggested by normal engineering practice, when the plant was built, but non-return valves were not fitted at regular intervals along the pipe lines as in the laboratory practice above. These non-return valves were later suspected of initiating explosions, and were either rubber-lined or removed altogether (depending on whether they were really desirable or not), but after this had been done, explosions still continued.

Effect of ring-packing of empty spaces

Table 5 shows the effects of packing a pipe with raschig rings. Expts. 1-7 cover the treatment of the forechamber. The 60 mm. empty forechamber is better than the 300 mm. forechamber, and packing the 300 mm. forechamber with rings (25 mm. x 25 mm.) is advantageous.

The remaining two series show that packing the whole length of the pipe with rings is an effective protection against the development of a detonation even at 6 atmos initial pressure. Expts. 15-17 are especially remarkable in that there was not even any penetration at 6 atmos when the pipe was packed with 25 x 25 mm. stoneware rings.

These results are of great importance in justifying the packing of large vessels such as liquid-gas separators (800 mm. internal dia.) with rings.

The authors' reading of Table 5 is that 35 x 35 mm. iron rings are as effective a packing as 10 mm. bore tubes, and that 25 x 25 mm. stoneware rings are even more effective.

Effect of wire-gauze filters

In an effort to improve the efficacy of the tube bundle packing, the effect of filters of wire-wool (steel wool as used for pot-scourers) was tried. These filters were tight wads of steel wool about $1\frac{1}{2}$ pipe diameters long, held together by perforated steel end plates and fitting tightly within the pipe. Some of the results are quoted in Table 6.

With filters alone (5 wads fairly close together at the forechamber end of a 30 m. pipe) there was no penetration at 3 atmos initial pressure, but at 4 atmos decomposition began after about 5 minutes, and accelerated slowly, until a detonation occurred after 15 minutes. With 8 filters in the same length of pipe a detonation occurred after 20 minutes.

When filters were used in front of a tube bundle penetrations still occurred after about 20 minutes, but did not develop into detonations.

The effect of these filters is to isolate the main length of pipe from the forechamber. The spark in the forechamber produces more or less of an explosion, and the first filter gradually becomes heated through by acetylene decomposing on the surface of its wires: when the hot spot reaches the adjacent chamber it may initiate a decomposition there which may be sufficiently violent to spread into the next small partitioned space, and eventually reach the main length of pipe, where it would almost inevitably produce a detonation.

Thus their effect may be only to delay the onset of detonation: this at first gave a spurious appearance of safety. It was suggested that where filters were fitted thermometers should be inserted in them and wired to an alarm system, so that a temperature rise in the filter might give warning of an imminent explosion: the pipe could then be flooded with nitrogen.

The detonations which occurred must be classed as serious. Of Expt. 3, Table 6, it is observed that the end of the pipe was blown out like the opening petals of a tulip: a workman was injured, and the oscillograph instrument (which judging by photographs was several yards away from the end of the pipe) was destroyed: this series of experiments was then discontinued.

The use of filters was eventually rejected on the grounds of inefficient protection and high resistance to gas flow in pipe lines.

Working pressure of plant

With an initial pressure of 5-6 atmos, explosion peak pressures of the order of 60-80 atmos may be expected. It was recommended that the plant should be built for a working pressure of 100 atmos, which would be safe for the peak pressures and also (since the failing pressure would be very much higher) for the highest impact pressures likely to occur. It was not considered safe to build the plant for 64 atmos working pressure, which is the next lower constructional standard.

It was recognised as impracticable to build any really large vessel (the converters are 18 m. high x 1.5 m. internal diameter) to withstand a detonation.

Conclusion

The violence of an acetylene decomposition depends on the nature of the initiation, the purity of the gas, and its pressure, upon the size and shape of the containing vessel, as well as on other factors less easily characterised. Whether the decomposition proceeds as a slow and in some cases incomplete decomposition, an explosion (scilicet, a bump), or a detonation (scilicet, resulting in the destruction of the container) can be controlled to a very large extent by packing the gas space with narrow tubes or raschig rings: the effect of this is to break up large gas volumes into small volumes, and to increase the overall thermal conductivity of the gas space. It is suggested that the material of the packing should have a high thermal conductivity and a high specific heat (i).

In the particular case of the butinediol process the plant conditions are less liable to cause decompositions than the experimental conditions under which the precautions were tested. Thus the initiating source in the experimental work was melting platinum,

(i) An unusual combination of properties. A little calculation of heat capacity is instructive.

which is unusually vigorous: in the plant converters (the largest volumes of acetylene under pressure) the total pressure is 5.5 atmos, of which only about half is partial pressure of acetylene, the remainder being water vapour; and the temperature is about 110°C., so that the density of the acetylene, and hence the mass present, is less by a factor of $293/383$ or about 0.75.

The following is a translation of the summary from the report dated 24.9.42 upon which the safety code for the butinediol plant was based:-

"Tests on the protection of acetylene pipe lines, "packed with either bundles of narrow tubes or with raschig "rings, against detonation of the gas have been carried "out at pressures up to 15 atmos, i.e. well over the "pressure (5-7 atmos) necessary for the Reppe synthesis of "butinediol. This work fully confirmed earlier experiments: "at pressures of 5-6 atmos the pressure rise was small at "the end of a pipe packed with narrow tubes. Pipe lines "packed with raschig rings quenched the explosion at low "pressures, and even with initial pressures of 6-8 atmos the "braking action on the explosion was sufficient to make such "a filling a completely satisfactory safety measure. With "higher initial pressures even narrow tube bundles show "high peak pressures, and the ratio of peak pressure to "initial pressure increases with the diameter of the narrow "tubes. The higher the initial pressure, the narrower "must be the packing tubes. At all costs, large unpacked "volumes must be avoided; they allow a detonation to "develop to a stage where it cannot be restrained by the "best preventive measures.

"The experimental results given here" (they are all quoted in this account) "terminate the work required by "the Chemische Technische Reichsanstalt on the safety "precautions necessary to prevent detonations of acetylene "in the Reppe butinediol process".

3. Authors' comments

Attention has already been drawn, in an otherwise objective account, to conclusions drawn from evidence which appears to the authors inconclusive or even insufficient.

Lest this should bias any who seek to base a safety code upon this account, and who may think that the experimenters were led into over-optimism by the importance of the butynediol process to their war-production, it is fair also to indicate strong points.

Firstly, the tone of the reports, and of Dr. Büche who took part in the work, is confident. Omissions from the formal reports, which are disconcerting to the objective reader, may well have been supplied by the knowledge of the men who had followed the progress of the work from day to day.

Secondly, two of the experiments reported here resulted in detonations. The significance of this is not so much to emphasise that detonations can occur when proper precautions are not taken (for this is already known), but to throw into higher relief the fact that detonations did not occur in the other 128 experiments quoted.

Thirdly, the precautions have been given a full scale test in a plant in which the total volume of vessels containing compressed acetylene (not allowing for the space occupied by solid packing) is of the order of 250 cbm., and have proved satisfactory. The operators of this plant have experienced a number of acetylene explosions, and remain confident.

TABLE 2. Acetylene decomposition: effects of catalyst, moisture, and temperature
Pipe 1.00 m. long, 90 mm. bore, 0.4 litres volume

1 Serial No.	2 Gas	3 Pipe filling	4 Tet with	5 Temp. °C.	6 Pi. ata	7 Peak pressure ata	8 Seconds	9 P/Pi	10 Remarks
1	Cylinder	empty	(dry)	40	6.45	63.5	.25	8.5	
2	"	"	"	100	6.0	51	.32	8.2	
3	"	"	"	100	7.5	49	.24	10.2	
4	"	"	water	100	6.45	76.5	.18	10.3	
5	"	"	"	40	6.45	65.5	.27	9.8	
6	"	"	"	100	8.4	77	.26	9.3	
7	"	"	"	100	8.4	70	.22	8.3	
8	Plant	"	"	40	6.0	62	.21	10.3	
9	"	"	"	40	6.0	66	.20	11.0	
10	"	"	"	40	6.0	49	.35	8.8	
11	"	"	"	100	6.0	49	.32	9.8	
12	"	500 g. fresh CuC ₂	"	100	6.0	84	.04-.02	13.0	Sharp crack
13	"	500 g. CuC ₂ 6 weeks' old unused	"	40	6.45	140	.02-.01	14.0	"
14	"	"	"	40	6.45	84	.04-.03	13.0	"
15	"	"	"	40	6.45	140	.025-.01	14.0	"
16	"	1 l. fresh catalyst on pumice	"	40	10.0	140			"
17	"	"	butynediol solution	30	6.0	68	.03	11.5	"
18	"	"	"	30	6.0	74	.02	12.3	"
19	"	"	"	30	6.0	83	.03	13.8	"
20	"	"	"	130	6.0	49	.075	8.2	Dull bang
21	Plant	"	"	30	6.0	77	.02	13.8	Sharp crack
22	"	"	"	130	6.0	54	.21	15.7	Inaudible
23	"	"	"	130	6.0	42	.104	10.0	Sharp crack
24	"	"	"	130	4.0	42	.173	9.75	Inaudible
25	"	"	"	130	4.0	11	.06-.01	7.2	Dull bang
26	"	"	"	130	5.0	36	.11	2.4	Inaudible
27	"	"	"	30	5.0	50	.06-.025	10.0	Sharp crack
28	"	"	"	110	5.0	31	.26	6.2	Inaudible
29	"	1 l. catalyst as above, used 4 days	"	110	5.0	28	.17	5.6	"
30	60% cyl. 40% N ₂	5 l. catalyst as above used 2 1/2 weeks	"	30	5.0	5			No ignition
31	67% cyl. 33% N ₂	3 l. catalyst as above used 4 days	"	30	5.0	21	.03-.06	3.5	Inaudible

Column 6. Pi - initial pressure of gas.

" 7-9. Oscillograph measurements.

TABLE 3. Acetylene decomposition: in long narrow tubes. Forechamber 300 mm. long unless otherwise stated.

Initial gas temperature - room.

1	2	3	4	5	6	7	8
Serial No.	Tube bore mm.	Tube length m.	Pi atmos	Peak pressure, atmos	Impact pressure atmos. at spark at end		Remarks
(a) Straight horizontal tube							
1	1/2 inch	60	5.1				P only after 5 min. End of tube warm
2	"	"	5.1				P immediately
3	"	"	5.2				"
4	"	"	6.8				"
5	"	"	7.5		200?		P, hissing noise
6	"	"	8.0		150?		P, but without explosion
(b) Straight vertical tube, sparked at lower end							
7	10	50	5				No P, burned after about 1/2 min.
8			5				"
9			6				"
10			7	off range			Very weak P
11			9	"			Weak P
12			11	"	230?	350?	
13			12	"	350?	350?	
14			13	"	350?	350?	
15			9	133			
16			10	160			
17			11	185			
18			12	225			
19			13	215			
20			14	327			
21			15	278			
22	12.5	30	5	-	39	200	
23			6	81	76	295	
24			7	80	76	305	
25			8	97	102	260	
26			9	117	235?	230?	
27			10	173	-	-	
28			5	67	57	207	
29			6	79	74	230	
30			8	-	74	287	
31			8	117	120	280	
32			8	80	-	-	
33			6	107	-	-	
34			7	123			
35			8	140			
36			9	155			
37			10	199			
38	16	50	5	20			
39			6	125			
40			7	130			
41			8	160			
42			9	174			
43			10	277			
44			11	256			Very high impact pressures made measuring unsafe
45			12	315			Series discontinued
(c) As above, but with forechamber 70 mm. bore x 500 mm. long							
46	10	30	5	144		180	
47			6	185		224	
48			7	-		257	
49			8	220		317	
50			10	275		off range	

TABLE 3. (contd.)

1	2	3	4	5	6	7	8
Serial No.	Tube bore mm.	Tube length m.	Pi atmos	Peak pressure atmos	Impact pressure atmos. at spark at end		Remarks
(d) Horizontal tube, bent as U							
51	1/2 inch	60	5.2			143?	P, end only warm
(e) Zig-zag coil (Fig.2), legs horizontal							
52	1/2 inch	60	7.0			181?	Decomposition throughout tube
53	"	"	7.5			218?	" " "
54	10	60	8.5			176?	" " "
55	"	"	9			162?	" " "
56	"	"	10			191?	" " "
57	1 inch	30	2			152?	P, end only warm
(f) Figure-of-eight coil in water bath at 13-14°C.							
58	10		3.5			155	Decomposition throughout tube
59			10.1			218	" " "

Column 5. Oscillograph measurements.

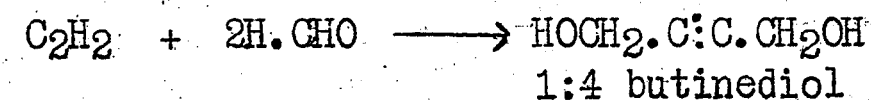
Column 8. P = penetration of decomposition into end chamber.

PART III. BUTINEDIOL STAGE

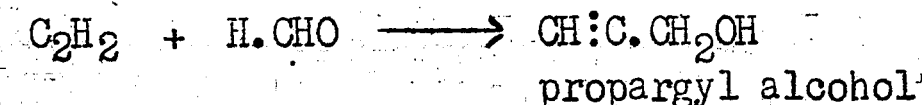
The information in this section was obtained by interrogations of Dr. Reppe at Frankfurt, and a scrutiny of his private file of I.G. reports; and by interrogation of the plant staff at Ludwigshafen, Dr. Niemann, Dr. Steinhofer, Dr. Pistor and Mr. Spohn, by inspection of the plant, and from flowsheets and documents produced, and in some cases specially prepared, by Dr. Pistor and Mr. Spohn.

1. Outline of Process

Acetylene and aqueous formaldehyde diluted with recycle liquors to a maximum strength of about 12%, are passed co-current downwards over a copper-bismuth acetylide catalyst supported on granular silica gel, at about 5 atmos. pressure and 90-110°C. The main reaction is:-



and a subsidiary reaction largely suppressed in the presence of excess formaldehyde is:-



Part of the butinediol solution is recirculated, such that the converter product contains about 33% of butinediol. Methanol (entering with the formaldehyde), unused formaldehyde, and propargyl alcohol are removed by distillation, leaving a 35-40% solution of butinediol in water to be passed forward for hydrogenation. Formaldehyde and propargyl alcohol are recirculated to the converters.

2. Description of Process

General layout of plant

The pump house contains a row of eight cubicles (Fig. 1) each designed to contain the following major plant items:-

TABLE 6. Acetylene decomposition; wire-wool filters spaced along wide pipes.

1 Serial No.	2 Pipe bore mm.	3 Pipe filling	4 Pi atmos	5 Impact spark	6 pressure atmos end	7 Remarks
1	200	5 filters	5.0	-	250?	No penetration. Free space 300 mm. After 5 minutes no effect, then slow pressure rise. At 15 minutes pressure was still rising; detonation occurred, and pipe burst.
2	200	5 filters	4.0	52	400-500?	After 20 minutes, penetration followed by detonation, pipe end burst.
3	200	8 filters	4.0	-	30-40	Filter penetrated, slow decomposition in bundle without perceptible knock. Let out after 1 hour.
4	100	8 filters preceded by 1/2 in. bundle	5.0	46	90-110	Penetration after 23 minutes, dull bang.
5	100	"	6.5	35	110-150	Penetration after 22 minutes, dull bang. Let out after 1 1/2 hours.
6	100	"	7.0	-	-	-

2 x 2-stage Elmo rotary compressors for fresh acetylene, rated at 350 cbm./hr. free gas from 10 in. w.g. to 5.5 atmos., 1 working, 1 spare;

1 x gas-water separator to remove entrained water from the compressed gas and to return it as sealing water to the compressors, with centrifugal pumps for circulating the sealing water;

3 x 1-stage Elmo rotary compressors for circulating acetylene, rated at 400 cbm./hr. free gas from 4 atmos. to 5.5 atmos., 2 working, 1 spare;

1 x gas-water separator serving the circulating pumps.

The converter house contains eight corresponding stalls (Fig.1) each containing:-

1 x converter, 1.5 m. internal diameter and 18 m. high, lined 18:8:3:1 steel, packed with granular catalyst (3-5 mm. size) to a depth of 16.7 m. Catalyst volume 24 cbm;

1 x liquid feed preheater;

1 x hot separator, disengaging hot liquor from gas at foot of converter;

1 x gas-cooler, cooling gases disengaged from hot separator;

1 x cold separator, disengaging liquor from gas leaving the gas cooler.

Centrifugal pumps for feeding and circulating liquid.

These plant items together constitute a "converter set", and the flowsheet for them is given in Fig.5. The converter sets are interconnected by common lines in a very flexible system, the purpose of which will appear

later.

The pump house also contains a central room for the automatic controls which regulate the gas circulation and fresh gas feed.

The converter house also accommodates the filter-room (where all the liquids entering the converters are filtered); the off-gas column for disengaging acetylene from the make butinediol solution; and a small still for recovering methanol, etc., from the compressor sealing water.

The still house and the tank farm constitute a common service to the eight converter sets: the flowsheets are shown in Figs.6 and 7.

The process which will be described now can be regarded as the normal process under good conditions: there are many deviations, which are dealt with in the Notes on the Process. It is important to make clear the reasons for deviations:-

(a) The life of the catalyst is 3-4 months, during which time it is deteriorating more or less slowly: this life has to be coaxed out of the catalyst by suitably arranging its working conditions.

(b) In spite of the great size of the plant, it is still in its experimental stages. It has never been run exactly as designed, some items have never been run at all, and there has been frequent air-raid damage.

(c) Certain modifications have been proposed and never carried into effect.

In the normal process, then, six of the converter sets are used in three pairs. The remaining two sets are used as spares or for recovering acetylene from the purge gas from the main converters. An outline flowsheet for one pair of sets and the distillation is given in Fig.3: it should be understood that in full operation three pairs of sets are run in parallel and their combined output sent to the stills. All the flow rates and compositions are given only to the nearest 0.1 cbm./hr.

Liquid circulation

See Fig. 3. The liquid feed is made up in the mixing tank 1 from:-

3.8 cbm./hr.	fresh formaldehyde solution, containing 40% formaldehyde and 1% methanol.
0.3 " "	recycled formaldehyde-propargyl alcohol solution from column 15.
2.2 " "	water.
5.7 " "	recycled butinediol solution from the hot separator of Converter 2.

The total feed is 12 cbm./hr. and contains 10-12% formaldehyde. It also contains a trace of formic acid from the recycled liquors, and sodium bicarbonate is added (about 0.04%) to bring the pH to 4.0-5.0. The feed is preheated to 60-70°C. in the preheater 2, and enters the top of the converter 3, where it is distributed, first by a sparge ring and then by about 0.3 m. depth of ring packing, over the cross-section of the converter. As the liquid stream flows down over the catalyst it reacts with the atmosphere of acetylene to give mainly butinediol and smaller amounts of propargyl alcohol. The heat of the main reaction is 55 k.cal./kg.mol. in the vapour phase, and 22 k.cal./kg.mol. in the liquid phase: the liquid phase reaction is predominant. The temperature of this converter is 90-110°C. The liquid and gas together drop from the foot of the converter into the hot separator 4, which runs at about 90°C.; the liquid contains about 30% butinediol. The disengaged gases pass through the gas-cooler 5 and into the cold separator 6, which runs at about 30°C.; here the liquid is an aqueous solution of propargyl alcohol, methanol and formaldehyde, total about 0.1 cbm./hr.

The two liquid streams from 4 and 6 are combined, giving again 12 cbm./hr. now containing about 5% formaldehyde and pumped through the preheater 8 to the second converter 9. This converter is run at 100-120°C. The liquid from the hot separator (90°C.) 10 contains about

33% butinediol, and the formaldehyde content has been reduced to a control figure of 0.5%: 6.1 cbm./hr. are passed for distillation to column 14, and 5.7 cbm./hr. returned as recycle to the feed mixer 1.

The disengaged gas is cooled as before in the gas cooler 11, and the liquid from the cold separator (30°C.) 12, about 0.1 cbm./hr. containing propargyl alcohol, methanol, and formaldehyde, is sent through the degassing column to the crude methanol column 15.

When the full plant is being run, that is three pairs of make converters and one pair of acetylene washing converters, the liquid circulations are not kept separate as Fig. 3 might suggest. The total amount of feed solution - that is four times the quantity above - is made up in the mixer 1, and split into four: three streams go to the three first converters, and the fourth to the first acetylene recovery converter. The first converter output (combined liquid from separators 4 and 6) goes direct to the second converter of each pair: these transfers are kept separate. Likewise the output from the first acetylene recovery converter goes direct to the second. The outputs from all three hot separators (second converters) 10 are combined into the common main and split into still 14 feed and recycle to mixer 1: the outputs from all three cold separators 12 are combined and go to still 15. The output from the second acetylene recovery converter all goes back to the feed mixer, where it replaces part of the water used to dilute the feed.

Automatic controls operating on the liquid levels in the separators are used to regulate the discharge from the converters. The feeds of liquids to the feed mixer and to the individual converters are regulated by hand-wheel valves against recording flowmeters.

Gas circulations

The feed gas to the first converter 3 is made up of:-

800 cbm./hr. free gas from the cold separator 6
420 cbm./hr. free gas fresh acetylene.

This gas contains 85% acetylene and is delivered at 5.5 atmos. About 60% is fed in at the top of the converter, and the remainder through the side entries (for positions see Fig.4): the relative amounts are adjusted to keep the temperatures within the converter steady and inside the correct range.

The second converter 13 is run similarly to the first, except that only 270 cbm./hr. free gas fresh acetylene is required as make up.

The fresh acetylene used for make up contains 96% acetylene and 4% of inert gases (hydrogen, carbon monoxide, and carbon dioxide). The inerts are kept down to 15% in the circulating gas by bleeding off a proportion, preferably to acetylene recovery converters.

When the full plant is being run, the gas circulations are not kept separate as indicated in Fig.5. Sufficient of the two-stage compressors are run to keep the common fresh-gas line which serves all the converters filled at 5.5 atmos. All the converter off-gases (from the cold separators) are taken into a common return-gas line, which supplies gas to as many of the single-stage circulating compressors as are necessary to maintain the common recycle gas line also filled at 5.5 atmos. The purge of acetylene to the recovery converters is taken from this line.

The gas-flows to the individual converters are controlled automatically by a centralised installation of Askania controllers. The pressure in the common recycle-gas line is held at 5.5 atmos. by one set of controls, which adjusts by-pass valves round the circulating compressors. The admission of fresh gas to the converters is controlled by the pressure at the head of each converter; when this falls below 5.5 atmos. the controller operates to admit fresh gas from the common line into that particular converter feed line.

Distillation

The butinediol section of the still house contains four stills of fairly conventional design - bubble-plate columns, steam-heated calandrias, and pumped reflux.

The descriptions are:-

Column No. (Fig.3)	14	15	16	(See Fig.6)
Description	Main	Crude methanol	Pure methanol	Propargyl
No. of bubble plates	35	44	10	35
Feed on n th plate from bottom	25-35	18-27	6	(25-35)
Diameter	2.0 m.	1.0 m.	750 mm.	2.0 m.
Reflux ratio	3:1	1:1-1.5:1	low	-
Head pressure	1.5-2.0 atmos.	0 atmos.	0 atmos.	(120 mm.Hg.)
Head temperature °C.	122-123	64	65	-
Reboiler temperature °C.	130	100	100	-

The feed to the main column is the 33% solution of butinediol from the hot separator 10 (6.1 cbm./hr. from one pair of converters) containing small amounts - 0.1-1.0% each - of methanol, formaldehyde, propargyl alcohol, and a small amount of involatile material from polymerisation reactions, etc. (Butinediol itself is practically involatile under the conditions of this still). The bottoms are a 35% butinediol solution (5.7 cbm./hr.), with the involatile residues: this comes from the still at 2 atmos. gauge pressure, and is let down in a flash-kettle (the vapour from which is condensed and run to drain) and sent to filtration and storage as pure butinediol solution. The overhead is a 50% solution of the volatiles in water, and is combined with the similar solution from the cold separator 12 to form the feed to the crude methanol column 15 (0.4 cbm./hr.).

The bottoms from the crude methanol column

contains about 20% formaldehyde and 20% propargyl alcohol, and is returned to the mixer 1 for recirculation (0.3 cbm./hr.). The overhead is a 70% solution of methanol (0.1 cbm./hr.) which is fractionated in the pure methanol column 16 to give 95% methanol at the head and water at the foot. The methanol is returned to the formaldehyde plant, and the bottoms (which contain traces of propargyl alcohol too small to worry about) go to drain. (So far the methanol thus recovered has not been accepted by the formaldehyde plant, and has been disposed of otherwise).

Filtration of butinediol solution

The 35% butinediol solution from the main still bottoms contains a small amount of dissolved silica from the catalyst support (as well as process by-products) which would deposit upon and de-activate the hydrogenation catalyst in the next stage. It is also slightly acid with formic acid (supposedly formed in the reboiler by a Cannizaro-type reaction of formaldehyde into formic acid and methanol). It is neutralised to pH 5.0 with caustic soda, and passed through three settlers in series, total hold-up time 1 hr. The flowsheet is given in Fig. 8. The clear liquor overflow goes to the main storage for "pure butinediol", which has a total buffer capacity of about 3 days. The settled slurry is drawn off the bottoms of the separators and filtered in Scheibler filters: the filtrates go also to pure butinediol storage, and the sludges, which are only a few kg. per day, are dumped.

