REPORT NO. 8.

WESTFALIA SEPARATOR A.G. C22/2190

OELDE

Object of Visit To inspect these works and to see what new developments have been made.

Persons Interviewed Werner Habig (President)

Dr. Hugo Habig (Vice-President)

Condition of Works Practically undamaged.

Production This firm specializes in high speed centrifuges of the 'cream separator' or Laval type, and had pre-war a considerable export trade. The number of men employed was about 1,000.

The works has been specially laid out for the manufacture of high speed centrifuges, with specialised machine tools where necessary, and a first class tool room.

Milking machines and a special type of butter churn are also produced, although this manufacture is very much subsidiary to that of centrifuges.

The quality of work is excellent.

Technical Data The types of high speed separators built include:-

1. Standard small cream separators, hand and motor driven.

Technical Data (Contd.)

2. Large cream separators, motor driven.

3. Nozzle discharge type centrifuges for yeast or starch, and similar products.

4. Centrifuges for varnish, trichlorethylene, and other dry cleaning solvents.

5. A special type of centrifuge in which the separated solids are discharged intermittently by the upper half of the bowl, moving axially relative to the lower half.

Recommendations

That a British controlled firm making or considering making high speed clarifiers should inspect these works.

The installation of the complete plant in Britain under British contrel is worth considering.

REPORT NO. 9.

ESCHER WYSS. C22/2603

RAVENSBURG

Object of Visit — To inspect these works, particularly in connection with chemical plant manufacture.

Persons Interviewed — Major Stoffel (Director)

Herr Schwab (Chief of Commercial Dept.)

Condition of Works — Practically undamaged.

Production — This firm is associated with Escher Wyss of Switzerland. Their manufacture is :-

1. Water Turbines up to 70,000 k.W. maximum.

Secondary to Water Turbines are:-

2. Steam Turbines up to 10,000 k.W.

3. Spray Dryers of special design.

4. Paper Making Machinery.

The works are well equipped with machine tools and has its own foundry.

Technical Data — Centrifuges

These are of two types:-

(a) Horizontal Spindle Ploughing Centrifuges

Technical Data (Contd.)

with full width ploughs, and frequently with automatic control.

Parts of these machines were available for inspection.

(b) Horizontal Oscillating Piston Type Centrifuges, with continuous feed and discharge.

No machines of this type were available for inspection.

Spray Dryers

Each dryer has a pair of heated rotating cylinders.

The liquor to be treated is sprayed on to these cylinders, and the evaporated liquor taken away through ducting.

These dryers are used for concentrating milk and juices, and it is claimed that the low temperature of evaporation conserves the vitamin content.

Towards the end of the war Spray Dryers were given first priority in these works on the instructions of the Nazi Government.

Recommendations

(1) Centrifuges

That detailed drawings of the Escher Wyss Continuous Centrifuges be dispatched to Britain for examination.

(2) Spray Dryers

That a specialist in Spray Dryers is sent to examine the Spray Dryers at these works.

copy 1

FINAL REPORT No. 92
ITEM No. 22

PRODUCTION OF ACRYLONITRILE AT LEVERKUSEN PLANT OF I.G. FARBENINDUSTRIE

Cambron, A.

"This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement."

REC'D. JUN 1946
TIIC L.E. & L. S-C.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON • H.M. STATIONERY OFFICE

PRODUCTION OF ACRYLONITRILE AT LEVERKUSEN PLANT OF I.G. FARBENINDUSTRIE

Reported by

A.Cambron - National Research Council

Target No 22/1 (e)

BRITISH INTELLIGENCE OBJECTIVE SUB-COMMITTEE
32 Bryanston Square, W.1.

(1946)

10 p. incl. illus. & diagrs

TABLE OF CONTENTS

SUBJECT			Page
1.	Introduction	-----	1
2.	Part I -- HCN Generator	-----	2
	Part II -- Reaction	-----	2
	Part III -- Recovery of Acrylonitrile	-----	3
Appendix I	-- Photographs of HCN generator, of Reactor, and general view of plant.	-----	
Appendix II	-- Flowsheet of Reaction unit.	-----	
Appendix III	-- Flowsheet of Recovery unit.	-----	
Appendix IV	-- Operating data, Recovery unit.	-----	

Personnel of Team

A. Cambron - National Research Council

SUMMARY

The production of acrylonitrile from acetylene and hydrocyanic acid was one of the items at Leverkusen investigated by a team who visited that I.G. plant in April. The information obtained at that time was included in the C.I.O.S. Report released under File No XXIII-25. Additional process information has been obtained in the course of a later visit to the Leverkusen plant, and this has been included in the present report to supplement the information already available. The present report contains additional information on the acetylene-HCN reactor, and on the recovery of acrylonitrile. Flow sheets of these two operations have been obtained and are included in this report.

1. INTRODUCTION

The information contained in this report was obtained in the course of an inspection of the acrylonitrile unit with Dr.Ludwig, Director of the Intermediater Department, on September 11th, The development of this process at Leverkusen was expected to provide an important source of one of the essential chemicals for the production of synthetic rubber during the war. The full capacity of the Leverkusen plant, however, was never sufficient to meet requirements, and air raids in '44 and '45 reduced production to about half. In order to provide additional production it had been planned to erect plants similar in design and capacity to the Leverkusen plant at Ludwigshafen and Auschwitz (Poland), Construction of these plants had not begun when the war ended.

According to Dr.Ludwig the development of this process was based on original work done at Leverkusen by Dr.Boyer, who was director of the Research Laboratory there.

2. PART I

Hydrocyanic acid generator

A photograph in Appendix I shows a view of the first HCN generator installed at Leverkusen (left center). This consists of a tower, 2½ ft diameter and 30 ft long. This tower was replaced later by another tower about 15 in. diameter and of the same height. It was reported that it was found necessary to use a column of that height in order to free the sodium sulphate completely from HCN before disposal, The operation of the HCN generator has been described in the report mentioned above.

The HCN produced was liquified, and stored as in the liquid form in two brine jacketed tanks on the roof of an adjacent building until required. It was observed that all lines handling liquid HCN were brine cooled.

PART II

Reactor

A photograph in Appendix I shows a view of the upper part of the reactor, and a flow sheet of the reaction system is attached as Appendix II. Another photograph shows a general view of the Acrylonitrile plant, the reactor being shown at left centre.

Acrylonitrile is introduced into the reactor through a single opening at the bottom, HCN is introduced through openings in the reactor wall about 4 ft. from the bottom, but some HCN may also be introduced through the bottom, the depth of the contact solution in the converter is about 14 ft. the depth of the reactor being about 20 ft.

The composition of the cuprous chloride solution used as catalyst, as given by Dr.Ludwig, was as follows:-

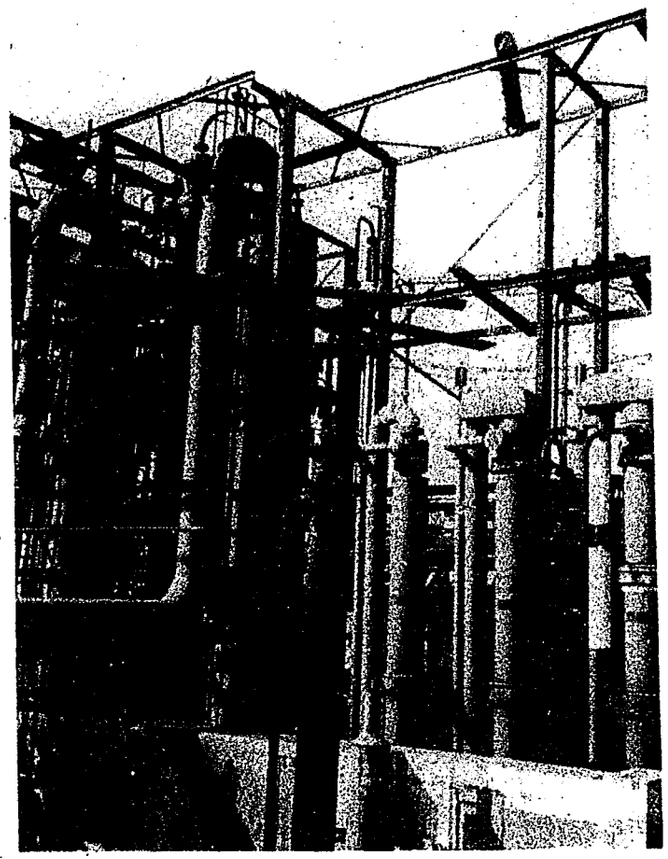
560	Parts	- Water
650	"	- Cu Cl
350	"	- NH_4Cl
20	"	- conc. HCL

This information is at variance with that in the previous report on the same plant, according to which the solution contained KCl and Na Cl but no NH_4Cl.

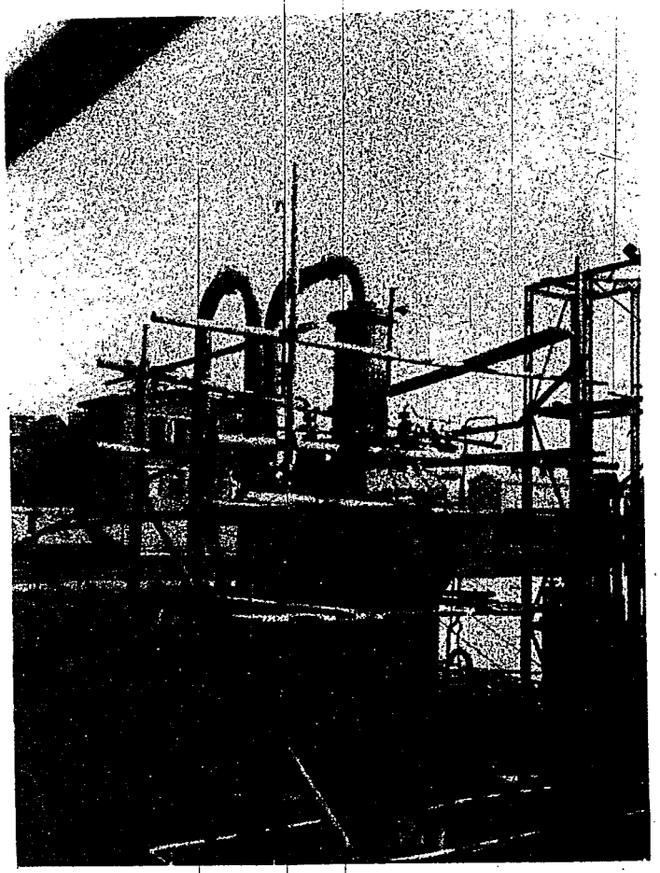
PART III

Recovery of Acrylonitrile

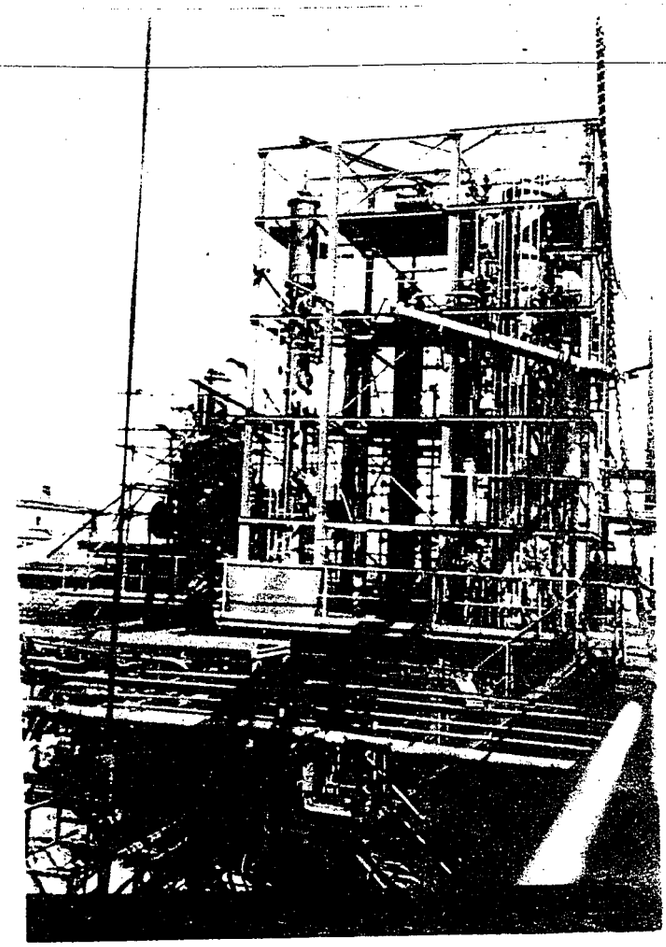
A flowsheet of the acrylonitrile recovery unit is attached as Appendix III, and a table of operating data for this unit is attached as Appendix IV, This table refers to the use of three fractionating columns, actually a fourth column has been used in the plant for fractionating the bottoms from the third column, and recover lacto-nitrile and other high boiling by-products.



HCN Generator



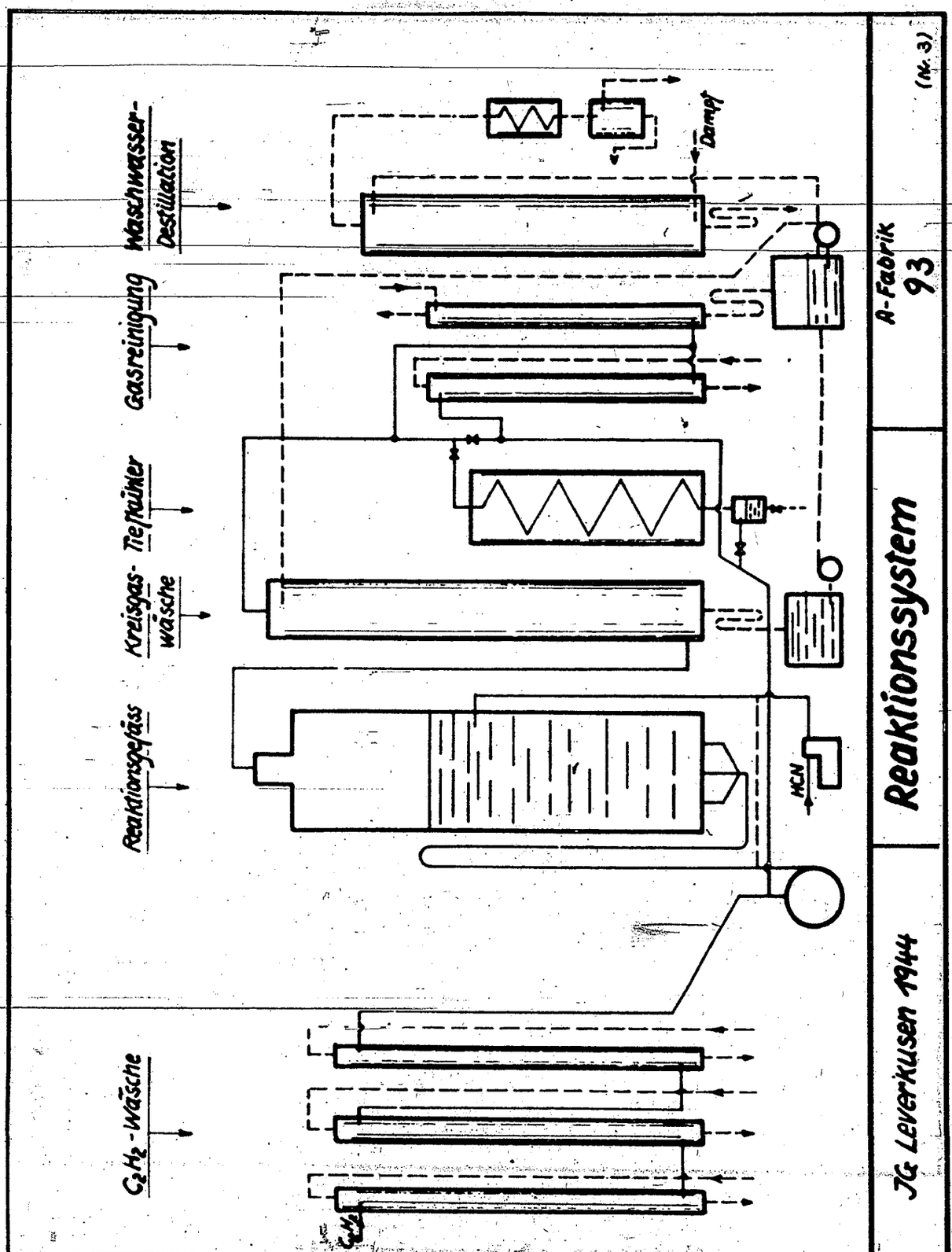
Reactor



General View of Plant.

APPENDIX II

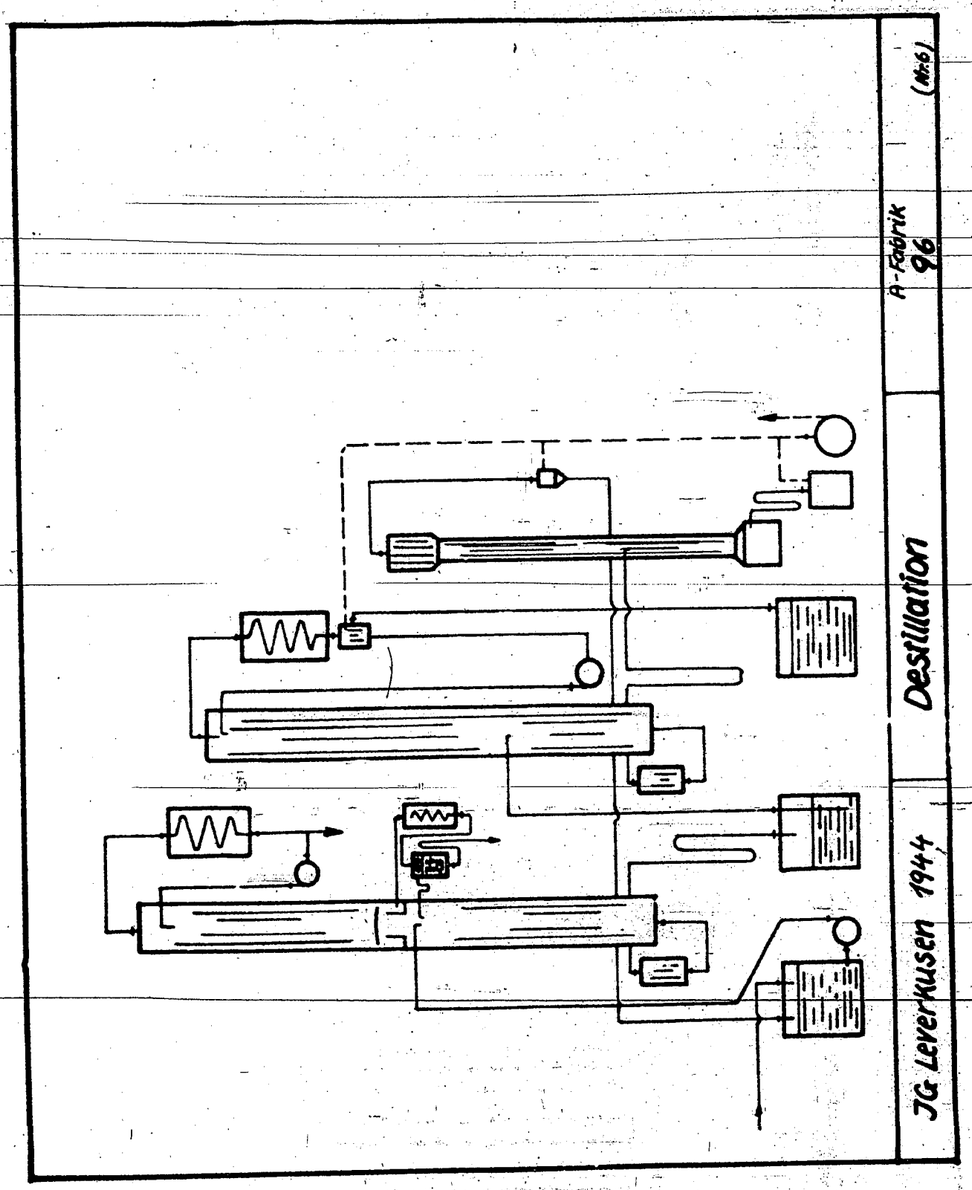
Page 1.



Flowsheet of Reaction Unit.

APPENDIX III

Page 1.



Flowsheet of Recovery Unit.

APPENDIX IV

Page 1.

Zusammensetzung und Fraktionen des Rohnitrils

	% vom Rohnitril	Sdp 760 Torr	Sdp. 140 Torr	
Azetylen Mova	0,5 3,0	- 5°	- -	Entlüftung 1te Kol.
Azetaldehyd Blausäure Chloropren	4,0 1÷2 1,0	21° 27° 59°	- -	Vorlauf 1te Kol.
Wasser als azeotropes Gemisch mit ACN	3,5	70°	-	Mitte 1te Kol.
Acrylnitril Dira	80,0 0,2÷0,4	77,5° 83÷84°	28°	Kopf 2te Kol. zu % %
(Acrylnitril)			28°	Kopf 3te Kol. zu 10%
Cyanbutadien Milchsäurenitril	4,0 2,0	135° 182°	81° 128	Sumpf 3te Kol.
JG. Leverkusen 1944				A-Fabrik 95 (Nr 5)

Operating data, Recovery unit.

BIOS FINAL REPORT No. 425
ITEM No. 22

Copy 1

A.G. Für Chemische Industrie, Gelsenkirchenschalke

(a controlled subsidiary of the I.G.)

MANUFACTURE OF CARBON BI-SULPHIDE.

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

Clayton, J. H.

BRITISH INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

LIBRARY
of the
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION
Bureau of Mines
SEP - 1946

LONDON—H.M. STATIONERY OFFICE

A.G. für CHEMISCHE INDUSTRIE, GELSENKIRCHEN-SCHALKE

(A controlled subsidiary of the I.G.)

Manufacture of Carbon Bi-Sulphide

Reported by:

J.H. Clayton - British Civilian,
Ministry of Supply.

BIOS Target No. C22/2193.

Miscellaneous Chemicals

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

9 pp. 3 fold diagrs.

TABLE OF CONTENTS

Subject.		Page No.
1.	Particulars of Target	2
2.	Condition of Plant	2
3.	Number of Retorts.	2
4.	General..	2
5.	Capacity.	3
6.	Output	3
7.	Retorts	3
8.	Sulphur	4
9.	Charcoal.	6
10.	Temperatures	6
11.	Fuel..	6
12.	Retort Replacement	7
13.	Carbon Bi-Sulphide Recovery and distillation	7
14.	Labour	7
15.	Efficiencies	8
	Flowsheet	
	Retort	
	Sulphur Feed Control	

A.G. für Chemische Industrie, Gelsenkirchen-Schalke

(A controlled subsidiary of the I.G.)

CARBON BI-SULPHIDE

1. Particulars of Target:

Date of visit:	12th, 13th & 19th October, 1945
Plant visited by:	J.H. Clayton - British Civilian.
Personnel interrogated:	Dr. Mueller, Technical Director Dr. Bolle, Works Manager Dr. Kettler, Commercial Director
Objectives:	The target was chosen to follow up information supplied by Dr. Jacob of Chemische Fabrik. Dr. Jacob, Bad Kreutznach to the effect that the Company was operating the I.G. design of carbon bi-sulphide plant.

2. Condition of Plant:

Plant not damaged and could be operated if gas was available. The plant had not been operated since early in 1945 and an inspection showed that a considerable general overhaul would be necessary before the plant could, in fact, be restarted.

3. Number of Retorts:

The plant consists of 5 settings, each setting containing 3 retorts, there being a few feet in between each setting, making 15 retorts in all.

4. General:

The firm had, until recently been run by Dr. Wissel, who died early in 1945, and both Dr.

Mueller and Dr. Bolle are newcomers to the firm and have never actually seen the plant in operation, which made a proper interrogation difficult. As far as was possible, the information supplied by these two gentlemen was checked by interrogating the foreman in charge of the plant.

The plant was built in 1938 and is laid out on very spacious lines and occupies, in total, an area of approximately 150 metres x 150 metres. The retort house itself is a lofty building with sufficient headroom to house an overhead crane for the removal of the retorts and has a dimension of approximately 100 metres x 25 metres.

5. Capacity:

The capacity of the plant is 9,000 tons per annum.

6. Output:

Actual outputs were:

1941..... 8,000 tons.
1942..... 9,000 tons.
1943..... 7,700 tons.