Charging and development of catalyst

The catalyst as delivered from the catalyst plant consists of 3-5 mm. mesh silica gel granules impregnated with 12% copper and 3% bismuth as oxides. The dry catalyst is filled into the converter by a telescoping chute so arranged that the fall of the catalyst is arrested at the lower end of the chute, which is always held 1 m. from the upper surface of the bed as it rises: thus the free fall of the catalyst granules from the end of the chute to the surface of the bed is 1 m. This gives a loose but even filling. The converter is closed up, and nitrogen is circulated and purged till oxygen is practically absent from the gas circulation. With nitrogen still

circulating, the catalyst is flooded with 8% aqueous formaldehyde preheated to 60°C., which reduces the cupric oxide to cuprous oxide. Acetylene is then introduced into the circulating gas, at first to the extent of 10%. The temperature is held at 70°C. maximum, and the metal oxides are converted to acetylides, and then to addition compounds of acetylide with acetylene: these reactions are exothermic, and care is taken to keep the temperature from rising above 70°C. The acetylene content of the gas is gradually raised to 85%, and formaldehyde circulation started: the converter is then gradually worked up to its proper operating conditions for production of butinediol. The whole process takes from 3-4 days.

Discharging catalyst

The useful life of the catalyst is limited to 2-4 months; deposition of cuprene on its surface leads to inactivation. The condition is indicated by a rise in the gas circulation pressure drop, which rises almost imperceptibly from say 0.1 atmos. for fresh catalyst to 0.3 atmos. over 10 weeks, and then may rise sharply to 1.5 atmos. over 1 week. An exhausted converter is purged with nitrogen: then the gas outlet pipe at the foot (Fig. 4) is withdrawn, which allows any loose rings and catalyst at the bottom to drop. Then the bottom end cover is taken off (the catalyst mass is so cemented together that it does not drop out freely), and a wide grid is fixed over the opening to act as a partial support during discharge. The catalyst mass is then hosed down with water jets (and an occasional rodding) from below, and finally from above, into a wide pyramidal brick lined sump, where excess water drains away. The moist mass is sent by truck back to the catalyst plant for roasting.

3. Notes on Process

(1) Control of converters

It is quite possible to run a single converter so that 10% formaldehyde is stripped down to 2-3% formaldehyde in one pass, but this requires a rather high operating temperature and leads to rapid inactivation

of the catalyst, life probably only one month. The routine flowsheet is two converters in series, but three have been run in series quite frequently. This sort of decision is made on the experience of the operators, and so far no firm set of rules seems to have been drawn up.

The variables used to control reaction temperature are:-

- (a) Total gas circulation: increasing circulation reduces temperature.
- (b) Diluting feed with water reduces temperature.
- (c) Raising acetylene concentration by increasing make-up gas input increases temperature.
- (d) Temperature gradients within the converter are controlled by adjusting the intermediate gas feeds.
- (e) A small amount of open steam feed at each acetylene inlet point is used to increase temperature. These feeds are generally kept on at low rates, as they are believed to assist stability of the reaction.

The operators must take great care to prevent the reaction getting out of control, since temperature rise above 120-130°C. leads to rapid deposition of cuprene and inactivation of the catalyst.

There are also occasionally acetylene decompositions within the converter; it is not known why they occur, but it is suspected that they may start at local hot spots within the catalyst. These are accompanied by a very loud explosion - "like a bomb" - but so far the heavy construction of the plant has contained the pressure rise. Sometimes an explosion will spread to a second or even a third converter. It was not ascertained exactly how often these explosions occurred, but it was certainly not unusual, for the operators referred to them in a most casual manner. After an explosion it was usually possible to get the converter working properly again: the catalyst did not always suffer permanent inactivation.

(2) Acetylene recovery

The operation of a pair of acetylene recovery converters has been described as routine, but it is not at all clear that this was ever achieved. It was certainly recognised as essential to an economic utilisation of acetylene: the inert gases entering with 690 cbm. of make-up gas amount to about 28 cbm., and if this is purged as 85% acetylene, the amount of purge must be 187 cbm., which fixes the upper limit of acetylene efficiency at 76%. The official figure for acetylene efficiency is 80%, and this was usually substantially exceeded during good running, so that it seems probable that some form of acetylene recovery was operated. The principle of the recovery is that the purge gases should be recirculated round a pair of converters supplied with formaldehyde-butenediol solution until the acetylene content of the gas is so far reduced as to make its final rejection economic.

The problem of attaining an acetylene efficiency of the order of 95% is dealt with in a report by Dr. Joost dated 21.1.42, which lays down three prescriptions:-

The acetylene content of the main converter exit gases shall be not above 85%;

There must be an acetylene recovery system operating at 60-70% efficiency;

Sodium bicarbonate must not be used for neutralising the feed to the converters, but this is less important than the first two points.

(3) Distillation

The flowsheet for the distillation section is given in Figure 6. Standby pumps have not been shown. The only essential difference from the simplified flowsheet in Figure 3 is that the propargyl alcohol-formaldehyde solution from the bottoms of the crude methanol column (15) is run back to the propargyl alcohol column (17), which separates propargyl alcohol azeotrope at the overhead from formaldehyde in the bottoms. The formaldehyde returns to make up the converter feed, and the propargyl alcohol is

exported. This column has never been operated for this duty. The column is of the same design as for the main butinediol column (14), except that its working pressure is 120 mm. Hg abs., and the reboilers are a once-through pattern (detail of the type in Fig.9) designed to minimise hold-up time in the reboiler and hence polymerisation of formaldehyde.

As the plant stands at present the main column (14) and the pure methanol column (16) have been damaged; the propargyl alcohol column is being used as the main butinediol column, operating for this purpose at atmospheric pressure, and the crude methanol column for separating aqueous methanol overhead from propargyl alcohol-formaldehyde solution.

Experimental work on the design of the main butinediol column is described in a report "Destillation formaldehydhaltiger Butindiollösungen in die Glockenboden-Kolonne Lu 109" by Dr. Joost, dated 18.8.42. The experimental column was 10 m. high and 350 mm. diameter and had 45 bubble-plates, each with 7 caps, spaced at 200 mm. The feed was on plate 37 from the bottom. The operating pressure was 1.5 atmos. gauge, the calculated vapour-velocity 0.5 m./sec. (empty shell) and the boil-up 250-300 kg./hr.

The ranges of conditions explored, and the best found, were:-

Feed formaldehyde content	1.0-1.6% ;	best 1.1%
Feed butinediol content	about 33% ;	
Bottoms formaldehyde content	0.1-0.5% ;	" 0.3%
Distillate formaldehyde content	4.0-8.0% ;	" 4.2%
Distillate/feed, ratio	1:4-1:10 ;	" 1:6
Distillate/reflux, ratio	1:2-1:3 ;	" 1:2

It was recommended that a once-through reboiler should be used to minimise self-condensation of formaldehyde, but this was not carried into effect.

Previous work in Ludwigshafen had shown that under conditions similar to those recommended, propargyl alcohol present in the feed would be reduced to below 0.1% (usually below 0.02%) in the bottoms, provided that the

formaldehyde was reduced to 0.5-0.6%. The recommended conditions therefore gave practically complete removal of propargyl alcohol.

It is possible for explosions, apparently of a quite subdued nature, to occur in the reboiler of the main butinediol column. This is ascribed to the decomposition of butinediol at 130°C. back into formaldehyde and acetylene, and spontaneous decomposition of the acetylene.

Another report by Dr. Joost, "Der Weg des Methanols in die Butindiolsynthese", dated 15.12.42, gives experimental results and plant design calculations for the recovery of methanol. The 40% feed formaldehyde solution contains 1.4% methanol, the bulk of which comes out in the cold separators. Some is carried forward as saturation vapour with the off-gases from the cold separators, and is scrubbed out by the sealing water of the circulating compressors. This sealing water is distilled for methanol in a small column, which takes the methanol off as a dilute aqueous solution in the bottoms (this can be passed to the crude methanol column, 15), and gives light boilers as an aqueous solution overhead. The light components are:-

	b. p. °C.	Approx. concn. in converter effluent %
Acetaldehyde	25	0.001
Methyl formate	32	0.001
Formaldehydedimethylformal	41	0.001
"Acetal" (unidentified)	57	0.01

The calculated column for separating this "acetal" of b. p. 57°C. from methanol would have 8 theoretical plates with the feed on the 5th from the bottom, operating at 3:1 reflux ratio.

(It appears that this column was never operated, and that the light boilers found their way into the crude methanol column, where they appeared along with the

methanol in the overhead, and then naturally contaminated the pure methanol in the overhead of the pure methanol column 16).

The design is also given for the pure methanol column; i.e. 10 plates, 700 mm. diameter.

(4) Neutralisation and filtration of "pure butinediol" solution

The flow diagram in Fig.8 shows the original design of the filtration plant. It was intended to use bowl centrifuges for the slurry from the three settlers, but although they were installed they have never been used; and the Scheibler filters were installed and used instead. The active carbon treatment plant has not been installed.

Experimental work on the improvement of the neutralisation stage is described in a report "Die Eptkieselung und Neutralisation der Technischen Butindiol-lösung in einem Arbeitsgang", by Dr. Trieschmann dated 15.6.44. The butinediol solution from the converters has a pH of 4.0-4.5, and after the formaldehyde, methanol, and propargyl alcohol have been distilled off, the remaining butinediol solution is neutralised, in current practice, with sodium hydroxide to pH 7.0-7.5. The disadvantages of this treatment are:-

- (a) there is a tendency to flocculate the silicic acid which has been dissolved out of the butinediol catalyst support instead of precipitating it, and it then passes the filters and goes through to the hydrogenation stage;
- (b) the presence of sodium hydroxide promotes the formation of sugary condensation products from formaldehyde, which interfere also in the subsequent hydrogenation and distillations;
- (c) the presence of sodium hydroxide also promotes the formation of formic acid (and methanol) from formaldehyde: the formic acid holds up sodium-ions, which are later removed in the Wofatik (base-exchange) treatment at the tetrahydrofuran stage (Part V), and give rise to development of

acidity in tetrahydrofuran storage;

- (d) any over-alkalinity with sodium hydroxide produces stable froths in the butinediol solution storage tanks.

The analyses of typical butinediol solutions are:-

	<u>Distilled, unneutralised</u>		<u>Distilled, neutralised with NaOH</u>
	I	II	
pH	4.03	4.1	7.1
SiO ₂ %	0.02	0.024	0.013
Mg	tr.	tr.	tr.
Na	0.021	0.016	0.065
Cl	below 0.5	-	-
Formaldehyde %	1.4	0.2-0.48	0.15-0.21
Butinediol %	-	42.9	39.7
Involatile residue %	-	0.7	1.0-1.1

- signifies, not determined.

Neutralisation with lime had been tried in 1939, but trouble arose in the hydrogenation stage. In 1943 "Hergan", an air-sifted magnesium oxide, became available, and was investigated as a substitute for sodium hydroxide. A first series of experiments demonstrated that ordinary ground magnesium oxide did not give good results; the particle size was probably too large (the oxide was used as a slurry in water), and an abnormally large addition was required to adjust the pH to 7.0: also precipitation of the silica was incomplete. A second series with Hergan gave much better results, and suggested that the neutralisation should be done hot. The final process recommended for trial was to heat the butinediol solution to 95°C., add 0.125% by weight (calculated on the volume of butinediol solution) of Hergan as a slurry in water, cool with agitation to 50°C. during 1 hour, and filter. When this process was applied to the unneutralised distilled solution II above, the final analysis of the butinediol solution was:-

Distilled, neutralised with Hergan

pH	7.56
SiO ₂ %	0.0032
Mg %	0.016
Formaldehyde %	0.33
Butinediol %	44.0
Involatile residue %	0.8

The advantages claimed are:-

- (a) Almost complete removal of silica;
 - (b) Prevention of formation of sugary condensation products from the unused formaldehyde;
 - (c) Repression of loss of Na-ions from the butinediol solution and consequent tendency to after-acidification.
- (5) Precautions in using the catalyst

The final catalyst is supposed to be a complex of copper acetylide with 1 mol. of acetylene, which is stable only in an atmosphere of acetylene. The catalyst is therefore developed in presence of excess acetylene, and if a converter is temporarily taken off the line an atmosphere of acetylene is preserved in it. If this is not done, the catalyst reverts to copper acetylide, and when acetylene is again admitted the complex is formed again exothermically, which promotes deposition of cuprene on the catalyst and loss of activity.

The function of the bismuth in the catalyst is to act as a cuprene inhibitor. Mercury is very effective, and the converters are provided with seal-pots through which metallic mercury may be added when the plant is running: it presumably distributes itself over the catalyst, but eventually runs out and collects at the foot of the converter. Iodine is also very effective. Neither mercury nor iodine seems to have been used largely, or even at all, on the full scale plant on account of scarcity during the war, and bismuth by itself seems reasonably effective.

The spent catalyst, that is copper acetylide supported on silica gel, is surprisingly stable. At the time when the plant was inspected, there was a three-inch layer of the catalyst - admittedly moist - on the floor of one of the stalls, and workmen were walking about on it. One of the converters had been opened at the top, and still contained its full charge of catalyst; it had not been used for about 12 months, and was quite dry. The plant chemist, in response to a question on the hazard of keeping 24 cbm. of catalyst (which contains about 2 tons of copper acetylide) thus standing around, rubbed some of the granules vigorously against the lining of the converter. They sparked prettily. In short, this catalyst must not be regarded as copper acetylide, but as copper acetylide stabilised by being deposited in silica gel.

The undeveloped catalyst, as delivered to the plant, is naturally innocuous, consisting only of copper and bismuth oxides on silica gel.

(6) Deposition of copper acetylide in pipe lines

During the operation of the plant copper acetylide migrates from the catalyst and is deposited all along the liquid lines as a fine dark-red film. This is free copper acetylide and is really dangerous: every few months, and before a pipe-line is taken down for repair, strong hydrochloric acid is pumped round the lines to dissolve away the deposit. This practice possibly accounts for the use of 18.8.3.1 steel for the converter liners (18.8.1.1 is used throughout the rest of the plant) as being almost completely resistant to hydrochloric acid over short exposures. 18.8.1.1 is reasonably resistant, especially for parts which can be replaced readily.

(7) Alternative productions of the butinediol plant

(a) Propargyl alcohol

For the production of propargyl alcohol, 40% formaldehyde is diluted with an equal weight of tetrahydrofuran, and the acetylene pressure is 8-10 atmos. Reaction temperature is 100-110°C. and yields of 80% are claimed.

(b) 3-Hexine 2:5 diol and 1-Butine-3-ol
(acetaldehyde and acetylene)

For vinylating acetaldehyde, which gives 3-hexine 2:5 diol, $\text{CH}_3\text{CHOH.C!C.CHOH.CH}_3$, and 1-butine 3-ol, $\text{CH}_3\text{CHOH.C!CH}$, the conditions are generally as for butinediol, except that the acetylene pressure is higher at about 10 atmos.

Neither of these processes has been worked on the full-scale plant, but semi-technical trials have been carried out.

(8) Authors' Comments

The flowsheets of this plant generally give the impression of extraordinary flexibility. The pipework on the converter sets is so arranged that all the variations - two or three converters in series, three pairs in parallel, two converters used for acetylene recovery, and so on - can all be organised by setting valves. Similarly the flowsheet of the still house, and the ways described above in which the stills could be operated, convey a similar picture. The basic designs of the individual plant items, that is the volume of tanks, the area of heat exchangers, and the number of plates in the fractionating columns, etc., seem likewise to have been treated on a generous scale. The converters on the other hand, which are the most expensive single items, seem to have worked right on their rated capacity. This suggests that the plant was designed round the converters, and the designers were very careful that an ancillary unit should not prove too small for its duty, and that any reasonable variation in operating conditions could be catered for without plant modification. This plant had to work from the very beginning, even if it did not work exactly according to plan.

4. Summary of material flows and yield data

The following figures are those quoted officially at the time of the visit. As they were prepared for the benefit of the French Military Government, and represent a forecast of what should be achieved in the plant as it now stands, they are probably rather conservative.

Yield of 100% butinediol
on 100% formaldehyde entering - 90% of theory
on 100% acetylene entering - 80% of theory

Space time yield of catalyst, calculated for two converters in series -

1.0 kg. 100% butinediol/litre of catalyst, 24 hrs.

Feed of 10-12% formaldehyde to a first converter -
12 cbm./hr. maximum

Feed of make-up acetylene to a converter -
350 cbm./hr. as free gas

Concentration of acetylene in off gases from a converter -
85%

Concentration of butinediol in crude butinediol solution -
33%

From the block materials flowsheet, see Table 1, p. 6 :

Catalyst (code number 526) -
1 tonne for 100 tonnes butinediol

Therefore life of catalyst approximately -
100 days.

The following notes are added by the authors:-

Physical properties of process materials

	MW	b. p. °C.	m. p. °C.	Density g./cc.
Butinediol	86	145°/15 mm.	55	-
Butinediol 33% solution	-	-	-	d_4^{20} 1.010
Propargyl alcohol	56	114-115	-17	0.9715/20°

Converter volume and catalyst volume; liquid and gas loads

The dimensions of the converters as drawn and quoted are 1.50 m. internal dia. and 18.0 m. long between flanges. The volume of this cylinder is 31.8 cbm.; and the volume of the quoted catalyst bed (length 16.7 m.) is 29.5 cbm. This does not check with the catalyst charge quoted as 24 cbm., but the figure of 24 seems to be correct.

12 cbm./hr. of liquid flow over a cross-section of 1.768 sq.m. gives a load of 6.8 cbm./sq.m., hr. (160 gall./sq.ft., hr.). 1100 cbm./hr. of free gas at 5 atmos. pressure gives a gas velocity calculated for the empty shell of 0.029 m./sec. (0.1 ft./sec.).

5. Notes on plant construction

General note on corrosion resisting steels used in construction

Three types of corrosion resisting steels were generally used on the manufacturing and distillation plants. These were supplied by Krupps and referred to as "V.2.A", "V.4.A", and "chrome steel" or "V.17.F".

The last was an alloy containing 17% of chromium with addition of titanium. It was used mainly on small pipe lines (1½" diameter and below) when the exigencies of war made it difficult to obtain the alternative materials, but was difficult to weld and unpopular with the maintenance engineer. In some instances, Raschig rings were made from it.

The nominal compositions of the first two types of steel are set out below. These figures were obtained from a catalogue issued by Krupps.

Makers' reference	Carbon %	Chromium %	Nickel %	Molybdenum %	Other Elements
V.2.A Normal	0.10	18	8	-	
V.2.A Supra	< 0.07	18	8	-	
V.2.A Extra	0.10	18	8	-	Ti
V.4.A Normal	0.10	18	8	2.2	
V.4.A Supra	< 0.07	18	8	2.2	
V.4.A Extra	0.10	18	8	2.2	Ti

To avoid the necessity for back reference, the designation "18/8/1/1" (18% Cr, 8% Ni, 1% W and 1% Ti) is used in place of V.2.A and "18/8/3/1" (18% Cr, 8% Ni, 3% Mo and 1% Ti) in place of V.4.A, throughout this report.

Steels of these nominal compositions are supplied under various names by a number of makers in Britain and elsewhere.

In addition to the above, a small amount of 14% chromium steel was used.

Electrical equipment used in buildings

All electric motors, starters and lighting fittings in the compressor house, the distillation plant and elsewhere where acetylene gas might occur were of the "explosion proof" type to the standards of the V.D.E.

This type of enclosure would not meet British flameproof requirements for Group II gases and vapours, but is used in Ludwigshafen for sheds with solvent hazards.

It should be pointed out here that there are no British standards for electrical gear suitable to work in mixtures of acetylene and air.

The lower explosive limit for acetylene in air is 2.5% by volume and its density relative to air is 0.91. In a well ventilated shed therefore the possibility of an explosive mixture occurring under normal conditions is

remote.

No danger from this type of electrical gear was envisaged by the area engineer.

Valves and pipe lines

(a) Valves for compressed acetylene

These were supplied by the firm of Schumann of Liepzig. They are essentially parallel slide valves, of "venturi" form with a cast steel body. The valve seats were inserted rings of compressed asbestos fibre and the slide was a plate of 18/8/1/1. When open, a hole in the slide corresponded with the throat opening in the valve.

(b) Liquor valves

On the high pressure (100 atmosphere) liquor lines, piston type Klinger valves were used, while on the low pressure lines inclined spindle full bore valves were adopted.

(c) Joints on pipe lines

Recessed joints were used on all the high pressure acetylene pipe lines (see detail on Fig.4) with compressed asbestos fibre gaskets. The steel used for these pipe lines was designated St. 45 x 29 to DIN.1629 having a tensile strength of 45 Kg./sq.mm.

The flange and hub were rolled in one ring and joined to the pipe line by a circumferential weld.

Flange joints on the high and low pressure stainless steel pipe lines were fitted with backing flanges.

Cranes

The butynediol and butanediol converters were both serviced by one Goliath crane which was provided with two blocks, with capacities of 130 and 45 tons respectively.

In addition, a jib crane was provided running along the top girder of the main crain, having a capacity

of 7½ tons and used mainly for lifting catalyst hoppers to the top of the staging.

Plant items were run in on a rail track on the east side of the converter house (see Fig.1).

The crane was fed by a trailing cable, supported from a subsidiary structure running alongside the crane track.

In addition to the above, there was a small crane having a capacity of 7 tons running along the top of the butynediol converter building and used for catalyst loading.

Compressors and circulators for acetylene

These machines were of the rotary water ring type and were supplied by Siemens Schuckerts under the name of ELMO.

Particulars of the compressors are as follows:-

Number of stages - 2.

Duty - 350 M³/hr. free acetylene compressed from 250 mm. water gauge to 5.2 atmos. 1st stage to 2.6 atmos.

Motor - Explosion proof, 88K.W. 1425 R.P.M.

Material of construction - All internal parts of 18/8/1/1.

The machines were designed for a safe working pressure of 100 atmospheres and a test pressure of 150 atmospheres. The glands were water cooled.

Fig.11 shows, in diagrammatic form, the system of operation of this type of compressor.

The circulators were similar except that they were single stage and delivered 420 M³/hr. of free gas, with a suction pressure of 4.0 atmos. and a delivery pressure of 5.2 atmos.

The cooling and sealing water to each set of compressors and circulators passed with the gases to a separating vessel, was extracted from this vessel and circulated through a tubular water cooler.

All this equipment, including the centrifugal pumps was designed for a safe working pressure of 100 atmospheres and a test pressure of 150 atmospheres.

Make up water was fed into the separators through a float controlled valve.

The temperature of the cooling water was kept below 50°C.

Compression in this type of machine will probably approximate to isothermal, with a very limited temperature rise of the gas, where in the normal type of rotary compressor, a temperature rise of the order of 100°C. might occur.

Converters

Fig.4 shows the general construction of these.

They consist essentially of tubes, flanged at each end, 18 M. long and 1.5 M. internal diameter, and provided with end covers.

They were fabricated by fusion welding in accordance with a specification calling for X-ray examination of seams and preparation of test specimens, seven being made by Krupps and the last by Mannesman and Heinrich Billwes.

The material of construction of the body was an alloy steel (M.III) having an ultimate tensile strength of 70 kg./mm.², the shell thickness being 73 mms. The factor of safety on the designed working pressure of 100 atmospheres was thus approximately 6.5.

Each converter was lined with 18/8/3/1 steel fixed to the inside of the body with false rivets at approximately 6" centres. This construction was necessary owing to the fact that the coefficient of expansion of

18/8/3/1 steel is approximately 50% greater than that of the body material. Thermometer pockets of conventional type were provided spirally round the body of the converter, to house the resistance thermometer elements.

The shell was fabricated in two sections joined by a circumferential weld and the end flanges were made from rolled rings, incorporating hubs for connection to the shell.

Protection of plant against acetylene detonations

The prevention of acetylene explosions developing into detonations has been dealt with in Part II, where the general precautions observed on this plant were described.

It is sufficient to emphasise here that all vessels and pipes which held acetylene under pressure are packed so as to break up the gas space into small volumes, the pipes with small tubes, and the vessels with rings. The whole volume of the gas-liquid separators is packed with 35 x 35 mm. 17% Cr steel rings; they run about one-third full of liquid, and of course the packing above this level is continually drenched with liquid from the entry port. The converter space below the catalyst (see Fig.4) is packed with 15 x 15 mm. and 35 x 35 mm. rings. After the catalyst has been filled in, and the acetylene and formaldehyde feed distributors fixed in position, the converter shell is filled up with 15 x 15 mm. porcelain rings, which are heaped up above the edge, so that when the top domed cover is put on, the whole space between it and the upper level of the catalyst bed is packed with rings.

The pipes used in construction of the heat exchangers are so narrow that no packing is necessary in them.

3 Pass evaporator ("Durchlaufverdampfer")

This type of evaporator was used in the distillation plant on column P.2 (item 17, Fig.6). The construction, shown schematically in Fig.9, ensures a high liquor velocity through the tubes.

The direction of flow is upwards in each pass.

This is an advantage in the case of liquors liable to frothing, the large liquor space at the head of the evaporator allowing the vapour to disengage itself at the end of each pass. The body of the evaporators was made from 18/8/1/1 steel, and the tubes from 14% chromium steel.

Condensers - distillation plant

These are the horizontal tubular type with cooling water inside the tubes. The tubes are so arranged that the condensate drip from one tube falls clear of the ones immediately below it.

The lower part of each condenser can be arranged to act as a condensate cooler, with an adjustable outlet.

In condensers on vacuum stills the vacuum pipe to the condenser is fitted with an inverted hood-shaped baffle to prevent liquid being entrained into the vapour pipe.

Construction and efficiency of bubble plate columns

The bubble plates are of conventional design, except that in some cases a very neat way of arranging parallel liquid flow on the plates, ascribed to Kirschbaum, has been used. The plate is removable, and is bolted down round its periphery to a shelf inside the column shell, which is one-piece welded construction. The plate carries a false wall of radius about 50 mm. less than the column shell, so that there is an annulus about 50 mm. wide all round the plate. The bubblers are inside the false wall; they are about 75 mm. diameter, of spun or pressed metal, and the slots are tapered from about 4 mm. wide at the lower edge to 2 mm. at the top. The slots are about 30 mm. high, and the lower edge of the cap is about 30 mm. clear of the plate. The downtake weir is inside the false wall, and leads to the annulus of the plate beneath: the liquid flows round the annulus both ways and enters the plate over an entry weir cut away in the false wall, diametrically opposite the downtake weir. The entry weir is heavily notched (V-notches 25 mm. deep x 12 mm. wide at top) and the downtake weir is saw-toothed (2 mm. wide notches).

In some columns the whole volume of the plate spacing has been filled with raschig rings: the object is to stop entrainment and allow the column to be loaded more heavily.

Nothing is known of the plate efficiency in the butynediol plant columns: the design has been empirical and developed from fairly large scale trials on bubble-plate columns.

Instrumentation and automatic controls

In both the manufacturing and distillation plants the principle of centralising all important instruments and controls was carried out as far as possible.

In the case of the manufacturing plant, each converter unit is provided with a control panel on which are mounted:-

- I. 4 flowmeters for acetylene (one to each of the four feed levels on the converter).
- II. 2 - 6 point temperature recorders (liquor and gas entries and catalyst temperatures at 10 levels).
- III. 2 temperature indicators. These cover temperatures at cooler outlets and intermediate levels in converter body.
- IV. Formaldehyde flow recorder.
- V. Automatic controller for formaldehyde preheater.
- VI. Recorder for top steam supply to the converter.
- VII. 2 pressure indicators (inlet and outlet to converter).
- VIII. 1 pressure recorder - acetylene pressure.
- IX. 1 gas analyser for recording the percentage of acetylene in the gases (installed but not put into operation). It was hoped by use of this instrument to improve the acetylene efficiency of the plant.

In addition to the above main control panel each cubicle in the compressor house is provided with a subsidiary panel with instruments for recording or indicating acetylene flows, pressures and temperatures and cooling water temperatures and flows.

A typical control panel in the distillation plant is that provided on column P.2, where the following instruments are grouped together:-

- (1) Temperature indicators.
- (2) Recorder for feed to column.
- (3) Recorder for reflux to column.
- (4) Recorder-temperature of each of two evaporators.
- (5) Recorder-pressure of column.
- (6) Indicator-pressure drop across column.
- (7) Recorder-flow from bottom of column.
- (8) Recorder-distillate from top of column.
- (9) Indicator-distillate release vessel-pressure.
- (10) Indicator-condenser water flow.

Where necessary the handwheels of the control valves are mounted on the face of the panel, the actual valves being mounted behind the blast wall (in the case of the manufacturing plant).

The instruments are generally of conventional pattern, orifice plates being used for flow measurement and resistance elements for temperature measurement.

All instruments on the 100 atmosphere section of the manufacturing plant were designed for this safe working pressure. In the case of pressure gauges, the necessary sensitivity was got by providing a coiled Bourdon tube 1.5 M. long.

Automatic controls (except for the Askania controls dealt with below) were of the compressed air operated pattern supplied by the firm of G.S.T. (Berlin).

These were extensively used for the control of liquor levels.

Temperature indicators were supplied by Hartmann and Braun and flowmeters by Bopp and Keuther (Mannheim) while the ring balance type of flowmeter used on the service lines were apparently made by the I.G.

The Askania automatic controls which regulate the pressure in the system by controlling the amount of fresh acetylene pumped into it and the rate of circulation, are operated by oil at an initial pressure of 7 atmos. The instruments appear to be of conventional pattern in which the pressure of a jet of oil is varied by the movement of a vane (actuated from the pressure to be controlled). This oil pressure is then transmitted to a servo motor which adjusts the position of the controlling valve through a linkage.

All the instruments are centralised in the Askania room in the compressor house.

Two pressures are controlled in each converter unit - the pressure in the converter head and the pressure in the acetylene manifold. The first is controlled by varying the fresh acetylene and the second by varying the rate of circulation. The object of this second control is apparently to make easier the adjustment of the acetylene flow through each of the inlets. If this pressure is kept constant adjustment of the flow through any pipe line will not affect the flow through the others.

As a general point, the I.G. do not seem to have adopted flow controllers. Process flows are always regulated by manually operated valves against indicating or recording flowmeters. Pressure in feed lines and levels are automatically controlled. The steam supplies to still reboilers are automatically controlled by temperature in the reboiler vapour line.

6. Summary of experience on pilot plant

This section is an abstract of a series of reports headed generally "Zweiter (etc., the first was not found) Bericht über die Butindiolherstellung in der technischen

Versuchsanlage Lu 606", by Drs. Gaus, Jorst and Trieschmann, covering the period early 1940 to late 1942. This is the 600 ton/yr. pilot plant upon which the main 8-converter plant at Ludwigshafen was designed. No flowsheet or plant description was found, but it is clear from the internal evidence of the reports that the flowsheet was very similar to that of the main plant. There were two converters; one 18 m. high x 500 mm. internal diameter, volume 2000 litres, catalyst volume 1700 litres; and the other 18 m. high, volume 700 litres, catalyst volume 600 litres. The smaller converter was part of the preceding pilot plant, the 100 ton/yr. model. The larger converter is described as having three zones, upper, middle, and bottom, in which temperatures were measured and to which acetylene could be admitted independently; but the bed of catalyst was not divided between these zones.

2nd report, dated 15.4.41

Period covered - May-December, 1940. Shut down during June and August-September due to plant troubles.

The 2000-litre converter was used alone with the feed liquid running once through. The catalyst was "nach Curtius", which means apparently that the silica gel catalyst granules were mixed with 25% weight of unimpregnated silica gel and marble chips, and filled in dry through a telescoping chute. A separate concurrent investigation, which was not traced, was dealing with the physical form and activity of the catalyst.

The distillation of formaldehyde, etc., away from the butinediol solution was done for the first time at 1.3-1.5 atmos. gauge pressure, and gave better stripping than the atmospheric pressure distillation previously used. The objects of investigation during the period were the influence of formaldehyde feed concentration upon the reaction and the influence of method of packing the catalyst

‡ (The volume calculated from the dimensions is 3530 litres. The cross-section is checked by the liquid rates 55 litres/sq.dm., hr. and 1100 litres/hr. being given as equivalents: the volume is repeated several times. Hence probably the height is in error. This probably applies to the height of the smaller converter also).

upon liquid distribution.

The conditions of running were:-

Working pressure - 5 atmos. Formaldehyde feed concentration 15-30%, mostly at 25%; pH of feed 6-7.

Converter temp. °C.	% CH ₂ O out	Feed rate kg. 100% CH ₂ O/sq. dm., hr.	Pressure drop atmos.
80-120 mostly at 100-115	0.2-3.1 mostly at 0.5-0.7	1.8-3.4 mostly at 2.7-2.8	zero rising to 1.5 at finish of run

The yields expressed on formaldehyde feed were:-

As butinediol	93.2-94.8% theory
As propargyl alcohol	0.2- 1.2% "
As unused formaldehyde	2.5- 3.3% "
As "residue"	2.2- 3.0% "

"Residue" appears to mean involatile condensation products, equated to formaldehyde at the ratio of approx. 1.3 kg. per kg. formaldehyde 100%.

There was one acetylene detonation, which started in the gas circulating compressor. This was a Wittig compressor, which is a dry oil-lubricated rotary blower. The effects were serious enough to be remembered, and the Wittig compressors were replaced by Siemens-Schukert water-sealed compressors. This was the only acetylene detonation ever reported.

3rd report, dated 17.4.41

Period covered - February-March, 1941.

The catalyst investigation was dealing with optimum copper and bismuth contents; and the preparation and properties of the silica gel support-water adsorption, hardness, roasting temperature, best type of oven. The objects of the investigation on the pilot plant were the same as before - formaldehyde feed concentration and liquid distribution over the catalyst, and the plant and

method of catalyst packing were again the same. It was found that filtering the liquid feeds to the converter was most beneficial to the life of the catalyst, and that high temperatures in the converter tended to produce high concentrations of "residue" in the butinediol solution. The mechanical loss of formaldehyde and butinediol was reduced to 1.0-1.5%. Efforts were made to keep the temperature within the catalyst bed uniform by admitting acetylene to the middle and lower zones. Mercury was used as a catalyst activator (cuprene suppresser).

The history of the run was briefly:-

Working pressure, 5 atmos. Formaldehyde feed concentration, 22.5%.

Days running	Converter temp. °C.		% CH ₂ O out	Feed rate litres/hr.	Pressure drop atmos.
	1/2 *	2/3 *			
0	90	110	0.5	260	0.2
56	115	116	4.0	260	0.25
6	Water circulated for 6 days to clean catalyst				
5	100	112	7.8	545	0.5 rising
4	Output of last 5 days put through again				
	118	124	0.4-0.9	545	1.6 stop

* 1/2 signifies thermocouple at junction of first and second zones, i.e. one third down converter.

When the catalyst was dropped out, it was found to be stuck together in lumps, and the liquid had been channelling.

Yields were much as before.

4th report, dated 17.12.41

Periods covered - 18.4.41 - 27.5.41 and
11.6.41 - 26.7.41.

Catalyst packing and plant as before; objects as before.

There were two distinct periods, and the history was briefly:-

Days running	Converter temp. °C.		% CH ₂ O out	Feed rate litres/hr.	Pressure drop atmos.
	1/2	2/3			

Working pressure 5.0 atmos. Formaldehyde in feed, 22.5%. Feed preheat temperature 70°C. Gas circulation 100 cbm./hr., 70 at head, 30 at middle zone.

40	100	110	5-10	520	0 rising to 1.0 stop
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Fresh catalyst. Output of above run put through again, approx. 4% formaldehyde. All acetylene fed at head.

27	110	104	0.2-0.5	600-900	
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Feed returned to fresh 22.5% formaldehyde.

19					rising to 1.5 stop
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Yields were much as before. This run confirmed the possibility of doubling the formaldehyde rate, but the increase in output was quite small, from 45 kg. butinediol/litre catalyst to 55.

5th report, dated 26.2.42

Periods covered - 16.8.41 - 30.9.41 and
October - November.

The two converters were now run in series, the 2000 litre first, and the 700 litre second as an exhausting converter. The catalyst packing was the same as before.

<u>Days running</u>	<u>Converter temp. °C.</u>	<u>% Formaldehyde out</u>		<u>Feed rate litres/hr.</u>
		1	2	
45	100-115	4-5	1.5	430-530
	New catalyst			
33	100-115	4.0	1.5	495

The conclusions reached from the work so far were that the high feed rates were beneficial, and that the dilution of catalyst with marble chips was of no value. The last 33-day run was disappointing, and the catalyst was deemed an inferior batch. Channelling was still occurring. The pH of the feed was of no consequence between 4-6.

6th report, dated 27.2.42

Period covered - 9.12.41 - 5.1.42.

The plant was run as in the 5th report, but the catalyst packing and liquid distribution was changed. The catalyst was not diluted with marble chips or silica gel, and it was (apparently) charged by filling the converter with water and floating the granules down. The liquid distributor was "nach Buche" and a sketch is given in Fig.10.

The catalyst development is described in detail:-

- 22.5% Formaldehyde at 65°C. was circulated for 16 hr., with nitrogen circulation.
- Acetylene introduced increasing from 10% to 20% during 3 hr., and then held at 20% for 24 hr. Temperature 70°C.
- Acetylene gradually increased to 80% over 24 hours.

(It is worth noting that when two converters are being started up in series, the catalyst in the second converter must be developed first).

There followed a thoroughly bad run, with the catalyst lasting only 26 days and the yield down to 87%. There seemed to be no good explanation of anything, except that the catalyst had certainly been packed too tightly.

(This is interesting, for when the authors first (saw the method of charging the catalyst by telescopic chute (they regarded it as ingenious but complicated, and asked (whether charging by floating down a water-filled converter (had been tried. The answer was yes, but it had been (found unsatisfactory).

7th report, dated 18.12.42

Period covered - 10.4.42 - 26.6.42.

This is a significant report: for the first time the tone of the reporting is confident, and it is clear that the process was now taking shape.

The two converters were again run in series. The catalyst was charged by telescopic chute, and the liquid was distributed as in Fig.10.

The catalyst was mounted on silica gel granules, as now used on the plant, having 93% water adsorption, packing density 0.56 g./cc., sized 40% below 3.5 mm. and 4% below 2 mm. The metal content was 32% (c.f. present 15%). The charge to the large converter was 1700 litres catalyst plus 29 kg. mercury, and to the small 600 litres catalyst plus 10 kg. mercury.

Development of the catalyst followed this schedule:-

- Cold 22.5% formaldehyde at pH 5.5 was circulated at 250 litres/hr. for 12 hr. Nitrogen circulation 25 cbm./hr. at 5 atmos.
- The formaldehyde feed temperature was raised to 65-75°C. to reduce the cupric oxide to cuprous oxide. Feed rates:

250 litres/hr. for 13 hr.
 100 " " " 4 "
 50 " " " 48 "

The copper content of the exit liquor was 0.2%, formic acid 0.3%. Since circulation of this liquid would have deposited copper (which would later form copper acetylide) on the rings and in the pipework, it was all put down the drain.

(c) The catalyst was washed with 300 litres/hr. of water at 65°C. for 20 hr. Still at 25 cbm./hr. of nitrogen at 5 atmos.

(d) To form copper acetylide, the water circulation was maintained at 300 litres/hr. at 65°C., and the acetylene concentration increased from 0% to 76% over 12 hr. Gas rate 25 cbm./hr., all to the head of the converter, 5 atmos. pressure. Temperature held at 60-70°C. by adjusting the acetylene rate.

Hours from start	0	4	8	12	16	18
Acetylene absorbed total cbm.	0	12	23	30.6	41.5	43.5

(e) The reaction proper was started by feeding 22.5% formaldehyde at 260 litres/hr. The acetylene concentration was increased from 76% to 93% over 14 hr., and the circulation rate was increased to 65-70 cbm./hr. (40 cbm./hr. to the head, 25-30 to the middle zone). Pressure 5 atmos. A feed of steam was used to the head at 14-15 kg./hr., and this was maintained all through the succeeding run. After 14 hours the original uniform temperature of 65°C. in the converter had been increased thus:

Thermocouple	1/2	2/3	outlet
Temperature °C.	86	97	88

External electrical heat was turned on the outside of the converter, to bring the 1/2 thermocouple up to 102°C.

The above procedure occupied in all 132 hours.

The history of the run proper was:-

Days running	Converter temp. °C.	Feed rate litres/hr.	% CH ₂ O out	Make kg. bd./l., day
10	85-100	250 at 22.5% pH 6.0 65-70°C.	1.5 fed into 700 l. converter	0.996
26		380 at 22.5% pH 5.5	4.5-5.5	1.24

pH dropped to 3.3-3.6 for 10 days to check effects of acidity: no effect. First beginnings of pressure drop noted.

8	96-112	ditto	rising to 9.0	0.968 (falling; point reading at end 0.89)
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The 700 litre converter could only strip its feed to 4.0% formaldehyde, and the still allowed 1.4% formaldehyde to remain in the butinediol. Pressure drop up to 0.1 atmos.

It was now clear that if the temperature had gone on rising at the same rate, either cuprene formation would have stopped the run or there would have been a rapid fall in output.

31	90-110	1100 at 10% to 600 at 12-13%	5.0	0.91
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380 litre/hr. of the make was sent to the second converter, the rest (720 litre/hr.) was returned to the converter and mixed with formaldehyde-propargyl alcohol distillate, fresh formaldehyde, and distilled butinediol to give the 10% feed. Feed gradually cut down and formaldehyde concentration correspondingly increased.

Pressure drop at beginning was 0.3 atmos. At last day of run pressure drop rose from 0.6 atmos. to 1.2 atmos. in 24 hours.

Mercury was added throughout the whole run at 400 g./day to the large converter and 200 g./day to the small.

The overall result of this run was that the two converters together (total catalyst volume 2300 litres) produced 75.5 kg. butinediol per litre catalyst, and the large converter alone produced 78.0 kg. Compare the 45-55 kg. bd./litre quoted in the 4th report.

The yields expressed on formaldehyde feed were:-

As butinediol	91.90%
" propargyl alcohol	0.86
" unused formaldehyde	3.60
" "residue"	3.40
	<hr/>
	99.76

The conclusions of the report are:-

- (a) The chute charging, the (new) silica granule support, and the method of liquid distribution are proven.
- (b) A feed pH of 3.3-3.6 is not harmful.
- (c) Increasing the liquid feed rate by a factor of 3 and reducing the formaldehyde concentration to 10% or so by recycling the make butinediol is most beneficial: the catalyst life was increased to 7 weeks and the output was the best yet achieved.
- (d) The method of developing the catalyst is too slow and wasteful for works use. In Schkopau, where this method is always used, the waste formaldehyde solution containing copper is kept separately till the end of the run, when it is put through the converter. (This apparently refers to the Schkopau pilot plant).

8th report (date missing)

Period covered - July - September, 1942.

This report, being the last found, is given as a full translation. Authors' additions are bracketed.

A. Procedure

(a) The method of charging the catalyst and the liquid distribution were the same as before.

(b) The silica gel granule catalyst 526 was used in the 2000-litre converter: mercury was not added either to the charge of catalyst or during the run, as it was desired to discover whether mercury had any effect on the full scale. The catalyst for the 700-litre converter was the same except that the bismuth oxide was omitted: again no mercury was used.

(c) Since high feed rates had been found beneficial in the previous run, a flow of 55 litres/sq.dm., hr. (1100 litres/hr.) was used throughout this one; it was formed by the same procedure of recycling make solution.

(d) The development of the catalyst was put through more quickly.

(e) The pH of the liquid feed was kept below 5.0, since when make liquors are brought to a higher pH they precipitate silicic acid.

(f) The make-up acetylene was put in after the recirculating compressor in order to be able to continue working when the converter pressure drop rose, and so to increase the length of the run.

B. Development of the catalyst

(a) The catalyst was saturated by circulating 20% formaldehyde at 250 litres/hr. for 12 hr.; nitrogen circulation 35 cbm./hr., 5 atmos. pressure.

(b) The formaldehyde feed was preheated to give 65°C. at the 1/2 thermocouple as quickly as possible. This took 2 hr.

(c) Acetylene was now added to the gas. The temperature at the converter outlet rose to 65-70°C. during 2-3 hr., and further increases were prevented by reducing the acetylene input. The catalyst was developed at 70°C. and an acetylene concentration of 10-20% during

10 hr. For the first 6 hr. the exit liquor was rejected (1800 litres of 10% formaldehyde), but after this it was recycled. The whole development occupied about 24 hr.

Over the next 4 hours the reaction temperature was increased to 90-100°C., and over the next 8 hr. the acetylene concentration was increased from 20% to 90%.

C. Conduct of run

The data are given in Tables (7 and 9). The run falls into five periods.

(a) Converter 1 was given a light load for 2 days after development, after which the full load was imposed:-

Liquid load	55 litres/sq.dm., hr.
Feed rate	1100 litres/hr.

380 litres/hr. of the make was passed to Converter 2. The rest of the make was mixed with distilled (topped) butinediol solution and fresh formaldehyde (and presumably recycled formaldehyde) to make up again 1100 litres/hr. of feed. The quantities were calculated to give a formaldehyde concentration in the feed of 10%.

As shown in Table (7) the formaldehyde loading during the 47 days of this period was 5.4 kg. 100% CH₂O/sq.dm., hr. The production of butinediol was 0.978 kg./litre converter, day; or 1.15 kg./litre catalyst, day (i.e. 1700 litres of catalyst). From the 30th day onwards the formaldehyde content of the make began to rise a little, and the temperature was increased after the 39th day from 100° to 110-114°C. In order to alter the temperature in the lower zone without affecting the upper, a steam point was installed at 1/2, and thereafter the temperature at 1/2 and at the bottom was controlled by the addition of steam. A pressure drop - 0.05 atmos. - was observed for the first time on the 40th day, and the gas circulation of 35 cbm./hr. at the head was reduced to 30 cbm./hr. The plant was shut down on the 11th and 12th days by an accident (nature not stated).

(b) On the 48th day, the 700 litre converter had to be shut down with a cuprene blockage, ascribed to the

absence of bismuth. It was refilled again with bismuth-free catalyst to check the result.

During the recharging of Converter 2 and the development of the new catalyst, Converter 1 was run at 1100 litres/hr., but with the formaldehyde concentration reduced to 5%. During this period of 7 days the formaldehyde loading was 2.9 kg. 100% CH₂O/sq.dm., hr., and the production of butinediol was 0.532 kg./litre converter, day or 0.626 kg./litre catalyst, day.

(c) On the 55th day Converter 2 was restarted and the full load put back on Converter 1. After 2 more days, during which the pressure drop (Converter 1) rose to 0.5 atmos., the feed rate had to be lowered again; and the gas circulation was likewise reduced on the 56th day to 25 cbm./hr. During these 4 days the formaldehyde loading on Converter 1 was 4.6 kg. 100% CH₂O/sq.dm., hr., and the butinediol production was 0.773 kg./litre converter, day or 0.910 kg./litre catalyst, day.

(d) During the next 10 days the liquid feed was gradually lowered to 500 litres/hr. With this feed rate and a gas circulation of 20 cbm./hr. the pressure drop rose to 0.7 atmos. By concurrently increasing the formaldehyde concentration the butinediol production was kept up to 0.882 kg./litre converter, day or 1.038 kg./litre catalyst, day.

(e) During the next 4 days the production of butinediol fell to 0.620 kg./litre converter, day or 0.730 kg./litre catalyst, day with a loading of 3.55 to 3.2 kg. 100% CH₂O/sq.dm., hr. On the 72nd day Converter 1 was shut down due to high pressure drop.

For days 1-18 the pH of the feed was 3.7 and of the make 3.5; and for the remainder of the run the pH of the feed was 4.5 and of the make 4.1.

Table (8) gives the formaldehyde balance and the yields for the whole run.

Table (9) compares the productions from Converters 1 and 2: the production from Converter 2 is the difference between the total for the 3rd quarter - that is the whole of this run - and the production from Converter 1,

calculated on the input of formaldehyde over the total running time of 75½ days. Calculating more exactly gives a running time of 70½ days in Converter 2, because of the interruption occasioned by the double charging with bismuth-free catalyst: alternatively the effective volume of Converter 2 should be reckoned as 660 litres instead of 700 litres to allow for this interruption.

Table (9) shows that the output of the two converters together was 67.2 kg. butinediol/litre catalyst, i.e. below the performance in the preceding run 14 (7th report: the corresponding figure there is 75.5), but the production of Converter 1 alone was 75.3 kg./litre catalyst, almost the same as before. (The figure is 78.0). The reason is that whereas the performance of Converter 1 was practically the same in both runs 14 and 15, Converter 2 was operated in run 15 for one-third less time than in run 14.

D. Conclusions

The performance of the 526 catalyst incorporating bismuth but without any mercury additions under the experimental conditions is 75.3 kg. butinediol/litre catalyst, which is almost as high as the result from run 14, 78.0 kg./litre.

The use of 526 catalyst without bismuth is unpromising. Converter 2 run without either bismuth or mercury had to be shut down after relatively short periods of 48 days and 18 days due to cuprene formation.

The increased feed rate of 1100 litres/hr., obtained by recycling make liquor, combined with a formaldehyde content of 10%, and giving a formaldehyde loading of not more than 5.4 kg. 100% CH₂O/sq. dm., hr., gave good results. The catalyst life was nearly 11 weeks.

Transferring the inlet point for fresh acetylene to the delivery side of the circulating compressor is justified. The gas circulation rate should be controlled by checking the delivery of the pump and not on the suction side.

Converter temperature can be controlled by injecting steam into the lower zones.

TABLE 7. Log sheet for butinediol pilot plant, run 14

Day	Converter temp. °C.			Feed l./hr.	Feed % CH ₂ O	Make % CH ₂ O	Load Kg CH ₂ O/sq. dm., hr.	Pressure drop atmos.
	1/2	2/3	bottom					
0	70-90	75-100	60-80	300	10	-	-	-
1	90	99	83	300		0.8	3.1	-
2	90	100	90	280		0.9	3.1	-
3	86	92	90	1100		3.2	5.4	-
4	90	98	100			3.1		-
5	90	100	100			3.2		-
6	89	98	98			3.5		-
7	90	100	105			3.3		-
8	90	100	103			3.1		-
9	91	99	103			3.3		-
10	91	101	105			3.2		-
11	90	99	104			3.2		-
12	-	-	-	-	-	-	-	-
13	93	104	106	1100	10	3.1	5.4	-
14	92	102	106			3.3		-
15	91	100	107			3.6		-
16	90	98	105			3.5		-
17	91	102	108			3.1		-
18	91	103	107			2.6		-
19	90	102	106			2.7		-
20	91	104	106			3.3		-
21	91	105	107			3.5		-
22	91	103	104			3.4		-
23	91	105	106			3.5		-
24	92	106	109			3.5		-
25	91	105	107			3.6		-
26	92	106	108			3.7		-
27	92	106	107			3.7		-
28	93	106	108			3.7		-
29	95	106	109			4.1		-
30	94	106	108			4.4		-
31	95	109	111			4.4		-
32	95	108	108			4.2		-
33	96	107	111			4.2		-
34	97	108	112			4.4		-
35	98	110	112			4.6		-

TABLE 7. (contd.)