The output per retort per day is 1.5. to 1.7 tons, or 4.5. to 5 tons per setting. The output when the retorts are new is 2 tons per retort per day, this lasting for 6/7 months. The output falls to one ton per retort per day by the end of the life of a retort. The output is very dependent upon the quality of the sulphur (see below)

7. Retorts:

The retorts are cast steel of the following composition:

Carbon ..... 0.25 to 0.30%
Silica..... 0.3 to 0.4%
Manganese..... 0.6 to 0.7%
Phosphorous..... up to 0.05%
Sulphur ..... 0.03 to 0.05%

The steel is Siemen Martin 27 basic and is manufactured by the Ruhrstahl A.G., Gelsenkirchen. The retorts measure 381 centimetres in height, 210 centimetres on the long axis and 75 centimetres on the short axis and they are tested on fabrication up to 4 atmospheres. The weight of a retort with a single vaporiser (see below) is 7,885 Kg. and with the double Vaporiser is 8,385 Kg. The cost of replacing a setting of 3 retorts is 21,000 R.M.

The retorts are brick lined.

The average life of the retorts is 14 months, although during the war a much shorter life was experienced due to war difficulties. The retorts grow 6/8 centimetres and provision is made for this by not building in the retorts at the top and by the provision of an expansion joint in the CS_2 offtake pipe.

8. Sulphur:

Preferably good quality yellow sulphur is used on this plant, as otherwise difficulty is experienced in the purification of the liquid sulphur necessary to avoid trouble in the prevaporisers. Sulphur is melted in open cast iron pots, steam jacketted, of approximately 4 feet in diameter and 4 feet deep, provided with slow agitators. The liquid sulphur runs from these two melting pots into a short open trough heated with steam pipes from which it runs into a further steam jacketted pot provided with a coarse filter to remove the coarser extraneous matter. A filter consits of a steel pyramid sieve of 2 mm mesh.

From the filter pot it is plunged by means of steam jacketted pumps of the plunger type through steam jacketted mains to two gravel filters of approximate size 4 ft. in diameter x 5 ft. high. The flow through these filters is downwards and the size of the gravel of the top few inches is that of a fine sand; 3-ft. of coarse sand size and approximately 1-ft. of walnut size. These gravel filters are steam jacketted. From these gravel filters the liquid sulphur is again pumped through steam jacketted pipes to a small heated storage

vessel situated high in the retort house, from which it runs, by gravity, through a common feed main to the 15 retorts and is fed to the retorts through a feed control and measuring device.

The rate of sulphur feed is regulated according to the specific gravity of the crude carbon bisulphide produced, which, when the plant is running well, contains 4/5% of sulphur.

The rate of flow of sulphur is measured once per hour by weighing the amount of sulphur flowing through the feed control device in one minute.

The sulphur is fed into annular tubes built into either end of the retort. In this manner the molten sulphur falls the height of the retort within the tube and enters the retort proper at the bottom at a temperature estimated at 500°C.in the form of vapour. 12 of their retorts are of the new design with 2 annular tubes at either end of the retort, and 3 of their retorts of the old design with only one annular tube at the end of the retort. They had gone over to the two tubes on the basis of technical information supplied to them from the I.G. Works at Premnitz, and although according to the technical information supplied to them by Premnitz a small increased output was to be expected and having the 2 sulphur feeds and not bricks, they had found that this innovation only permitted them to increase their sulphur feed from 80 Kg. per hour of sulphur to 90 Kg. per hour of sulphur but they stressed that this result was not to be taken as too reliable as the change had been made under war conditions at a time when they were finding it extremely difficult to operate their plant at all.

With poor quality sulphur, difficulty is experienced with the filters which must be cleaned much more frequently and with the valves, particularly the feed control and measuring device, which block up.

It could usefully be stated here that the Company, as a subsidiary of the I.G., carried out no original work of its own and depended entirely upon Premnitz for technical information and designs.

9. Charcoal: The charcoal is purchased from Holzverkohlungs Industrie, A.G., a subsidiary of the Deutsche Gold- und Silberscheideanstalt.

The charcoal is made in externally heated retorts and is normally made of Beech or Birchwood charcoal and averages 3% ash. The charcoal is obviously of a good and reliable quality and little attention is paid to it by the firm. No activity test is employed and no activating materials are added.

The charcoal is pre-roasted, the heat being provided by the combustion of a small percentage of the charcoal itself. The charcoal pre-roasters are brick lined vessels provided with air suction for maintaining the fire and air blowers for venting (see sketch). The temperature of pre-roasting is 600/650°C.and the charcoal is at that temperature for approximately one hour, after which it is dropped into small storage wagons, each of sufficient capacity for one charge for one retort. The retorts are charged every four hours. The charcoal is fed hot to the retorts but there is provision in the form of bunkers for storing roasted charcoal, from which store it is fed to retorts cold.

The retorts are ashed every 10-14 days, an operation which takes two hours per setting.

10. Temperatures:
The external temperature is maintained at 800°C. to 850°C. the temperature being measured just above the gas flame. Great attention is paid to the temperature and 850°C. as an external temperature at the point mentioned above is considered as the absolute maximum and never exceeded.

11. Fuel:
The settings are heated by coke-oven gas, which is led into the settings through burners running the width of the settings between the retorts. The waste gases go away at 500°C. and are not utilised.

12. Retort Replacement:

It takes about 21 days to replace a setting and all 3 retorts are replaced if one retort fails, despite the thin dividing wall between the retorts.

13. Carbon Bi-sulphide Recovery and Distillation:

The carbon bi-sulphide produced goes into a common main, one main per setting of 3 retorts. This main is water cooled by water sprays inside and outside and the main sits in a water bath. The excess sulphur is deposited in this main and the main must be cleaned out every 24 hours. Approximately two-thirds of the carbon bi-sulphide condenses in this main. The gases are then sent forward to a refrigeration system in which they are cooled to minus 10°C. The gases from the refrigeration system contain between 350 and 400 grammes per m^3 of carbon bi-sulphide and are washed through a Feld washer, which strips them down to 0,0 grammes of the CS_2. The oil used in the washer is paraffin oil.

The Feld washer is manufactured by W. Feld & Company, Heckstrasse 77, Essen/Werden, and consists of a tower built in sections, in which there are eight revolving plates driven on a shaft. The plates revolve at several hundred r.p.m. spraying oil, which is run through independent feed pipelines on to the centre of each plate. In this manner a mist is formed and the oil striking the sides of the tower runs down and leaves the tower through a common outlet. The gases enter the tower at the bottom and leave at the top, completely free of carbon bi-sulphide. The CS_2 containing oil is sent to a stripping still where it is stripped completely of CS_2.

The crude CS_2 is refined by distillation in a column-type still, the operating temperature of which is 51/52°C.

14. Labour:

7 men per shift (3 shifts)	=	21 men
Day labourers	=	4 "
Total		25 "

This is for the production of 750 tons per month.

This excludes the foreman chemist and all office staff.

15. Efficiencies:

We are advised not to take the efficiencies during the war, as these have been seriously upset by war conditions. 1939 figures were supplied, which were as follows;-

Per 100 Kg. Crude CS_2;-

Sulphur (nett)	84.8
Charcoal	21.2
Gas	32.7 m^3
Power	0.8 k.w.h.
Water	0.1 m^3
Steam	19.6 Kg.

To purify the CS_2 are required:

Steam	15.9 Kg.
Water	0.1 m^3.

The loss of CS_2 over purification and distillation is 6% when the sulphur content of the crude is 4/5%.

Schnitt E-F

Schnitt A-B

Schnitt C-D

Die Breite der Platten ist den gegossenen Recorten zu entnehmen

20 Stück

2 Stück

Die Seitenflächen müssen gut aufeinander passen, sämtliche Kanten müssen rechtwinklig und scharfkantig sein

Die Innenflächen der Rasenrost sind besonders sauber und glatt zu ziehen.

Reinigungsstutzen muß an dieser Fläche anliegen! Achtung! Von Versand sind diese Maße genau zu prüfen, bzw. die Reinigungsstutzen anzupassen

Löcher anfasen

Text zur Ans. 2 u. 3 Die Plattenmassen sind in der Nähe verschieden lassen sich praktisch spielfrei in der Richtung der Platten-breite gegenüber der Nähe darf - eine gewisse Schräglage der Platten-ebene gegenüber der Rasenrostauflage ist zulässig. Soll aber der Ansatz der Rasenroststangen, die die Platten müssen so aufeinander passen, daß sie sich nicht über die ganze Länge der Platte gegenüber der Rasenrostauflage verspannen auf derartige Verspannungen ist zu achten. Die Entlüftung ist in Mastenrost einzubauen. Laufflächen ungünstig sind zu vermeiden. Löcher können Teile bewegen, sich mit merklichem Spiel hinein-

nach Schablone anreißen

Maße genau einhalten

zulässige Toleranz ± 5mm.

Stück	Benennung	Teil-Nr.	Werkst.	Zeich.-Nr.	Maß-Nr.	Stücklgst.
2	Platten ca 235 x 210 x 10					
20	Platten ca 770 x 210 x 10					
	Rasenrost					

Ruhrstahl Aktiengesellschaft
Gelsenkirchener Gußstahlwerke

Tag | Name

Maßstab 1:10

DIV. 33292

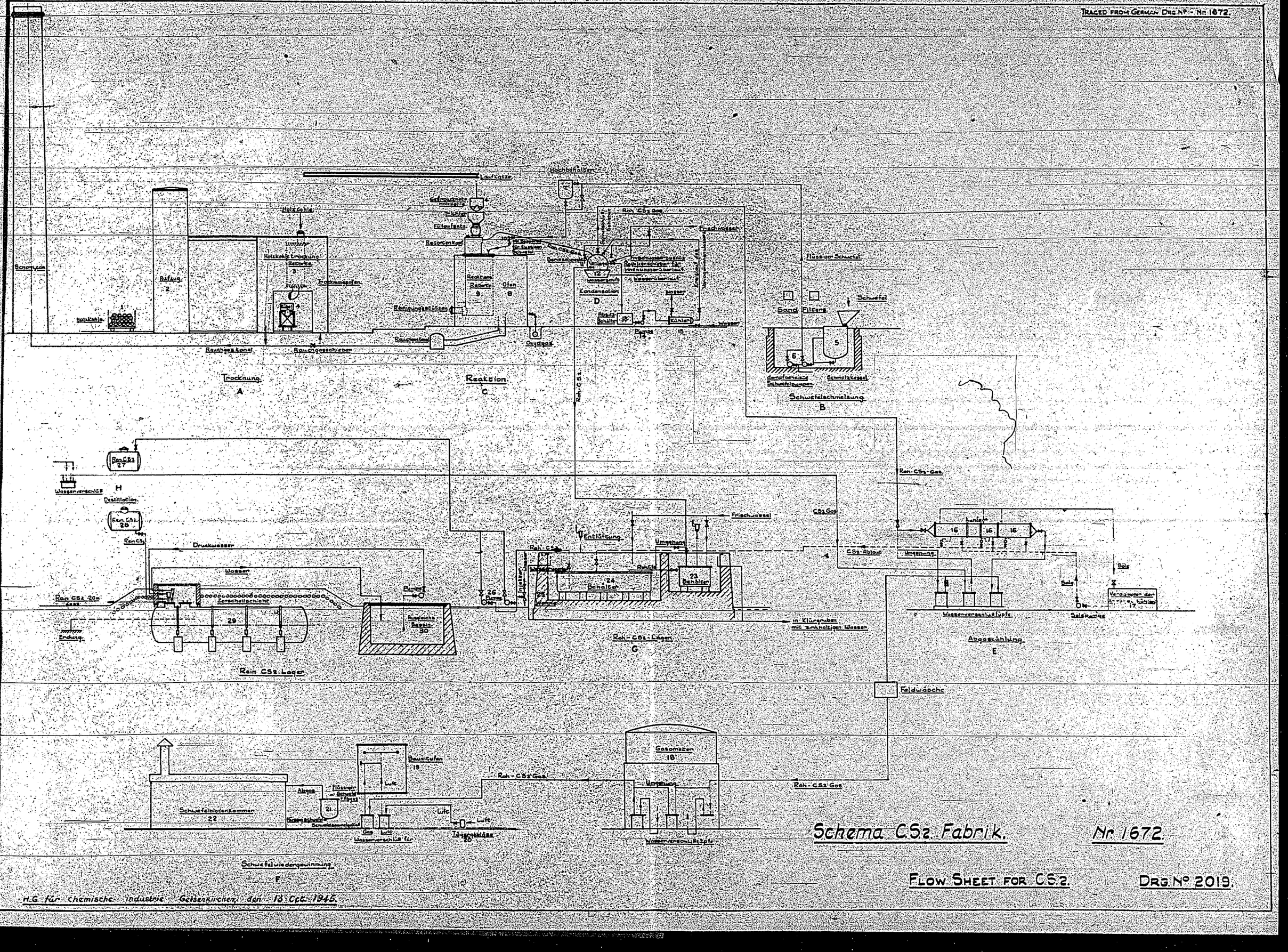
PS 55-0

Ersatz für PS 77-0

Ersetzt durch

DRG No 2011

TRACED FROM GERMAN DRG. Nº - Nr 1872.



Schema CS2 Fabrik. Nr 1672.

FLOW SHEET FOR C.S.2. DRG. Nº 2019.

H.G. für Chemische Industrie Gelsenkirchen, den 18 Oct. 1945.

TRACED FROM GERMAN DRG. NR. (NR. 672)

Schnitt A-B

Nahtl. Rohr 67 x 2,75 St
Din 2440

Dampfrohr Din 2441

Schliessweite 37

Nahtl. Rohr 108 x 3,75 Din 2440

Nahtl. Rohr 89 x 3,25 Din 2440

Mutt

Flügelmutter M4
Stiftschraube

Deckel aus Aluminium

Aluminium

Steigung gleich.

Kupferring

Kupferring 6 x 4
Ring aus Klingerit

Nahtl. Dampfrohr ¼"
Din 2441

Nahtl. Rohr 38 x 2,5 Din 2440

Nahtl. Dampfrohr ½"
Din 2441

Nahtl. Dampfrohr ¼"
Din 2441

Nahtl. Dampfrohr ¼"
Din 2441

Schr M4

Deckel aus Aluminium

C-D

Meßapparat für Schwefel M. 1:1

Chemische Industrie Gelsenkirchen den 16 Okt. 1945.

DRG. Nº 2020

Copy 1

FINAL REPORT NO. 341

ITEM NO. 31, 22

GERMAN CHEMICAL PLANT MANUFACTURE

Gobbing, J. H. W.

"This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement."

LIBRARY
of the
FOR[illegible]Y THETIC
LIQUI[illegible]ELS DIVISION
Bureau of Mines
SEP - 1946

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE
LONDON — H. M. STATIONERY OFFICE

GERMAN CHEMICAL PLANT MANUFACTURE

Reported by

Major J.H.W.Cobbing B. of T.

BIOS Trip No.1373

BIOS Target Numbers
C31/742, C22/2875

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

17 p. Illus.

TABLE OF CONTENTS

Subject	Page No.
Object of visit	1
General	1
Mixing Machine developments	1
Rubber Mixers and Sifters	2
Grinders	3
Capacity of Plant	3

Object of visit - To investigate the developments made in Mixing and Grinding Machines for chemical processes during the War, and to ascertain the general conditions of this plant at the present time.

Name of Target: WERNER & PFLEIDERER

Type: ENGINEERING WORKS (CHEMICAL)

Location: STUTTGART / FEUERBACH

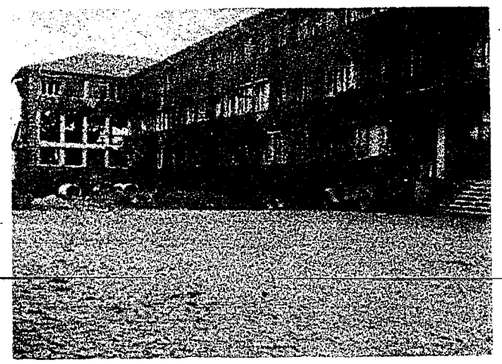
Physical condition: This target was bombed four times (not heavily) and with the exception of the damaged shops shown on photographs enclosed, the remaining shops have been repaired, with the result that an output of about 75% of pre-War production could be obtained.

(Photograph No.1)

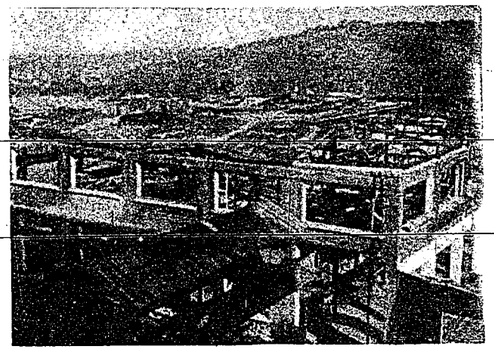
Mixing Machines. (Photographs Nos.2 and 3)

Single bladed Mixers and two-bladed Mixers have been built in a large variety of sizes up to 7,500 litres during the War and many different constructions have been developed as illustrated (Werner & Pfleiderer catalogue).

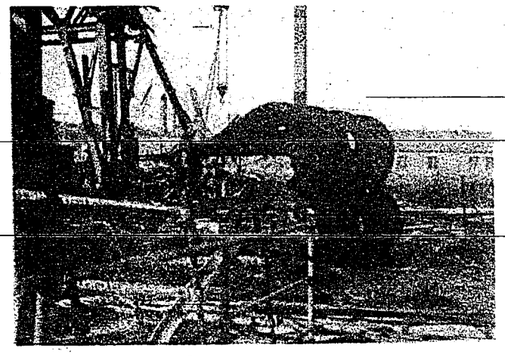
The construction of the single blade Mixers (referred to as SIMPLEX MACHINES) has been developed in size and there have been several different types of drive arranged, but the main form of the blade as illustrated on page 63 has not been altered. Very few of these machines have been made in special metals, such as stainless steel, but this has been due more to the shortage of this material in Germany than to any other cause. A number of their machines in various stages of completion now exist in this Works.



OFFICES



EXTERIOR

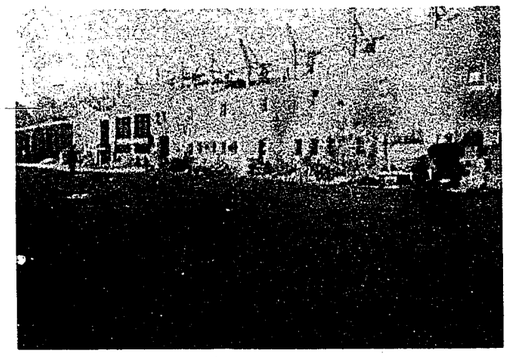


INTERIOR

SHOP No. 31.



INTERIOR

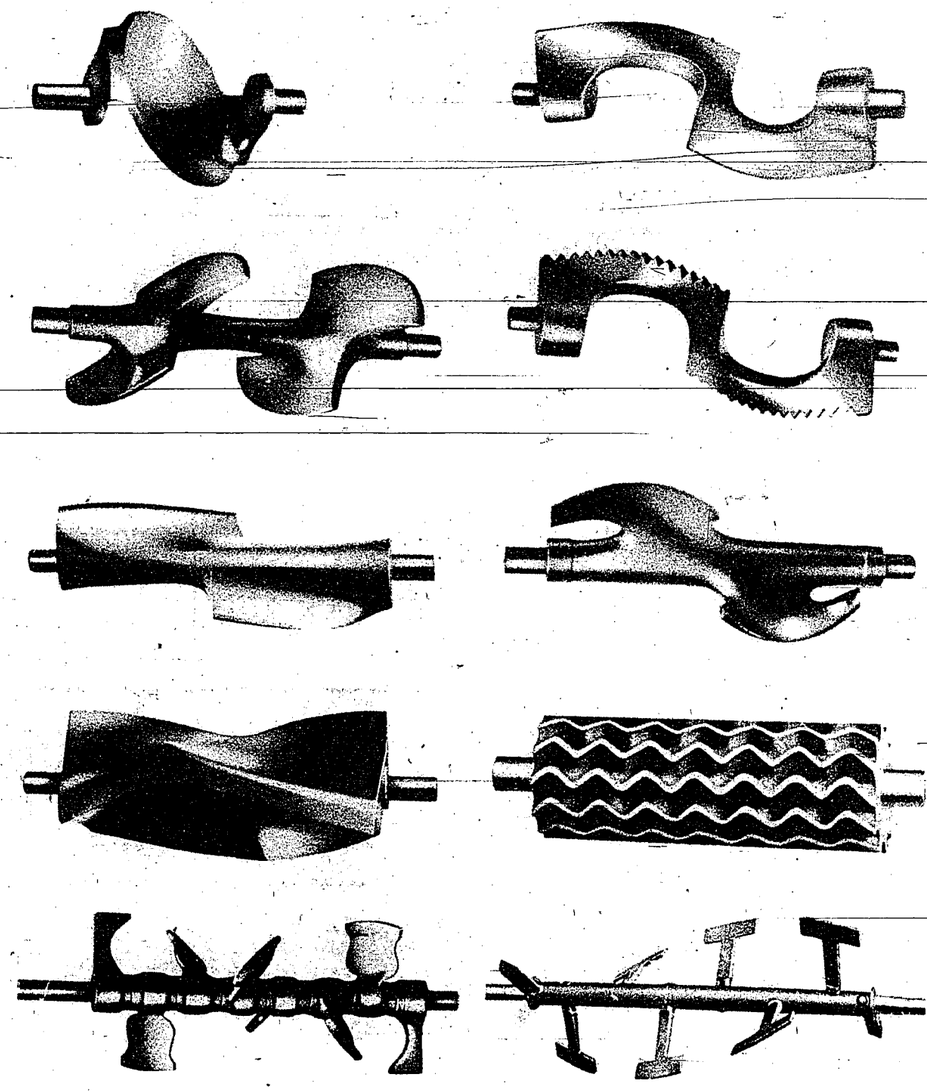


EXTERIOR

SHOP No.8.

CHIEF BOMB DAMAGE AT WERNER & PFLEIDERER . STUTTGART.

PHOTO No.1.



PAGE 63.

PHOTO. No. 2.

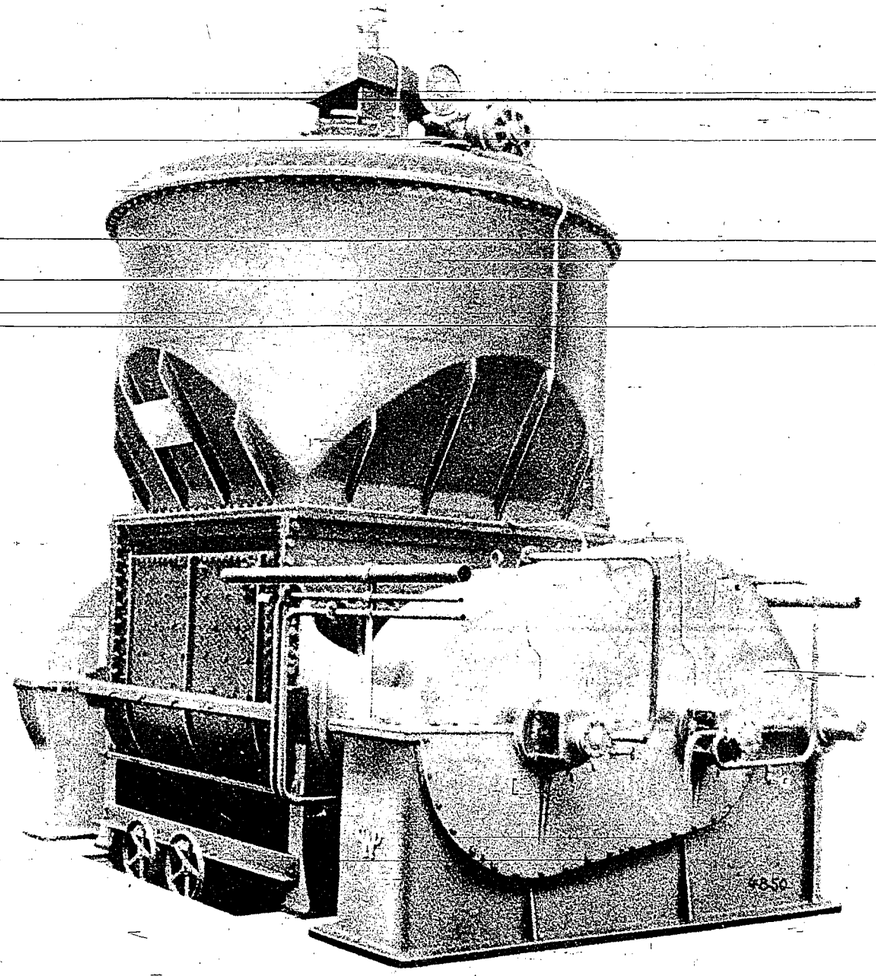


Photo No. 3.