Day	Converter temp. °C.			Feed l./hr.	Feed % CH ₂ O	Make % CH ₂ O	Load Kg. CH ₂ O/ sq. dm., hr.	Pressure drop atmos.
	1/2	2/3	bottom					
36	100	109	112			4.6		-
37	100	110	112			4.7		-
38	100	110	112			4.8		-
39	100	110	114			4.9		-
40	100	110	113			5.1		0.05
41	100	109	113			5.0		0.05
42	100	112	117			4.9		0.15
43	100	113	116			4.8		0.2
44	102	112	122			5.0		
45	102	113	121	1100/800		5.6		
46	100	110	120	1100	10	5.7	5.4	
47	100	110	122		10	4.8	5.4	
48	100	110	124		5	2.6	2.9	0.15
49	99	107	124			2.1		0.2
50	98	108	123			2.0		0.2
51	102	114	120			1.8		0.15
52	101	115	122			1.8		0.15
53	99	116	124			1.8		0.2
54	102	115	120		6	2.5		0.2
55	100	115	120	1070	8	3.5	4.35	0.3
56	100	114	120	1000	10	4.3	5.1	0.45
57	100	115	120	900		4.6	4.6	0.5
58	100	116	118	850		4.9	4.35	0.6
59	100	114	120	750		5.0	4.6	0.6
60	100	114	120		12	5.0		0.45
61	100	112	118	700		5.1	4.5	0.5
62	102	116	122		12.5	4.7		0.6
63	102	116	123	600	14	4.5	4.3	0.6
64	102	120	122			4.3		0.6
65	102	120	120			4.2		0.65
66	102	124	122	550		3.4	3.9	0.7
67	102	126	124	500		3.5	3.55	0.75
68	98	118	120			4.0		0.7
69	98	119	120			4.5		0.7
70	100	120	118			4.5		0.5
71	100	118	116			5.5		0.8
72	102	118	118	450		6.3	3.2	0.8

TABLE 8. Formaldehyde balance and yields
July-September, 1942

	Wt. kg.	Equiv. 100% CH ₂ O kg.	Yield % calc. on CH ₂ O stock used (114802 kg)	Yield % calc. on CH ₂ O unused *	Dis- crep- ancy
Butenediol produced	154473	107772	93.90	93.90	
Propargyl alcohol as product	280	151	0.13	0.13	
Propargyl alcohol in make	1195	640	0.56	0.56	
Formaldehyde unused	3045	3045	2.65	1.55	1.10
"Residues"	4299	3540	2.91	-	2.91
		114948	100.15	96.14	4.01

* Based on uninterrupted running and excluding that deliberately run away.

TABLE 9. Production in individual converters

	Days running	Production kg. butinediol	% of total production	Production rate			
				on converter volume per day		on catalyst volume per day	
	47	91860		45.95	0.978	54.00	1.15
	7	7451		3.73	0.532	4.37	0.626
	4	6185		3.09	0.773	3.64	0.91
	10	17646		8.82	0.882	10.38	1.038
	4	4960		2.48	0.620	2.98	0.730
Converter 1	72	128102	82.9	64.07	0.89	75.31	1.046
" 2	66	23371(2)	17.1	37.7	0.571	43.90	0.665
Both together	70.5	154473 (1)	100.0	57.2	0.811	67.2	0.953

Converter 1 - 2000 litres volume, 1700 litres catalyst.
 " 2 - 700 litres volume, 600 litres catalyst.

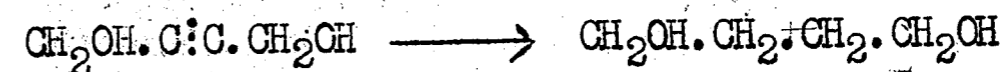
- (1) Total production in period.
- (2) Difference between total production and the production in Converter 1 as calculated from the formaldehyde feed and performance for Converter 1.

PART IV. BUTANEDIOL STAGE

The information in this section was obtained by interrogation of Dr. Steinhöfer and Mr. Spohn, and inspection of the plant, in November, 1945.

1. Outline of process

35-40% butinediol solution is hydrogenated in co-current downwards flow at 40-130°C./200-300 atmos. over a nickel-copper-manganese catalyst. Butanol is topped off from the product, and the resulting approx. 40% butanediol solution is sent to the tetrahydrofuran stage. Alternatively 100% butanediol may be produced by a complete distillation.



2. Description of process

General layout of plant

See Figure 1. The plant consists of two main buildings, the compressor room and the converter house; liquid feed and product storage are provided in the tank farm, and the fractionating columns are housed along with the butinediol columns in the still house. The compressor room is a large high building, and contains the butinediol feed pumps (eight 3-ram single-stage reciprocating pumps), and the hydrogen circulating pumps (seven single-stage reciprocating compressors). The converter house is an open structure running parallel to the compressor room, and on the same line as the butinediol converter house: the same Goliath crane serves both converter houses. The converter house contains eight stalls in two groups of four: three stalls in each group are used, and each contains a converter with its own heat exchanger. The converters in the six occupied stalls are:-

- 4 converters 18 m. high x 0.8 m. internal diameter, steel lined with copper. The copper lining is not essential, and was omitted in one case owing to war shortage, but it is distinctly desirable. These are the main make converters, and are worked in parallel.

1 converter 18 m. high x 0.8 m. internal diameter, lined with 18.8.1.1. This is kept on a separate liquid circulation system and is used only for reworking defective (incompletely hydrogenated) butanediol.

1 converter 18 m. high x 0.6 m. internal diameter, steel lined with acid-resisting tiles (same shell as above five). This is used for hydrogen purification only, and works dry.

A control room runs parallel to and between the buildings. On the open ground between the compressor room and the control room are the pipes and surge-tanks for circulating hydrogen and nitrogen: again in open ground between the control room and the converter house are the gas coolers, gas preheaters, and liquid-gas separators. All the pressure plant is built for 340 atmos. working pressure.

This plant has been rather badly damaged, and is now being restarted.

Normal running process

The flowsheet showing one converter set - normally four sets are run in parallel - and all the principal items for the common gas circulation and liquid feed, is shown in Fig.12.

35-40% purified butinediol solution is pumped by the 3-stage liquid-feed ram pumps 1 through the heat exchanger 10 to the top of the converter 12. The flow to each converter is 3 cbm./hr., and the entering temperature is 40°C. The maximum capacity of the feed pumps is 6 cbm./hr.

Hydrogen from the purification converters is pumped at 12-15000 cbm. free gas/hr. to the top of the converter. This gas may pass through a steam-heated preheater, which is never used, and (as an alternative to the butinediol solution feed) through the heat exchanger 10; but this is not done in normal practice. The maximum capacity of the circulating compressors is 75000 cbm./hr.

The pressure in the converters is 200-300 atmos., and is maintained as high as the supply pressure (from the hydrogen plant at Oppau) will allow. The reaction is exothermic with a heat liberation of 65 K.cal./g.mol., and the temperature at the bottom of the converter is 120-130°C.: this is controlled by varying the hydrogen flow. The conversion is practically complete, and the control test is that the liquid effluent should show practically no reaction with iodine. The life of the catalyst is 6-8 months, and as it ages the temperature in the converter may be raised little by little to maintain the speed of reaction. The temperature however must not rise above 130°C. or there is danger of hydrogenation proceeding to butanol.

The liquid and gas discharged together from the bottom of the converter pass downwards through the heat exchanger 10, and then through the trombone water-jacketed cooler 13 to the separator 14. The disengaged gas is taken into the common suction line to the hydrogen circulating pumps, and the liquid, crude butanediol, is let down into low-pressure tanks and pumped to distillation.

Starting hydrogenation plant

The catalyst is supplied from the catalyst plant as silica rods 3 mm. dia. x 5-8 mm. long impregnated with nickel, copper, and manganese oxides, containing 16% nickel, 5% copper, and 0.7% manganese as metals. These pellets are loaded dry into the converter. The converter is sealed up, and nitrogen is circulated at 6000 cbm. free gas/hr. at 50-100 atmos. by two of the gas circulating compressors (6) which are kept for nitrogen. The items in this circulation are:-

Nitrogen storage bottle	(5)
Compressor	(6)
Compressor surge tanks	(7)
Nitrogen pressure-side separator	(9)
Heat exchanger	(10)
Electrical preheater	(11)
Converter	(12)
Cooler	(13)
Separator	(14)
Nitrogen suction side separator	(9)

The pressure- and suction-side separators are introduced to keep lubricant from the compressors out of the converters, and liquid from the converters out of the compressors.

The electrical preheater is a trombone pipe the walls of which act as the heating resistance: a low-voltage current from a variable transformer is passed directly along the pipe. It is used only for heating the nitrogen circulation, and thus the converter and catalyst, to the catalyst reduction temperature.

When the catalyst bed is at 250-300°C., one of the hydrogen dosing bottles (5) is opened carefully into the circulation, so that only a few cubic metres of hydrogen enter: this causes a slight kick in temperature at the top of the converter. This small addition of hydrogen is repeated until the catalyst is practically all reduced, and there is no kick in temperature after the addition. Hydrogen is then admitted rapidly, to give a circulation of 12000 cbm. free gas/hr. of 50% hydrogen: this circulation is continued for 6 hr. to complete the reduction of the catalyst.

The circulation is now turned over to use the hydrogen pressure- and suction-side separators (8), and the electrical preheater is cut out of circuit. Hydrogen pressure is built up until the full circulation rate of 15000 cbm./hr. is reached; as nitrogen has not been purged, the gas composition is now about 70% hydrogen, 30% nitrogen at 300 atmos. The converter temperature rapidly falls to 40°C. at the top, and the feed of butenediol solution is started at its full rate of 3 cbm./hr.

Spent catalyst at the conclusion of a run is sold for metal recovery.

Hydrogen purification

Hydrogen is made at Oppau factory on a water-gas plant, and purified there by washing with copper solutions which remove the bulk of the carbon monoxide. On its arrival in the butenediol plant it is circulated round a converter packed with a nickel-on-silica catalyst which

hydrogenates the trace of carbon monoxide still remaining to methanol. The 10 sq. m. gas cooler shown under (8) in the flowsheet is used to cool this make-up gas as it is admitted to the main circulation. The plant control limit for carbon monoxide in the hydrogen circulation is below 0.001%; if this is exceeded there is a tendency for the hydrogenation to go on to butanol.

The make-up hydrogen contains 3% nitrogen, and a purge is taken to maintain the nitrogen content of the circulation at 30%.

Instrumentation and control on the hydrogenation side

All the hydrogen flows are controlled by manually operated valves, except certain main control valves which are motor-operated and centrally controlled so that the whole circulation can be shut down quickly in emergencies. Flows are recorded on ring-balance gauges operating from orifice plates. The gas pressure drop through the converters is about 5 atmos., although drops as high as 20 atmos. occur, and as it is necessary to hold four converters balanced in parallel, special attention to the overall pressure drop is necessary. This is done by a differential pressure gauge sensitive to 1 atmos. at 300 atmos., working on the position taken up inside a straight cylinder by a spring-loaded lapped-fitting piston.

Distillation

The complete flowsheet for the distillation section is given in Fig. 13.

In the butadiene sequence only the first of the seven columns comes into use. The rectifying section of this column has 32 plates 1200 mm. dia., and the stripping section 10 plates 1800 mm. dia. It operates at atmospheric pressure. The feed is crude butenediol from the converter house, containing:

Butanediol	about 35%
Butanol	1-2%
Light overheads)	0.1%
Involatile residue)	
Water	to 100%

Butanol azeotrope, b.p. 92°C., comes over at the top and is separated into its layers: the lower aqueous layer is pumped as reflux and the upper alcohol layer pumped away as wet butanol for use elsewhere in Ludwigshafen. The very light overheads are collected in a separate condenser. The bottoms is a 35-40% solution of butanediol, still containing the involatile residue, and is pumped to the storage tanks which supply the tetrahydrofuran plant.

The remainder of the plant is only used for producing 100% butanediol. The schedule is:-

Column	Feed	Overhead	Bottoms	Head pressure mm. Hg. abs.	Temperature °C.	
					Head	Bottom
2(W)	Col.1 bottoms	Most of water, to drain	To 4	760	100	112
4(VW)	Col.2 bottoms	Rest of water, to drain	To 5	80	56	165
5 (Crude lights)	Col.4 bottoms	Very small amounts of indeterm- inate products	To 7	50	145	155
6 (Pure lights)	Standby for Column 5, or for special purposes not very clearly designated.					

Column	Feed	Overhead	Bottoms	Head pressure mm. Hg. abs.	Temperature °C.	
					Head	Bottom
7 (Pure butane- diol)	Col.5 bottoms	Pure butane- diol	To 3	20	115	180
3 (Residues)	Tarry bottoms from 7	rework in 7	waste	5	110	185

This distillation plant is again of a most flexible and generous nature, and it is quite clear that the designers intended that there should be ample capacity for the most unlikely contingencies.

Two research reports were found bearing upon the distillation section. One, "Über die Verwendung der 1:4-butandioldestillationsrückstände der Bu III Anlage" by Krzikalla and Flickinger, dated 30.11.44, describes the residue left by the distillation of butanediol at 180°C./10-11 mm. (comparable to the bottoms from Column 3), as a tenacious black sticky tar containing 9% ash (from the catalyst), water-soluble, with a pH in aqueous solution of 9-11. The full output of this tar would be 220 tons/month. When mixed with an acid catalyst such as ammonium chloride and heated to 160-170°C. it gives a water- and soda-insoluble resin. The tar was mixed with 8% of water and sold as "Sucol B" for making linoleum, pressed cork building blocks, etc., and possible outlets as a wetting agent or in paper manufacture were suggested.

The other report, "Die Abtrennung und Aufarbeitung der von den Rohbutandiollosungen abgetrennten Mono-ole", by Dr.Hrubesch, dated 26.7.40, deals with an early proposal, not adopted, to separate the light alcohols (ethanol, propanol, and butanol) formed as by-products in the hydrogenation from the butanediol by azeotropic distillation with trichloroethylene. A number of phase diagrams

were worked out, but it was clear that the problem of designing the columns was going to be tackled empirically.

3. Yield and output data

The official yield figure at present quoted for 100% butanediol calculated on 100% butinediol entering is 95% of theory.

The space-time yield of the catalyst is 3 Kg. 100% butanediol/litre catalyst, day.

From the materials list in Part I 6 tonnes of catalyst 13340 are required for 1520 tonnes of butanediol. The catalyst life is thus approx. 250 days.

4. Notes on construction details of plant

Joints for copper lined high pressure pipe

These joints were of the lens ring type the lens ring being of 18/8/1/1 stainless steel. The copper lining (approx. 1/16" thick) was fitted inside the steel pipe. At each lens ring face a ring of copper 1/16" thick was fitted to cover the face and to lap over the copper tube. The lap joint between the two was then sealed by welding.

Cranes

In addition to the Goliath crane which serves the converter stalls, small cranes are provided over the pipework on top of the control building and also over the gas distribution network outside the compressor house.

Motor operated high pressure valves - control gear

This gear was supplied by A.E.G. and incorporated an illuminated indicator showing the amount of valve opening at any time.

Electric preheaters

Two of these units were provided - one to each

set of converters. Heating was effected by passing a low voltage current through H.P. steel tubing. The diagrammatic arrangement is shown in Fig. 12.

The H.P. tubing is provided with connectors integral with the tubing (or welded to it) and the U tubes are formed in one section.

The low voltage supply is from a transformer (supplied by Koch and Sterzel - Dresden) having a maximum output of 1000 KVA. The output voltage is varied by changing the depth of immersion of the core in the two secondary coils. The input voltage is 6000 and the maximum output voltage on each coil is 70. The electric motors which raise or lower the transformer cores are operated from temperature controllers.

Instrumentation

Meters used for measuring the flow of butinediol to the plant were "ovalradmesser" and were of the gear type with elliptical gears. They were supplied by Bopp and Reuther. This type of instrument was generally adopted for liquor measurement.

The control panels on the high pressure gas side in the machine room are provided with the following instruments:-

Temperature indicator.

Temperature recorder.

3 Analysers recording the percentage of hydrogen or nitrogen in the circuit gases. (Pollux meters, made by a Ludwigshafen firm and working on gas densities).

A pressure difference meter, across converters. (Made by I.G. instrument workshops).

Two recording pressure gauges and two indicating pressure gauges. Supplied by Schaeffer and Budenberg - Magdeburg.

Records are kept of the hydrogen and nitrogen suction and delivery pressures at the separators, of the nitrogen and hydrogen inlet pressures from the pipe bridge, and of the hydrogen dosing line.

The control building was divided into two rooms, corresponding to the two ranges of converters.

Each room contained one control panel for the electric preheater. This included an instrument showing the percentage of core immersion, the automatic temperature controllers, temperature recorders and indicators.

In addition there were three control panels, corresponding to each converter. The ring balance meters recording gas flows were not mounted on these panels (which carried only temperature recorders and indicators) but mounted alongside.

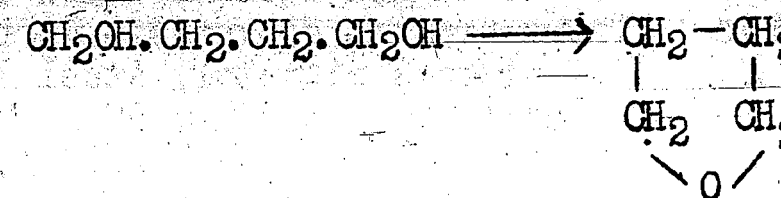
As in the case of the butanediol converters, a number of temperature points were arranged at different levels around the converters, records being taken from some and indications from others.

PART V. TETRAHYDROFURAN STAGE

The information in this section was obtained by interrogation of Dr. Steinhöfer and Mr. Fiegl (plant engineer) and inspection of the plant in November, 1945.

1. Outline of process

35-40% Butanediol solution is fed with 0.3% phosphoric acid as catalyst into a liquid-phase converter at 280°C./100 atmos. The tetrahydrofuran is isolated from the product practically free from water by fractionation.



2. Description of process

General layout of plant

All the items of this plant are housed inside a single building, which is of remarkably heavy construction especially at the roof. Its ground floor is about 4 m. below normal ground level. For location see Figure 1. The building is rectangular in plan, and is divided longitudinally: on one side of the partition the main plant items - preheaters, converters, heat exchangers, columns - are accommodated on three floors (in all about 22 m. to the roof); on the other side of the partition the roof is lower, the feed pumps occupy the ground floor and the control room the first floor.

The flowsheet is given in Figure 14.

Normal running process

35-40% Butanediol solution from the butanediol distillation section, containing rather less than 1% butanol and about 1.5% of non-volatile residues, is treated with Wofatik, a base exchange zeolite of the Permutit type, whereby the sodium ions (which were

introduced as caustic soda or sodium bicarbonate in the butinediol process) are removed and the pH is reduced to 1.5-2.0.

This solution is pumped up to 100 atmos. pressure and fed at 10-15 cbm./hr. through three preheaters in series: the first heated by 20 atmos. steam, the second by 100 atmos. steam, and the third by electric resistance windings applied to the pipes. Its temperature is then 290°C.

60% Phosphoric acid is now injected to give a concentration of 0.3% in the liquid stream, which is fed into the converter. There are two converters in parallel, each 12 m. high x 0.5 m. internal diameter, steel lined with 18.8.1.1: they run full of liquid at 270-280°C. The heat of reaction is almost negligible, about 3 K.cal./g. mol., and the converters are heated by external electrical resistance elements.

The discharge from the converters passes through a cooler fed with hot water, which reduces its temperature to about 110°C., and it is then let down to atmospheric pressure by flashing into the first fractionating column. Steam is generated in this cooler, at 18 atmos. pressure, and is used to heat the reboilers of the fractionating columns.

Sodium hydroxide solution is injected into the feed to the first column to neutralise the phosphoric acid: the distillation plant is in mild steel. Both columns operate at atmospheric pressure. The first column removes tetrahydrofuran, the small amounts of butanol that entered with the original feed butanediol, and water, leaving an aqueous bottoms containing sodium phosphate and all the involatile resins which have been collecting during the butinediol, butanediol, and tetrahydrofuran formation stages. These separate as a gummy layer on the surface of the water, and are drummed off for disposal.

In the second column virtually 100% tetrahydrofuran (b.p. 65°C.) comes over as distillate; the bottoms is water containing traces of butanol, and is run down the drain.

These columns were put up on the basis of laboratory experiments without any pilot-scale trial.

3. Yield and output data

There is no present official yield figure, for although the plant is (superficially at least) little damaged, it is not being started up. The yields are quoted as generally 93-94%, but higher yields were sometimes obtained.

The space-time yield of the converter volume is 20 kg. 100% tetrahydrofuran/litre, day.

PART VI. CATALYST PLANT

The information in this section was obtained from an interrogation of Dr. Wimmer and inspection of the plant on 15.11.45, and from an interrogation of Dr. von Susich on 20.11.45.

1. Manufacture of the butinediol catalyst

Principles

Sodium silicate solution is precipitated with sulphuric acid, and the silicic acid filtered off, washed free from electrolyte, extruded into rods, and dried at about 150°C. The rods are broken up into granules and roasted at about 700°C. The ignited granules are impregnated with a solution of copper and bismuth nitrates and roasted again at about 500°C., to give the catalyst as supplied to the butinediol plant: this contains 12% copper and 3% bismuth as oxides. The flowsheet is given in Fig. 15 (A and B).

Process

Sodium silicate is stored in tanks as a solution of density 1.37-1.38 g./cc. containing 25% SiO₂ and 8.3% Na₂O: this is diluted with an equal weight of water and held in a subsidiary storage tank which supplies the measure vessel delivering to the precipitation pan.

The precipitation pan is a 4 cbm. rubber-lined, mild steel, hemispherical bottom pan, fitted with a jacket for cooling water and a turbine agitator driven at 80 r.p.m. The sodium silicate solution is charged, and sulphuric acid of density 1.125 g./cc., containing 17-18%, added till the pH is 4.5. 25% Ammonia liquor is then added till the pH is 7.0. This precipitation is carried out at room temperature and takes about 1 hr. The slurry is then blown by compressed air to filter-presses, which takes about 6 hr.

The filter-presses have 36 wood plates and frames 1200 x 1200 x 50 mm., arranged for thorough-extraction washing. The cloths are preferably polyvinyl chloride.

The cakes are washed with water at 40°C. till free from electrolytes, as shown by testing for sulphate ion: this takes 36-48 hr.

The composition of the washed cakes is approximately SiO₂.2H₂O - 20%, free water - 80%. They are dropped into bogeys, and about three-quarters of a batch are loaded into a continuous rotary dryer, dried at 150°C. to very nearly 100% SiO₂.2H₂O, and ground in a mill to a fairly fine powder. This powder is mixed with the remaining one-quarter of the 20% press-cake (and some returned dry material, see below) to give a stiff paste of about 50% free water content, ready for extrusion into rods. The rotary dryer is 10 m. long x 1 m. diameter, built of 18.8.1.1 steel; the air for drying passes co-current with the load, and is heated in a calandria heated by 20 atmos. steam; some of the air is recirculated. The dryer turns at about 1 r.p.m. The average internal temperature is 150°C., and the maximum inlet air temperature is 180°C. The mixer for making the 50% paste is a Werner-Pfleiderer; there are three mixers of 400, 600 and 800 litres capacity (to suit the size of catalyst batch being made), and are all in mild steel.

The 50% paste is extruded into rods in a hydraulic press with a ram-loading of 200 atmos. The size of the dies varies with the purpose of the catalyst, and for the butinediol catalyst is 10 mm. dia. (A - refer here in description of butanediol catalyst preparation). The rods are about 100 mm. long. They are fed into a continuous band dryer; 5 passes, bands 1.1 m. wide of 18.8.1.1 chain-weave wire gauze, contact time 4 hr., heating air derived from the off-gases from the calcining furnace (below) and circulated within the dryer, temperature 150°C.: builder, Benno-Schilder. The rods come out as white fairly hard sticks.

The rods are put through a double-roller breaking mill, which discharges into a set of two flat shaking sieves. The fines, below 3 mm. mesh, and only about 10% in quantity, are returned to the Werner-Pfleiderer mixer for making up fresh 50% paste. The oversize, above 8 mm. mesh, is returned to the breaking mill. The granules 3-8 mm. mesh are fed into a continuous rotary

dryer and calcined at a nominal temperature of 700°C.: the probable temperature is 600-700°C. The dryer is 12 m. long x 1 m. internal diameter, and is lined with firebrick and heat-insulating brick (silicate cement setting): it is direct fired with town's gas, and the off-gases are used to heat the continuous band dryer (above). The granules from the calcining furnace are sieved, and the fines below 3 mm. mesh discarded: the remaining 3-8 mesh granules are known as "kieselplit"; they are hard, irregularly shaped as befits their formation by breaking up the rods, and are coloured a very faint yellowish-pink.

The silica granules are loaded into baskets 1000 x 750 x 750 mm. made of 2 mm. thick 18.8.1.1 steel sheet perforated all over with 2 mm. holes on 5 mm. centres, and the baskets are immersed in 18.8.1.1 tanks containing the impregnating solution, which contains copper and bismuth nitrates: the ratio of copper to bismuth is 12:3 and the density of the solution is 1.44 g./cc. Impregnation takes place at room temperature, and requires about 20 minutes: complete impregnation is marked by air-bubbles ceasing to rise from the granules. The absorption of the solution by the silica is not selective: that is, the solution is replenished but not restored to strength by addition of salts or water. The baskets are taken out and allowed to drain, and the moist granules fed to the roasting furnace. All handling of the baskets is done by a block and tackle running along an overhead rail.

The roasting furnace is a continuous rotary furnace, 6 m. long x 600 mm. internal diameter. It is lined with acid-resisting brick set in silicate cement (Hoechst SW.20, composition 4% sodium silicofluoride, 2% clay, 94% quartz sand pasted with sodium silicate solution containing 26% SiO₂, 8% Na₂O). It is direct fired by town's gas to a temperature of 500°C., and the off-gases are taken through scrubbers to remove nitrogen oxides before discharge to atmosphere. The contact time is 15-20 minutes, and is controlled by keeping the catalyst at the discharge end free from nitrate ion.

The roasted catalyst granules, now oxides deposited on silica, are screened to remove fines and sent to the butinediol plant.

The following information is added by the authors. An impregnating solution prepared to the specification given contained 152.5 g./litre of copper and 38.2 g./litre of bismuth. A sample of catalyst taken from the plant analysed thus:-

Bismuth as Bi 5.5%

Copper as Cu 11.5%

Spectrographic examination did not reveal the presence in significant amounts of any other metals.

2. Treatment of spent catalyst from butinediol plant

The spent catalyst from the butinediol plant consists of copper-bismuth acetylides on silica contaminated with cuprene. It is delivered wet in trucks to the catalyst plant, and loaded wet direct into the gas-fired rotary furnace at 500°C. used for igniting the nitrate-impregnated granules. This treatment oxidises the acetylides back to oxides, and has so far been carried out without accidents, although there are occasional "whoofs". The oxidised granules are sent to a refinery at Hamburg for recovery of the metals.

Some experimental work had been done on recovering nitrate solution from the oxidised granules for re-use on the Ludwigshafen catalyst plant, and also upon re-using the oxidised granules directly in the butinediol converters, but this had been interrupted at an early stage and had never reached plant scale.

3. Manufacture of the butanediol catalyst

Principles

These are the same as for the butinediol catalyst

except that the finished catalyst contains 16% nickel, 5% copper, and 0.7% manganese as oxides.

Process

The process is identical with the butinediol catalyst process up to the extrusion stage (marked A in text). The rods formed by extrusion are 3 mm. dia.: these also pass through the band dryer exactly as before, but then go straight to the calcining furnace without being broken into granules: their form is then 3 mm. dia. cylinders about 5-8 mm. long. They are calcined at nominal 700°C. as before, and the fines and dust sieved out. The calcined rods are charged into baskets and impregnated as before, except that the impregnating solution contains copper, nickel and manganese nitrates; the ratios nickel:copper:manganese are 16:5:0.7, and the density of the solution is 1.50 g./cc.

The impregnated rods are dried in tray dryers at 110°C., and loaded into an inclined tumbling bowl mixer (rather like a cement mixer, but without lifting flights) and sprayed with the impregnating solution at the rate of 2 litres of solution to 10 litres of catalyst. The moist rods are then roasted to form the oxide in the same rotary furnace at 500°C. as was used before. This is the catalyst as delivered to the butanediol plant.

The following information is added by the authors. An impregnating solution prepared to the specification given contained 155 g./litre of nickel, 48.5 g./litre of copper, and 6.8 g./litre of manganese, and showed a tendency to precipitate crystals at 15°C. A sample of catalyst taken from the plant analysed thus:-

Nickel	as Ni	14.8%
Copper	as Cu	4.2%
Manganese	as Mn	0.62%

Spectrographic examination did not reveal the presence in significant amounts of any other metals.

4. Output of catalyst plant

The nominal output of the catalyst plant for

silica-supported catalysts is 5 cbm./day of 24 hr., of which 60% goes to butinediol and 40% to butanediol catalysts. Some parts of the plant can be pushed to an output of 10 cbm./day.

The plant also manufactures the butadiene catalyst, which is sodium phosphate supported on coke.

5. Experimental development of a porous stoneware support for the butinediol catalyst

The silica support for the present butinediol catalyst has one major disadvantage in that it dissolves to a slight extent in the acidic reaction product, and this dissolved silica must be removed in a separate step on the plant before the butinediol solution is passed forward for hydrogenation. The experimental work by Dr. von Susich described here was directed towards the development of an improved support derived from kaolin.

The prime requirements of a support are:-

- (a) Mechanical strength (it should be noted that the present silica support, though rather friable in the hand, is still robust enough to stand packing in a bed 16.7 m. deep without crushing);
- (b) Adsorptive capacity;
- (c) Chemical indifference.

Silica is encountered in four forms - amorphous (silicic acid), quartz (formed at about 800°C.), and the glasses tridymite and cristobalite which are of no interest as catalyst supports. Quartz is strong mechanically but has a low adsorptivity; silicic acid is adsorptive but weak mechanically and is soluble in acids. The temperature of 700°C. nominally used in the manufacturing process represents a compromise; in fact however owing to the short contact time in the calcining furnace most of the support is not heated to 700°C.

Kaolin from which impurities have been removed

by leaching with dilute hydrochloric acid consists of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. On heating at 450-500°C. metakaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is found; the solubility of the kaolin in dilute hydrochloric acid, initially low, increases tremendously, but as heating is taken up to 900°C. the solubility decreases again towards zero. At temperatures well above 1000°C., mullite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ begins to decompose into the inactive sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{SiO}_2$. The water adsorption of kaolin heat-treated to just above 1000°C. varies between 100% and 150%, compared with the silica at present used, which has an adsorption rather below 100%. A mullite support would therefore have been worth a full scale trial, but there were no sufficiently large furnaces in Ludwigshafen capable of working to the high temperature.

Attempts had been made to increase the adsorptivity of kaolin supports by artificially increasing the porosity. One part of purified kaolin powder is mixed with one part of some very finely ground organic substance, kneaded with water, and extruded as rods. Wood meal and infusible phenol-formaldehyde or urea-formaldehyde resins had been used: it was advisable to use a specifiably pure organic substance, since impurities in the ash would pass into the support when they might have uncontrolled trace element effects on the final catalyst. The rods are ignited: at about 300°C. the organic material chars and the mass goes black, and then with excess air at about 800°C. the carbon is burned out. Finally the rods are heated to 1100-1200°C. for 1 hour. Early preparations had been done in crucibles, but these were unsatisfactory because it was difficult to disperse the air-blast for burning out the carbon, and later preparations had been made in a narrow cylindrical vertical electric furnace or in a rotary direct-gas fired furnace about 2 m. long x 300 mm. internal diameter.

A butinediol catalyst supported on porous mullite made in this way had given a life test of 3 months total, working on days only over a period of 8 months (as usual, a severer test than uninterrupted working). The acid extraction figure, done by boiling during 27 hr. with 0.5% formic acid, showed practically no soluble silica. Alkali solubility tests had not been done, but could almost be guaranteed to be zero.

This catalyst support was similar to a porous synthetic stone which had been developed at Waldenburg, Upper Silesia. This was produced in the form of large flat blocks for furnace insulation. It had also been produced as small cubes as the support for the manganese dioxide-phosphoric acid catalyst ("T-stoff kontakt") used to decompose 80% hydrogen peroxide used as fuel in U-boats, torpedoes, aircraft and V-weapons. Some of these small cubes had been tried for the butinediol catalyst; their edges had been rounded off by tumbling in a mill so as to form rough spheres. The porosity had been found to vary widely, and those spheres showing a large number of fine holes, and no blow holes, had been sorted out by hand-picking. Eventually the firm producing the blocks (name not known) had succeeded in making the porosity uniform.

PART VII. CAPITAL AND OPERATING COST ESTIMATES

The information in this section was obtained from I.G. files collected at Griesheim Document Centre in November, 1945. At this time the American authorities had only just started to scrutinise the documents, and they were most helpful in finding such few relevant documents as had been unpacked. It is a pity that only estimates were found, but in view of the disturbed history of the plant, estimates are probably as enlightening as actual running figures.

Overall cost calculations for a Buna Plant, Reppe route, in Norway. I.G. Ludwigshafen File No.S.33/V-D-3 dated 1941

Manufacturing cost, RM/tonne Buna S

	<u>Schkopau estimates</u>	<u>Norway calculations</u>
Raw materials including coal	36.34	-
Auxiliary chemicals	10.68	-
Total raw materials	(47.02)	42.27
Electric power	-	1.77
Coal for services	-	9.45
Total services	16.69	(11.22)
Maintenance materials	5.41	5.41
Wages and salaries	22.30	22.30
Office administration	2.12	2.12
Amortisation	-	33.00
Interest	-	21.00
Total charge on investment	50.86	(54.00)
	<u>144.40</u>	<u>137.32</u>

Services estimates for Ludwigshafen Buna Plant I.G. Ludwigshafen File No.S.33/VI-A-6 ("Buna Lu Historie I", Dr.Ambros' file), dated 12.11.40

	Butinediol	Butinediol dist'n.	Butanediol dist'n.	Tank farm	Butanediol	Tetrahydrofuran	Catalyst Plant
Output T/hr. (24000 T/yr. Buna S)	4.25	-	-	-	4.32	3.38	.25
Power Kw.	390	40	20	40	1200	450	80
Steam 100 atmos. T/hr. 20 "	-	-	-	-	-	4.2	-
2.5 "	0.8	-	1	-	-	1.6	0.1
	3.2	16	6	0.5	2.5	0.4	0.5
Water cbm./hr.	120	550	170	100	160	100	40
Nitrogen cbm./hr.	-	10	10	50	40	10	5
Hydrogen cbm./hr.	-	-	-	-	3200	-	-
Gas cbm./hr. 2300 W.E.	-	-	-	-	-	-	80

For other parts of the plant, as comparison:-

	Carbide plant	Acetylene generation and purification	Butadiene converters and distillation
Output T/hr.	6.3	1.8	2.4
Power Kw.	25470	140	-

Capital cost estimates, for whole Buna plant

Same file as above; scale 30000 T/yr., dated 10.3.41

	<u>1000's R.M.</u>
Clearing land	900
Drains	600
Preparing site	300
Demolition	10
Lavatories	15
Road lighting	40
Road connections	250
Rail tracks	500
Tank cars	150
Road cars for catalyst	10
Workshops for 300 fitters	480
Workshops, carbide plant	200
Offices and laboratories	850
Rubber testing laboratory	505
Extension to telephone system	128
Air raid shelters	900
Steam plant	9160
Pipe bridges	553
Extension of pipe bridge for steam and gases	1400
Extension of works nitrogen system and low pressure line to carbide plant	300
Extension of river-water system	320
Extension of well-water system	38
Extension of drinking-water system	42
3 New cooling towers	900
4 New wells	60
Filters for river water	800
6 kv. hightension station	900
6 Cross-linked and 1 main distribution stations	650
20 kv. and 6 kv. feeders	420
Low tension wiring	330
Connection to pipe bridge	150

1000's R.M.

* Catalyst plant	2140
Formaldehyde plant, 3 converters	1430
* Tank farm	150
2 Furnace transformers	800
Raw material storage, carbide plant	1770
Coke silo, carbide plant	1040
Carbide furnace rooms 1 and 2	6110
Carbide handling plant 1 and 2	1205
Acetylene generation	980
Granulating plant	250
Hydrated lime handling	600
Carbon monoxide gas-holder	110
Acetylene crude gas-holder	110
Acetylene purification	450
Acetylene pure gas-holder	72
* Butenediol converter house (8 converters)	6300
* Butenediol distillation	1800
* Butenediol converter house (6 converters, including hydrogen purification)	6750
* Butenediol compressor room	3070
* Butenediol distillation	2500
Tank farm for butadiene (in, out, intermediate, auxiliaries storage)	1200
* Tetrahydrofuran plant	2150
Butadiene converter house	3900
Butadiene distillation and compressor room	2600
Gas holder for crude butadiene	90
Styrene converter house	2440
Styrene distillation	1270
Ethylbenzene tank farm	350

	<u>1000's R.M.</u>
Extension of styrene tank farm	100
Polymerisation plant	6580
Tank farm for polymerisation	595
Milling, etc.	3500
Buna plant	1500
Connections to pipe bridge	500
Workmen's baths	500
Contingency	1227
	<u>38000</u>

This list has been reproduced in full, because whereas isolated costs may be difficult to interpret, a full capital cost may permit cross-correspondences. The plants which are relevant to this report have been starred. A rough classification of this list shows for a complete 30000 T/yr. Buna S plant:-

	<u>1000's R.M.</u>
Site work, roads, transport Services	2760
Workshops	16501
Storage for materials	680
Plant:	5622
Catalyst plant	2140
Tank farm	150
Butinediol converters	6300
Butinediol distillation	1800
Butanediol converters	6750
Butanediol compressors	3070
Butanediol distillation	2500
Tetrahydrofuran	2150
Other plant	33580
Offices and laboratories	58440
Amenities	1355
A. R. P.	515
Contingency	900
	1227
	<u>88,000,000</u>

The construction of the plant started towards the end of 1940, and it was put into operation at the end of 1942.

Staffing and labour requirements

Same file as above.

The total staff for the whole of the Buna area was estimated to be as follows:-

Chemists and Physicists	-	12
Engineers (Site 3, Workshops 5)	-	8
"Technicians"	-	13
Foremen	-	27
Assistant foremen	-	59
Workers	-	1140

Labour requirements for each of the plants covered by this report were as follows:-

<u>Plant</u>	<u>Day</u> <u>workers</u>	<u>Shift</u> <u>workers(3 shifts)</u>	<u>Total</u>
Butinediol	6	42	48
Butanediol	6	36	42
Distillation	6	36	42
Tank farms	10	12	22
Tetrahydrofuran	5	21	26

Two chemists (or physicists) were allocated on each of the butinediol, butanediol and distillation plants and one chemist to the tetrahydrofuran plant.

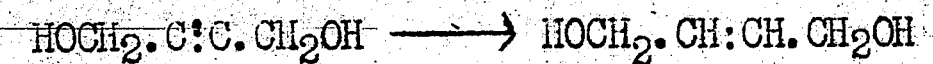
No engineers were allocated specifically to these plants as it was apparently intended to concentrate most of the engineering staff in the workshops. This building which was to be approximately 500 ft. long x 75 ft. wide, and was intended to house the engineering offices as well as the workshop, was apparently never completed.

APPENDIX I. PARTIAL HYDROGENATION OF BUTINEDIOL TO BUTENEDIOL

This process is not a part of the Buna process, nor has it been operated except on a pilot plant scale. It is included in this report to save cross-references. The information was obtained by interrogation of Dr. von Susich on 20.11.45 and Dr. Friedrich on 22.11.45 at Ludwigshafen.

Principles

A 34% aqueous solution of butinediol is hydrogenated at 50-90°C./200 atmos. over an iron catalyst. The yield of butenediol is about 83%.



Process

The outline flowsheet of the semi-technical plant is given in Fig. 16.

34% Butinediol solution pumped from the stock tanks into the feed measure vessel 1 and thence by the high-pressure ram-pump 2 through the preheater 3 into the converter 4. Recycled hydrogen plus make-up is also admitted at the top of the converter. The converter is 5 m. long and 120 mm. internal diameter, and holds a charge of 50 litres of catalyst, which is finely divided iron supported on pumice granules. The operating pressure in the converter is 200 atmos., and the temperature 50°C. at the beginning of a run: as the catalyst deteriorates over its useful working life of 5-6 weeks, the operating temperature is progressively raised to 90°C. Operation over 90° even with an old catalyst leads to over-hydrogenation. The reaction is exothermic, and the heat liberated is 35-40 k.cal./g.mol. The discharge at the bottom of the converter drops into the catchpot 5, and the gas is led off through the gas cooler 6 and the second catchpot 7 to the hydrogen circulating pump 8. The feed of butinediol solution is 20-25 litres/hr., and the hydrogen circulation rate 4000 litres free gas/hr. at 200 atmos.

The liquid product from the two catchpots collected in the product measure 9, and most of the water is evaporated off in 10. (In the actual plant this piece of apparatus seems to have been of a most intricate and curious design, but its purpose is straightforward enough). The final product contains 15% water and 85% crude butenediol. The yields calculated on input butenediol are:-

Butenediol	-	83%
Butanediol	-	10%
Butenediol recovered	-	0-2%

Operation of the process

About 5 tonnes were made on this semi-technical plant, which implies that it was operated for about 1000 hr. in all, equivalent to say 6 weeks steady running, i.e. one run at a catalyst life of 6 weeks.

The process was also operated in a 330 litre converter, which made 15-20 tonnes.

Preparation of the iron catalyst

The catalyst for the laboratory development work was prepared by extruding a paste of pure iron (made from iron carbonyl) and butanol into small rods. These were heated in a furnace at 500°C. in a stream of hydrogen, where they stuck together rather, and the aggregates had to be broken up by hand into the individual rods.

This catalyst used large quantities of fairly expensive iron, and the catalyst for the semi-technical work was made by coating the iron-butanol paste on to pumice granules of about 5 mm. mesh in a Jager mixer (a tilted rotating bowl), and heating the coated granules in hydrogen as before. This catalyst had been prepared in batches of 12 litres, 80 litres, and 5 tonnes.

The iron catalyst was not regenerated after use in the process.

The partial reduction also works with Raney iron, but partially-poisoned nickel and cobalt catalysts are unsatisfactory in that they operate only at rather higher temperatures and lead to the formation of tarry by-products.

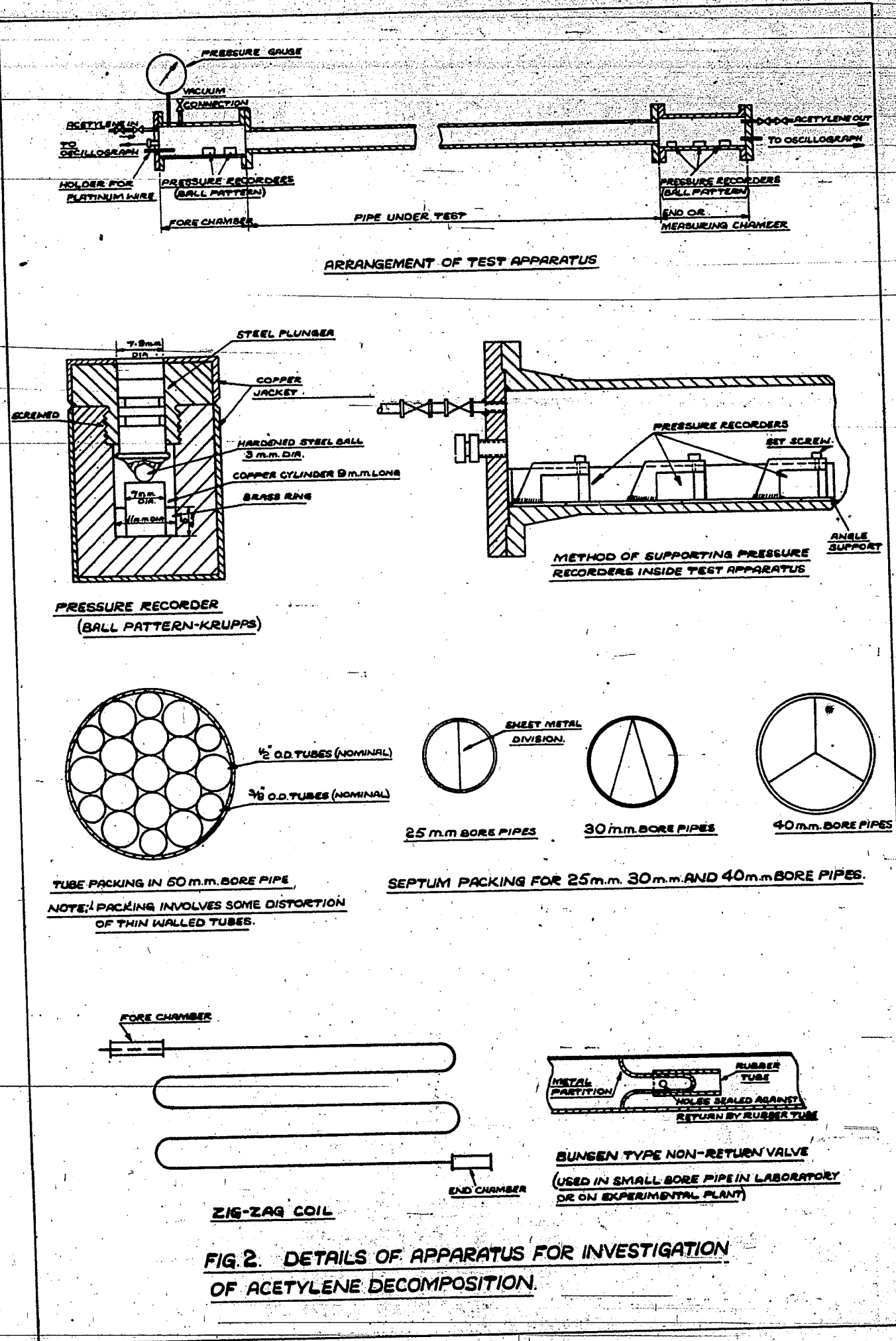


FIG. 2. DETAILS OF APPARATUS FOR INVESTIGATION OF ACETYLENE DECOMPOSITION.

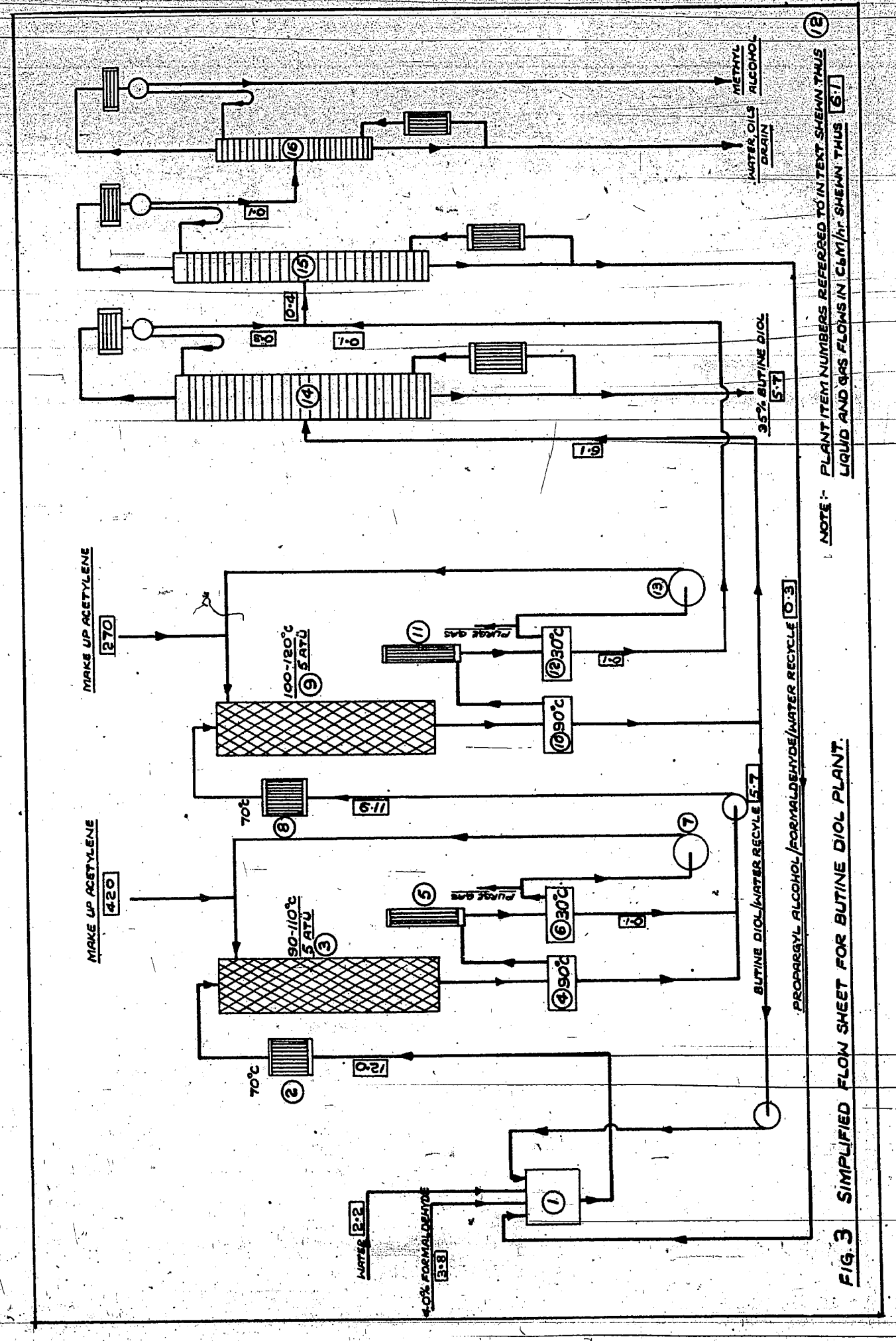


FIG. 3. SIMPLIFIED FLOW SHEET FOR BUTYNE DIOL PLANT.