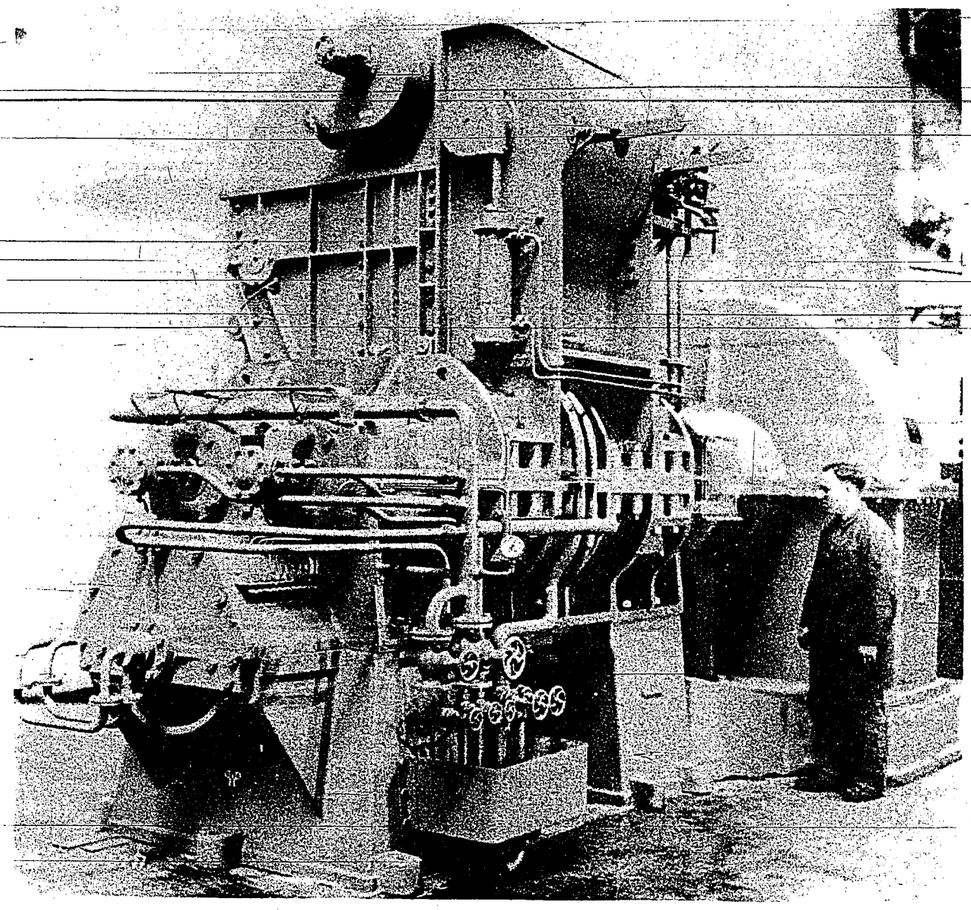


Photo No. 4.

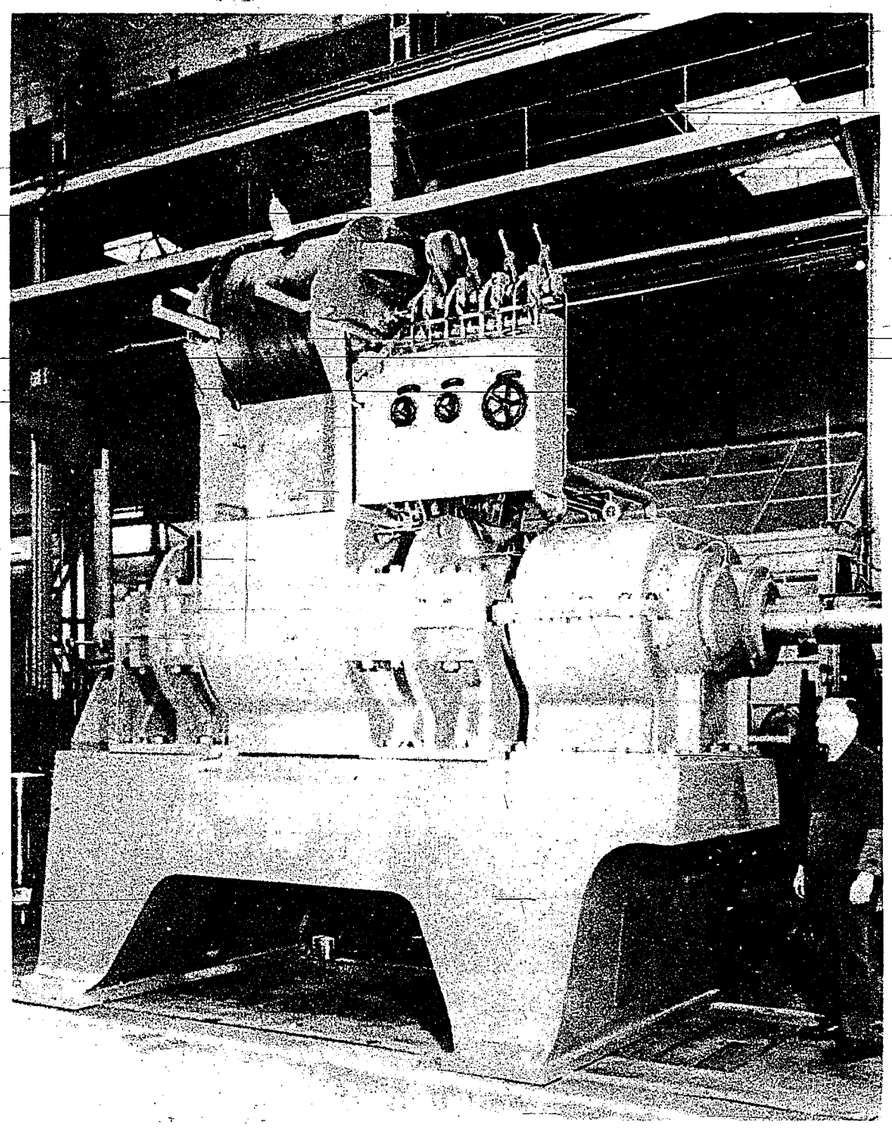


Photo No. 5.



Photo No. 6.

The two-bladed Mixers (known as the UNIVERSAL MIXERS) have been developed and built in sizes up to a total capacity of 15,000 litres woth a top stirring blade to keep the upper layers of the material being treated in a state of agitation. The smaller sizes of these machines have frequently been made in special metals such as bronze and stainless steel, but none of the constructions employed seem to be any advance upon the methods used by us at the present time. Certain of the driving arrangements have been modified and there is a general tendency to encase the gears in more substantial guards, usually made in cast iron.

The very large machines have mostly been made for the Rayon Industry and a very considerable number of these have been made during the War (a photograph of one of these is attached).

Rubber Mixers. (Photographs Nos.4 and 5)

A new Internal Rubber Mixer has been developed which contains many new features, but its efficiency can only be confirmed by actual tests. The new blade form, the method of feeding, the construction of the main body of the trough, together with many minor modifications in the construction of these machines, are new practice, and it is recommended that one of these machines be shipped to U.K. and tested out. (Two photographs of this machine are attached). A Laboratory size of this machine is also made. In addition a laboratory model (Size 5) with overhanging blades has been made.

Shredders for Rayon Industry. (Photograph No.6)

In addition to the standard Pulpers in general use in this country, a Disc Shredder has been developed and built in Germany during

the War. Outputs of 800 kgs. to 1000 kgs. of Alkali Cellulose per hour are obtained. It chiefly consists of one disc with hard serrated segments fitted to it revolving just above a stationary disc of similar construction. This method of treating Alkali Cellulose sheet has not been employed in the U.K. and it should be investigated on a practical scale. A Worm Shredder has also been made but so far no production machine of this type has been made. (An illustration of the Disc Shredder is attached).

Centrifuge Sifter (Photograph No. 7)

This is a machine for screening viscose and consists of a set of screens revolving outside baffles so arranged that the screens are kept clean throughout the passage of the viscose through the machine. A photograph of this machine is attached.

Rotary Mixer and Grinder.

A small liquid Mixer and Grinder of a conical type has been developed and only one of these has been put into operation. It consists of a stirrer placed at the bottom of the container with two rollers or rubbers revolving round the walls of the container. No real data as to the bahavious of this machine is yet available, as it is only in the development stage.

Printed for H.M. Stationery Office by W. R. Royle & Son Ltd., 36 - 209.

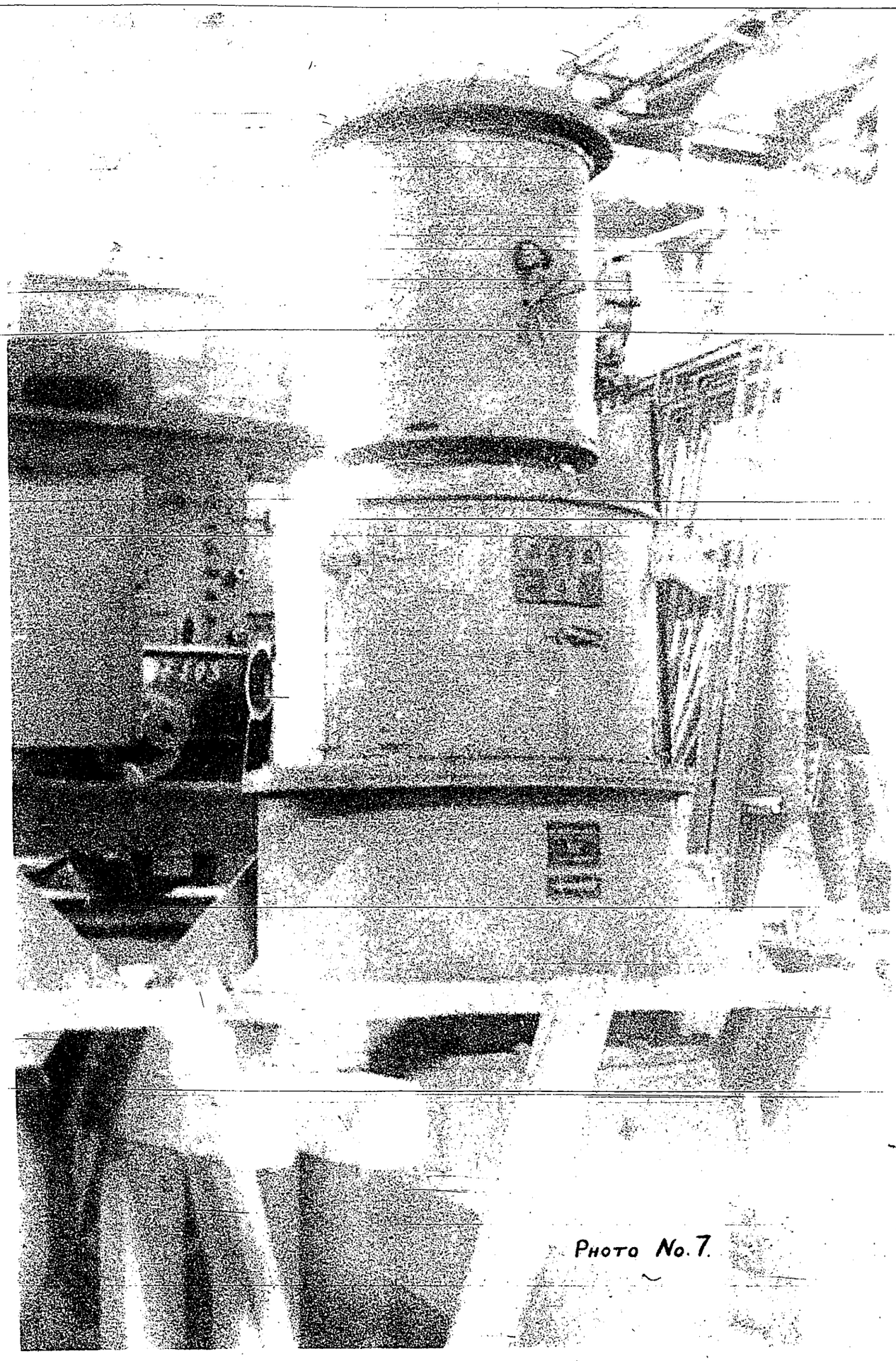


Photo No. 7.

Copy 1

BIOS Final Report No. 523

Item No. 30

CARL ALEXANDER MINE, BAESWEILER NEAR ALSDORF

THE DE-ASHING OF COAL BY FROTH FLOTATION AND ACID EXTRACTION AND THE RUHRWERKS COAL CLEANING PROCESS

Crawford, A.

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LIBRARY
LONDON—H.M. STATIONERY OFFICE
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION
Bureau of Mines
SEP — 1946

CARL ALEXANDER MINE, RAESWEILER NEAR ALSDORF.
The De-Ashing of Coal by Froth Flotation and Acid Extraction and the Rührwerks Coal Cleaning Process.

Reported by

A. Crawford,

Ministry of Fuel and Power.

BIOS Target No. C30/348

(1946)

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

1 Appendix, 4 Illus., 4 Folding Diags.

TABLE OF CONTENTS.

Subject	Page No.
REPORT I. - Visit to Carl Alexander Mine at Baesweiler near Alsdorf on February 14th, 1946.	
Introduction	1
Object of Visit	1
Summary	1
Personnel interviewed	2
General description of colliery	3
Coal Preparation Plant	3
Washery	3
Pre-flotation cells	4
Main flotation cells	5
Chemical extraction plant	6
Coking Plant	7
Cost of Processing	8
Conclusions	8
REPORT 2. - Interview with Dipl. Ing Mijo Matkovic.	
Introduction	8
Object of Discussion	9
Summary	9
Principle of process	9
Commercial application	10
Published reference in Glückauf	11
Motion films at Freiberg	12
Conclusions	12
Diagrams and photograph	End.

Personnel of Team

A. Crawford, Ministry of Fuel and Power.

REPORT I

Visit to Carl Alexander Mine.

Introduction.

The normal raw material for the manufacture of carbon electrodes employed in the electrolytic smelting of aluminium from bauxite is either pitch coke or petroleum coke. During the war both these substances were in short supply in Germany and a number of processes were developed to obtain a substitute for them from coal. In use the life of an electrode and the quality of the metallic aluminium produced depend to a large extent on the purity of the carbon forming the electrodes, particularly the anode. All the ash (especially any iron and silicon present) goes into the aluminium. Therefore a first essential in the use of coal was its freedom from mineral matter and other impurities.

This does not imply that processes for the preparation of ultra-clean coal have no value for purposes other than the manufacture of electrode carbon. It merely states the main force behind the German drive for ultra-clean coal.

Object of visit.

To obtain information regarding the process in use at the Carl Alexander mine for the separation of ultra-clean coal by froth flotation, and its subsequent treatment by acid extraction to remove soluble impurities.

Summary.

Coal dust sized below 0.75 m.ms. with an addition of lump coal milled to the same size is froth floated to a purity of 0.9 per cent of ash. Extraction with a dilute mixture of hydrochloric and hydrofluoric acids reduces this figure to 0.5. After washing to remove the acid the coal is coked at 1300°C and forwarded to the electrode manufacturers.

Personnel interviewed.

Director Vahle - mine manager
Dipl.-ing Matkovic - mine engineer.

N.B. Throughout this Report the word "ton" denotes the metric ton (2204 lbs.)

General description of Colliery.

The Carl Alexander mine was half German and half French owned (Roechling and Longwy). Its normal output is 2,200 tons per day but the surface buildings have suffered damage by shell fire and at the time of the visit the output was 900 - 950 tons per day. With the cessation of hostilities there is now no demand for extremely pure coal, and consequently the main flotation and the chemical extraction plants were not working. They last operated in September, 1944.

The coal mined consists of bituminous coking coal with a volatile content of 16 - 18 per cent except in seam D where the figure rises to 20 - 21 per cent.

Of the seams worked, N, P, O and D, the latter is the most important as it yields a high percentage of low ash coal. Table I. shows the characteristics of the seams:-

Table I.

Seam	D	N	P
per cent ash.	per cent yield.	per cent yield.	per cent yield.
0.3	2	0	0
0.3 - 0.4	4	0	0
0.4 - 0.5	5	0	0
0.5 - 0.6	8	2	0
0.6 - 0.7	10	4	0
0.7 - 0.8	12	8	0
0.8 - 0.9	14	10	0
0.9 - 1.0	15	11	4
- 1.0	30	65	96

Whereas seam D is able to give a theoretical yield of 70 per cent of coal containing less than 1.0 per cent of ash, seam N yields only 35 per cent and seam P is unuseable.

For this reason the underground workings were arranged to give a preponderance of seam D in the mine output. In addition the preparation plant was arranged so that lumps of seam D collected from the hand-picking belts could be crushed (to 0.75 m.m's) and introduced into the main flotation system. An attempt was made to keep the

proportion of crushed coal down to the bare minimum for successful operation since lumps commanded 18 marks and fines only 13 marks per ton. Three tons of lumps yields 1 ton of pure coal so the final coked product costs 20 marks more per ton from lumps than from fines.

Coal Preparation Plant.

This section of the report should be read in conjuction with the flow sheet to which the bracketed numbers refer.

Washery.

The washery can conveniently be divided into two parts, a normal part for making coking coal and a special part for making electrode coal.

The raw coal is screened at 80 m.m. the oversize being dealt with by hand-picking. The under-size is again screened at 30 m.m. and 10 m.m. giving 80 x 30 m.m. nuts cleaned in jig (1) and 30 x 10 m.m. nuts cleaned in jig (2). Wet screening of the 10 x 0 m.m. fraction on high speed pulsating screens (5) separates a 10 x 0.75 m.m. product cleaned in jig (3) and 0.75 x 0 m.m. coal which passes to the pre-flotation cells. Jig (4) takes middlings from the first three jigs and provides boiler fuel, or the washed middlings may be mixed off with the coking smalls.

Pre-flotation cells.

These consist of 19 cells similar to the Mineral Separation type and manufactured by Schuchtermann and Kremer-Baum of Dortmund. In addition to the main feed of 0.75 x 0 m.m. coal which contains 20 - 25 per cent ash the pre-flotation unit receives settlings from the washery service cone (6) and the discarded coal from the main flotation unit via a thickener (7), a pump (8) and a high speed pulsating screen fitted with 0.75 m.m. mesh (9).

The cells are arranged in line, the first three yielding about 25 per cent of the input at an ash content of 4 per cent, (at 21 tons per hour of dry solids this forms the greater proportion of the feed to the main flotation cells), 45 per cent is separated at an ash content of 6 - 7 per cent and is vacuum filtered at (10) before it is added to the normal coking coal; and the remaining 30 per cent proceed by way of a 0.75 m.m. oversize screen (11) to the stone tip. These rejects contain 70 per cent ash.

The flotation oil used is beech wood tar oil (Buchenholtzteerol) and this is added to the entering feed. Sometimes it is also necessary to add a little oil in the later stages.

Main Flotation Cells.

There are 96 main flotation cells plus 20 standby cells, arranged in groups of four.

The circuit is a little unusual and is due to Dr. Biesel a former employee at Carl Alexander. Patent rights have been granted to the colliery company under German patent No. DRP 668720. Briefly the arrangement is as follows:- froth from the first cell is transferred to the second by a bucket elevator; that from the second cell to the third and so on. Froth from the pre-flotation unit is therefore 4 times re-floated in the main flotation unit. Tailings from the third and fourth cells are combined and re-circulated to the first cell, and the discard from the first and second cells is removed and returned to the pre-flotation unit as described under that heading.

As well as the 21 tons per hour input of pre-frothed dust, the main bank of cells receives a quota of 5 tons per hour of crushed lumps from seam D. These are hand-picked and contain not more than 4 per cent ash; hence it is unnecessary for them to pass through the pre-flotation cells. Crushing of the lumps is effected by a jaw crusher (12) swing hammer crusher (13) and coarse, medium and fine roll crushers (14), the final size being nominally 0.75 x 0 m.m. It will be noted that over-size is picked up by a 0.75 m.m. screen from the coal discarded by the main flotation unit. This oversize is crushed in the wet state in a ball mill (15) and returned to the main flotation unit.

In the four stages of re-flotation the ash content is reduced from 4.0 percent in the feed to:-

	Ash content (dry basis)
Stage I	2.5
" 2	1.8
" 3	1.1
" 4	0.9

From the 26 tons per hour introduced, 12 tons per hour are obtained with the lowest ash and are recovered by filtration on rotary disc filters (16), before proceeding to the chemical extraction plant. This corresponds to about 80 percent of the possible yield predicted by laboratory float and sink tests.

Chemical Extraction Plant.

The chemical extraction plant was covered by German Patent No. D.R.P.B. 185549 VI b/1a. Thirteen acid extraction pots had been constructed of which ten had been in use. They each measured 3 metres in diameter and 6 metres in height, with conical shaped bottoms tapering to a plug hole.

The outer lining of the pots was in re-inforced concrete whilst the inner lining, in contact with the acid, consisted of accurately moulded and tightly jointed carbon blocks cemented in position by pitch. Siemens Planierwerke of Berlin Lichterfelde mould the blocks from the purest coal made at Carl Alexander, employing pitch as a binder. In manufacturing the blocks the final operation is stated to be carbonisation at 1500 - 2000°C.

These blocks are 45 m.m's thick, and several shapes are employed to line the pots internally and also to form an arched roof. A pipe of 75 m.m's bore and 55 m.m. walls moulded from the same material, conducts steam into the acid liquor for heating purposes.

The ratio of coal to solvent liquid is 1 : 2.

The solvent is prepared by mixing in the proportion of:

2 k.gm. hydrofluoric acid (40 per cent acid by volume)
4 k.gm. hydrochloric acid (70 " " " " ")
200 k.gm. water. No evidence was obtained of the use of any other acids beyond those described.

The contact time is 1 hour at 100°C; the heat being supplied by blowing in live steam.

After filtering to remove the coal the acid is said to be spent and almost neutral; it was therefore discarded. Acid resistant filters are necessary however, and rubber lined disc filters (17) supplied by Firma Wolff of Buchau were employed. Acid proof filter cloth for these was prepared from synthetic plastic material named "Spalatite", a product of I.G. Farbenindustrie.

Leaving the rubbered filters the still acid filter cake was stirred in water and filtered again on disc filters of the normal type, fitted with phosphor bronze wire cloth.

At this stage the filter cake contained 25 per cent moisture which was too wet for carbonisation. A portion was therefore dried in a Haas horizontal rotary dryer, and added back to the remainder so that an average moisture content of 18 per cent in the mixture was attained.

On leaving the chemical extraction and de-watering processes the ash content of the coal is 0.5 per cent on the dry basis. The advantage of the acid extraction process is that the effective yield at 1.1 per cent ash in the froth flotation circuit can be adhered to. Reference to Table 1. will show the very low yield of 0.5 per cent ash coal obtainable by float and sink methods alone.

Coking Plant.

The coking plant is of normal type consisting of a bench of Otto underjet ovens constructed in silica brick to withstand flue temperatures of 1400°C. A high coking temperature is required to counteract the effect of high moisture in the charge, to reduce the volatile matter in the coke to 0.5 per cent, and to yield a coke of high electrical conductivity.

The ovens are 9 metres long x 3 metres high x 400 m.m's wide, and a charge is carbonised in 24 hours the maximum temperature attained being 1300°C.

Hand quenching of the coke is carried out carefully so that the moisture in the final product is 0.5 percent.

A yield of 6,000 tons per month was obtained with an average analysis of :-

	per cent
Moisture content	0.5
Ash content	0.65
Volatile matter	0.5

As work was continuous during 24 hours for seven days per week the hourly capacity is

$$\frac{6,000}{24 \times 30} = 8.4 \text{ tons per hour (electrode coke)}$$

The production of normal coke at the plant was about 1,000 tons per day.

It was stated than no deleterious effect of halogen acids on the refractory oven walls had been observed, and it was claimed that 100 parts of electrode coke contained

0.11 parts of silicon (as Si)
0.12 parts of iron (as Fe)

the remainder (0.42) being mainly alumina.

Confirmation of this statement in respect of the iron content of the coke was obtained from a separate source but the claim for the silicon content appears to be exaggerated. Messrs. Greisheim - electrode manufacturers - report the ash analysis of the Carl Alexander coke taken over a period of a month to be as follows:-

Table 2.

Average Analysis of Ash from Carl Alexander. Electrode Coke by Greisheim over period of 1 month.

		per cent
Total ash content.		0.6 to 0.7
Silica	SiO_2	46.12
Ferric Oxide	Fe_2O_3	15.32
Alumina	Al_2O_3	23.65
Lime	CaO	3.92
Magnesia	MgO	0.50
Titania	TiO_2	3.90
Sulphate	not determined	-
Alkalies	" "	-
		93.41

Cost of Processing

Unfortunately detailed process costs were not available owing to documents being destroyed in the blitz. The following information was collected:-

1. Cost of crushing plant, main flotation and chemical treatment plant and all accessories ---------- 5×10^6 marks.
2. Labour (excluding jig washer pre-flotation cells). 85 men per day (excluding coking) 125 men per day (including coking)

3. Power. 1100K.w./hr. for jigs and pre-flotation unit.
1000K.w./hr. for mills, main flotation, acid extraction and coking plant.

4. Water. The water requirements are high and a plentiful supply must be available. For the whole washery and pure coal plant the consumption was 450 cu. metres per hour (1650 gallons per minute).

5. Selling Price. The price for electrode coke was fixed at 90 marks per ton.

Conclusions.