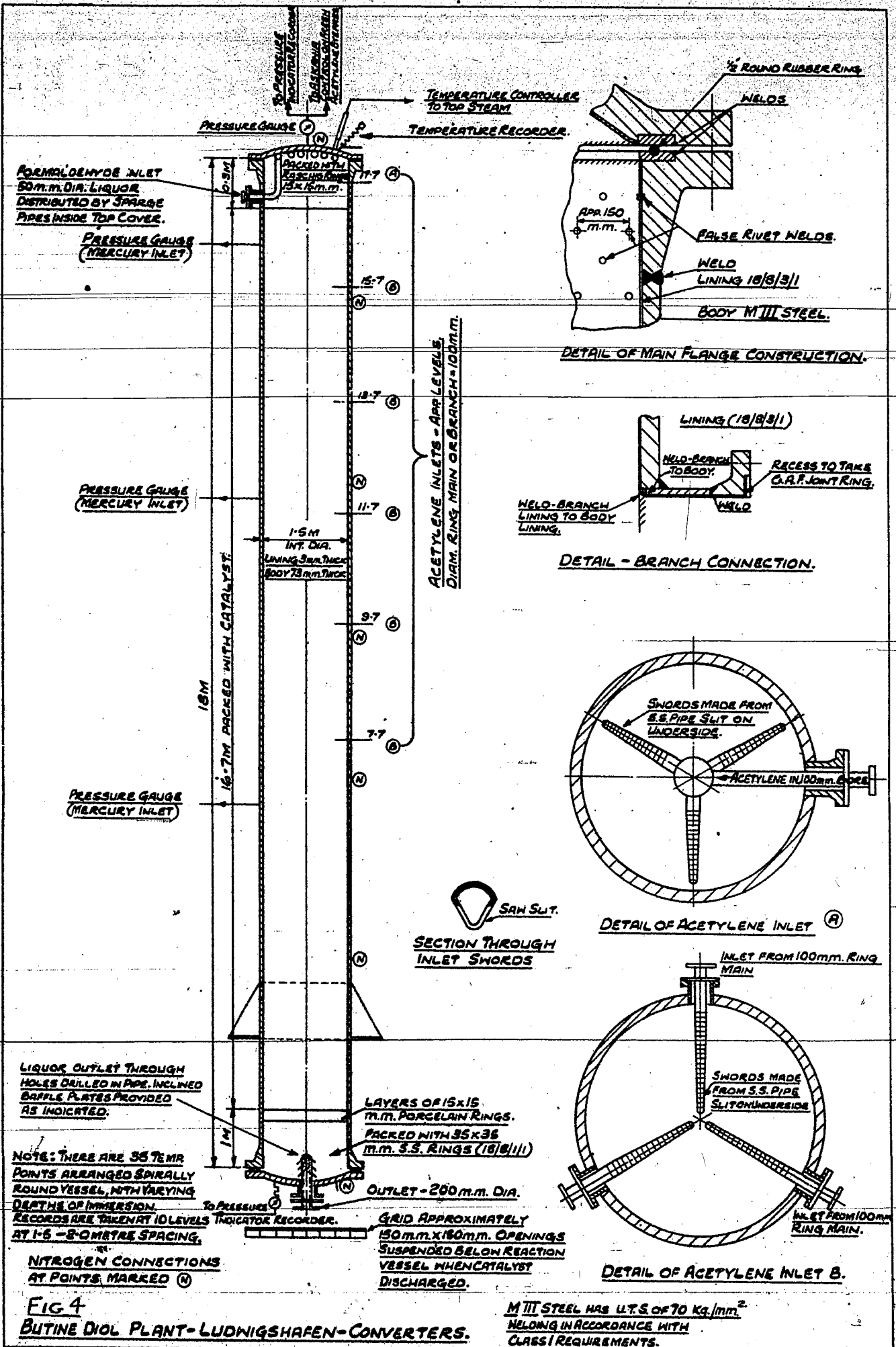
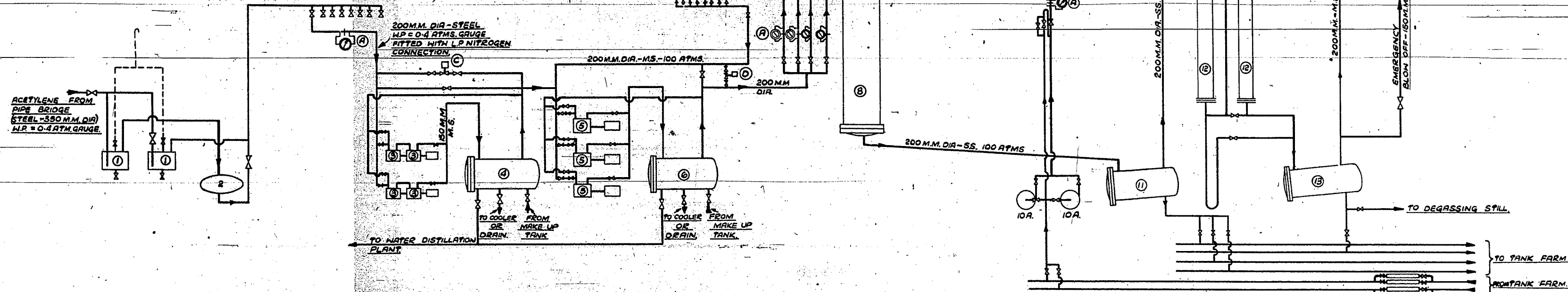


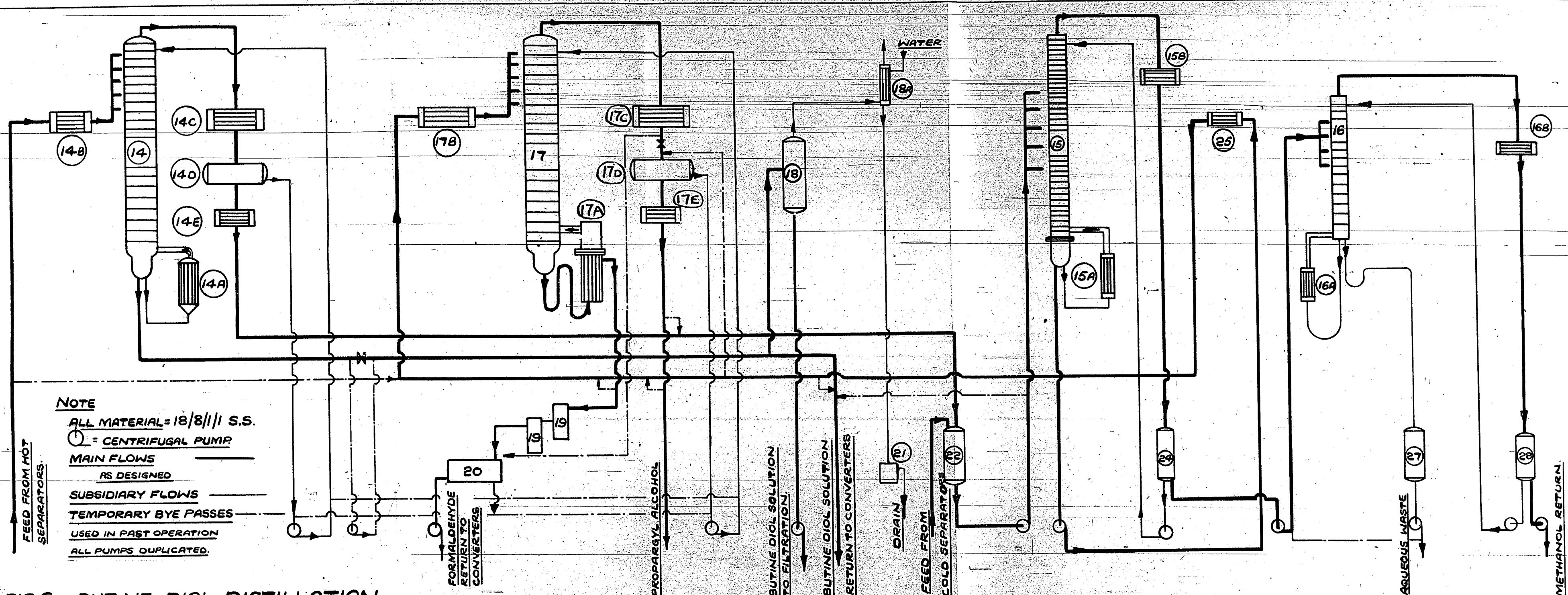
FIG 4
BUTENE DIOL PLANT - LUDWIGSHAFEN - CONVERTERS.

**FIG. 5 BUTINE DIOL PLANT
FLOW SHEET FOR CONVERTER AND PUMP-HOUSE, 1 UNIT.**

TOTAL NUMBER OF UNITS = 8
EXCEPT WHERE SHOWN, FLOW SHEET REFERS
TO ONE UNIT ONLY. INSTRUMENTS MARKED 'A'
ARE ON MAIN CONTROL PANEL.



ITEM NO	1	2	3	4	5	6	7	8	9	10	10A	11	12	13	14
DESCRIPTION	CATCH POTS.	ROTARY COMPRESSOR FOR FRESH ACETYLENE.	WATER AND ACETYLENE COMPRESSORS (SIEMENS) (SUCKLETS-ELMO) STAGE	RECEIVER.	WATER AND ACETYLENE COMPRESSORS (SIEMENS) (SUCKLETS-ELMO) STAGE	RECEIVER.	SEPARATORS.	CONVERTER.	TUBULAR HEATER.	FILTER.	PUMPS	RECEIVER	TUBULAR COOLERS	RECEIVER	FILTERS
NO OFF.	2 FOR WHOLE 8 UNITS.	1 FOR WHOLE 8 UNITS.	1 FOR EACH UNIT (WORKING), 1 SPARE.	1 FOR EACH UNIT.	1 FOR EACH UNIT (WORKING), 1 SPARE.	1 FOR EACH UNIT.	4 FOR EACH UNIT.	1 FOR EACH UNIT.	1 FOR EACH UNIT.	2 FOR EACH UNIT DITTO.			2 FOR EACH UNIT.	1 TO EACH UNIT.	2 ON EACH PIPE LINE SERVING ALL 8 UNITS.
FUNCTION	DEAN LIQUOR FROM ACETYLENE GAS.	MEASURE TOTAL FLOW TO WHOLE 8 UNITS.	ACETYLENE MAKE-UP COMPRESSORS.	CATCH VESSEL FOR WATER FROM ROTARY COMPRESSORS.	ACETYLENE MAKE-UP COMPRESSORS.	CATCH VESSEL FOR WATER FROM ROTARY COMPRESSORS.	FINAL SEPARATION OF WATER FROM ACETYLENE.	REACTION OF FORMALDEHYDE AND ACETYLENE.	PREHEATER FOR FORMALDEHYDE.	FOR FORMALDEHYDE.		PRIMARY SEPARATOR FOR BUTINE DIOL (HOT).	FOR BUTINE DIOL.	SECONDARY SEPARATOR FOR FORMALDEHYDE FEED.	FOR FORMALDEHYDE FEED.
CAPACITY.	APP 30 CU. FT. EACH.	PEAK RATE 3000 CU. M ACETYLENE/HOUR.	350 M ³ /HR. EACH.	1/2 M ³ APP.	400 M ³ /HR. EACH.	1/2 M ³ APP.	100 LITRES. APP.	18 M. LONG X 1.5 M INTERNAL DIA.	TOTAL AREA = 24 M ² (3 SECTIONS 8 M ² EACH).	EACH FILTER 7 CANDLES 0.6 10 M ² AGAINST BATH.		0.9 M. DIA. X 3 M. LONG.	EACH COOLER 4 M ² WATER OUTSIDE, GAS INSIDE. TUBES 10 M. LONG.	0.9 M. DIA. X 3 M. LONG.	CANDLE TYPE FILTER AREA = 18.6 M ²
MATERIAL OF CONSTRUCTION.	M.S.		ALL WORKING PARTS CAST 18/8	WELDED STEEL INTER PAINTED WITH BAKING ENAMEL.	ALL WORKING PARTS CAST 18/8	WELDED STEEL INTER PAINTED WITH BAKING ENAMEL.	WELDED STEEL.	WELDED STEEL LINED WITH 18/8/11	18/8/11	18/8/11	18/8/11	WELDED STEEL LINED 18/8/11	18/8/11	AS ①	18/8/11
TEMPERATURE RANGE.	ATMOSPHERIC.	ATMOSPHERIC.	MAX 50°C	MAX 50°C.	MAX 50°C.	MAX 50°C.	MAX 180°C.	MAX 150°C.	MAX 150°C	MAX 50°C	MAX 50°C.	MAX 150°C.	MAX. INLET TEMP 150°C.	40°C.	ATMOSPHERIC.
NORMAL WORKING PRESSURE.	5 LB./SQ. IN. GAUGE (MAX.)	5 LB./SQ. IN. GAUGE (MAX.)	STAGE 110-8 ATMOS. GAUGE STAGE 125-12 ATMOS. GAUGE	5-2 ATMOSPHERES GAUGE.	SUCTION 40 ATMOS GAUGE DELIVERY 5-2 ATMOS. GAUGE	5-2 ATMOS. GAUGE.	5-2 ATMOS. GAUGE.	5-2 ATMOS. GAUGE.	5 ATMOS. GAUGE	5-2 ATMOS. GAUGE.	5-7 ATMOS. GAUGE.	5 ATMOS.	5 ATMOS. GAUGE.	5 ATMOS. GAUGE.	5 ATMOS. GAUGE.
DESIGN PRESSURE	DITTO	DITTO.	100 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	10 ATMOS.	100 ATMOS.	100 ATMOS.	100 ATMOS.	5 ATMOS GAUGE.
SERVICES.			COOLING WATER TO BODY AND GLANDS THROUGH CIRC. SYSTEM. NITROGEN TO PUMP SUCTIONS (0.5 LB. IN.) CONNECTION FROM DELIVERY TO THROU. (VENT FOR NITROGEN)	WATER TO AND FROM COOLING SYSTEM.	COOLING WATER TO BODY AND GLANDS THROUGH CIRC. SYSTEM. NITROGEN TO PUMP SUCTIONS (0.5 LB. IN.) CONNECTION FROM DELIVERY TO THROU. (VENT FOR NITROGEN)	WATER TO AND FROM COOLING SYSTEM.	16 ATM. STEAM AT POINTS MARKED 'S'.	NITROGEN CONNECTIONS TO BODY.	5 ATM. STEAM TO TOWNS JACKETS OF PIPES.	TOWNS WATER.	TOWNS WATER.	NITROGEN (20 ATM)	WATER.		NONE.
POWER.			EACH MOTOR-88 KW. 1425 R.P.M.		EACH MOTOR-88 KW. 1425 R.P.M.						TO PUMP MOTORS				
INSTRUMENTS.	LEVEL GAUGE ON EACH CATCH POT.		INDICATING FLOW METER ON SUCTION OF EACH PUMP. DITTO ON WATER TO EACH STAGE. INDICATING PRESSURE GAUGE ON PUMP SUCTION INTERMEDIATE STAGE DELIVERY STAGE TEMPERATURE RECORDERS ON DELIVERY.	INDICATING PRESSURE GAUGE. LEVEL GAUGE. AUTOMATIC LEVEL CONT. (COMPRESSED AIR OPERATED) ON MAKE-UP WATER LINE.	AS FOR ITEM ③	AS FOR ITEM ④	INDICATING FLOW METERS ON TWO BOTTOM STEAM CONNECTIONS. RECORDING FLOW METER ON TOP STEAM CONNECTION.	TEMPERATURE RECORDERS AND INDICATORS IN TOP & BOTTOM OF TOWER.	TEMP. INDICATOR TO INLET. TEMP. RECORDER AND CONTROLLER ON OUTLET. COMPRESSED AIR OPERATED.	NONE.		LEVEL INDICATOR AUTOMATIC LEVEL CONTROLLER (AIR OPERATED).	TEMP INDICATORS ON OUTLET WATER-DITTO ON GAS INLET AND OUTLETS FROM EACH COOLER-FLOW INDICATOR WATER TO COOLERS.	LEVEL INDICATOR AUTOMATIC LEVEL CONTROLLER (AIR OPERATED)	NONE.
REMARKS.			AUTOMATIC VALVE 'C' CONTROLLED BY PRESSURE AT CONVERTER HEAD.	FILLED WITH 17% CR. STEEL RASCHIG RINGS 35 MM. X 35 MM.	AS FOR ITEM ④	NON-RETURN VALVES ON STEAM CONNECTIONS AUTOMATIC CONTROLLED BY PRESSURE IN ACETYLENE DISTRIBUTION MANIFOLD.	FOR DETAILS SEE FIG. 5.	HEATERS ARE BUILT UP FROM STEAM JACKETED TUBES. 30 M.M. DIA.	FILTERS ARE SINGLE STAGE OF COTTON CLOTH. CENTRIFUGAL PUMPS	FILLED WITH 17% CR. STEEL RASCHIG RINGS 35 MM. X 35 MM.		FILLED WITH 17% CR. STEEL RASCHIG RINGS 35 MM. X 35 MM.	FILTERS ARE OF COTTON CLOTH.		



NOTE
 ALL MATERIAL = 18/8/1/1 S.S.
 ○ = CENTRIFUGAL PUMP
 ——— MAIN FLOWS AS DESIGNED
 - - - - - SUBSIDIARY FLOWS
 ······ TEMPORARY BY-PASSES USED IN PAST OPERATION
 ALL PUMPS DUPLICATED.

FIG 6 BUTINE DIOL DISTILLATION.

ITEM NO.	14	14A	14B	14C	14D	14E	17	17A	17B	17C	17D	17E	19	20	18	18A	21	22	15	15A	15B	24	25	16	16A	16B	27	28
NUMBER OF DESCRIPTION	COLUMN	EVAPORATOR	PREHEATER	CONDENSER	RECEIVER	COOLER	COLUMN	EVAPORATOR	PREHEATER	CONDENSER	RECEIVER	COOLER	TAR CATCHERS	RECEIVER	LET DOWN VESSEL	CONDENSER	SEPARATOR	RECEIVER	COLUMN	EVAPORATOR	CONDENSER	RECEIVER	PREHEATER	COLUMN	EVAPORATOR	CONDENSER	RECEIVER	RECEIVER
AREA CAPACITY OR NO OF PLATES	35 PLATES 2M DIA.	200 M ² EACH		200 M ²	4M ³		35 PLATES 2M DIA.	200 M ² EACH 3 PASS		200 M ²	4 M ³			4.5 M ³				6M ³	44 PLATE 1M DIA.	40 M ²	100 M ²	4 M ³		10 PLATES	5 M ²	5 M ²	4 M ³	1.5 M ³

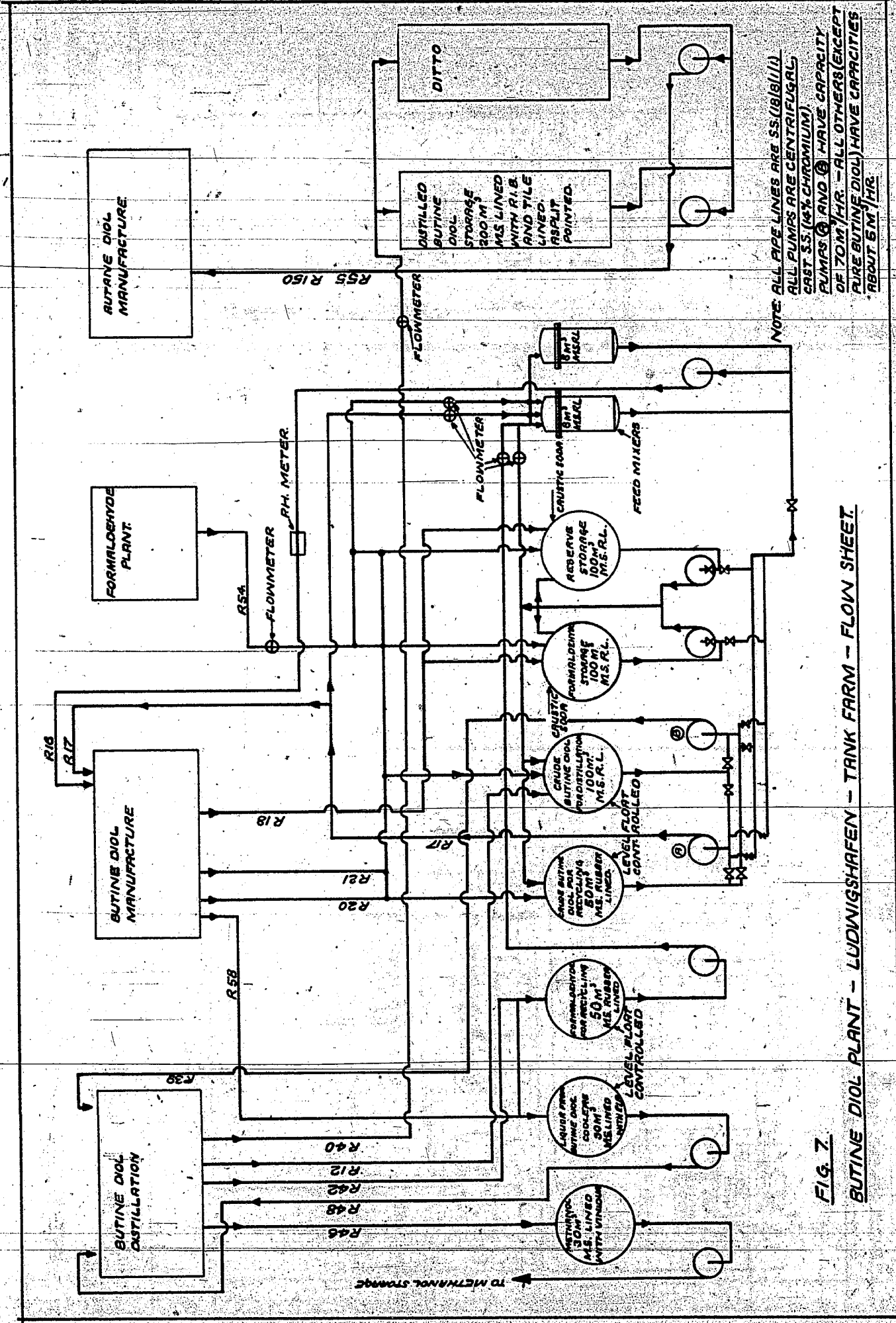
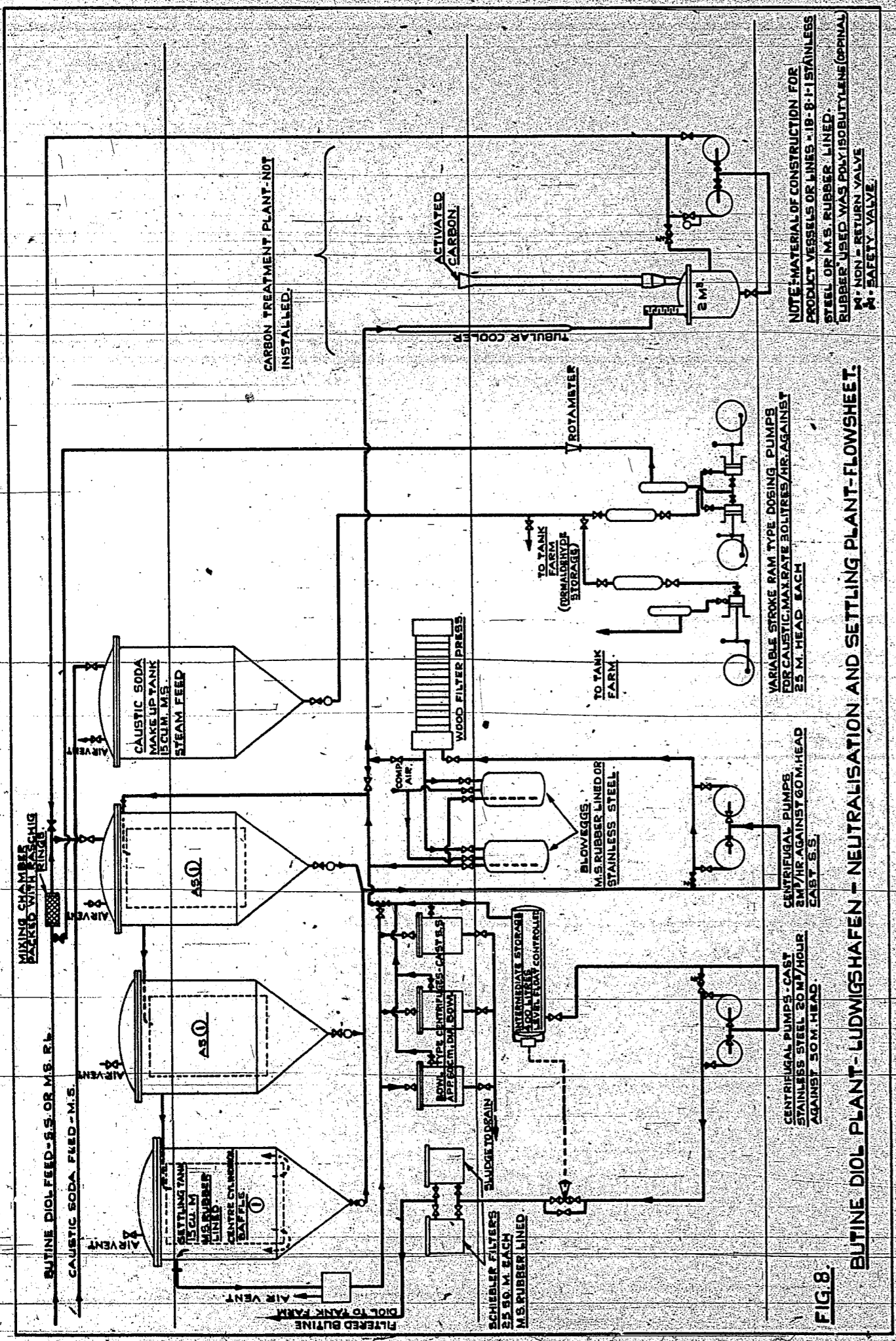


Fig. 7.

BUTYNE DIOL PLANT - LUDWIGSHAFEN - TANK FARM - FLOW SHEET.



NOTE: MATERIAL OF CONSTRUCTION FOR PRODUCT VESSELS OR LINES - 18-8-1 STAINLESS STEEL OR M.S. RUBBER LINED. RUBBER USED WAS POLYISOBUTYLENE (ORINAL M. NON) - RETURN VALVE M. SAFETY VALVE.

VARIABLE STROKE RAM TYPE DOSEING PUMPS FOR CAUSTIC/MATERIAL SOLID/HR. AGAINST 25 M. HEAD EACH

CENTRIFUGAL PUMPS - CAST STAINLESS STEEL 20 M³/HOUR. AGAINST 3.0 M. HEAD.

CENTRIFUGAL PUMPS - M.S. RUBBER LINED OR STAINLESS STEEL 2 M³/HOUR. AGAINST 3.0 M. HEAD. CAST S.S.

FIG. 8.

BUTINE DIOL PLANT - LUDWIGSHAFEN - NEUTRALISATION AND SETTLING PLANT - FLOWSHEET.

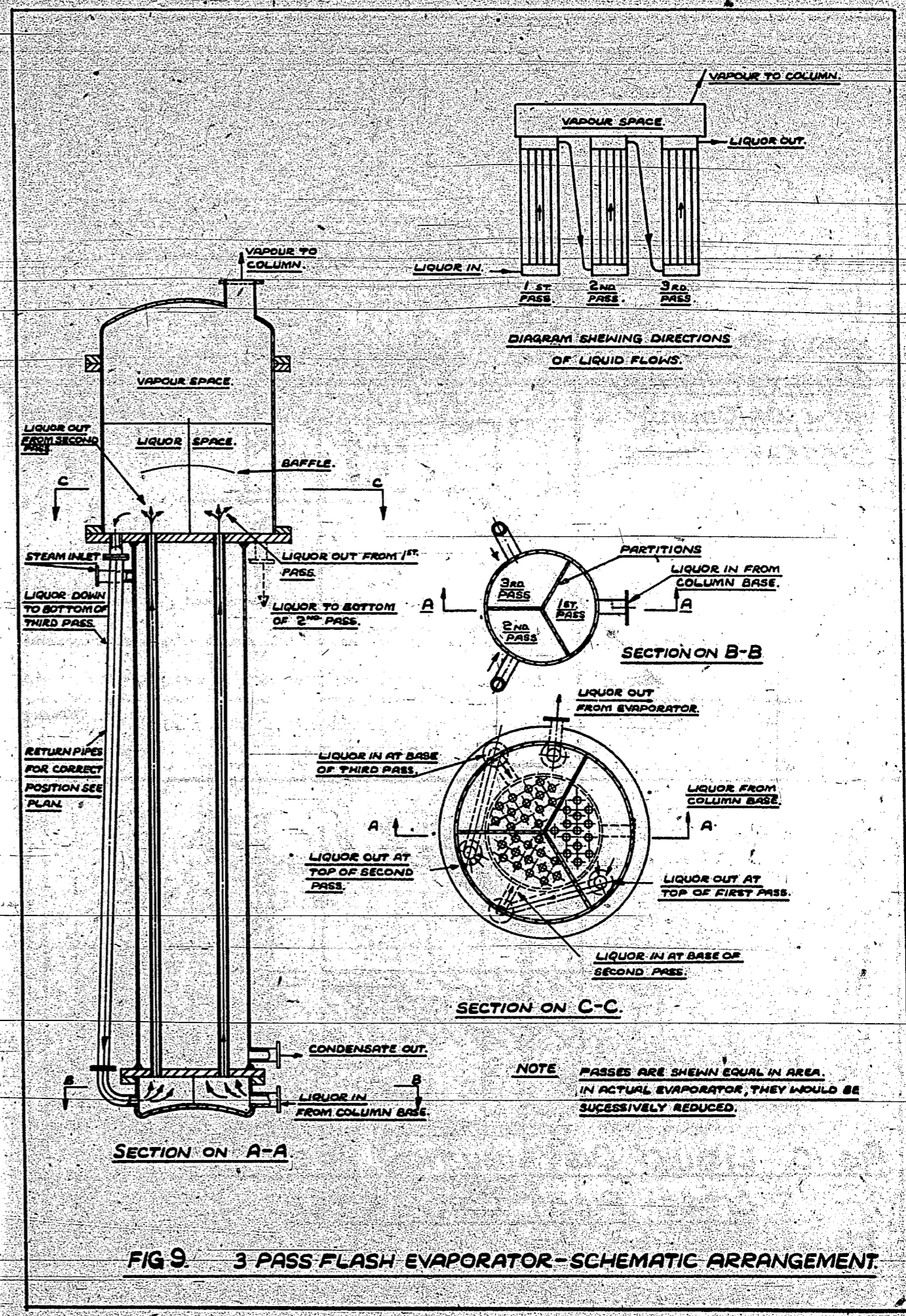


FIG. 9. 3 PASS FLASH EVAPORATOR - SCHEMATIC ARRANGEMENT.

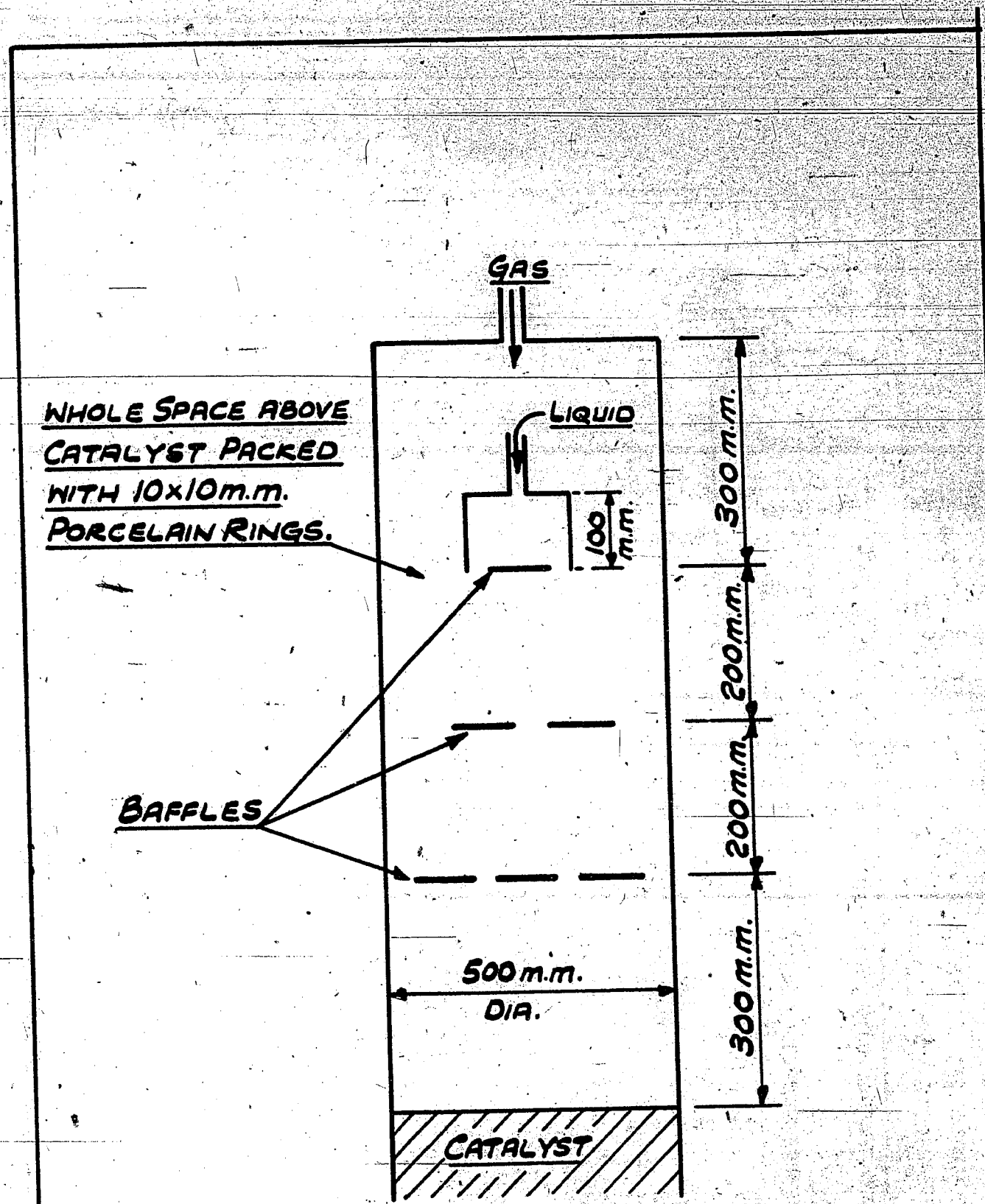


FIG. 10. LIQUID DISTRIBUTION FOR 2,000 LITRE PILOT CONVERTER.

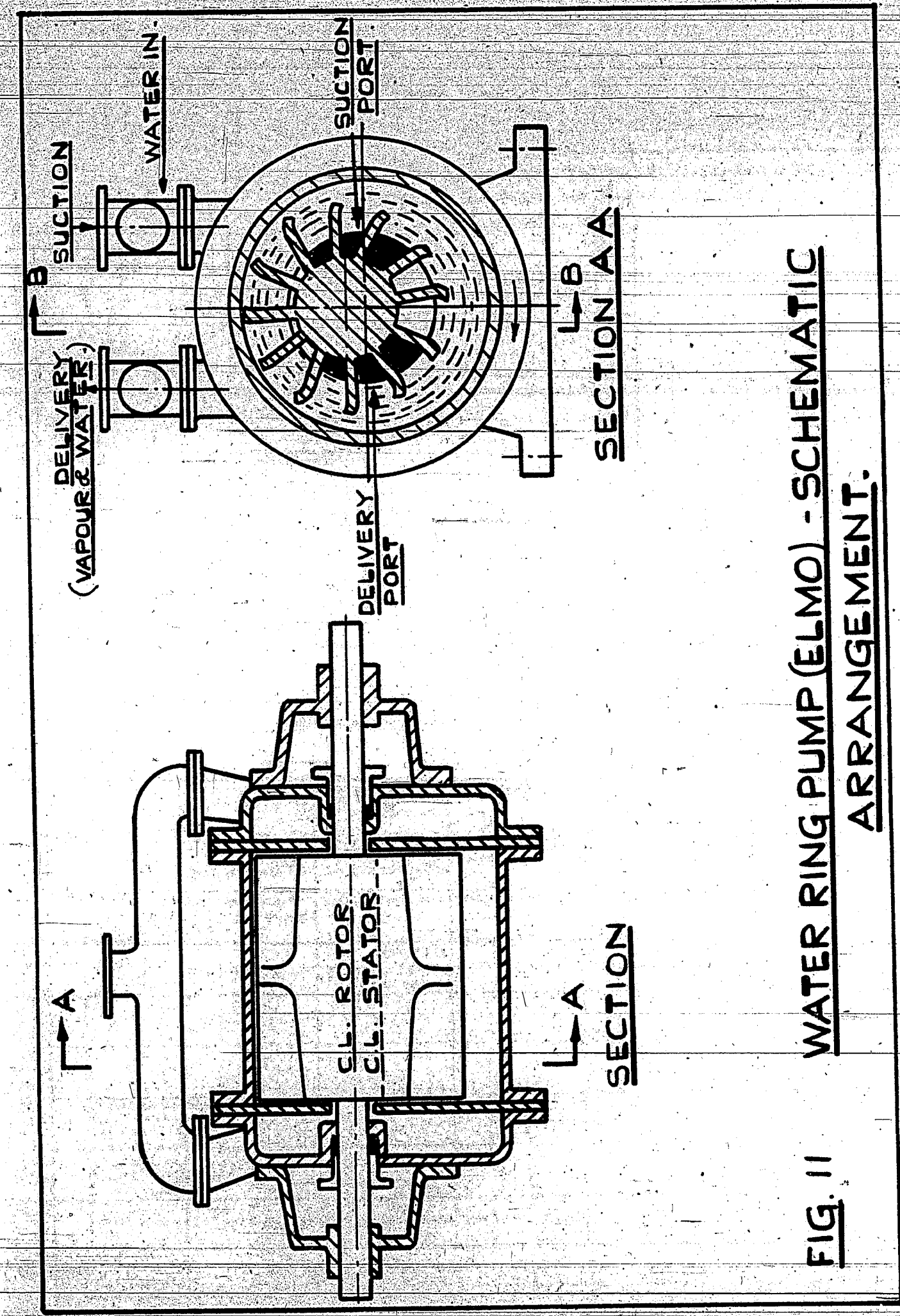
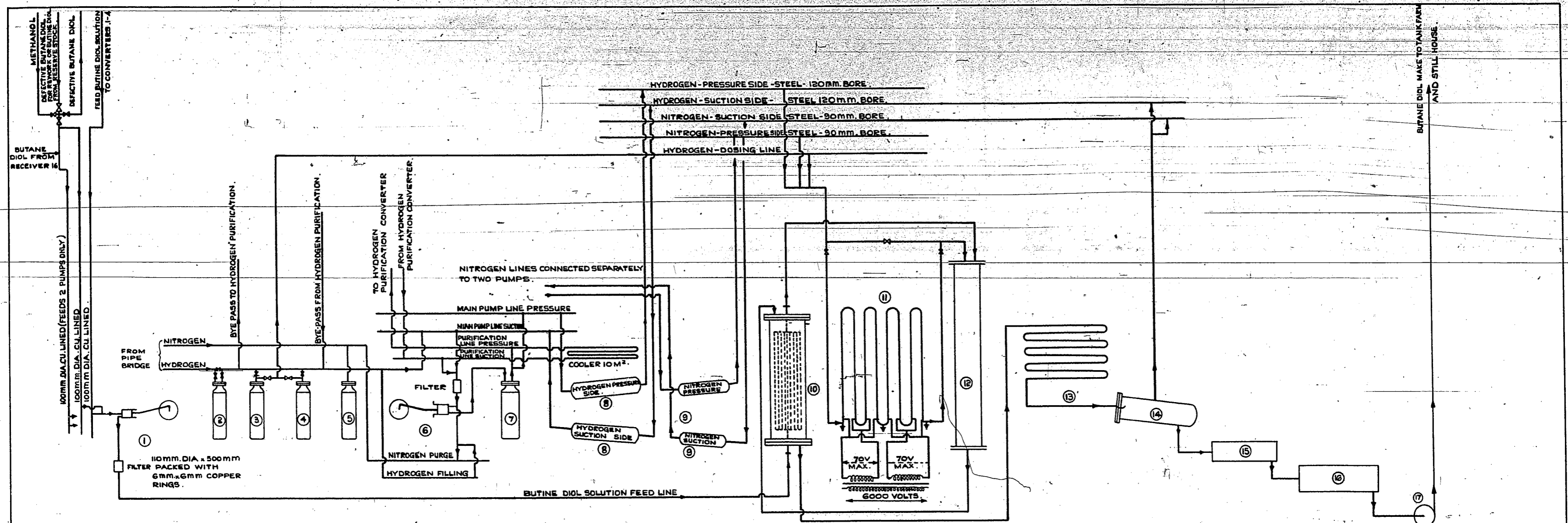


FIG. 11 WATER RING PUMP (ELMO) - SCHEMATIC ARRANGEMENT.



ITEM NO. AND DESCRIPTION	1 BUTANE DIOL FEED PUMPS - 3 PLUNGER SINGLE STAGE, SINGLE ACTING, HORIZONTAL.	2 MAKE UP HYDROGEN STORAGE BOTTLES 3, 4. HYDROGEN DOSING BOTTLES 5. NITROGEN STORAGE BOTTLE.	6 HYDROGEN & NITROGEN CIRCULATING PUMPS SINGLE STAGE DOUBLE ACTING	7 GAS SURGE TANKS	8 SEPARATORS FOR HYDROGEN.	9 SEPARATORS FOR NITROGEN.	10 HEAT EXCHANGER	11 PREHEATER FOR NITROGEN.	12 CONVERTERS.	13 COOLERS.	14 LIQUID-GAS SEPARATOR.	15 LET DOWN RECEIVER	16 PUMPING TANKS	17 PUMPS.
No. OFF	5 WORKING, 3 SPARE.	4	7 (2 ONLY USED FOR CIRCULATING NITROGEN)	7 (1 TO EACH HYDROGEN PUMP)	2 (1 ON PRESSURE SIDE, 1 ON SUCTION)	2 (1 ON PRESSURE SIDE, 1 ON SUCTION)	6 (1 TO EACH REACTION TOWER)	2 (1 TO EACH SET OF REACTION VESSELS)	6 (4 MAIN PROCESS FOR HYDROGEN PURIFICATION FOR DEFECTIVE BUTANE DIOL)	6 (1 TO EACH REACTION VESSEL)	6	2 (1 TO EACH SET OF 3 REACTION TOWERS)	4 (2 TO EACH SET OF 3 REACTION VESSELS)	
DUTY OR SIZE	6 M ³ /HR. MAX. DELIVERY PRESSURE 340 ATMS. 140 R.P.M.	0.5 m DIA. 4 m LONG.	75000 M ³ /HR (MEASURED AT 15°C 735 MM) MAX. PRESSURE 340 ATMS. 130 R.P.M.	0.5 m DIA. 4 m LONG.	1 m DIA. 6 m LONG.	0.7 m DIA. 4.6 m LONG.	0.5 m DIA. 12 m LONG 520 TUBES 6 mm BORE 13 mm O.D.	8 TUBES 90 mm BORE 125 mm O.D. 10.5 m HEATED LENGTH EACH.	18 m LONG BORE 600 mm (HYDROGEN PURIFICATION) 800 mm (ALL OTHER UNITS)	200 M ² ; 23 m LENGTHS OF 70 mm BORE WATER JACKETED PIPE	NOMINAL 6 M ³ EACH.	1.2 m DIA. x 5 m LONG	2.4 m DIA. x 7 m LONG	CAPACITY REQUIRED - 30 M ³ /HR. EACH.
MATERIAL OF CONSTRUCTION	PUMP BARREL STEEL PLUNGER 18/8/1/1	STEEL.	STEEL.	STEEL.	STEEL.	STEEL.	STEEL-COPPER LINED MANGANESE BRONZE TUBES & TUBE PLATES	STEEL.	HYDROGEN PURIFICATION TIE LINED. LINED WITH 18-8-1-1 LINED WITH COPPER	COPPER LINED STEEL	COPPER LINED STEEL	ALUMINIUM	ALUMINIUM (RUBBER LINED M.S. MAY BE USED)	SILICON ALUMINIUM
POWER	90 KW.		450 KW.					ELECTRICALLY HEATED BY CURRENT ALONG TUBE WALLS. TOTAL OUTPUT OF TRANSFORMER 100 KW.						
SERVICES										WATER.				
INSTRUMENTS	EACH PUMP HAS METER ON SUCTION	PRESSURE GAUGE ON EACH VESSEL.	PRESSURE GAUGES ON SUCTION AND DELIVERY SIDE SUPPLIED BY BERLINER					OUTPUT OF TRANSFORMER THERMOSTATICALLY CONTROLLED.	TEMPERATURE RECORDS AT 4 LEVELS ON TOWER TOGETHER WITH GAS AND LIQUOR INLET AND OUTLET TEMPERATURES.	COOLING WATER INLET & OUTLET TEMPERATURES RECORDED.				
COMMENTS	SUPPLIED BY MICHAEL & SOHN, FRETAL DRESDEN.		MASCHINEN FABRIK 4 PUMPS ARE WORKED IN PARALLEL.					USED DURING REDUCTION OF CATALYST ONLY.						DELIVER TO TANK FARM.
WORKING PRESSURE	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	340 ATMS.	2-4 ATMOSPHERES	ATMOSPHERIC PRESSURE	MAX. 5. ATMS.

FIG 12. BUTANE DIOL PLANT - LUDWIGSHAFEN - FLOW SHEET.

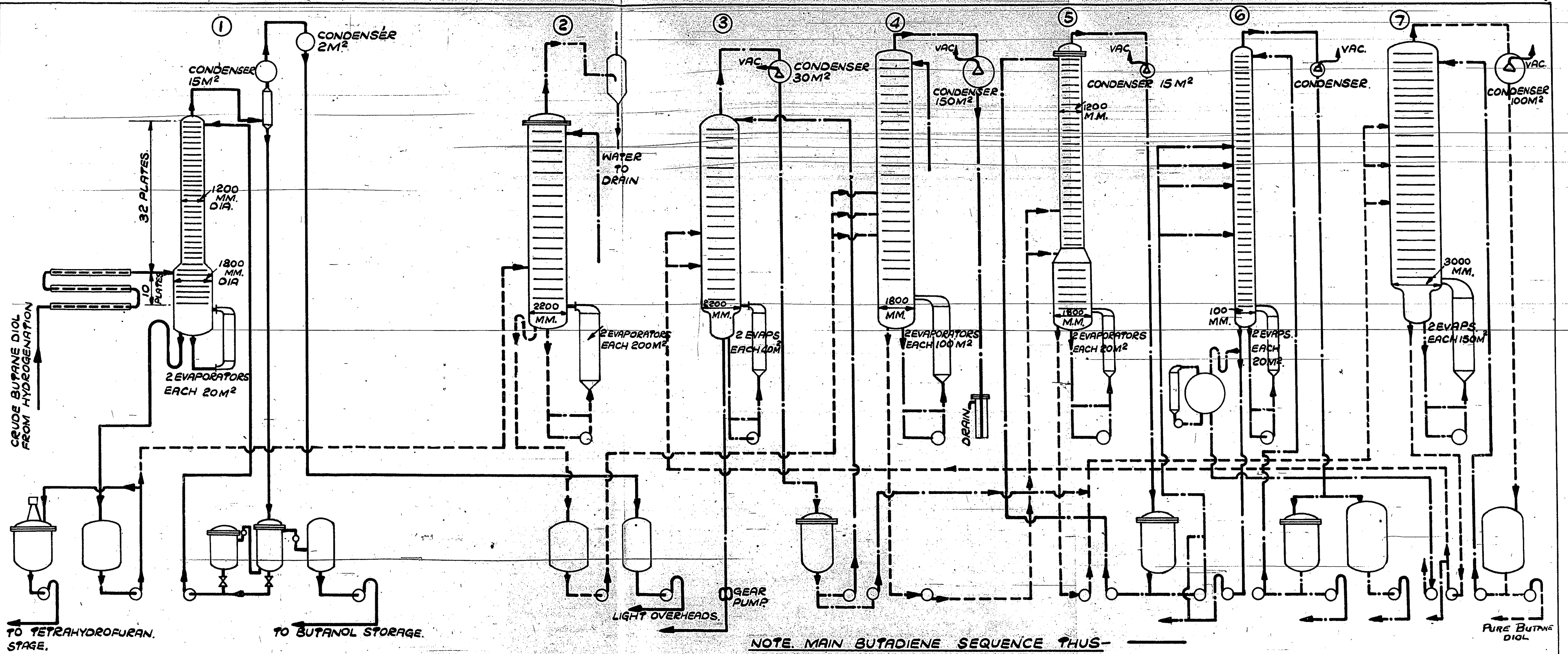
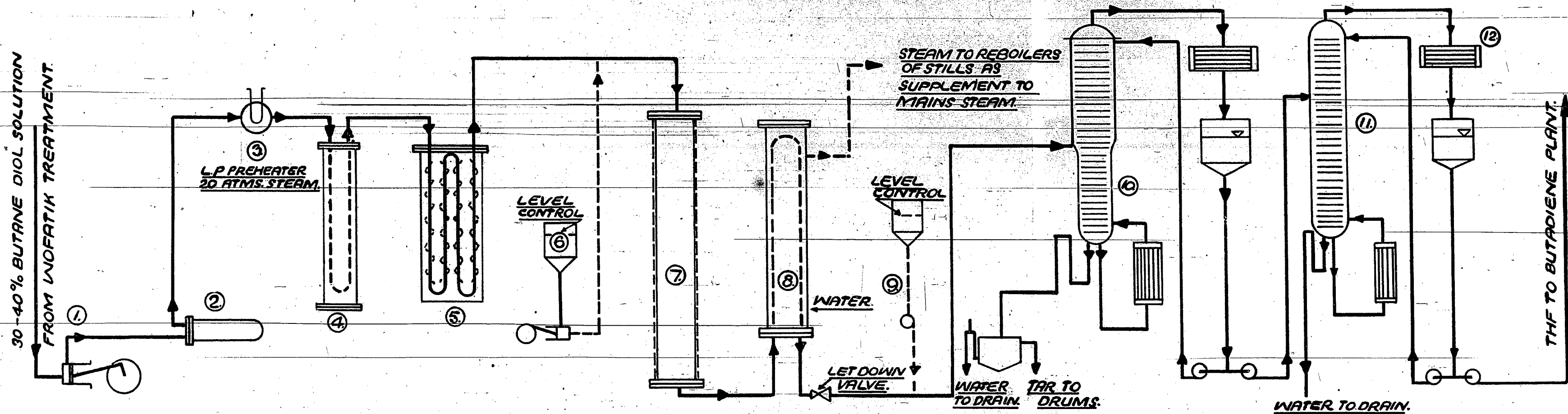


FIG 13. BUTANE DIOL DISTILLATION.