Despite the fact that arrangements were in hand to increase the production of electrode coke from 6,000 to 10,000 tons per month, the writer is of the opinion that the whole scheme is far too costly to be even considered under normal circumstances.

More-over the electrodes produced from coke have a different structure from those prepared by coking pitch. Broadly speaking micro photographs indicate pitch coke as having a cellular structure arising from the expansion of a molten mass by internal gas evolution. The cell walls are dense and thick. On the other hand micro photographs of coke produced by carbonising coke from pure coal with an admixture of a pitch binder give the impression of discreet particles fritted together.

At any rate the electrodes produced from pitch and low ash coke were not up to the standard required, and the practice finally adopted was to blend pitch, Pott Broche extract, and coke from pure coal to obtain the desired qualities in the finished article.

It therefore seems unlikely that the de-ashing of coal by acid extraction will have any wide application at the present time, if ever.

Report 2.

Interview with Dipl. - ing. Mijo Matkovic.

Introduction.

Dipl. - ing Mijo Matkovic was the chief engineer at Carl Alexander colliery having replaced Dr. Biesel, as

explained in Report I. He is of Czech origin.

Matković was of the firm opinion that the chemical extraction process was a costly extravagance. He thought that it was possible to recover pure coal more cheaply by a new method of coal cleaning described as the Ruhrwerksverfahren.

Object of Interview.

To obtain details of the process referred to by Matković.

Summary.

The Ruhrwerks process of coal cleaning, applicable to sizes below 0.1 m.m. depends on centrifugal force for separating materials of different specific gravities. With metalliferous ores 93 per cent of the theoretical yield at any desired S/G is claimed; with coal the corresponding figure is about 78 per cent.

Principle of Process.

(See diagram to which the bracketed numbers refer). A Cylindrical cell fitted with four fixed baffles (1) has a propellor or stirrer (2) arranged at its lower extremity. Above this a set of annular rings (3) of semi-circular cross section are arranged. The latter can either be submerged in the liquid in the cell, or withdrawn from it. Both the rings and the stirrer rotate at sufficiently high speed to bring centrifugal force into action.

The heavier particles tend to accumulate on the stationary walls of the cell but are constantly flung back into the interior by the action of the fixed baffles. With the rings submerged some of the heavy particles are trapped on the innerside and by withdrawal of the rings are removed from the liquid.

In the raised position the rings are washed clean by a jet of water and the heavy particles caught in a fixed launder terminating in an outlet (4). The lighter particles remain in suspension in the cell.

In use the material to be cleaned is crushed to 0.1 m.m. and suspended in water. A continuous flow is maintained through the cells which may be connected in series or parallel as in the case of froth flotation practice. The rings are continually raised and lowered the time submerged being 30 seconds.

The process was originally devised by Profs. Neunhoffer of Breslau and Grunder of Freiberg for oxide ores which were difficult to treat by froth flotation. Matkovic did the experimental work at Freiberg. He claims that where the divergence in specific gravity of concentrate and gangue is relatively wide, as in the case of metalliferous ores, a yield of 93 per cent of that predicted by theory is attainable. With coals the corresponding figure is 78 per cent.

Dr. Meyer of the Bergbau-Verein, Essen-Heisingen subsequently supplied the following data regarding a laboratory scale test on coal from the Konigin Elizabeth mine:

Raw Coal:	7.3 per cent ash
Crushed to:	0.5 m.m.
Coal water ratio:	1 : 6.
Stirring time	2 Mins
Operation repeated	20 times
Speed of Stirrer	300 revs. per min.

Results.

49.5 per cent yield	0.96 per cent ash
46.6 " " "	12.97 " " "
Difference	Due to loss of fine coal in water.

Remarks. These results could be improved upon by finer grinding and the use of more than one cell.

Commercial Application.

Messrs. Krupp-Gruson of Magdeberg handle the patent rights of this process and have erected two large scale plants as follows:-

1. A plant for cleaning coal at the Grube Donnersmark at Beuthen, Upper Silesia; which separated coal of 0.2 per cent ash content, confirming the laboratory scale tests.

2. A plant for recovering arsenical pyrites belonging to W. Guttler, Reichenstein, Lower Silesia.

Information regarding the capacity of these plants was not available.

Published reference in Gluckauf.

So far as is known the only published reference to this method of cleaning appeared in Gluckauf, vol.80., 1st April, 1944, No. 13/14,page 139. A translation is as follows:-

"Professor Grunder spoke about the stirring blade process for the preparation of the finest sizes of ore and coal. This process is a wet mechanical process, especially (suitable) for the finest sizes, in which the pulp is brought to a cell containing a stirring propellor and put into rotation. By the centrifugal force developed and by the sinking of a basket the heavy particles are trapped. They are lifted from the pulp and the lighter ones remain in the pulp. The process is used in such cases where other mechanical processes e.g., froth flotation, are insufficient.

The process was invented by dual experiments with Professor Neunhoffer,of Breslau, (the holder of the patents), by using the so-called Breslau bell shaped stirring apparatus in which the pure ore particles gave a deposit. An automatic device had to be developed to take out these deposits.

For this purpose Professor Neunhoffer devised a catching basket of rings, with openings between the rings, which is submerged in the pulp, and lifted after a certain time (30 - 40 secs.) in order to spray out the concentrate with water sprays.

There are two different pots or containers, the first being Neunhoffer's fitted with ribs to deflect the heavy particles into the interior of the container. Afterwards Professor Grunder developed a parabolic pot in which there are no ribs. This avoids turbulence and the pulp rotates in the form of a parabola. Generally it can be said the first gives the better enrichment but the lower yield and the second the better yield but the lower enrichment.

At Freiberg different laboratory tests were made with these devices which gave satisfactory results. Krupp-Grusonwerke have taken over the process for commercial application. At present it is not yet possible to say anything about its use in commercial plants.

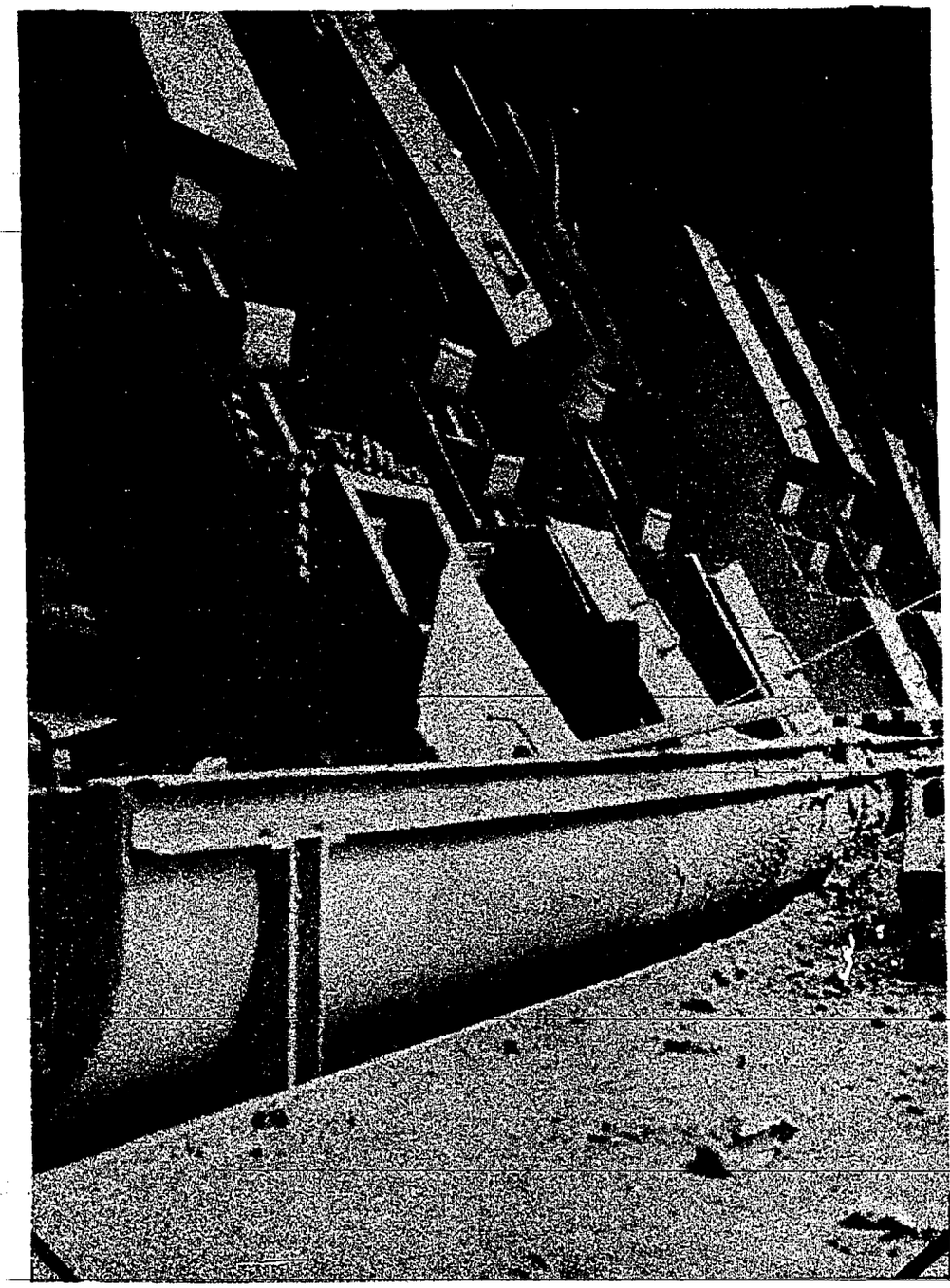
Professor Grunder showed some films after the paper".

Motion-films at Freiberg.

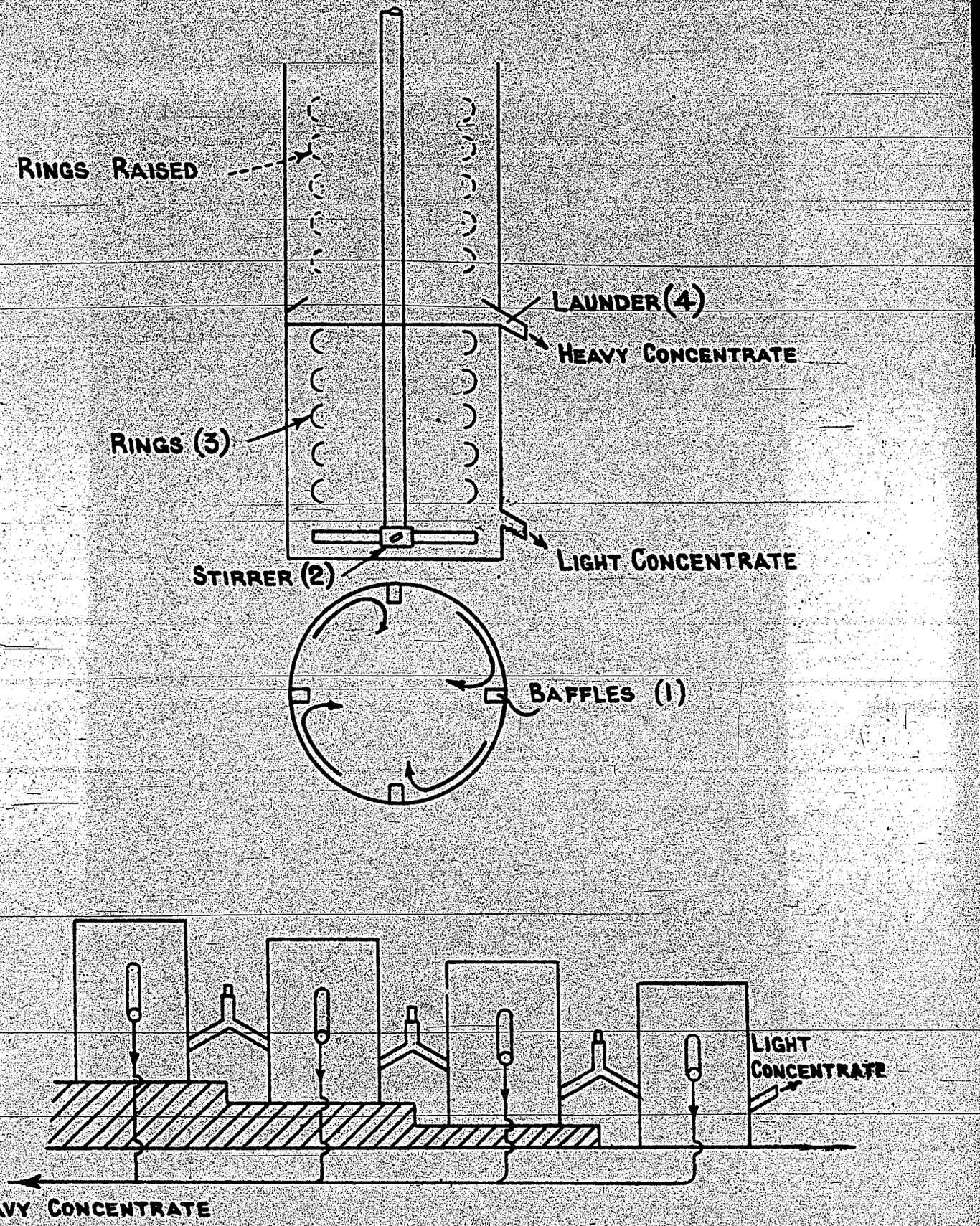
Professor Grunder is described as an expert on making motion films of coal cleaning processes showing the principles involved. About 35 to 40 films are available at Freiberg dealing with various methods of coal cleaning. Amongst these are 3 or 4 dealing with the Ruhrwerks process.

Conclusions.

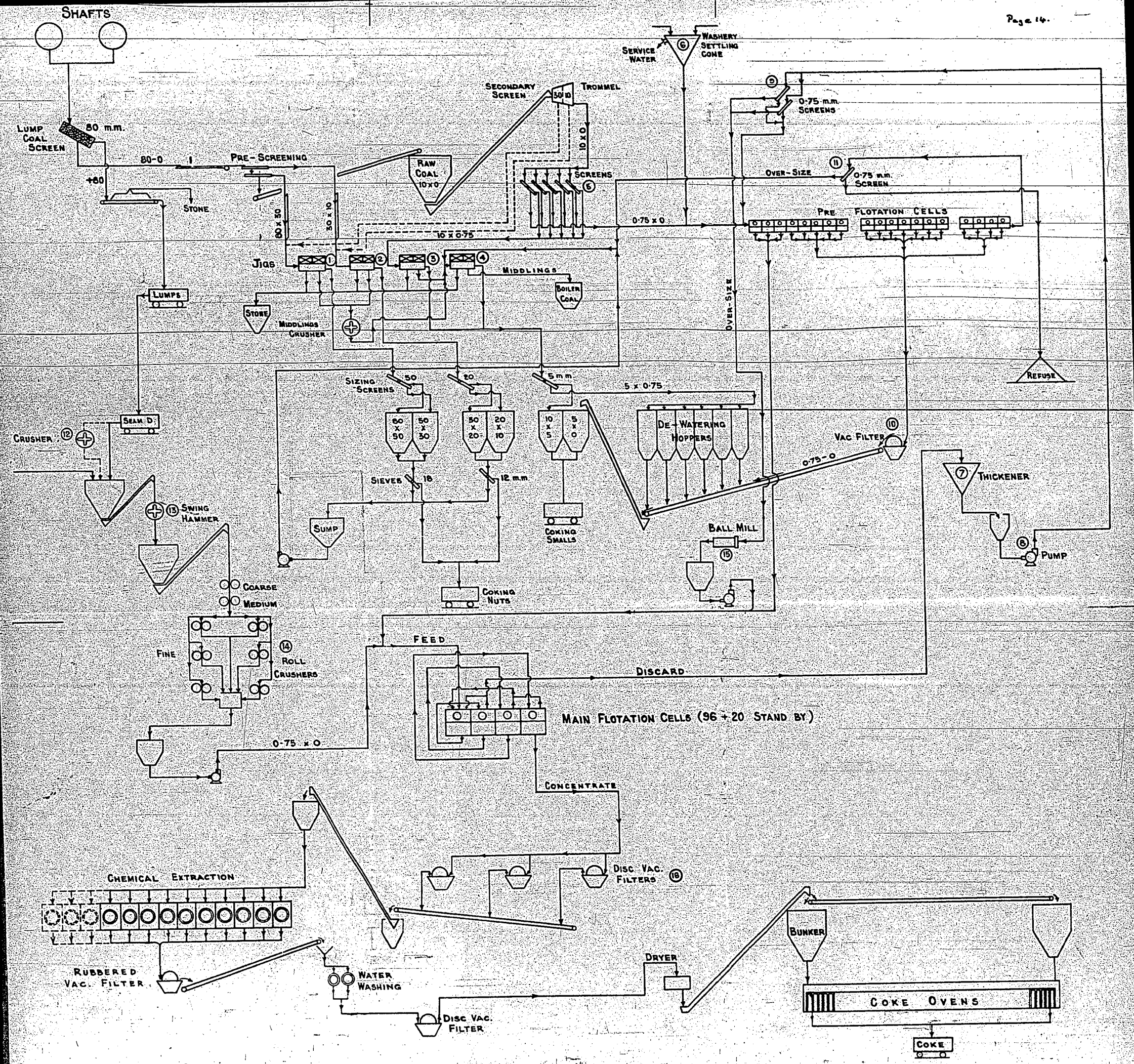
This process appears to have definite possibilities and warrants further investigation.



FROTH ELEVATORS ON FLOTATION CELLS, CARL ALEXANDER MINE, BAESWEILER.



RUHRWERKS PROCESS
DIAGRAM — NEUNHOFFERS ARRANGEMENT



Preparation of Ultra-clean Coal

CARL ALEXANDER

Baeswieler

Copy 1

BIOS Final Report No. 522
Item No. 30

I.G. FARBENINDUSTRIE A.G., HÖCHST

THE DE-ASHING OF COAL BY COMBINED JIG WASHING, FROTH-FLOTATION, AND EXTRACTION WITH CAUSTIC SODA

Crawford, A.

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

FOREIGN SYNTHETIC LIQUID FUELS DIVISION
Bureau of Mines
SEP - 1946

I.G. FARBENINDUSTRIE A.G., HÖCHST

The De-Ashing of Coal by Combined Jig Washing, Froth - Flotation, and Extraction with Caustic Soda.

Reported by

A. Crawford,

Ministry of Fuel and Power.

BIOS Target No. C30/188

(1946)

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

3801

A

13 p. 2 fld diags.

TABLE OF CONTENTS

Subject	Page No.
Introduction	1
Summary	2
Personnel interviewed	2
Outline of Process:	
Jig Washing	3
Froth Flotation	3
Chemical Extraction Process	5
Effect of Treatment on Coal and Coal Ash	7
Coking	7
Cost of Processing	8
Conclusions	11
Diagrams 1 - 3	End.

Personnel of Team

A. Crawford, Ministry of Fuel and Power.

The De-ashing of Coal by combined Jig Washing, Froth - flotation, and Extraction with Caustic Soda.

Date of visit. 19th February, 1946.

Introduction.

The normal raw material for the manufacture of carbon electrodes employed in the electrolytic smelting of aluminium from bauxite is either pitch coke or petroleum coke. During the war both these substances were in short supply in Germany and a number of processes were developed to obtain a substitute for them from coal. In use the life of an electrode and the quality of the metallic aluminium produced depends to a large extent on the purity of the carbon forming the electrodes, particularly the anode. All the ash (especially any iron and silicon present) goes into the aluminium. Therefore a first essential in the use of coal was its freedom from mineral matter and other impurities.

This does not imply that processes for the preparation of ultra-clean coal have no value for purposes other than the manufacture of electrode carbon. It merely states the main force behind the German drive for ultra-clean coal.

This report is an account of the process evolved by the I.G.Farbenindustrie, for installation at their Auguste Viktoria mine, Hüls, Recklinghausen.

In actual fact, the plant, though constructed, was never erected there owing to bomb damage at the mine, and it was decided to apply the process to coal drawn from the Hohenzollern pit near Beuthen in Upper Silesia. The controlling interests in this mine are held by Messrs. Schaffgotsch.

The Hohenzollern mine is equipped with a trough washer, and investigation disclosed the fact that by withdrawing coal from the top trough in the system a sufficiently pure product (containing 1.5 - 2.0 per cent ash) could be obtained to dispense with the creaming jigs in the Auguste Viktoria project.

N.B. The word "ton" throughout this report denotes the metric ton (2204 lbs.).

At least some of the plant, if not all, was despatched to Upper Silesia, but there is no definite information as to its present where-abouts. The one thing certain is that the process has not yet functioned on the large scale.

Under these circumstances it is felt that a description of the Auguste Viktoria project will at least show the extent to which Germany was prepared to go to satisfy the requirements of her light metal industry, as well as giving the main details of the scheme.

Summary.

Coking coal of 22 per cent volatile content and 12.5 m.m. in size is cleaned in a first stage of jig washing to 4 - 5 per cent ash. This product is creamed in a second stage of jig washing to 1.8 per cent ash, then ground finely and froth floated to 0.8 per cent ash. Finally the low ash coal is extracted with caustic soda at an effective concentration of 2.5 per cent for 20 minutes at 120 atmospheres pressure and 250°C. The product is both acid and water washed, and contains 0.28 per cent ash.

Personnel Interviewed. Dr. Geissler.

The coal research laboratories of the I.G. at Höchst were formerly headed by Dr. Winnacker, who has since been removed by the U.S.A. Military Government for his Nazi activities prior to the occupation. He now resides at Hofheim.

Dr. Geissler worked with Winnacker from 1938 onwards and now replaces him. For his degree, Geissler studied coals at Dresden under Professor Foerster; he has several publications dealing with coal to his credit, and is also a boiler and feed water specialist.

The laboratory apparatus at Höchst will extract 200 k.g. of coal per day with caustic soda, and a small experimental coke oven, 20 c.m. x 90 c.m. x 2 metres, produces 120 k.g. of coke per day. With this apparatus 20 tons of coke were produced for manufacture and testing as carbon electrodes.

Outline of Process.

Jig washing.

The Auguste Viktoria mine produces coking coal having an ash content of 12 per cent in the raw state and a volatile content of 22 per cent on the dry ash free basis.

Before it was damaged an existing jig washer yielded some 126 tons per hour (dry basis) of washed fines sized 12.5 x 0 m.m's, containing 8 per cent of ash. These fines constituted the raw material for the recovery of ultra-clean coal.

Referring to Fig 1. the intention was to deslime the fines on screens fitted with 0.5 m.m. mesh the undersize going forward for boiler or coking coal with an ash content bordering on 12 per cent. The oversize grains with 4 per cent ash are sprayed with clean water and re-washed in nine new creaming jigs, yielding four products. Expressing the weights on the dry basis these are:-

1. About 28 tons per hour of coal with 1.8 per cent ash for further treatment.
2. Some 24.6 tons per hour of coal with 4 per cent ash returned to the normal coking coal.
3. 5.7 tons per hour of middlings containing roughly 18 per cent ash for boiler fuel.
4. 4.7 tons per hour of slurry returned to the coking mixture.

The final operation shown on Fig 1. is the de-watering of the pure coal in two centrifuges having a capacity of 40 tons per hour each, (one machine acting as a standby).

Froth Flotation.

From the de-watering operation the coal of lowest ash passes to two coarse crushers and six Teutonia disc mills by Gröpnel of Dinnendahl, shown in Fig 2. The latter have a capacity of 5 tons per hour each and reduce the particle size from < 12.5 m.m's to the following grading:-

Grinding in Gröpnel 'Teutonia' mills.

Yield. per cent.	Size. per cent.
1	> 0.52 m.m.
5	0.25
16	0.12
10	0.09
17	0.06
51	< 0.06

Fig 2. also shows the three banks of froth flotation cells, containing 14 cells in the first and ten in each of the succeeding groups. A conditioner precedes and a froth breaker succeeds each stage of frothing.

The coal is therefore flotated three times, the discard proceeding by way of pumps and thickeners to disc filters, and from there to the blending bunkers to augment the normal coking coal supply by 12.6 tons per hour.

From the input to the froth flotation circuit a yield of 55.0 per cent or 15.4 tons per hour of coal was anticipated, containing 0.8 per cent of ash. This was to be de-watered in two Escher-Wyss centrifuges (made at Zurich, Switzerland), the product being delivered to the chemical extraction plant with an average moisture content of 10 per cent.

As well as providing low ash coal, the froth flotation treatment is described as having the advantage of removing iron compounds which, if present, would increase the consumption and contaminate the reagents employed in the chemical extraction process.

Recapitulating, up to the chemical extraction stage, from 1,000 tons of coal fed into the creaming jigs, sized at 12.5 x 0.5 m.m. and containing 4 per cent of ash, the yields expected were:-

Yield. tons	Class.	Ash. per cent.	Destination.
245	Pure coal	0.8	Chemical Extraction Plant.
590	Coking "	3.9	Coke oven bunkers.
90	Middlings.	18.0	Boilers for steam raising.
75	Sludge.	?	Coke oven bunkers.

Chemical Extraction Process.

Fig 3. is an abridged version of a drawing by Dr. O. Otto of Bochum. It is schematic and does not attempt to show all the plant i.e., it does not include all the centrifuges, storage tanks, collecting pots, pumps, etc. The bracketed numbers refer to this figure.

10 tons per hour of flotated coking fines containing 10 per cent moisture and 0.8 per cent ash are fed over a belt weighing machine (1) to either one or the other of three tanks (2) fitted with stirrers. A 3 per cent solution of caustic soda is added in the ratio of

$$\frac{\text{Coal}}{\text{Caustic solution}} = \frac{1.0}{0.4}$$

As the coal contains 10 per cent of moisture the effective alkali concentration is 2.5 per cent.

The mixture is stirred at 40 - 50°C. for 30 minutes and is then forced by three high pressure paste pumps(3) through a heat interchanger (4) where cold medium entering is heated by hot medium leaving the tube heating furnace (5).

From the pumps the paste leaves at a pressure of 100 - 200 atmospheres and the temperature is raised to 250°C. in the gas-fired furnace (5), for a period of 20 minutes; actually the paste is at an elevated temperature for 20 minutes, and under pressure for 30 minutes.

Having parted with some of its sensible heat in the interchanger the hot medium is cooled in a water-cooler (6), and passes through pressure reducing valves (7) to a collecting pot (8). Softened water is also laid on to this pot; hard water, of course, would deposit scum on the alkaline coal.

The extracted coal is then pumped at atmospheric pressure to a bank of five rubber lined Escher-Wyss centrifuges (9) which have, in all, six collecting pots attached to them. An arrangement of valves and connecting pipes enables the following operations to be carried out, the centrifuges being interchangeable so far as the removal of acid or alkali is concerned:-

1. The bulk of the caustic soda is centrifuged off and returned for re-use.

2. The coal is dropped into 5 per cent hydrochloric acid and stirred.

3. The hydrochloric acid is centrifuged off and returned for re-use.

4. The coal is dropped into water and stirred.

Caustic soda solution too dilute for further use as an extracting medium is employed for water-softening purposes, in the softener shown at (13). Any surplus is piped to the drain where it is neutralised by dilute washings from the hydrochloric acid treatment.

It appears essential to employ an acid washing stage since the removal of caustic alkali by numerous washes with water alone proved impossible. If acid is not employed the final result is an alkali-activated coke.

Apparently no attempt was contemplated to recover either acid or alkali by concentration of the dilute washings. The consumption of 100 per cent caustic soda is 21 k.g. and of 30 per cent hydrochloric acid 63 k.g. per ton of extracted coal.

From the Escher-Wyss centrifuges the coal suspended in slightly acid water is pumped to three vacuum filters (10), lined with rubber to prevent corrosion and employing filter cloth made from poly-vinyl chloride, a chlorinated synthetic resin.

The filter cake is again stirred inwater in tanks (11), and pumped to three Escher-Wyss centrifuges (12) which yield a product containing 10 per cent of moisture and 0.28 per cent of ash. This is the final operation for purifying the coal.

Summarising the chemical treatment the process may be regarded as:-

1. Addition of 3 per cent caustic soda solution.
2. Pressure raised to 120 atmospheres.
3. Temperature raised to 250°C for 20 minutes.
4. Alkali centrifuged off.
5. Addition of 5 per cent hydrochloric acid solution.
6. Acid centrifuged off.
7. Water added and filtered off.
8. Water added again and centrifuged off.

Effect of Treatment on Coal and Coal ash:

Table I shows the effect of the various treatments on the analysis of the coal ash:-

Table I.

Stage.	Raw Coal.		Flotated Coal.		Extracted Coal.	
Ash, per cent.	4.7		0.76		0.26	
Constituent.	100pts. ash	100pts. Coal	100pts. ash	100pts. Coal	100pts ash	100pts. Coal
SiO_2	43.52	2.04	28.96	0.22	24.26	0.063
Fe_2O_3	12.38	0.58	29.38	0.22	38.72	0.101
Al_2O_3	32.72	1.54	34.19	0.26	27.51	0.072
CaO	3.36	0.15	2.18	0.016	1.79	0.005
MgO	1.31	0.06	1.59	0.012	1.04	0.003
SO_3	2.63	0.12	1.09	0.008	0.56	0.0015
Alk.	3.41	0.76	2.21	0.017	5.32	0.014
TiO_2	--	--	0.40	0.003	0.50	0.0013

As well as the removal of ash the extraction process destroys at least half the caking properties of a good coking coal. Auguste Viktoria coal, however, retained some caking power even after extraction for two days. Three days reaction time left a non-caking residue.

The Upper Silesian coal of the Hohenzollern mine contained 35 per cent volatile matter and was not a good coking coal. Consequently if this project had gone forward it would have been necessary to add 20 per cent of pitch to the purified coal before passing it on to the coke ovens.

Coking.

As the process has not functioned on the large scale, the following remarks apply only to the small experimental oven installed at the laboratories of the I. G. at Höchst.

As high a carbonising temperature as possible was required in order to yield electrode coke of the maximum conductivity.

The experimental oven was:-

20 c.m's. wide.
90 c.m's. high.
2 metres long.

It held a charge of 200 k.g. coal and carbonised at 1100°C in the chamber with a flue temperature of 1300°C. A yield of 120 k.g. of good coke was obtained per day, and - as explained previously - Geissler made 20 tons of coke in this oven for full scale electrode trials.

In deciding the quality of the coke, (apart from its purity), the most important laboratory test was its resistance, and a brief description may not be out of place. A sample of the coke ground and sieved to a grain size of 0.06 x 0.09 m.m. was placed in a steel cylinder of 30 m.m. bore, fitted with insulated electrodes 25 m.m. apart. The cell is filled under standard conditions of packing, and a small hydraulic ram inserted at one end raises the pressure to 5 atmospheres. The resistance of the 25 m.m. column of coke is measured under these conditions with a testing set; a good coke registers a resistance of 300 ohms.

Cost of processing.

The cost of processing can only be estimated. Tables II and III give the main details:-

Table II.

I.G. Farbenindustrie plant to yield 72,000 tons coal (50,000 tons coke) per annum.

Process.	Cost of Plant.	Cost of Buildings.	Men per day. (÷ 3 for shifts)	
	R- marks.	R- marks.		
Jigs for creaming raw coal.....	760,000	415,000	9	6 day week.
Flotation cells and auxiliaries.....	1,540,000	585,000	21	
Chemical Treatment..	2,435,000	500,000	30	7 day week.
Coking.....	1,100,000	500,000	25	
Totals.	5,835,000	2,000,000	85	

Table III.

Cost of Processing by Jig Washing, Froth-flotation, and Alkali Extraction for 72,000 tons per year of ultra-clean coal.

Running Costs.	Washing.	Froth-Flotation.	Chemical Extraction.
Managerial expenses R.M. per yr.	7,800	15,600	19,500
Services:			
Electric power K.W.H. per day.	10,000	20,000	34,000
per year.....x 10⁶	3.72	6.24	11.4
Water in cubic metres per day.	1,200	1,200	1,800
Gas for furnace c.m. per hour	-v	- -	550
per year.....x 10⁶	- -	- -	4.4
Steam, tons per ton coal	- -	- -	0.25
tons per year.....	- -	80,000	18,000
Reagents.			
Frothing oil, R.M. per year	- -	- -	- -
tons per year.....	- -	60	1,500
NaOH (100 per cent) tons per yr.	- -	- -	4,500
HCl (30 " " "	- -	- -	- -
Cost of Working or Operating:			
Note: By this the author understands labour. R.M. per year.....	45,000	111,000	150,000

Neglecting the capital costs and introducing average figures for the cost of services and reagents where these are not stated the balance sheet is as follows:-

	R- marks per ton of ultra-clean coal.	Basis of Calculation. *
Managerial expenses.....	0.60	Quoted.
Electric power at 3.3 pfennigs per unit.....	9.89	0.4d per unit
Water at 5.5 pfennigs per cubic metre.....	1.06	3.0d per 1000 gals.
Coke oven gas at 3.0 pfennigs per cu.m.	1.82	10d per 1000 cu.ft.
Steam at 4.48 marks per ton.....	1.12	2/0 per 1000 lbs.
Reagents:		
1. Frothing oil.....	1.11	Quoted.
2. Caustic soda.....	7.19	£17.25 per ton.
3. Hydrochloric acid...	12.50	£10 per ton
Labour.....	4.25	Quoted.
Total.	39.54	

* Note: The value of the R- mark is here taken as 1/-.

The figure obtained does not include maintenance costs, stores, lighting, heating and insurance, nor does it include any coking charges.

The value of the ultra-clean coal was expected to be about 108 marks per ton.

Conclusions.

Unless there is an unprecedented demand for low ash coal there does not seem to be any wide scope for this process. The author cannot envisage it functioning on the large scale, except under the stress of war time conditions such as those which applied to Germany.

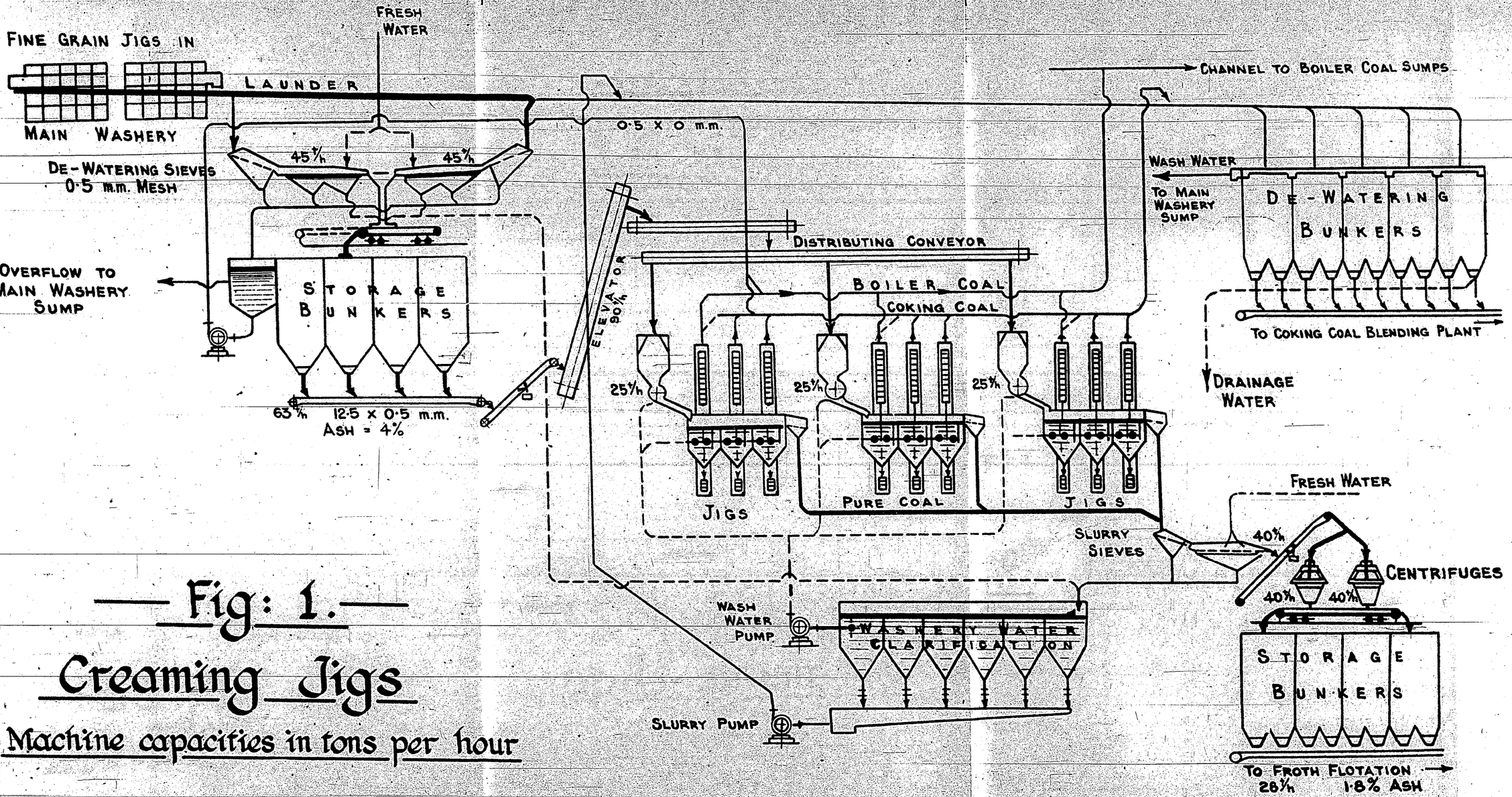


Fig: 1.

Creaming Jigs

Machine capacities in tons per hour

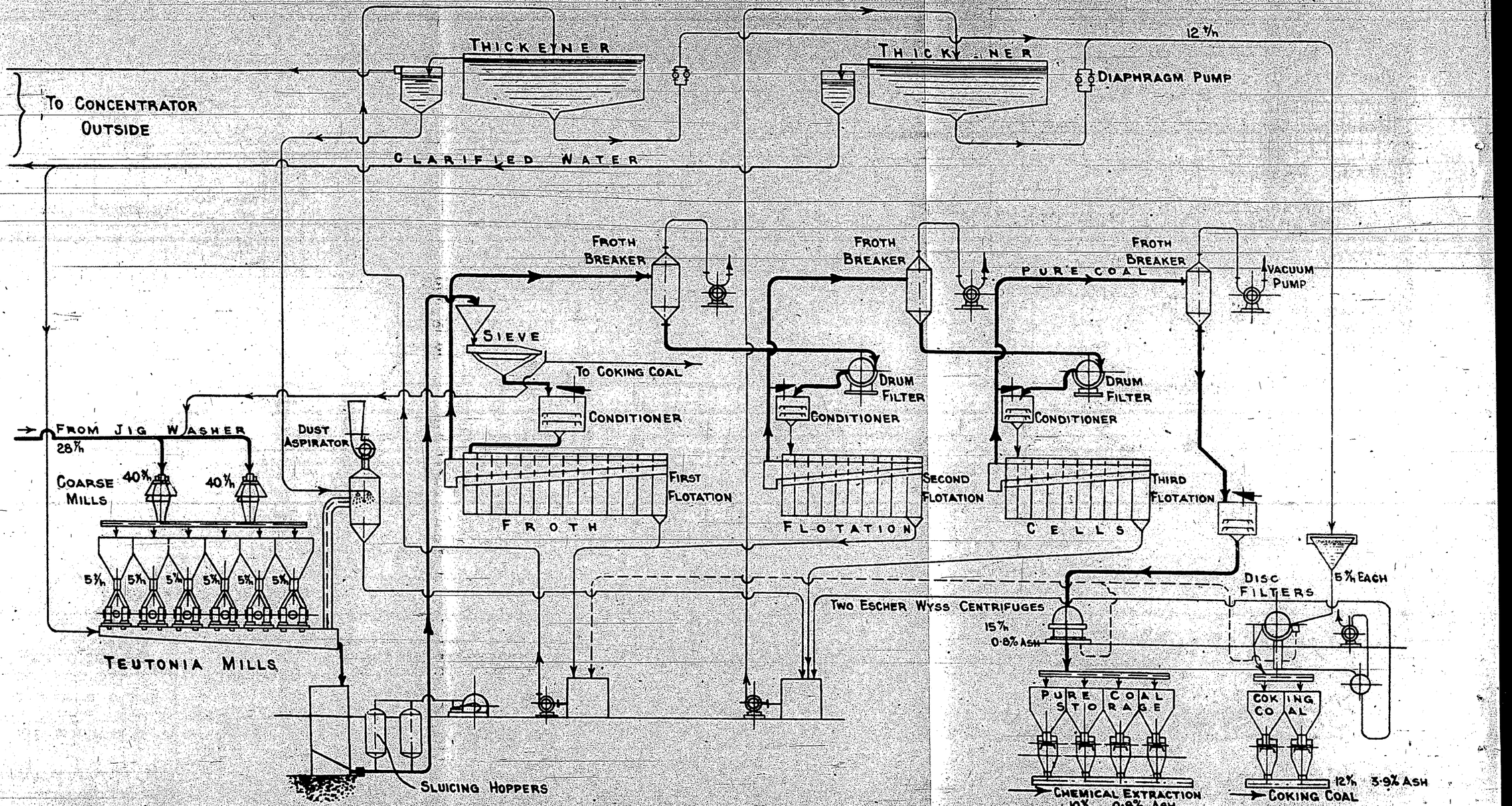
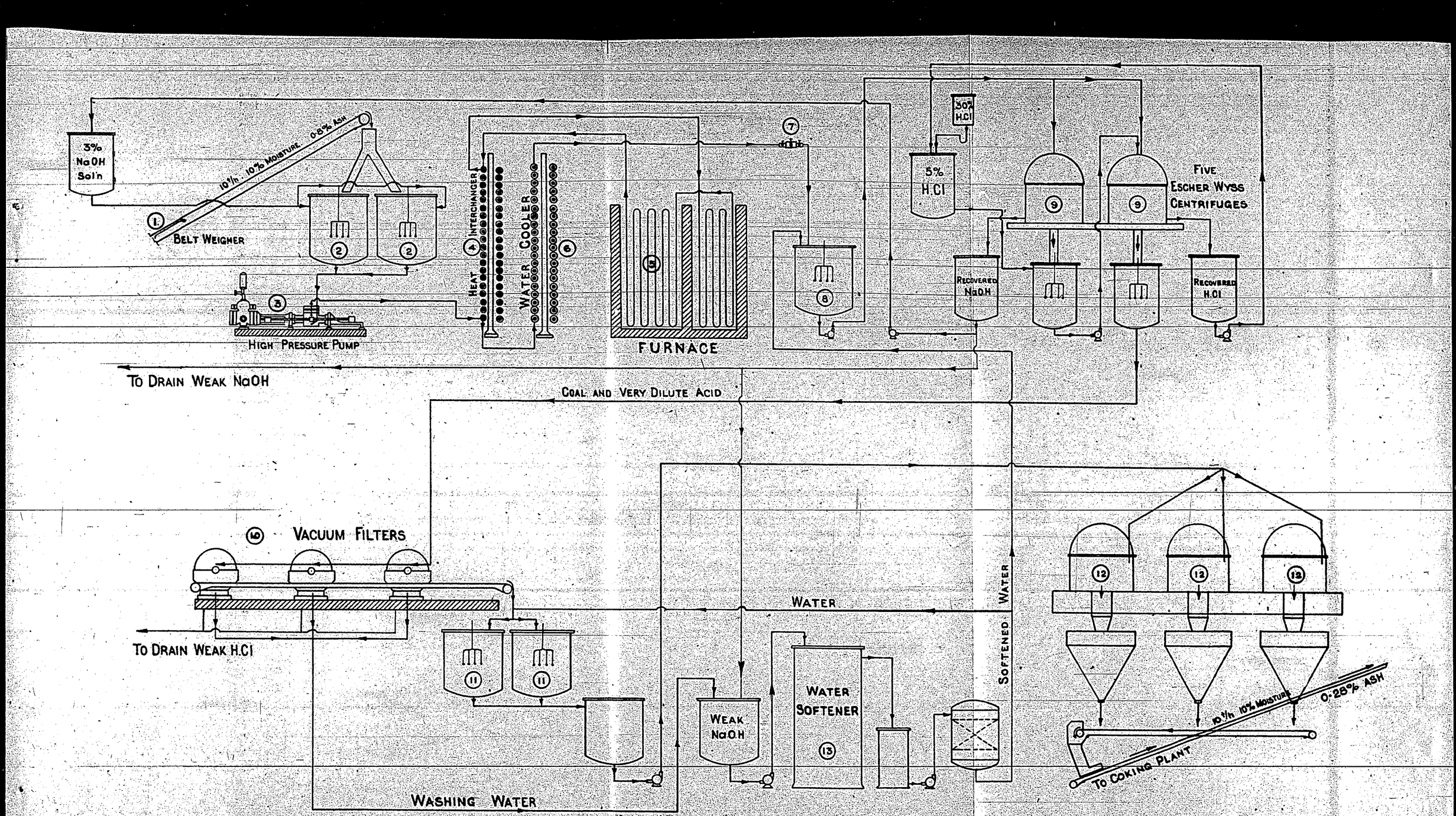


Fig: 2. Froth Flotation

Machine capacities in tons per hour



— EXTRACTION OF COAL WITH CAUSTIC SODA. —

— FIG.3 —

Copy 1

FINAL REPORT No. 266
ITEM No. 22

NEW TECHNICAL APPLICATIONS OF ACETYLENE

Evans, D. G.

LIBRARY
of the
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION
Bureau of Mines
SEP - 1946

"This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement."

BRITISH INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

LONDON - H. M. STATIONERY OFFICE

UNCLASSIFIED

NEW TECHNICAL APPLICATIONS OF ACETYLENE

Reported by

Major D.C. Evans, R.E., M. of S.

BIOS Item 22
Miscellaneous Chemicals
BIOS Target No. 22/1(f)

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

(1946)

34p.

NEW TECHNICAL APPLICATIONS OF ACETYLENE.

INTRODUCTION.

This report is based on a translation of a paper outlining the work of Dr. J. Walter Reppe of I.G. Farben on new technical applications of acetylene. It was obtained by a C.I.O.S. CAFT Assessment Team (Major A.J. Skey, C.M.H.Q., and Mr. K.T. Nilssen, U.S.A.) during a visit in May last to the Anorgana G.m.b.H. plant at Gendorf in Bavaria.

The report describes a number of new applications of acetylene under the following headings:-

1. Vinylation.
2. Ethinylation.
3. Carbonylation.
4. Cyclic polymerisation.

A translation of a report by Dr. Reppe on cyclopolyolefines has already been published as B.I.O.S. Final Report No. 137.

D.C. EVANS,
MAJOR, R.E.

for Chairman, Group III. B.I.O.S.

14th January, 1946.

THE CHEMISTRY OF SOME NEW TECHNICAL APPLICATIONS OF ACETYLENE.

(BY Dr. WALTER REPPE).

I. Vinylation.

By vinylation is meant the addition reactions of acetylene leading to a vinyl derivative. Addition can be brought about between acetylene and hydroxyl, sulphydryl, amino, amido and carboxylic acid groups as follows:

1) $R\text{-}OH$ + $HC \equiv CH \longrightarrow R\text{-}O\text{-}CH=CH_2$

Alcohol — Vinyl ether

2) $R\text{-}SH$ + $HC \equiv CH \longrightarrow R\text{-}S\text{-}CH=CH_2$

Mercaptan — Vinyl-thio-ether

3) $R\text{-}COOH$ + $HC \equiv CH \longrightarrow R\text{-}COO\text{-}CH=CH_2$

Carboxylic acid — Vinyl-ester

4) $R\text{-}NH\text{-}R_1$ + $HC \equiv CH \longrightarrow R\text{-}N(R_1)\text{-}CH=CH_2$

Primary ($R_1 = H$), or secondary amine. — Vinyl amine

5) $R\text{-}CO\text{-}N(H)\text{-}R_1$ + $HC \equiv CH \longrightarrow R\text{-}CO\text{-}N(CH=CH_2)\text{-}R_1$

N-substituted amide — N-Vinyl-N-alkyl amide

6) $[R_1\text{-}R_2\text{-}NH\text{-}R_3]^+$ + $HC \equiv CH \longrightarrow [R_1\text{-}R_2\text{-}N(CH=CH_2)\text{-}R_3]^+ \; OH^-$

Alkyl ammonium base — Trialkyl-vinyl ammonium base.

Vinyl ether is easily produced as shown above - by allowing acetylene under pressure, in the presence of a catalyst, to act on the alcohol concerned at a high temperature. As catalysts many substances of alkaline reaction are suitable, such as alkali and alkali earth metals, their hydroxides, alcoholates, phenates, cyanides, etc., and also the zinc and cadmium salts of organic acids.

From the alcohol and alkali hydroxide for instance, the alcoholate is first formed from which acetylene forms the salt of the vinyl ether, which, with further alcohol, is converted into the free vinyl ether and alcoholate:

1) $ROH + NaOH \rightarrow RONa + H_2O$

2) $RONa + HC \equiv CH \rightarrow RO-CH=CH-Na$

3) $RO-CH=CH-Na + ROH \rightarrow RO-CH=CH_2 + RONa$

Absorption of the acetylene proceeds with extraordinary ease in the primary and secondary alcohols of the aliphatic range up to the montane alcohols. Tertiary alcohols react only slowly.