NOTE. MAIN BUTADIENE SEQUENCE THUS- ———
 MAIN FLOW IN PURE BUTANE DIOL MANUFACTURE THUS- - - - -
 ALL OTHERS THUS- ———



ITEM No.	①	②	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫		
ITEM.	FEED PUMPS.	SURGE TANKS.	H.P. STEAM PREHEATER	ELECTRIC PREHEATER.	PHOSPHORIC ACID INJECTION	CONVERTER.	STEAM REGENERATOR COOLER.	CAUSTIC SODA INJECTION.	SEPARATOR.	CRUDE THF STILL.	CONDENSER RECEIVER & PUMPS	PURE THF STILL.	CONDENSER RECEIVER & PUMPS.
N° OF			4.	2.		2.	2.			1.		1.	
MAT. °.			18/8/1/1.	18/8/1/1.		18/8/1/1. LINED	18/8/1/1.			M. S.		M. S.	
W.P.	100 ATMS.	100 ATMS.	100 ATMS (STEAM AND PRODUCT)	100 ATMS.		100 ATMS.	100 ATMS.			ATMOS.		ATMOS.	
REMARKS	(DELIVERY)	LEVEL CONTROLLED AUTOMATICALLY	WORKING TEMP 20 - 250°C CONSISTS OF 3-4 SECTIONS AS REQUIRED TO EACH 50 M ²	WORKING TEMP 250 - 290°C ELECTRIC WINDINGS APPLIED TO PIPES.		500 M.M. BORE X 12M. LONG ELECTRIC WINDING ON OUTSIDE WORKING TEMP 280°C.	WORKING TEMP 280 - 180°C OUTLET STEAM PRESSURE = 18 ATMS.			40 PLATES 22 ABOVE 2.2m DIA. 18 BELOW 1.8m DIA. 400MM PLATE SPACING	LEVEL CONTROLLER IN RECEIVER.	35 PLATES 10 ABOVE 25 BELOW 2m DIA.	LEVEL CONTROLLER IN RECEIVER

FIG. 14

FLOW SHEET FOR TETRA HYDROFURAN.

ITEM NO.	FUNCTION	N ^o OFF.	CAPACITY, OUTPUT, OR SIZE.	METHOD OF HEATING OR COOLING.	MATERIAL OF CONSTRUCTION	PLANT DESCRIPTION	COMMENTS.
1	SUBSIDIARY STORAGE TANK FOR SODIUM SILICATE SOLUTION	1					SODIUM SILICATE SOLUTION (39-40° BAUME 25% SOLID) 9.3% NH ₄ OH LET DOWN WITH EQUAL VOLUME OF WATER
2	MEASURE VESSEL FOR SODIUM SILICATE SOLUTION	2	4 M ³	WATER JACKET PROVIDED BUT NOT USED.	RUBBER LINED M.S.	PROVIDED WITH 80 R.P.M. TURBINE TYPE AGITATOR, APP. 18" DIA. X 18" HIGH.	SULPHURIC ACID FED TILL PH=4.5. BROUGHT BACK BY 2.5% NH ₄ SOLUTION TO ABOUT 7.
3	PRECIPITATION VESSEL FOR SILICA GEL	2			HARDWOOD PLATES AND FRAMES	WASH TYPE PRESSES-THROUGH EXTRACTION P.V.C. FILTER CLOTHS	LIQUOR RUNS TO DRAIN VIA FLOOR CAKE WASHED WITH WATER AT 40°C TO REMOVE ELECTROLYTES MAINLY SILPHATES (80% WATER 20% SOLIDS IN CAKE)
4	FILTER PRESSES	12	EACH ABOUT 25 LITRE CAPACITY 10" LONG X 10" INT. DIAM.	COASTAL STEAM TO COOLERS AND HOT AIR CIRCULATION BY FAN (30)	19/8/1/1	FEED BY ROTATING TABLE SLICING PASTE INTO DRUM. DRUM ROTATES APP. 1 R.P.M.	NORMAL WORKING TEMP. = 150°C
5	ROTARY DRYER	1	ROTOR APP. 40 CMS. DIA.		C.I. AND STEEL.	HORIZONTAL SPIRAL PIN TYPE MILL-SCREEN 1/2" DIA. HOLES, COMPLETELY ENCLOSED. SHAKER TYPE FEED WITH MAGNETIC PULLEY	MAKERS - MASCHINENFABRIK GEISLINGEN-STUTTGART
6	GRINDING MILLS	2	1-100 LITRE 1-600 LITRE 1-800 LITRE	WATER JACKETED	MILD STEEL, CAST IRON	DOUGH TYPE MIXERS. DISCHARGE BY TIPPING.	MIX PROPORTION OF PASTE FROM PRESS WITH GROUND MATERIAL FROM MILL.
7	WERNER PLEIDERER MIXERS	3	EACH PRESS HAS ONE 40 LITRES OF PASTE AT EACH OPERATION		MILD STEEL, CAST IRON REMOVABLE INSERTS.	STANDARD HYDRAULIC PRESS.	BANDS 11 MM WIDE CHAIN WEAVE WIRE GAUZE. WORKING TEMP. 150°C.
8	EXTRUSION PRESS	2	OUTPUT 5 M ³ /DAY	OFF GASES FROM CALCINING OVEN-ITEM 10	S.S. 16/8/1/1	MAKERS - BENNO-SCHILDE	
9	SPASS BAND DRYER	1	APP. 10 M ³ /DAY		M.S. AND C.I.		
10	ROLL CRUSHER	1	ROLLS APP. 12"				
11	SIEVE	1				2 FLAT SHAKING SIEVES.	
12	CALCINING KILN	1	12 M LONG 1 M INSIDE DIA.	GAS FIRED	M.S. LINED WITH FIREBRICK	INSULATING BRICK BEHIND FIREBRICK OFF GASES TO TEMP. 500°C	
13	SIEVE	1					
14	IMPREGNATING TANK	1	1200 LITRES		M.S. TILE LINED-AS PLUIT POINTED WITH ACID RESISTING BRICK SET IN MORTAR BY ROCEMENT	NOT AGITATED OPEN TOP	CATALYST IMMERSED IN TANK IN BASKETS 1000 X 750 X 750 MM OF 18/18// PERFORATED WITH 2 MM HOLES AT 5 MM CENTRES.
15	ROASTING FURNACE	1	6 M LONG X 0.6 M INT. DIAM.	GAS FIRED		WORKING TEMPERATURE = 500°C	
16	TRAY TRUCK DRYER FOR BUTANE DIOL CATALYST	1					
17	BOWL TYPE MIXER, INCLINED AXIS	2	APPROX. 1-2 M		M.S. AND C.I.		CATALYST SPRAYED WITH SOLUTION INSIDE MILL

FIG. 15B. BUTANE & BUTANE DIOL PLANTS - LUDWIGSHAFEN. CATALYST PLANT-FLOW DIAGRAM-LIST OF PLANT ITEMS.

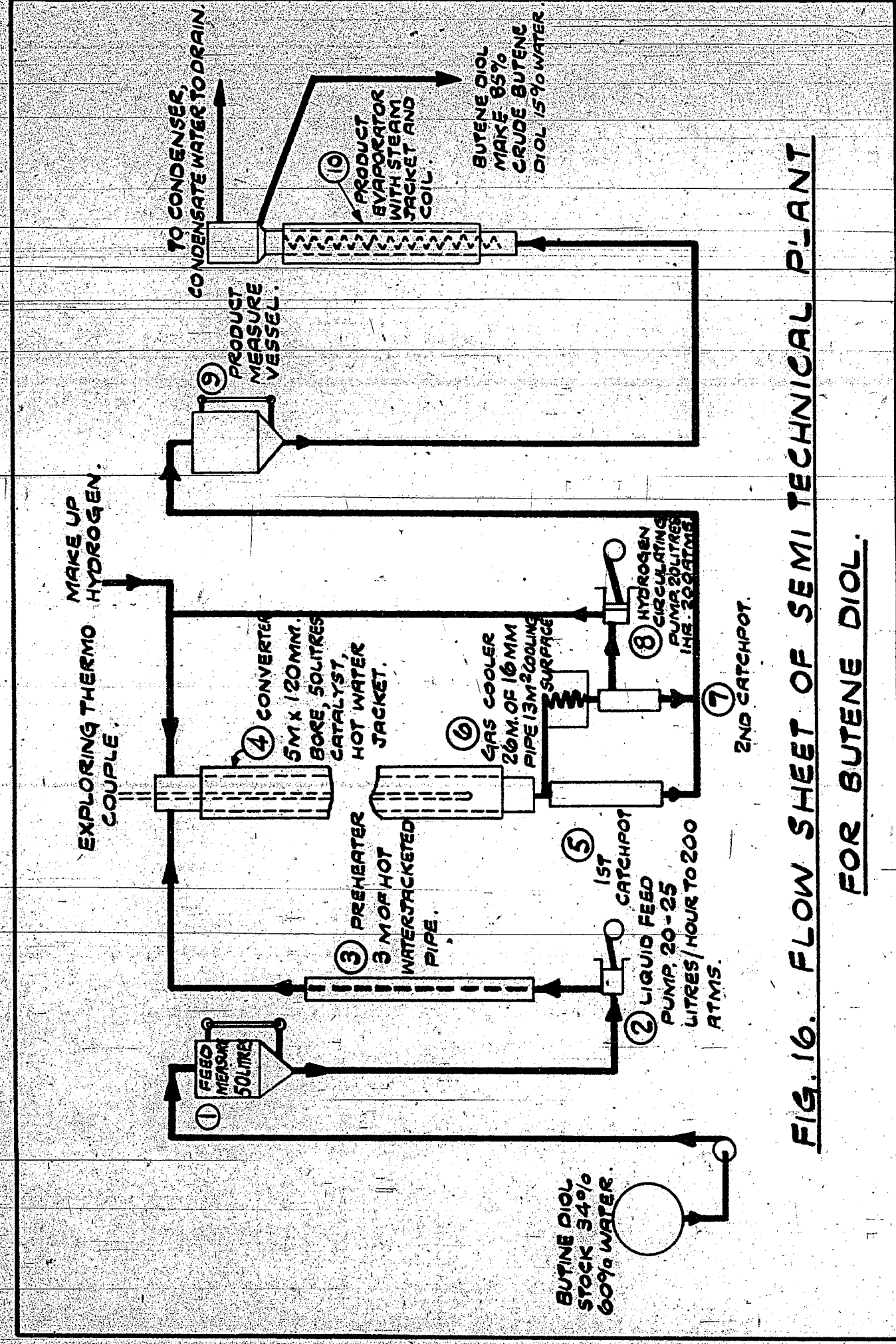


FIG. 16. FLOW SHEET OF SEMI TECHNICAL PLANT FOR BUTENE DIOL.

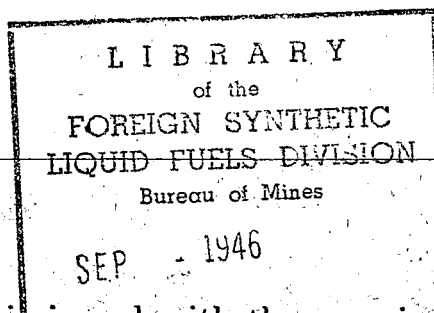
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**BIOS FINAL REPORT No. 419
ITEM No. 22**

I.G. WAXES:

Manufacture at Gersthofen and Oppau

Baird, W.



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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

I. G. WAXES: MANUFACTURE AT
GERSTHOFEN AND OPPAU

Reported by

W. BAIRD, M. of S.

BIOS Target No. 22/1(d)

(1946)

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE,
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TABLE OF CONTENTS

<u>SUBJECT.</u>	<u>PAGE NO.</u>
<u>OBJECT OF VISIT</u>	1
<u>SUMMARY</u>	1
<u>PERSONNEL INTERVIEWED</u>	1
<u>GENERAL</u>	1
<u>I.G. WAXES: Manufacture.</u>	2
Plant	2
<u>GERSTHOFEN WAXES</u>	
Wax S	2
Wax KP	3
Wax KPS	4
Wax BJ, unbleached	4
Wax BJ, bleached	5
Wax E	5
Wax EG	6
Wax N neu	6
Wax Spezial	6
Wax CR	7
Wax L	7
Wax G	8
Wax O	8
Wax OP	9
Wax AD	9
<u>OPPAU WAXES.</u>	
Wax S	9
Wax L	9
Wax Z	9
Wax OZK	10
<u>APPENDIX 1: production figures.</u>	11

PERSONNEL OF TEAM:

Dr. W. Baird, M. of S. (Gersthofen products -
16.10.45)
Mr. G.R. Perdue, M. of S. (Oppau products -
28.9.45)

OBJECT OF VISIT:

During an investigation into the manufacture of textile auxiliary products it was found that the I.G. used certain synthetic waxes in the formulation of water-repellent wax emulsion finishes. Data on the manufacture of these waxes was therefore desired and as the subject of synthetic waxes was considered to be of wider interest the scope of the investigation was extended to cover the range of waxes made at Gersthofen and Oppau.

SUMMARY:

The I.G. had quite an extensive business in synthetic waxes. These were made almost entirely at Gersthofen by chromic acid oxidation of Montan wax to varying degrees followed, in some cases, by esterification and other procedures to give the desired product. Details of the processes used are given in this report and the production figures for the more important products are listed in the Appendix. Some data on the waxes manufactured at Oppau has been included in this report.

PERSONNEL INTERVIEWED.

Dr. Heisel: director in charge at Gersthofen.
(Dr. Heisel had only recently been appointed to this post).

Dr. Schwarta: in charge of wax production at Oppau.

GENERAL:

The Gersthofen factory was undamaged. There was, however, no production of synthetic waxes as the raw Montan wax came from Riebeck, now in the Russian zone.

In Dr. Heisel's opinion, Riebeck Montan wax is quite unique as a raw material for the production of synthetic waxes. Similar products could be produced from other brown coal waxes but the wax content of these other coals was lower and hence costs would be higher. Peat wax, and especially German peat wax, was considered unsuitable by Dr. Heisel: peat is much younger geologically than brown coal and the wax therefore different chemically.

Riebeck montan wax was said to be essentially ester in chemical character and to contain very little paraffin. During the treatment with chromic acid the ester groups are hydrolysed, at least in part, and the alcohol residues oxidised to fatty acids.

I. G. WAXES: MANUFACTURE.

Plant.

The Gersthofen plant, though specially built for the manufacture of synthetic waxes based on Montan wax, was of a type common in the manufacture of organic chemicals and quite normal in lay-out.

It comprised, roughly, a mill for grinding the raw Montan wax; 10 oxidation kettles of 7 c.m. capacity, lead-lined, jacketed, fitted with stirrer etc., two smaller kettles for washing the crude oxidised wax; two vacuum kettles (3 c.m.) for drying the wax; 8 kettles for esterification and other processes. There was also a flaking drum for finishing the products.

GERSTHOFEN WAXES.

WAX S.

This is an oxidised Montan wax.

600 kg. raw, deresinified Montan wax is charged to the oxidation kettle containing 1000 l. chromic acid, and melted.

The mixture is stirred and 5000 l. of chromic acid is added during about $3\frac{1}{2}$ hr., at a temperature of 120°C . Stirring is continued for a further hour and after settling 1 hr. the spent liquor is run off. A further 4360 l. of chromic acid is now added during $4\frac{1}{2}$ hr. at 120°C . and stirring continued for $1\frac{1}{2}$ hr. The mixture is again settled for 1 hr. and the spent liquor run off.

The spent liquor is cooled to about 50°C . diluted to 39°Be with condenser water and pumped back to another unit of the factory for regeneration.

The wax is transferred to a settling kettle where it is settled for 4 hr., residual liquor separated and the wax then blown to a washing vessel containing

about 1000 l. hot water. After thorough stirring at the boil the mixture is allowed to settle for 4 hour and the acidity of the liquor tested. It should contain the equivalent of not more than 5 g. H_2SO_4 per litre. The wash water is run off through a sight glass and the wax transferred to the vacuum kettle where it is dried, while stirring, at 90-100°C. and 160-360 mm. pressure.

The wax is then run off to the flaker. It should possess the following properties:-

Melting point	80-83°C.
Acid value	142-157
Ester value	10-30
Sap. value	160-175
Unsap.	7-10%
Sp.gr. 20°	1.01-1.02

Notes:

- (1) The chromic acid used contains 110 g. CrO_3 per litre.
- (2) If the chromic acid is added too rapidly during the oxidation there is a danger of the reaction becoming too vigorous and the reaction mixture may froth over.
- (3) During the drying stage it is necessary to take care that the wax does not froth over.

WAX KP.

This is obtained by oxidation of Montan wax followed by esterification.

250 kg. deresinified Montan wax and 300 kg. raw Montan wax (not deresinified) are charged to an oxidation kettle containing 1000 l. chromic acid, and melted. 4860 l. of chromic acid is then added during $3\frac{1}{2}$ hr. at a temperature up to 120°C. and stirring continued a further $1\frac{1}{2}$ hr.

The spent liquor is run off, the wax transferred to a settling kettle for 4 hr. and then blown to another kettle where it is washed at about 100°C. with 30% sulphuric acid and then settled 4 hr. The wax is then thoroughly stirred with boiling water (1000 l.) and allowed to settle 4 hr; the wash water should contain not more than 5 g. H_2SO_4 per litre. The wash water is run off and the wax dried as before.

The wax is transferred to an esterification kettle where it is reacted with 4% by weight of ethylene glycol and 4% by weight of butylene glycol at 110-115°C. until the acid value falls to 20-25. 0.4% of Marseilles soap and 3% of G alcohol are added and stirred into the melt.

The wax should have the following characteristics:

Melting point	80-82°C.
Acid value	20-25
Sap. value	145-155

WAX KPS.

This is prepared in exactly the same way as wax KP using:-

350 kg. deresinified Montan wax
100 kg. non-deresinified Montan wax
6,135 l. chromic acid.

The wax has the same analytical criteria as wax KP.

WAX BJ, unbleached.

This is a complex mixture derived from fatty acids, wax S, glycol, wool fat and paraffin as follows:-

288 kg. palm kernel fatty acids, 108 kg. stearic acid, 162 kg. ethylene glycol and 750 cc. of 20% sulphuric acid are stirred together at 90°C. until the mixture has an acid value of 70.

1440 kg. wax S. 41 kg. ethylene glycol and 410 cc. of 20% sulphuric acid are added and the mixture again stirred at 90°C. until the acid value falls to 25.

47 kg. wool fat, 458 kg. paraffin and 700 g. "Aroma" are now stirred in and the mixture run to aluminium trays to solidify.

The wax should have the following characteristics:-

Melting point	72-74°C.
Acid value	33-43

Ester value	83-95
Sap. value	118-133
Unsap. "	22-26%
Sp.gr. 20°	0.97

WAX BJ Bleached.

500 kg. of the unbleached wax is bleached by the slow addition of 1364 l. of chromic acid at 115°C. The reaction is finished when the chrome liquor still contains 5 g. CrO₃ per litre and the CrO₃ content is followed during the reaction until this figure is reached.

After settling 1 hr. the spent liquor is run off and the wax washed with 10% sulphuric acid at the boil and then with water until the acid contents is not more than 5 g. H₂SO₄ per litre water. After drying in vacuo at 90° the wax is run to trays to cool.

The wax has the following characteristics:-

Melting point	70-73°C.
Acid value	66-86
Ester value	86-106
Sap. value	163-183
Unsap. "	21-24%
Sp.gr. 20°	0.96

WAX E.

This is derived from wax S by esterification.

100 kg. wax S is esterified with 10.5 kg. ethylene glycol using 30 cc. 20% sulphuric acid as catalyst, at 110-115°C., until the acid value is 18-20. 0.0005% of KOH (in water) is then added to neutralise the acid.

The wax has the following characteristics:-

Melting point	79-82°C.
Acid value	17-25
Ester value	140-156
Sap. value	158-178
Unsap.	5-8%
Sp.gr. 20°	1.01-1.02

WAX EG.

This also is an esterified wax s product.

100 kg. wax S, 12 kg. propylene glycol and 30 cc. of 20% sulphuric acid are stirred together at 110-115°C. until the acid value falls below 28.

The wax has the following characteristics:-

Melting point	72-75°C.
Acid value	18-26
Ester value	135-153
Sap. value	158-173
Unsap.	5-8%
Sp. gr. 20°	1.01-1.02

WAX N neu.

This product is analogous to Wax BJ, unbleached.

320 kg. wax S, 24 kg. palm kernel fatty acids, 40 kg. stearin, 8 kg. wool fat, 48 kg. ethylene glycol and 180 cc. 20% sulphuric acid are stirred together at 90°C. until the acid value falls to 55.

100 kg. paraffin, 20 kg. marseilles soap and 32 kg. Emulphor are then added, the mixture dried at 260-360 mm. pressure at a temp. not exceeding 90°C. The melt is run to trays to cool.

The wax has the following characteristics:-

Melting point	72-74°C.
Acid value	33-43
Ester value	83-95
Sap. value	118-133
Unsap.	22-26%
Sp. gr. 20°	0.97

WAX SPEZIAL.

This is a mixture of various esterified waxes.

1200 kg. deresinified Montan wax is esterified in a lead kettle with 34 kg. butylene glycol at 110°C. using 8.3 kg. conc. sulphuric acid in 3 kg. water as catalyst, until the acid value falls to 15-20. The melt is then neutralised with 1.7 kg. KOH.

420 kg. non-deresinified Montan wax, 200 kg. Wax G, 30 kg. butylene glycol, 3 kg. conc. sulphuric acid and 3kg. water are stirred together at 110-115°C. until the acid value falls to 20-25. 420 kg. G alcohol is then added and mixed in.

960 kg. Wax G, 56 kg. butylene glycol, 480 cc. conc. sulphuric acid and 520 cc. water are stirred together at 115-120°C. until the acid value falls to 55. 32 kg. lime (calcium hydroxide) is then added and the mixture stirred thoroughly.

The three components are then melted together and mixed thoroughly.

The wax has the following characteristics:-

Melting point	90-93°C.
Acid value	13-18
Ester value	80-90
Sap. value	95-110
Unsap.	20-22%
Sp.gr. 20°	1.00

WAX CR.

This is a mixture of Montan wax and esterified wax S.

600 kg. Wax S, 60 kg. butylene glycol, 60 cc. conc. sulphuric acid and 60 cc. water are stirred together at 110°C. until the acid value falls to 37. 900 kg. deresinified Montan wax is then added and the whole mixed thoroughly.

The wax has the following characteristics.

Melting point	80-83°C.
Acid value	31-37
Ester value	84-98
Sap. value	115-130
Unsap.	13-16%
Sp. gr. 20°	1.00-1.01

WAX L.

This is similar to wax S. Deresinified Montan wax is oxidised as described for Wax S only using a total

of chromic acid equivalent to 142 kg. CrO_3 per 100 kg. Montan wax. 6000 l. of chromic acid solution is used in the first oxidation step as in Wax S and 1730 l., added in $1\frac{1}{2}$ hr. followed by $2\frac{1}{2}$ hr. stirring, in the second oxidation step.

The wax has the following characteristics:-

Melting point	80-83°C.
Acid value	127-139
Ester value	22-37
Sap. value	155-170
Unsap.	7-10%
Sp.gr.20°	0.99-1.00

WAX G.

This is a lightly bleached Montan wax.

600 kg. deresinified Montan wax is treated with 5400 l. of chromic acid added during 3 hr; stirring is continued a further 2 hr. The procedure is otherwise exactly the same as for Wax S. Care however must be taken during the washing with water only to boil very gently as the wax readily forms an emulsion with water.

The wax has the following characteristics:-

Melting point	82-86°C
Acid value	100-110
Sap. value	145-155

WAX O.

This is a derivative of wax S.

100 kg. wax S, 5.9 kg. ethylene glycol and 30 cc. of 20% sulphuric acid are stirred together at 110-115°C. until the acid value falls to 50-55.

3 kg. calcium hydroxide is then added slowly with good stirring and the reaction continued until the acid value is 12-14. Care is necessary during the addition of the lime to prevent undue foaming.

The wax has the following characteristics.

Drop point	102-106°C.
Acid value	10-15

Ester value	103-120
Sap. value	111-133
Unsap.	5-8%
Sp.gr. 20°.	1.03-1.04

WAX OP.

This is similar to Wax O and is made using 8.5 kg. butylene glycol in place of ethylene glycol as described for wax O.

The analytical characteristics are substantially the same as those of wax O.

WAX AD.

This is a derivative of wax G.

It is made as described for wax O using 100 kg. wax G. 7.6 kg. propylene glycol, 10 cc. 20% sulphuric acid, esterifying to an acid value of 35 and then reacting with 1.5 kg. lime to an acid value of 18.

OPPAU WAXES.

WAX S.

The procedure used at Oppau differs somewhat from that used at Gersthofen. 600 kg. Montan wax, in small flakes, is stirred into 2,120 kg. sulphuric acid at about 114°C. to form a thick emulsion. A 50% aqueous solution of 1600 kg. potassium dichromate is added over a period of 2½ hr. The temperature rises to 116°C. during the addition of dichromate and after it has fallen to 112°C. the pan is sealed and the reaction completed at 133°C.; the product is worked up as described before and the chrome is recovered as chrome alum, and sold as a tanning agent.

WAX L.

The above procedure was also followed for Wax L in the Oppau Works, using 1200 kg. of potassium dichromate for 600 kg. Montan wax.

WAX Z.

This is derived from wax L.

Wax L is mixed with 2.5% by weight of iron powder and the mixture heated at 330°C. until elimination of carbon dioxide and water is completed. The resultant ketone is hydrogenated at 400°C. with hydrogen at 200 atm using 1.5% of nickel carbonate-kieselguhr catalyst containing 20% nickel. The catalyst is used only once and the nickel recovered for re-conversion.

The wax has m.p. 100°C.

WAX OZK.

This product was used as a substitute for ozokerite but none had been produced since about 1940.

It is made by subjecting to the process used for wax Z, a mixture comprising:-

50 parts Montan Wax
40 parts hardened train oil
10 parts raw train oil

- The wax has m.p. 75°C.

APPENDIX 1.

The following shows the production figures for the more important I.G. waxes manufactured at Gersthofen.

<u>Wax Brand.</u>	<u>Metric tons per annum.</u>	
	<u>1937.</u>	<u>1943.</u>
CR	108	234
G	86	205
KP	31	154
KPS	-	136
L	258	1487
S	2095	1173
Spezial	202	527