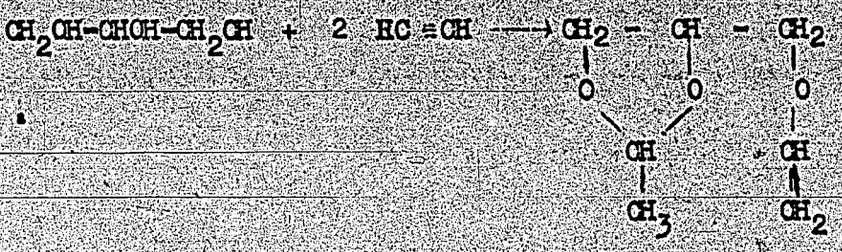
Polyhydroxy alcohols can also be vinylated satisfactorily, provided the reaction conditions are such that these alcohols are still stable. In this case, however, as a result of only partial vinylation, several products of reaction may occur; and in addition, cyclic acetals may be formed, favoured when two hydroxyl groups can form a stable 5 or 6 numbered ring. In other cases vinyl ethers are obtained, two or more vinyl groups being introduced. The formation of acetals is favoured by higher temperatures:

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HC \equiv CH \xrightarrow{150^\circ} \begin{array}{l} CH_2-O-CH=CH_2 \\ | \\ CH_2OH \end{array} \xrightarrow[150^\circ]{HC \equiv CH} \begin{array}{l} CH_2-O-CH=CH_2 \\ | \\ CH_2-O-CH=CH_2 \end{array}$$

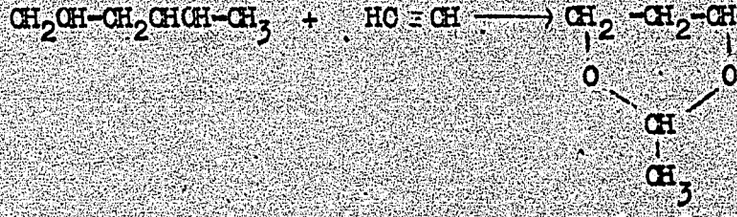
$$\begin{array}{l} CH_2OH \\ | \\ CH_2-O \\ \quad \backslash \\ \quad\quad CH-CH_3 \\ \quad / \\ CH_2-O \end{array} \quad \text{(180°)}$$

/Glycerol

Glycerol generally yields the acetal of mono-vinyl ether, butane 1.3 diol gives almost exclusively cyclic acetal, whilst from butane-diol-1.4 the divinyl ether can be obtained without difficulty:



1.2 ethylidene glycerol 3-vinyl ether.



butane diol-1.3-ethylidene acetal



butane diol-1.4-divinyl ether

It may be pointed out that high-boiling alcohols with a boiling point under atmospheric pressure above the reaction temperature can be converted into vinyl ethers (under normal pressure). Vinylation in the gas phase is also possible, but cannot be used in so many cases.

The reaction described for producing vinyl ethers from acetylene and alcohols can be applied, with few exceptions, to all compounds containing a hydroxyl group. In this way all the aliphatic alcohols with straight and branched chains can be vinylated, also cyclohexanol, its substitution products such as the alkyl cyclohexanols and ring homologues, such as the decalols, as well as phenol, the naphthols and their substitution products, terpene alcohols, dihydro-abietinol, and, partially alkylated or acetylated carbohydrates bearing free hydroxyl groups.

In earlier work it was also shown that contrary to statements in the literature, vinyl ether can be produced from alcohols and vinyl chloride in the presence of dissolved alkali-hydroxides or alcoholates in 90% yield:

$$RO\boxed{Na + Cl}CH{=}CH_2 \longrightarrow NaCl + ROCH{=}CH_2$$

Excess alcohol acts as solvent and using double the quantity of alkali, it is also possible to start from the more easily handled 1.2-dichlor-ethane or 1.1-dichlorethane.

Amongst the reactions of vinyl ether only brief reference can be made to the addition of hydrocyanic acid and halogen acid, as well as of alcohols and phenols. The ready hydrolysis of vinyl ether in an acid medium into acetaldehyde and the alcohol component

$$CH_3\text{-}O\text{-}CH{=}CH_2 + H_2O \xrightarrow{P_H < 7} CH_3OH + CH_3CHO$$

is theoretically interesting and technically important, and provides a facile route to acetaldehyde without the use of mercury salts.

Vinyl ether yields the corresponding mixed ethers which are otherwise difficult to prepare, on hydrogenation.

The most important reaction of the vinyl ethers, however, is polymerisation which follows the same course as that of styrol, vinyl chloride, vinyl acetate, etc., that is to say the vinyl groups combine 'head to tail' forming an ether substituted paraffin chain.

$$\begin{matrix} CH = CH \\ \quad | \\ \quad OR \end{matrix} \qquad \begin{matrix} CH_2{=}CH \\ \quad | \\ \quad OR \end{matrix} \qquad \begin{matrix} CH_2{=}CH \\ \quad | \\ \quad OR \end{matrix} \longrightarrow$$

$$-CH_2-\underset{\underset{OR}{|}}{CH}-CH_2-\underset{\underset{OR}{|}}{CH}-CH_2-\underset{\underset{OR}{|}}{CH}-$$

Cross linking is achieved by use of di- or poly vinyl ethers and in this way products are obtained which are no longer soluble in the usual solvent media, but are only capable of swelling. The divinyl ether forms bridges which bind the individual fibre molecules of the polyvinyl ether together.

/Polymerisation

Polymerisation of vinyl ether can be carried out in the well known ways, that is to say in bulk, in solution or in emulsion. The first two methods have proved most satisfactory, for which Friedel-Crafts reagents, such as aluminium chloride, iron chloride, titanium tetrachloride, tin tetrachloride and - particularly satisfactory - boron fluoride in the form of its organic addition compounds may be used as catalyst. The vinylation reaction thus places at our disposal a means of converting a wide range of organic substances into polymeric products.

The polyvinyl ethers, (trade name "Igevine") serve manifold purposes as raw material for varnishes, and adhesives, as well as textile auxiliary media and impregnating media, and also as leather preservatives and as latices for emulsions for making artificial leather.

From phenols using alkali-hydroxides or alkali-phenolates as catalysts, as already stated, the phenol vinyl ethers are obtained. With, however, salts of zinc or cadmium or organic amines as catalysers, resins of high molecular wright are formed which are of great interest as ingredients of buna and also as raw material for adhesives and varnishes. A phenol acetylene resin known as "Koresin", first made it possible to produce a sticky synthetic rubber, so that the phrase was coined "No buna without "Koresin" (Krauch).

Vinyl thio-ethers are produced from mercaptans and acetylene under similar conditions to those used for preparing the vinyl ethers. To the vinyl group also sodium sulphide, taurine, methyl taurine and the like, may be added to obtain from the higher vinyl sulphides textile assistants. The sulphur can be oxidised to the four-valent or six-valent state, which appreciably increases the reactivity of the vinyl group. The polymerisation capacity of these vinyl sulphides, vinyl sulphoxides and vinyl sulphones, however, is inferior to that of the vinyl ethers although the possibilities have not yet been by any means thoroughly explored.

Under pressure, the vinylation reaction also yields the vinyl esters of the higher fatty acids, the catalysts used are the zinc and cadium salts of the fatty acids concerned. The reaction apparently proceeds in a similar manner to the formation of vinyl ether. The zinc salt of the carboxylic acid first adds acetylene and this unstable intermediate product is split by a further acid molecules into the zinc salt and the vinyl ester:

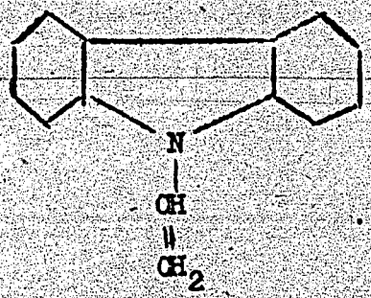
1) $$\begin{matrix} RCOO \\ RCOO \end{matrix}\!\!>\!Zn + 2\,HC{\equiv}CH \longrightarrow \begin{matrix} R\text{-}COOCH{=}CH \\ R\text{-}COOCH{=}CH \end{matrix}\!\!>\!Zn$$

2) $$\begin{matrix} R\text{-}COOCH{=}CH \\ R\text{-}COOCH{=}CH \end{matrix}\!\!>\!Zn + 2\,RCOOH \longrightarrow 2\,RCOOCH{=}CH + \begin{matrix} RCOO \\ RCOO \end{matrix}\!\!>\!Zn$$

In addition, vinyl esters of carboxylic acid can also be produced by vinylation under pressure in the gas phase, as for example vinyl benzoate.

The vinyl esters of the higher fatty acids constitute a further interesting group of substances capable of polymerisation.

The vinyl amines are important but only secondary amines, however, lead to monomers which are sufficiently stable to be of technical value. The most important here is carbazole, which gives N-vinyl carbazole under the conditions already described.



Oxidative polymerisation of this substance in alkaline suspension yields poly-N-vinyl-carbazole, a valuable product marketed under the name of "Luvican". It represents the first thermo-plastic synthetic material with high heat-resisting properties (Marten number 150), and at the same time with outstanding electrical properties (resistance to creeping current, frequency independence of the angle of loss). The production of Luvican also, for the first time, opened the way to a serviceable organic mica.

Mono substituted amides can be vinylated, producing N-alkyl-N-vinyl amides in accordance with the following scheme:

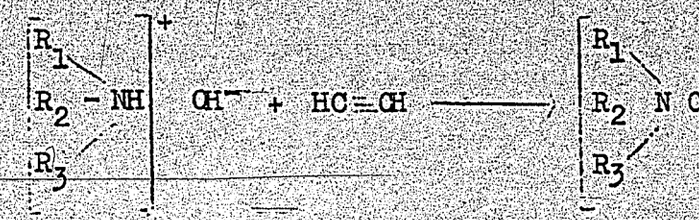
$$R\text{-}CO\text{-}N\!<\!\begin{matrix} H \\ R_1 \end{matrix} + HC{\equiv}CH \longrightarrow R\text{-}CO\text{-}N\!<\!\begin{matrix} CH{=}CH_2 \\ R_1 \end{matrix}$$

in which R may represent an alipatic, aromatic, arylalkyl, hydroaromatic or heterocyclic residue. R_1 is generally an alkyl

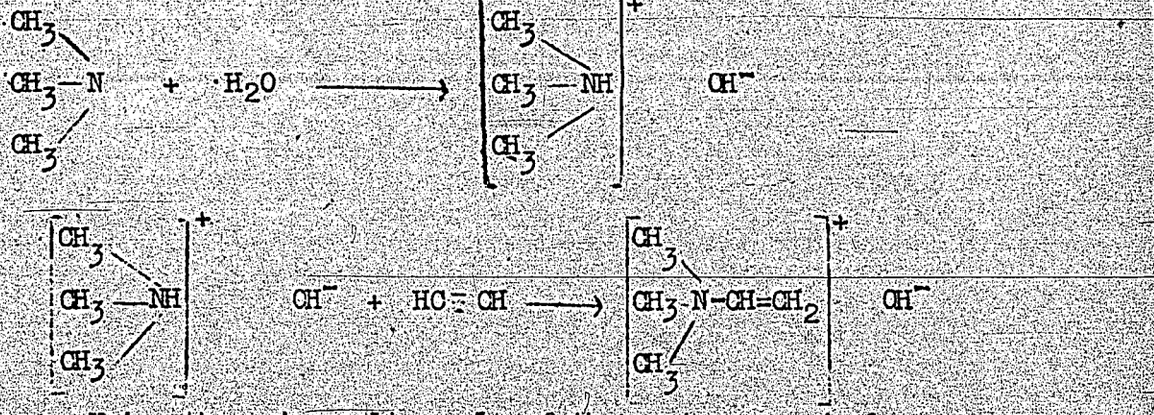
/or

or aryl group. The reaction of the unsubstituted acid amides, is being worked on at present.

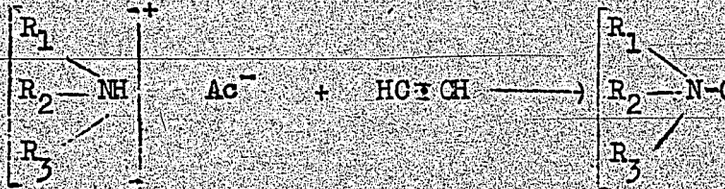
A particularly interesting example of vinylation is, however, the very recent (1942) discovery of direct conversion of tertiary amines in the presence of water into quaternary vinyl ammonium compounds:



in which R_1, R_2 and R_3 may be aliphatic, aromatic, arylalkyl, hydroaromatic or heterocyclic residues. In the case of the simple aliphatic amines reaction is practically quantitive. Thus using an aqueous solution of trimethyl amine with acetylene under pressure at low temperatures "Neurin" (= trimethyl-vinyl-ammonium-hydroxide) is obtained without the use of a catalyst:



Using the amine salt, a salt of the quaternary vinyl ammonium base is similarly produced:



in which H Ac represents any acid which may be selected.

/II. Ethinylation.

II. Ethinylation.

In 1937 Walter Reppe discovered a whole group of similar reactions of acetylene, brought about by the same catalysts. These reactions are also given by other acetylene hydrocarbons and their derivatives, provided the ethine is terminal.

These general reactions are described as ethinylation, an ethinyl group being added resulting in the formation of ethinyl compounds, alkinols or substituted propargyl amines. Three types of reaction have been studied:

1. Conversion of alkylol amines into substituted propargylamines (amino-propines),

2. Conversion of amines into amino-butines, and

3. Conversion of aldehydes and/or ketones into alkinols or alkin-diols.

Some of the substances formed according in reactions 1 and 3 are already known, but only obtained by complicated and costly processes which are far from easy to handle, and which it has never been possible to carry out catalytically. Amino-propines and alkinols produced by this process remained laboratory curiosities, effectively unobtainable.

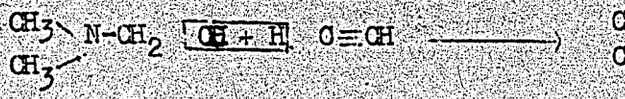
These ethinylation reactions are catalysed by the heavy metal acetylides of group IIb of the periodic system, that is to say copper, silver and gold, as well as by mercury acetylide. Compounds of these metals which are converted into acetylides under the conditions of reaction, are also suitable. The finely divided metals are effective but less satisfactory. In practice copper acetylide has been found best. To obtain as complete conversion as possible, it is advisable to work with acetylene under pressure, though reaction takes place without pressure with homologues, derivatives and substitute products of acetylene, of higher boiling point.

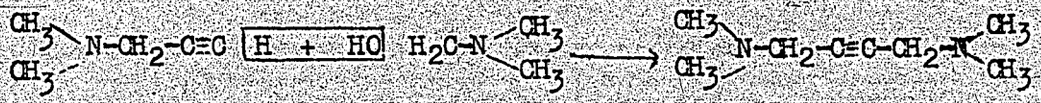
In order to avoid danger from the explosive acetylide reaction was at first attempted with copper compounds as catalysts under such conditions that no copper acetylide could form but it was only by adhering to the conditions under which copper acetylide was formed that the desired reactions took place, and then very easily. In numerous experiments the conditions for safe handling of copper acetylide were ascertained so that it became possible to

/carry

carry through the reactions without danger, even on the largest technical scale.

The conversion of alkylol amines with acetylene into substituted propargyl amines was first discovered. It was known from earlier work that phenyl acetylene or vinyl acetylene is converted by alkylol amines in dioxane solution, with loss of water, into propargyl amines but this procedure is ineffective with acetylene even under pressure. The hydrogen atoms of acetylene are not sufficiently reactive in absence of activation by the phenyl or vinyl group. If, however, the system is activated with copper acetylide formation of propargyl amines or substituted propargyl amines takes place readily and in part even at room temperature. For instance, dimethyl propargyl amine, together with a small quantity of tetra-methyl-diamino-butine is formed from dimethylol-amine from dimethyl amine + formaldehyde and acetylene:





A series of propargyl amines was produced in this way from a number of amines, and a range of new substances was thus opened up. In fact, these substances give many reactions of acetylene itself, so that they can be used again as starting materials for syntheses in the alkine series. The product of dimethylol urea and acetylene, which cannot be isolated unpolymerised is particularly interesting, should have the formula

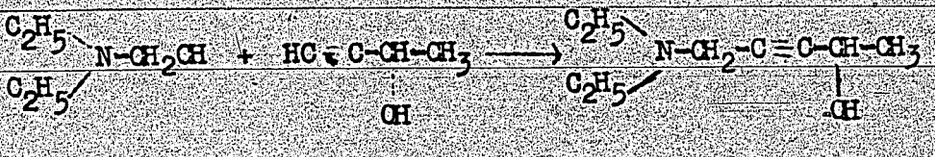
$$HOH_2C - NH - CO - NH - CH_2 - C \equiv CH$$

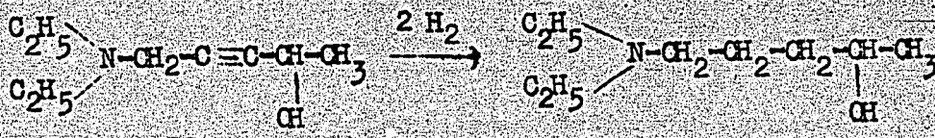
but yields very rapidly polymerised product which has become a component of an important raw material for varnishes.

As already stated, these ethinylation reactions are applicable, not only to acetylene itself, but also to its derivatives and substitution products which still have an "acid" hydrogen. Out of the multiplicity of the reactions, one may select that between

/butine

butine-ol-2 (obtainable by alkinol synthesis from acetylene and acetaldehyde) and diethyl-methylol amine (from diethyl amine and formaldehyde), which is effected practically quantitively in acetic acid solution with copper acetylide or butinol copper as catalyst:

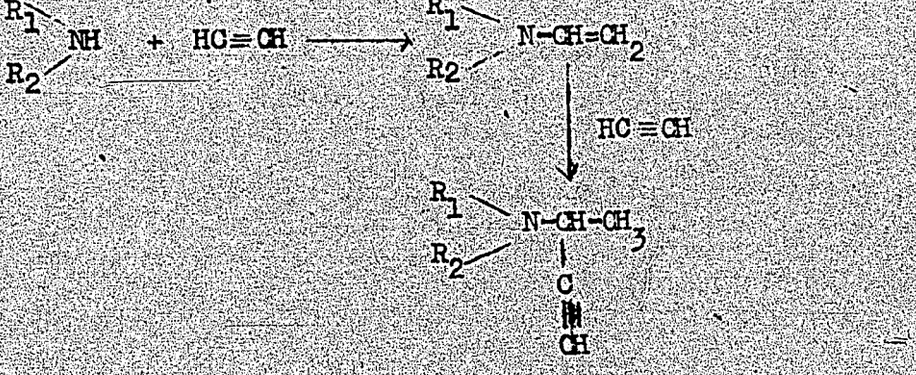




1-Diethyl-amino-pentanol-4 from hydrogenation of 1-diethyl-amino-pentin-2-ol-4 is the intermediate for the production of Plasmoquine obtained by condensation with 6-methoxy amino quinoline. 1-Diethyl-amino-pentanol-4 and 1-diethyl-amino-pentyl-amine-4 are easily obtained from the amino-alcohol referred to and are used for building up the anti-malarial "Atebrin".

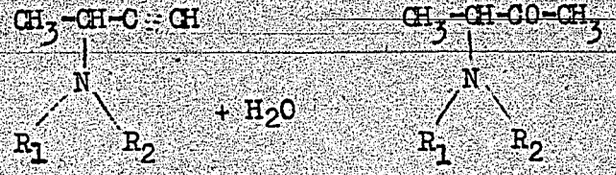
In the course of ethinylation chemistry we shall come across further reactions which lead to valuable therapeutic agents.

The amino-butines are similar to the propargyl amines, and are produced directly from the amines and acetylene under pressure. It has already been stated above that amines with acetylene, under the catalytic influence of alkalis, earth-alkalis and zinc or cadmium compounds, combine into vinyl amines. Heavy metal acetylides, and particularly copper acetylide, make possible a second addition, forming substituted 2-amino-butine-3-compounds:

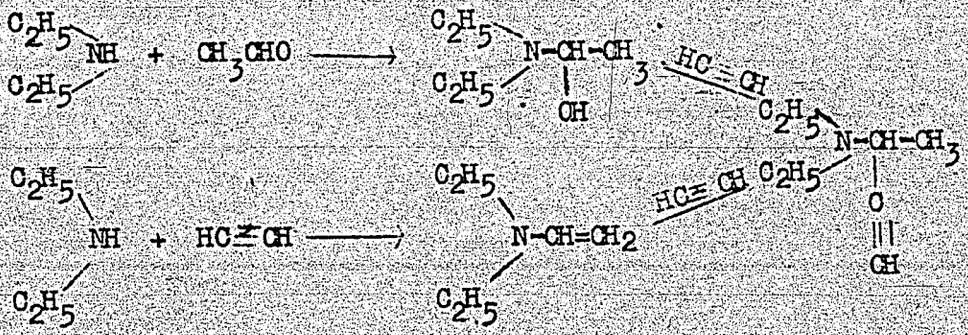


/in

in which R_1 and R_2 may be aliphatic, aromatic or heterocyclic residues, and R_2 also hydrogen. The reaction can therefore be carried out with both primary and secondary amines and it was possible to produce, inter alia, the amino-butine derivatives of dimethyl-amine, diethyl-amine, n-butylamine, di-n-butyl-amine, benzyl-amine, aniline, N-methyl-aniline, piperidine, pyrrolidone, cyclohexylamine, etc., and to study their properties. Proof of constitution was, inter alia, obtained by hydration to the ketone:



In addition the molecular refraction is in agreement with this constitution which was further supported by the same product, 2 diethylamino butine-3, by either of the routes:

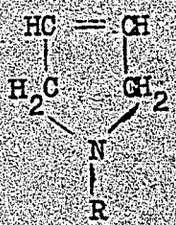


(not isolated)

The amino-butines - at least in the aromatic series - can be isomerised into the corresponding amino-butadiens.



In addition, small quantities of the isomeric pyrroline are formed:

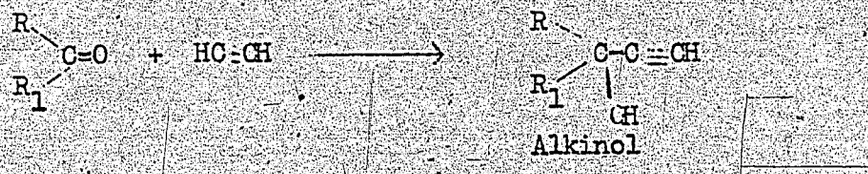


/By

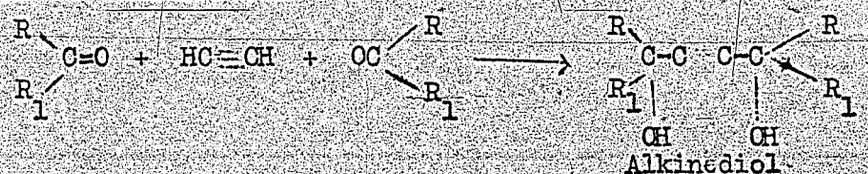
By the synthesis referred to, a large series of new, highly unsaturated and extremely reactive bodies were obtained with which the reactions of acetylene can be carried out again. Thus, inter alia, water, hydrogen halide, hydrocyanic acid, etc., can be added. They can also be subjected to partial and complete hydrogenation, as well as conversion with alcohols into vinyl ethers. In this way a multiplicity of new substances has become accessible, amongst which are many technically important products not referred to here.

The most important of the ethinylation reactions, however, is the alkinol synthesis from acetylene and aldehydes or ketones.

It can be carried out with one or two molecules of the carbonyl compound:



Alkinol

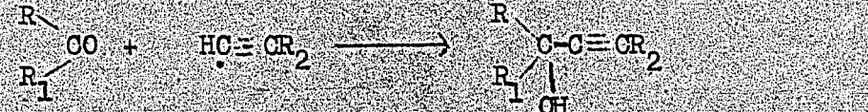


Alkinediol

Here, in the case of the aldehydes $R_1 = H$. Otherwise, R and R_1 may indicate alkyl, aralkyl, aryl, cycloalkyl or heterocyclic residues. $R = R_1 = H$ corresponds to the most important alkinol synthesis, the conversion of formaldehyde into propargyl-alcohol or butine-diol.

Different aldehydes or ketones can also be added to the alkinol originally formed, so that mixed alkine-diols are obtained.

With other alkynes, with the exception of diacetylene, mono substitution only is possible.



/Alkinols

Alkinols and alkine-diols have previously been produced from acetylene magnesium bromide and carbonyl compounds, a method not capable of technical utilisation. The same can be said of a second method applicable only to ketones in which the alkali compound of the ketone is reacted with acetylene. Technical utilisation being out of the question, these substances, which in themselves were extremely interesting and reactive, could only be considered laboratory curiosities.

The most important example of the alkinol reaction is that with formaldehyde. In this case, the propargyl alcohol which is first formed immediately reacts with further formaldehyde and forms butine-diol:

$$HCHO + HC\equiv CH \longrightarrow HOCH_2-C\equiv CH$$

Propargyl-alcohol

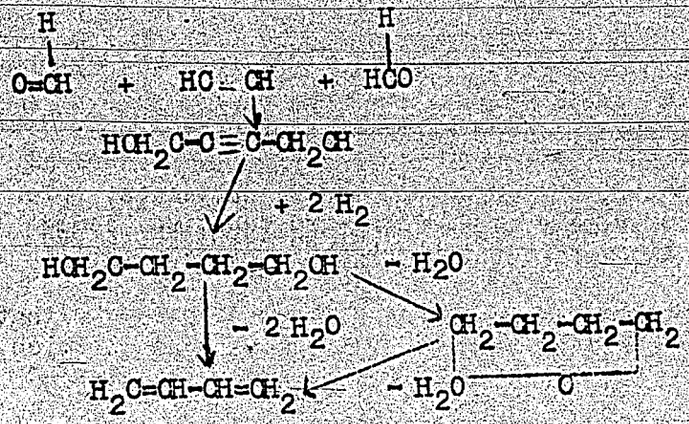
$$HOCH_2-C\equiv CH + HCHO \longrightarrow HOH_2C-C\equiv C-CH_2OH$$

Butine-diol

This conversion can be effected with extraordinary ease with the ordinary commercial 30% aqueous formaldehyde, with a yield of about 97%. The reaction is only possible by the use of copper acetylide as catalyst. On the basis of kinetic studies it may be considered that a loose additive compound is first formed from the copper acetylide and acetylene, the activated acetylene then reacting with formaldehyde, with the formation of propargyl-alcohol, which again unites, with further acetylene, through an active complex forming butine-diol.

In this way 30% technical formaldehyde yields an approximately 35% solution of butine-2-diol-1.4, containing about 2% of propargyl alcohol. The propargyl-alcohol can be removed from the solution by simple distillation, and by reaction with formaldehyde converted into butine-diol.

By the technical synthesis of butine-diol a new, extremely convenient synthesis of butadiene, the basic hydrocarbon for synthetic rubber was opened up. In this process the butine-diol is converted by hydrogenation into butane-diol, which, by dehydration yields butadiene by way of the intermediate stage of tetrahydrofurane:



A further report is given below on the technical development of the synthesis, and also on the advantages which it has over the older four-stage process (by way of acetaldehyde, aldol and butane-diol-1.3). The synthesis of butine-diol from formaldehyde and acetylene gives access, however, not only to product already produced technically by other means, but also opens up means of obtaining, by easy methods, classes of substances which have hitherto been obtainable only with difficulty.

The wide range of substances made accessible by the butine-diol synthesis can be seen on the attached Table I, in which, however, only the more important of the possible reactions are included.

We will here take up only a few particularly interesting compounds:

As stated above, the synthesis of butine-diol undoubtedly takes place in two stages by way of propargyl-alcohol as intermediate and it is possible, under suitable conditions (raising of the acetylene concentration, working with the addition of solvents, variation of the catalyst, counter-current principle, etc.), to conduct the reaction in such a way that propargyl-alcohol is the main product with only a small quantity of butine-diol. As a result of this propargyl-alcohol is available in any quantity as a cheap raw material for further syntheses. A few of the possibilities are referred to briefly.

By hydrogenation of propargyl-alcohol for example by varying the nature of the catalyst and the reaction conditions (as a general rule of p_H), either allyl-alcohol or n-propanol, or even propion aldehyde can be obtained without appreciable by-products. The allyl-alcohol can be converted into glycerol by known methods,

/by

by addition of hydrogen peroxide or by conversion with HOCl into chloro-hydrin and saponification. In this process a technically valuable synthesis is available for this valuable triol.

By oxidation two molecules of propargyl-alcohol yield hexadiene -2.4-diol-1.6. This compound is of particular interest as an intermediate for polyamide fibres. On hydrogenation it yields hexane-diol-1.6 which can be converted on the one hand by oxidation into adipic acid, and by dehydrogenation into γ-capro lactone, which, by treatment with ammonia, can be converted into the important δ-capro lactam.

Propargyl-alcohol can also be dehydrogenated to yield the exceptionally reactive propargyl-aldehyde. Of its many reactions reference may be made to condensation with guanidine to give 2-amino-pyrimidine, a component of the hitherto most effective sulphonamide "pyrimal" (effective against meningitis), and to the addition of water to produce methyl-glyoxal. The direct addition of water to propargyl alcohol results in acetol.

Butine-diol by addition of water, yields butanone-2-diol-1.4 which on hydrogenation, gives butane-triol-1.2.4, suitable as a substitute for glycerine for most varied purposes. Butane-triol-1.2.3, is also accessible (see below) by alkinol synthesis from acetaldehyde. The linking of three butine-diol molecules into cyclic hexamethylol benzene, which can be converted by oxidation into mellitic acid, is interesting. With ammonia, butine-diol forms the pyrrol ring which is particularly interesting for pharmacological purposes. In addition, by way of 1.4-dichlor-butine-2, diacetylene is available easily in absolutely pure form.

Butene-diol, the partial hydrogenation product of butine-diol, is also a valuable substance. By oxidation with hydrogen-peroxide, per-salts or hypochlorous acid, and saponification, a very good yield of erythritol is obtained. Oxidation with atmospheric oxygen gives maleic anhydride, whilst dehydration leads to dihydrofuran. Butene-diol can also be used in Diels-Alders syntheses.

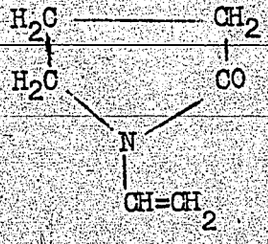
The butane-diol obtained by complete hydrogenation of butine-diol is an important material in the production of polyurethanes. Butane-diol is also an intermediate for poly-amides as shown in the attached Tables. Oxidation leads to succinic acid and by way of 3-keto-pimelic acid to pimelic acid. Butane-diol behaves in an interesting manner on dehydrogenation. Instead of succinic dialdehyde as one would expect, butyro lactone is produced almost quantitively by simply

/trickling

trickling over a copper catalyst at about 200°. This transformation of diols into the corresponding lactones has already been mentioned in the dehydrogenation of hexane-diol-1.6 to ε-capro lactone.

The accessibility of γ-butyro-lactone brings a range of substances into the sphere of technical possibilities, (Table II). We may refer to the easy production of dipropyl ether-γγ-dicarboxylic acid by reaction with caustic soda and thio dibutyric acid by the analogous reaction with sodium hydrosulphide.

Cyano-butyric acid obtained from sodium cyanide and butyro-lactone leads to glutaric acid, to penta-methylene-diamine-1.5 and to pentane-diol-1.5. The most important reaction of butyro-lactone, however, is conversion into α-pyrrolidon by means of ammonia α-pyrrolidon can be vinylated as already stated with formation of N-vinyl pyrrolidon.



This substance can be polymerised into poly-N-vinyl-pyrrolidon, which has attained importance as a plasma substitute. The preparation known to the trade under the name of "Periston" has already saved the lives of tens of thousands of soldiers. The product, which is absolutely non-toxic, and which has the carbo-amide grouping which is also present in albumen, is one of the most valuable pharmaceutical products of recent years, and may well be placed in importance alongside the sulphonamides. Tetrahydrofurane is also an extremely important intermediate from which, poly-amides can be derived. When treated with carbon monoxide and water it yields adipic acid practically quantitively (see under III). When treated with hydrochloric acid or thionyl-chloride, 1.4-dichlor-butane is formed by way of butanol chloride. From this adipic dinitrile can be obtained in the familiar manner using sodium cyanide. The dinitrile on hydrogenation yields hexa-methylene-diamine-1.6, and on saponification, adipic acid.

Reaction of acetaldehyde and acetylene is important yielding the expected products:

/Butine

Butine-3-ol-2 $CH_3-CH(OH)-C\equiv CH$

and

Hexine-3-diol-2.5 $CH_3-CH(OH)-C\equiv C-CH(OH)-CH_3$

in very satisfactory yield and in approximately equal quantity. The most important reactions of the butinol and hexine-diol can be seen from Table III. We may refer briefly to the quantitive convertion of butinol by formaldehyde into pentine-3-diol-2.5.

$$CH_3-CH(OH)-C\equiv C-CH_2OH$$

which leads by way of pentane-diol-2.5 to piperylene. Pentine-diol, like butine-diol, can be converted into the mixture of the isomeric pentane-triols, whereby a further glycerine substitute is produced.

Reference has already been made to the synthesis of 1-diethyl-amino-pentanol-4 and 1-diethylamino-pentylamine-4 leading to "Lasmochin" and "Atebrin". By hydration of butinol acetoin is formed, which on hydrogenation gives butane-diol-2.3. Diacetyl is now accessible from acetoin and by isomerisation of butinol, vinyl methyl ketone can be obtained.

From the partial hydrogenation product of butinol, butene-3-ol-2, 1.2.3-trihydroxy butane is readily available, whilst 1.2.4-trihydroxy butane, as already stated, is obtained from butine-diol.

By most vigorous hydrogenation butine-3-ol-2 yields butane-ol-2, and thence by dehydrogenation methyl ethyl ketone.

The reactions of hexine-diol, hexene-diol and hexane-diol correspond exactly to those of butine-diol, butene-diol and butane-diol. Thus from hexine-3-diol 2.5 hexane-triol-2.3.5 can be obtained, and from hexene-3-diol 2.5 1.4-dimethyl-erythritol. Hexane-diol-2.5, on dehydrogenation, yields hexane-dione-2.5 (acetonyl acetone).

The alkinol synthesis has also been carried out with other aldehydes and ketones, such as propion-aldehyde, n-butyric aldehyde, croton aldehyde, oenanthaldehyde, benzaldehyde and acetone.

/III. "Carbonylation".

II. "Carbonylation".

(a) Acetylene and carbon monoxide.

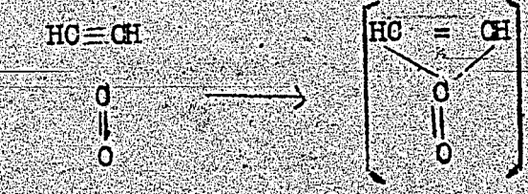
It was thought possible that in the presence of a metal carbonyl or of a metal capable of carbonyl formation acetylene might be made to yield aldehydes by reaction with carbon monoxide. The product isolated, however, from reaction of acetylene and carbon monoxide in presence of water proved to be acrylic acid, and it was found that other 'hydrogen donors' led to similar reaction. Thus alcohols with acetylene and carbon monoxide yield acrylic esters, amines, acrylamines, mercaptans thio-esters or the tautomeric thioacrylic ester, and organic acids the mixed anhydrides with acrylic acid.

As a first explanation of this reaction it was assumed that the acetylene reacted in its hypothetical isoform $H_2C = C <$ to give methylene ketene

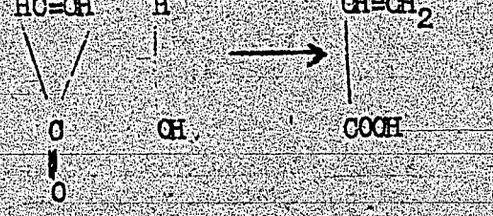
$$H_2C = C = CO$$

since it is known that ketenes with water, alcohols, etc. yield carboxylic acids, esters, etc. This theory, however, did not explain the reactivity of the di-substituted acetylenes, which cannot be converted into ketenes. Nor does it explain the occurrence of two different products of reaction from di-substituted acetylenes.

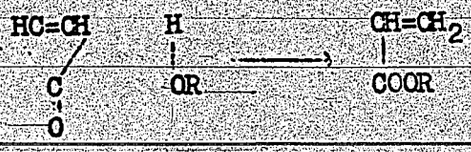
As a more satisfactory explanation the intermediate formation of cyclopropenone from acetylene and carbon monoxide was assumed, this then reacting with compounds containing hydrogen atoms, such as water, alcohols, mercaptans, amines and reactive carboxylic acids as follows:



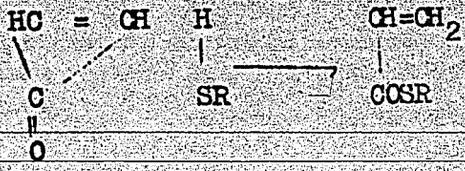
Cyclopropenone (hypothetical)



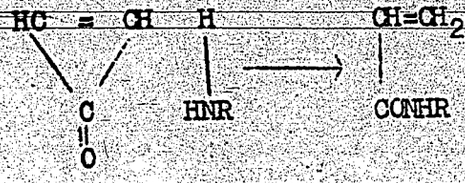
Acrylic acid



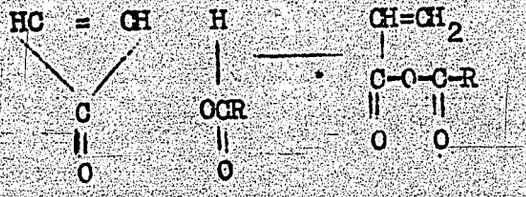
Acrylic esters



Acrylic thic-esters

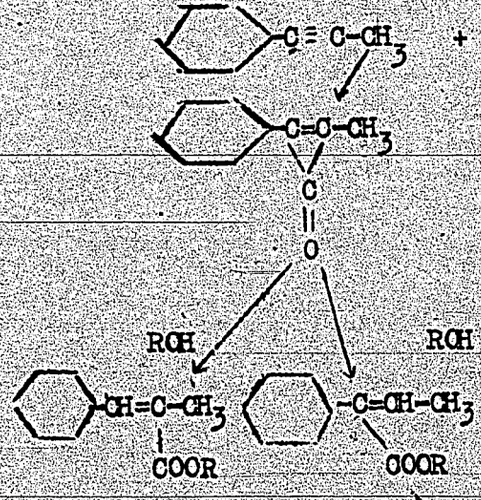


Acrylic amides



Mixed acrylic anhydrides

From methyl phenyl acetylene the expected isomeric α and β substituted acrylic acids and esters are actually obtained:



α-methyl cinnamic ester α-phenylcrotonic ester

/The

The reactions described can be brought about by introducing metal carbonyls or catalytically using carbonyl-forming metals or their compounds. Using metal carbonyls to yield CO, an acid or halogen must be present:

$$H_2O + CH \equiv CH + 1/4\ Ni(CO)_4 + 1/2\ HCl\ aq \longrightarrow$$

$$H_2C = CH-COOH + 1/4\ NiCl_2\ aq + 1/4\ H_2$$

Acrylic acid

$$RCH + HC \equiv CH + 1/4\ Ni(CO)_4 + 1/2\ HCl\ aq \longrightarrow$$

$$H_2C=CH-COOR + 1/4\ NiCl_2\ aq + 1/4\ H_2$$

Acrylic ester

$$RSH + HC \equiv CH + 1/4\ Ni(CO)_4 + 1/4\ HCl\ aq \longrightarrow$$

$$H_2C=CH-COSR + 1/4\ NiCl_2 \cdot aq + 1/4\ H_2$$

Nickel carbonyl is most suitable, cobalt carbonyl yields similar results, but is more difficult to obtain, but so far no reaction has been obtained with iron carbonyl. As acid component hydrohalic acid, acetic acid and phosphoric acid are suitable but in technical work concentrated hydrochloric acid is used. The acid should be used in aqueous solution, however, otherwise considerable formation of propionic esters occurs through the hydrogen produced in the course of the reaction, and in the presence of water these propionic acid esters are entirely absent.

The reaction occurs, unusually vigorously at a temperature of 40°-42°. The conversion is practically quantitative giving acrylic acid and its derivatives in about 96% yield.

For regeneration of the nickel carbonyl from the salt formed, nickel chloride, for instance, the nickel chloride solution is first treated with rather more ammonia than is necessary for the formation of the complex hexamine nickel chloride, and then treated with CO at about 80° and 50-100 atmospheres. In this process nickel carbonyl is produced quantitively. The aqueous solution, containing besides excess ammonia ammonium chloride and ammonium carbonate is treated with milk of lime and the ammonia regained. This simple conversion of nickel salts into nickel carbonyl in aqueous solution represents a considerable technical advance on previous methods.

$$Ni \underset{\uparrow 4\,CO}{|Cl_2 + 2\,NH_3 + H_2O + CO|} \longrightarrow Ni(CO)_4 + 2\,NH_4Cl + CO_2,$$

$$\text{or } \left[Ni(NH_3)_6\right]Cl_2 + 5CO + 2\,H_2O \longrightarrow Ni(CO)_4 + 2\,NH_4Cl + (NH_4)_2CO_3 + NH_3$$

The acrylic ester synthesis can in this way be carried out continuously by the sump process without pressure. The process can be applied to acetylene hydrocarbons, and also to alkinols and alkindiols and their ethers and esters, and also to amines and mercaptans carrying acetylene residues.

Nickel halides are most suitable catalysts and for the preparation of acrylic esters, the method used is to allow the alcohol to drip into a pressure tower at a temperature of 150° to 180° - the catalyst being already dissolved in the alcohol - whilst at the same time a mixture of acetylene and carbon monoxide is circulated through the apparatus directly or as a counter-current. At the foot of the tower high percentage acrylic ester can be drawn off, which can easily be worked up into the pure product.

The advance represented by this new synthesis is illustrated by comparing the procedure previously available for obtaining acrylic esters:

$$H_2C = CH_2 \xrightarrow{HOCl} ClCH_2CH_2OH \xrightarrow[-H_2O \,+\, ROH]{Ca(OH)_2}$$

$$H_2C\underset{O}{<}CH_2 \xrightarrow{HCN} HOCH_2CH_2CN \xrightarrow[\text{saponified}]{}$$

$$CH_2 = CH - COOR$$

(b) Olefins and carbon monoxide.

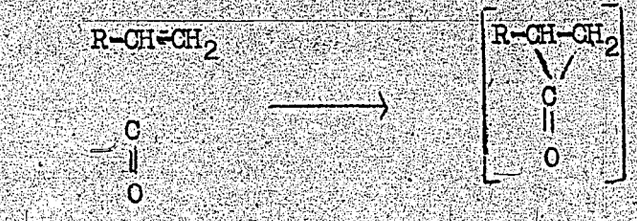
On the basis of the work with acetylene a similar procedure was applied to the olefins. It was to be expected that a cyclopropanone would then be formed, which, in the presence of an

/acceptors

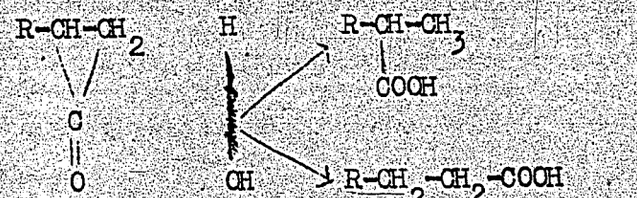
acceptors with a reactive hydrogen atom - such as water, alcohols, mercaptans, amines or carboxylic acids - would lead to esters thio-esters, amides and anhydrides of saturated carboxylic acids.

The actions of this type were in fact realised the hypothetical intermediate cyclopropanone undergoing fission to yield both possible products.

It may be noted that the cyclo-propanone can also be split by hydrogen. The following summarises the general reactions:

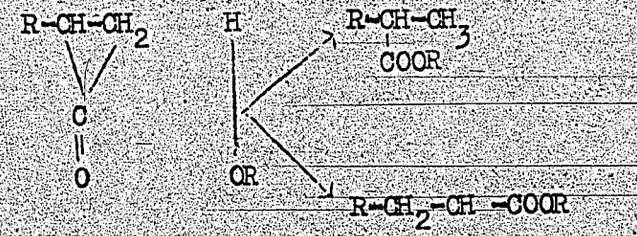


Alkyl cyclo propanone (hypothetical)



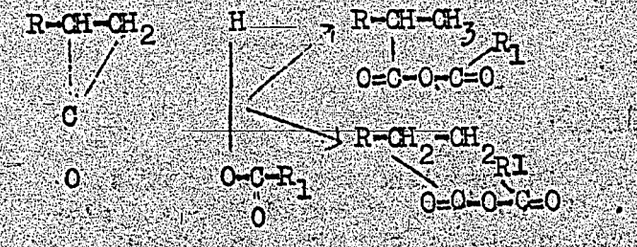
α-methyl-carboxylic acid

n-carboxylic acid

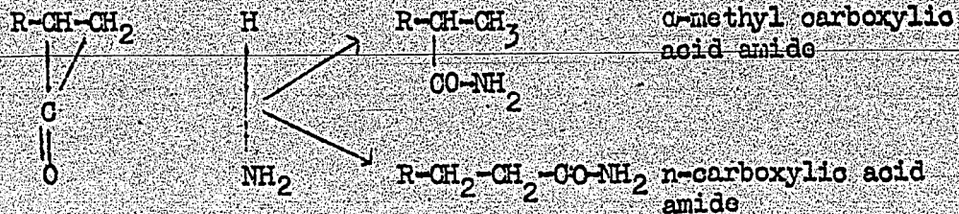


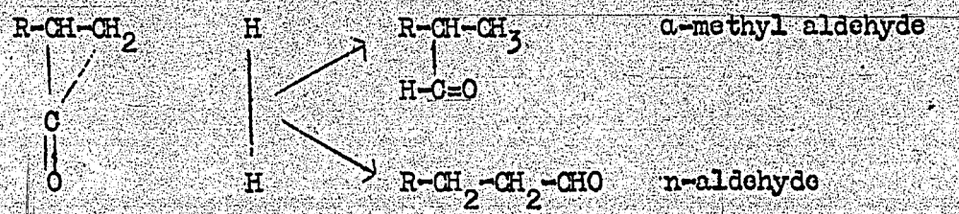
α-methyl carboxylic ester

n-carboxylic ester



Carboxylic acid anhydrides



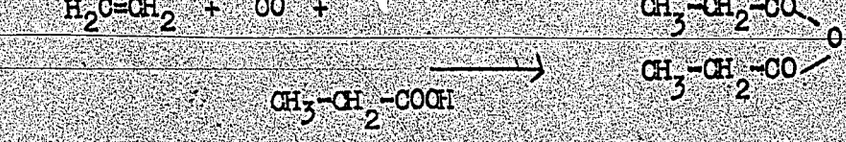


As in the case of the acetylenes, the reactions can be carried out using stoichiometric quantities of metal carbonyls in the presence of acid or catalytic ally.

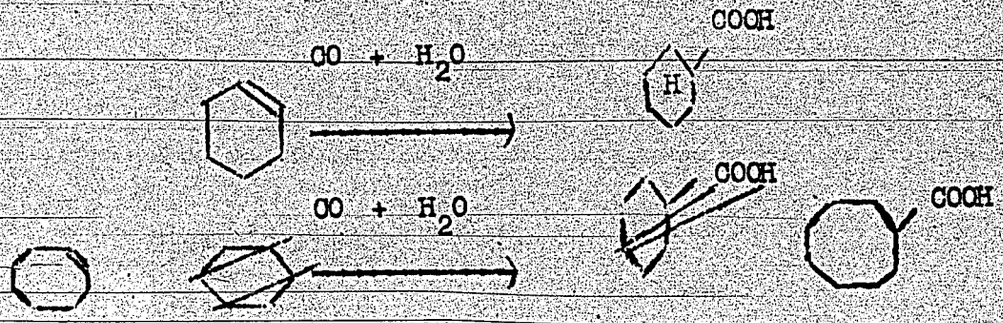
The greatest interest naturally attaches to the carboxylic ac id synthesis which proceeds with ease from the olefin, carbon monoxide and water, with nickel carbonyl as catalyst at 200 - 300° and 150 - 300 atmospheres.

The most important application is in obtaining sebacic acid from the appropriate cracked or synthetic olefin and of propianic anhydride. It is possible to obtain both propionic acid and propionic anhydride from ethylene, carbon monoxide and water by selecting the reaction conditions:

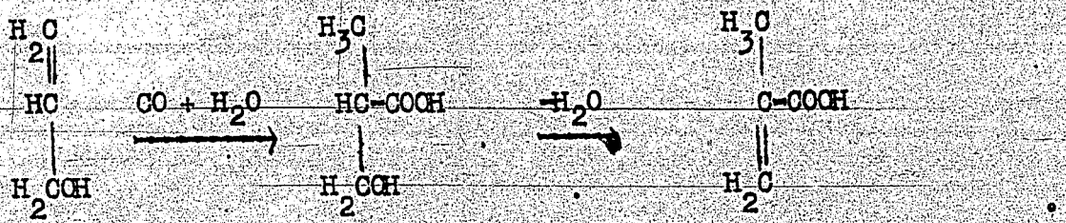




Cyclic olefins react in a similar manner. For instance, hexahydrobenzoic acid is produced from cyclohexene, carbon monoxide and water; cyclooctotetraene (see below) yields cyclooctylcarboxylic acid:



Olefin alcohols, olefin carboxylic acids and olefin ketones also exhibit the same reaction. For example, allyl alcohol yields β-hydroxyl-isobutyric acid, which, however, is dehydrated to methacrylic acid during the reaction.

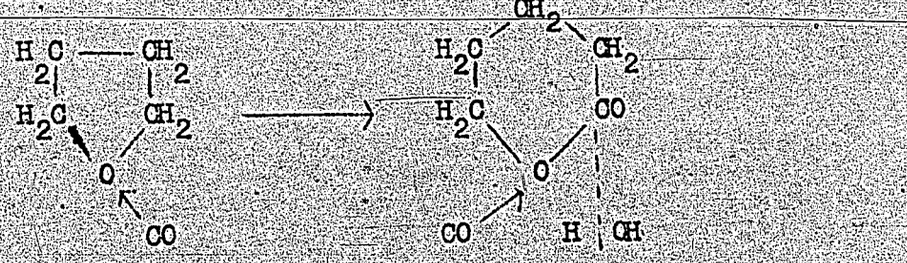


Allyl alcohol — β-hydroxy-iso-butyric acid — Methacrylic acid

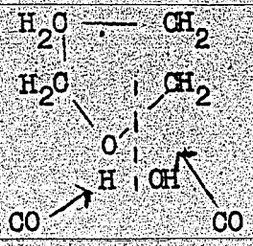
(c) Reaction of carbon monoxide with alcohols and ethers.

By the use of metal carbonyls, particularly nickel carbonyl, it is comparatively easy to introduce carbon monoxide into aliphatic and cyclic ethers. In contrast with the olefins, in which nickel carbonyl is effected alone, the analogous conversion with ethers and nickel carbonyl requires the presence of a halogen.

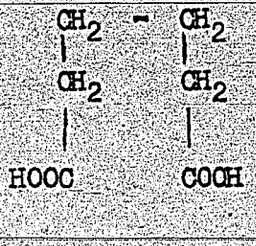
These findings led to a new synthesis of adipic acid from tetrahydrofurane:



Tetrahydrofurane — δ-Valerolactone



Tetrahydrofurane



Adipic acid

This synthesis can be effected as a continuous process in good yield and makes possible the production of polyamides in a cheap and simple manner on a large scale, without the use of phenol. Tetra hydropyrane can be converted into pimelic acid in a similar manner.

The diols corresponding to the cyclic ethers react the same way. Thus, butane diol-1.4 with two molecules of carbon monoxide yields adipic acid and hexane diol 1.6 suberic acid.

(d) Further applications.

Finally, we may refer briefly to two further basic reactions recently discovered (1941 and 1944), making use of catalysis by metal carbonyl hydrides.

This arose from the preparation of metal carbonyl hydrides - and particularly cobalt carbonyl hydride $HCO(CO)_4$ and iron carbonyl hydride $H_2Fe(CO)_4$ - in large quantities for the first time for the determination of their physical constants, and study of their chemistry.

It was found that cobalt carbonyl hydride belongs to the strongest known acids (corresponding approximately to HCl in strength), and iron carbonyl hydride behaves as a monobasic acid of medium strength.

By reaction with olefins in the presence of water alcohols, and from acetylene hydroquinone, was formed. The course of the reactions is complicated, and is far from being cleared up.

The overall reaction for the alcohol synthesis from olefins e.g. using ethylene is as follows:

$$H_2Fe(CO)_2 + 2\,H_2C{=}CH_2 + 4\,H_2O \longrightarrow$$

$$2\,CH_3{-}CH_2{-}CH_2{-}OH + Fe(HCO_3)_2$$

$$\downarrow$$

$$FeCO_3 + H_2O + CO_2$$

$$H_2C{=}CH_2 + 3\,CO + 2\,H_2O \longrightarrow CH_3{-}CH_2{-}CH_2CH + 2\,CO_2$$

Catalytic reaction

In the presence of ammonia amines are obtained:-

$$CH_2{=}CH_2 + 3\,CO + H_2O + NH_3 \longrightarrow$$

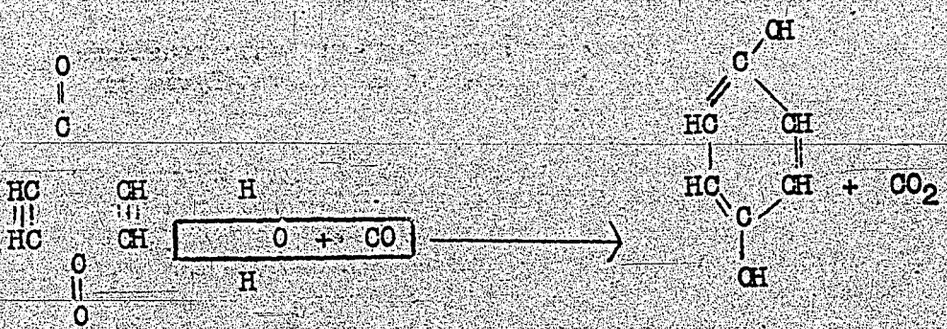
$$H_2N{-}CH_2{-}CH_2{-}CH_3 + 2\,CO_2$$

n-propyl-amine

the di- and tri-propyl-amines being also formed.

By the use of acetylene in the reaction with metal carbonyl hydrides, it was expected to obtain unsaturated alcohols. Unexpectedly, however, hydroquinone or from substituted acetylenes, hydroquinone derivatives, were formed, in about 30% yield.

The gross reaction can be formulated as follows:



or:

$$H_2Fe(CO)_4 + 4\,C_2H_2 + 2\,H_2O \longrightarrow 2\,C_6H_6O_2 + Fe(OH)_2$$

/The

The successes in the new carbon monoxide chemistry were here also attributable to the use for the first time of hitherto unused catalysts, in this case the metal carbonyls and metal carbonyl hydrides, or their substitution products, just as success was achieved in the case of the ethinylation reactions by the use for the first time of the heavy metal acetylides as catalysts.

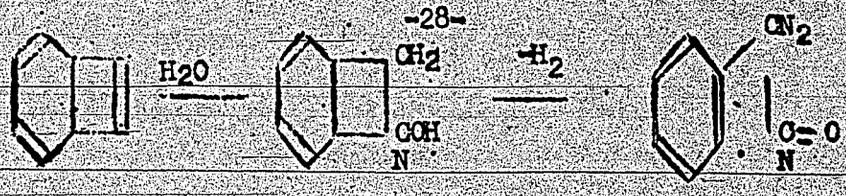
As a result of these experiments it has become possible to obtain technically important and complex substances from simple and readily available starting materials at low cost.

IV. Cyclic polymerisation of acetylene.

In 1940 systematic investigations led to the discovery of the polymerisation of acetylene into cyclooctatetrane, which had previously been prepared by Willstätter only by starting a series of reactions from pseudo-pelletierine in which the yield based on the alkalid employed, was less than 1%. By the new synthesis the technical production of cyclo-octo-tetrane has become possible.

Acetylene in an inert solvent, of which the most suitable is tetrahydrofuran, is compressed at more than 20 atmospheres in the presence of nickel compounds such as nickel cyanide, nickel thiocyanate or nickel aceto-acetic ester. The yield of cyclo-octo-tetrane is high and only small quantities of resinous products from polymerisation of the cyclooctatetrane occur. Small quantities of high-boiling unsaturated hydrocarbons are also formed, which, from their behaviour and properties, appear to be the hitherto unknown ring-homologues of cyclooctatetrane. It has not yet been possible to clear up their constitution. As a subsidiary product, an isomer of naphthaline-azulene - also occurs in small quantities, through dehydration and rearrangement of the primary product cyclo-decapentene. Cyclooctatetrane has the constitution I. Hydrogenation and oxidation with perbenzoic acid are readily explained on this formula. Most of its reactions, however, apparently proceed through II, where splitting of the four membered ring may also lead to derivatives of ethyl benzene. Halogenation and Diels-Alders syntheses, in particular, with maleic anhydride, acetylene-dicarboxylic ester and quinones supplies important information regarding the mode of reaction of cyclooctatetrane.

Hydration of cyclooctatetrane, gives a quantitive yield of phenyl acetaldehyde, which is best explained by formula II, assuming there is simultaneous dehydrogenation:



Cyclooctotetrane can react in á third way illustrated by the formation of terophthalic aldehyde by reaction with hypochlorite:



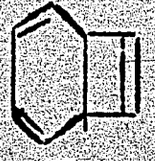
From analogy and without experimental support Hurd and Drake expressed doubt as to whether the four double band are conjugated in cyclooctotetrene. The physical properties of cyclooctotetrane do however confirm the cyclooctotetrene-1.3.5.7 formula postulated by Willstätter. This is shown, in particular by the Ramon spectrum, the few lines arguing the highest symmetry, and by the investigations carried out by Meeke, not yet published, of the infra-red spectrum. The zero dipole moment is in keeping with this.

Chemically cyclooctotetrene behaves in a way which compel the assumption that by the action of different reagents, it can react in the three following forms:



I

Cyclooctotetrane-1.3.5.7



II

Dicyclo-(0.2.4)-octatriene-2.4



III

1.2.4.5-Dimethylenecyclohexadiene-2.5

/The

The full results, which, also lead to the seven-ring series, cannot be referred to within the limits of this review. It can be seen however that cyclooctotetrene provides entirely new ways, of obtaining inaccessible benzene derivatives as well as of studying the chemistry of the eight numbered ring.

Technical application.

The technical application of the reactions described was possible only after safe conditions for handling acetylene under pressure had been found. In this direction Reppe may be considered to have contributed as much as in devising the basic reaction. Whilst acetylene under a pressure of 0.5 atmospheres was formerly considered dangerous and a pressure of over 1.5 atmospheres actually forbidden, it has now become possible to pump acetylene at 5 to 10 atmospheres and 100°C at several hundred cubic metres per hour with perfect safety.

Perhaps the most important application is in the preparation of butadiene via butine diol butane diol and tetrahydrofuran. Production of butine diol is carried out in towers 18 m. high and 1.5 m. diameter containing 25 m³ of catalyst, equivalent to 3000 Kg. of copper acetylide. 90% acetylene is fed in at 5 atmospheres the heat of formation of butine diol of 55 K.cal./mol. being carried away by evaporation of water vapour into the circulating gas. In the last stage of the preparation of butadiene a considerable improvement in yield was obtained by the circulation of tetrahydrofuran.

Reference may be made to the synthesis of tetra-hydrofurane from the approximately 35% crude aqueous solution of butane-diol. By adding 0.1% of acid and heating at 250 - 300°C. under about 100 atmospheres, a quantitive separation of water is secured even in this dilute aqueous solution.

For a large number of additional syntheses Reppe has already done all the preliminary experimental work, so as to be able to produce them on the largest scale. War conditions have prevented the development of further processes notably the manufacture of the acrylic esters from acetylene, carbon monoxide and alcohols, of alcohols from olefins and water, of acids, from olefins, carbon monoxide and water and of cyclooctotetrenes from acetylene.

In addition to the new reactions described Dr. Reppe has also been responsible for establishing on a technical basis processes already known of which the following may be mentioned:

/Inter

Inter conversion of alcohol and acetaldehyde, the production and applications of ethylene, and production of butadiene.

In 1926 ethylene was still being obtained by the classical method from ethyl alcohol. The dehydration catalyst was improved and attention turned to obtaining ethylene by cracking middle oils which got as far as the planning of a technical plant. The project was wrecked, however, by the impossibility of securing a reduction of the duty on middle oils.

The experience gained, however, was applied to another source of ethylene. In spite of its small ethylene content (about 1%) a number of works later used the process for obtaining ethylene oxide, glycol and other ethylene derivatives from coke oven gas.

Acetylene offers a further source of ethylene. Partial hydrogenation was thoroughly investigated and alkaline reduction with zinc found to be effective not only to convert acetylene into ethylene, but as a generally applicable method for the partial reduction of the triple bond.

This process was superseded by the partial hydrogenation of acetylene in the gas phase using a palladium catalyst.

Reference may also be made to the preparation of ethylene chlorohydrine required for the manufacture of hydroxy ethyl-aniline for the indigo synthesis. A mixture of chlorine and ethylene is pumped continuously through a reaction tower containing water, unreacted ethylene being recirculated. Ethylene chlorohydrin is obtained as an aqueous solution, water removed from the tower being replaced. The ethylene stream effects perfect mixing, the heat of the highly exothermic reaction being carried away by the evaporation of small quantities of water, and the temperature in this way is being maintained at the most favourable value of 50°. This so-called "sump process" devised by Reppe has been also applied to the manufacture of acetaldehyde, paraffin oxydation, carbo-hydrogenation and sulphochlorination.

Ethylene chlorohydrin in this way became a ready source of ethylene oxide, glycol and glycol ethers. The procedure, for converting chlorohydrin with milk of lime into ethylene oxide was perfected as a technical process, and the production of the pure oxide, in particular, was improved.

/The

The conversion of ethylene oxide into glycol or its ethers by reaction with water or alcohols in presence of sulphuric acid at normal pressure proved not to be feasible on a large scale, but was effected by pressure hydrolysis with water or alcohol without a catalyst under pressure. From ethylene oxide by reaction with hydrocyanic acid acrylo nitrile was obtained on a technical scale the intermediate ethylene cyanhydrin being dehydrated catalytically.

$$CH_2 - CH_2 \text{ (O)} + HCN \longrightarrow CH_2OH\text{-}CH_2\text{-}CN$$

$$CH_2\,OH\text{-}CH_2\text{-}CN \xrightarrow{-H_2O} CH_2{=}\,CH\text{-}CN$$

With this neat synthesis the unprofitable and far from safe method from ethylene chlorohydrine and sodium cyanide was finally abandoned, and a route to acrylic esters was also provided.

When, in 1925, the problem of the manufacture of artificial rubber was again taken up by the I.G. Farbenindustrie, Reppe undertook the preparation of butadiene by way of acetaldehyde acetaldol and 1-3-butylene-glycol. A competitive process using thermal decomposition of cyclohexane was superseded by the four-stage process developed between 1925 and 1928.

The chemical and technical development of the last two stages, hydrogenation of acetaldol and dehydration of 1.3-butylene glycol represent a great achievement. The dehydration of the 1.3-butylene glycol offered great difficultics overcome by the elaboration of a suitable catalyst. The known dehydration catalysts severely reduced the yield of butadiene owing to secondary reactions.

Acid alkali phosphates on graphite as carrier, to which amine phosphates such as butylamine phosphate were added as a source of free phosphoric acid, proved particularly satisfactory, the glycol, together with steam, being passed over this catalyst which has also been found effective in the manufacture of butadien from 1.4-butylene glycol as mentioned above.

1.3-Butylene

1.3-Butylene glycol will not withstand any appreciable over-heating, whilst the dehydration is a highly endothermic reaction, and in order to permit only very small differences in temperature in the reaction chamber it was necessary to equip the conversion receptacle with very large heating surfaces.

This work during 1925 - 1928 provided the basis for the manufacture of butadiene, of which, 100 tons were manufactured on a semi-technical scale as early as 1928.

Gendorf, 24 March 1945. SH(K)173

Copy 1

Final Report No. 370.
ITEM No. 22

MANUFACTURE OF ACETALDEHYDE.

Fisher, J. W.

"This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement"

LIBRARY
of the
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION
Bureau of Mines
SEP - 1946

4 JUN 1946

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H.M. STATIONERY OFFICE

MANUFACTURE OF ACETALDEHYDE.

Reported by:

J.W.Fisher, M.of S.

BIOS Target No. 22/1(f)

British Intelligence Objectives Sub-committee,
32, Bryanston Square, W.1.

12p. diagr.

TABLE OF CONTENTS.

Subject.	Page No.
Object of Visit.	2.
General.	2.
Description of Process.	3,4.
Vinylation.	3.
Hydrolysis.	4.
Production & Quantities.	4.
Yields.	5.
Steam, Power, Labour.	7.
Cost of Product.	8.
Cost of Installation.	9.

Personnel of Team.

J.D. Rose, M.of S.
J.W. Fisher, "
J.F.C. Gartshore, "
C.J.S. Appleyard, "
A.H.Andersen, "
P.W. Blaylock, "

MANUFACTURE OF ACETALDEHYDE.

(from acetylene and methanol).

Object of Visit.

A visit was paid to the Mainkur (Fechenheim)-Frankfurt Works of the I.G. Farbenindustrie during the period 26th-29th November, 1945 with the object of interviewing Dr. Walter Reppe, and, if possible, of securing access to 152 technical Reports understood to be in his possession. Among the documents so found, a file bearing the title "Acetylen" contained a Report (dated 13th October, 1937) on a projected manufacture of acetaldehyde from acetylene and methanol, and the information abstracted therefrom forms the subject of the present Report.

General.

Dr. Reppe was understood to claim that the process had never been operated on a large scale, but that there was now some likelihood that production of acetaldehyde by this route would be put in hand by I.G. There are, however, indications that this route for acetaldehyde has been run on semi-works scale at Ludwigshafen. The information taken from the Reppe Report of 13th October, 1937 relates to a projected plant for the manufacture of 5100 tons/month i.e. 170 tons/day of acetaldehyde. Details of the working of the process are given, together with some relevant calculations; and comparisons with the mercury-catalysed Schopau process are provided.

The Reppe Report claimed great advantages for the new process when compared with the usual hydration in presence of mercury catalysts, both as regards purity of product and in actual operation. For example, blemishes and decomposition spots in sheets or films, made from cellulose esters containing acetyl groups, have been traced to mercury impurity in the acetic acid used. Acetic acid from acetaldehyde by the new route would obviously be superior for cellulose esterification purposes, since no mercury is used in the proposed new process.

It is claimed further that difficulties inseparably connected with the use of mercury and its recovery are obviated, and that in the new process no trouble is experienced with poisoning of catalyst. Even when using relatively impure acetylene, the caustic potash catalyst is able to take care of the impurities.

Description of Process.

The numbers used in brackets in the following account refer to the flow-diagram given on page 11.

The process is based on the reaction of acetylene with methanol under pressure to give vinyl methyl ether, which in turn is hydrolysed to give acetaldehyde and methanol, the latter being recycled.

$$CH_3OH + CH{\equiv}CH \xrightarrow{KOH} CH_3O.CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3CHO + CH_3OH.$$

Vinylation Section.

The vinylation reaction is carried out in a tower 15 metres high and 2 metres inside diameter (I). The tower during operation is filled with a 20% $^{W}/_{w}$ solution of caustic potash in methanol, the reaction temperature i. 160°C., and the operating pressure is 16 ats. Into the pressure tower is pumped (4) continuously methanol containing a small quantity of dissolved caustic potash. The amount of the latter is not normally greater than 2% and is adjusted to maintain the concentration of caustic alkali in the tower at the 20% $^{W}/_{w}$ figure. The tower carries a gas-circulation system by means of which, via gas circulation pump (3), an acetylene/nitrogen mixture is pumped in at 16 ats. pressure. Gas entering the tower has 35-40% $^{V}/_{v}$ acetylene, but emerges, after deposition of the vinyl ether in the condensing system (7 and 8), with only 10-15% acetylene. The fresh acetylene required is taken from gasometer (1) and is forced by compressor (2) into the circulation system.

Through dephlegmator (6), which holds back methanol, the vinyl methyl ether passes in the gas stream to the water-cooled condenser (7), and on to the separator (8), which contains a heating element. The condensate in (8) is freed from dissolved gas by slight warming, and the liberated gas, together with the main stream, goes on through another cooler (9) into separator (10), where the remaining V.M. ether falls out. The gas passes out

of the top of separator (10), and, by way of the catch-pot (11), back to the suction side of pump (3). Any condensate in separator (10) runs back into separator (8), and from the latter crude V.M.ether goes to degassing column (12) at 6 ats. pressure, where it is completely freed from acetylene. The latter passes through the dephlegmator(13) at 6 ats. to a reducing valve, and so to the suction side of compressor (2). The crude ether from the degassing column is run to the storage tanks (14), where it is held under 3 ats. pressure of nitrogen.

Hydrolysis and Distillation Section.

The V.M.ether from storage (14) is fed continuously, with rotameter control (15) to hydrolysis tower (II), 10 metres high and 2.5 metres diam. This tower contains a 0.25% solution of sulphuric acid in water at 80°-100°C., and in this, at an operating pressure of 2.5 ats., the ether is hydrolysed. Make-up water and sulphuric acid are added from storage vessel (16) as required. All the acetaldehyde with some methanol and water passes via pipe (17) to the distillation column (III), which is 15 metres nigh, 2.6 metres diam., and is of the bell and plate type, - or is packed with Raschig rings. From the column top passes acetaldehyde, which is condensed in the cooler (19) and runs via buffer tank (20) to storage. Water rendered slightly acid with sulphuric acid is fed from vessel (18) to the column to prevent acetal formation.

From the base of column (III) aqueous methanol is run off to the stirred vessel (21) where it is made weakly alkaline with caustic soda solution, and then to the methanol distillation column (IV), 12 metres high and 2.5 metres diam., and of the bell and plate type. Any traces of aldehyde are resinified by the caustic alkali, and this is desirable, since the recycled methanol must be free from acetaldehyde. Methanol, distilling from the column top, is condensed at (22) and is pumped via receiver (23) back to the storage vessel (5), from where, after addition of caustic alkali, it is pumped back to tower (I).

Quantities involved.

For a production of 170 tons/day of acetaldehyde, 96,600 $m.^3$/day of acetylene must be handled. This will

give 264 tons/day crude vinyl methyl ether (85% ether + 15% methanol) to be saponified, and 163.5 tons/day of methanol to be fractionated from aqueous solution.

Yields.

In the research plant at Ludwigshafen the yield of vinyl methyl ether from acetylene was 97%, and the saponification stage to acetaldehyde was achieved with 99% yield. An overall yield of 96% was therefore assumed.

Flow rates.

(1) Vinylation section.

1 Converter. Height 15 m. Diameter 2 m.
Cross-section 3.14 m^2.
Volume 47 m^3.

Circulating gas - 1000 m^3/hr./20°C./16 ats.
Methanol vapour - 43 m^3/hr./20°C./16 ats.
(= 1.67 tons/hr./20°C./1 at.)
1043 m^3/hr./20°C./16 ats.

Velocity of vapour - 0.136 m/sec.

(2) Saponification section.

1 Converter. Height 10 m. Diameter 2.5 m.
Cross-section 4.9 m^2.
Volume 49 m^3.

Through tower pass -

6.82 tons: 7.15 tons/hr. CH_3CHO) = 9.3 tons V.M.E.
(5.15 " " CH_3OH)
(1.67 " " CH_3OH

equivalent to -

0.523 m^3/sec./80°C./2.5 ats. CH_3CHO.
0.686 m^3 " " " CH_3OH.
1.209 m^3 total.

Velocity of vapour - 0.25 m/sec./2.5 ats.

(3) Aldehyde/Methanol separation.

1 bell and plate tower. 15 m. high. 2.6 m.diameter.
Cross-section 5.3 m^2.

To separate -
7.15 tons/hour CH_3CHO
6.82 " " CH_3OH.
9.24 " " H_2O.

7.15 tons/hr. CH_3CHO = 1.985 kgrm./sec.
= 1.085 m^3/sec./20°C./1 at.

This permits, with up to 5 times reflux a linear velocity (at 2.5 ats.) of $\geq$ 40 cms./sec.

(4) Methanol distillation.

1 bell and plate column 12 m. high, 2.5 m. diam.

To separate -
6.82 tons/hour MeOH
9.24 " " H_2O.

With $2\frac{1}{2}$: 1 reflux, column known to be adequate.

Heats of Reaction.

$CH_3OH + CH{\equiv}CH \rightarrow CH_3O.CH{=}CH_2$ + 30.7 Kcals.

$CH_3O.CH{=}CH_2 + H_2O \rightarrow CH_3OH + CH_3CHO$ (no heat).

Heats of Vaporisation.

Vinyl methyl ether	-	104 Kcals./kg.
Methanol	-	263 " "
Acetaldehyde	-	~200 " " (incl.heat of solution)
Water	-	540 " "

Steam requirement.

(a) Total heat for vinylation - approx. 30,000 Kcals.

(b) " " " saponification - " 70,050 "

(c) Acetaldehyde column (3/1 reflux) - 60,000 "

(d) Methanol column (2.5/1 reflux) - 63,000 "

223,050 Kcals.

At 1 kg. steam = 500 Kcals.

steam reqrd. is $\frac{223050}{500}$ = 446 kg.

Plus 20% for losses = 535 kg. steam
(per 100 kg. CH_3CHO)

Electrical energy requirement.

15 k.w.h. per 100 kg. CH_3CHO.

Labour requirement.

10 men. (2 for one vinylation tower plus one degassing column. 2 for one saponification tower plus one distillation column. 1 for methanol distillation. 3 for servicing compressors and pumps. 2 for general work.)

Estimated Cost of Product.

based on Schkopau prices (Mercury process.)
5100 tons CH_3CHO/month = 170 tons/day.

Per 100 kg. acetaldehyde.

	Amount.	Rate. (Reichmarks)	Cost.	
(a) Raw Materials.				
Caustic potash (kg.)	2.00	48.00	0.96	
Alkali liquor (NaOH)	0.20	16.80	0.03	
Sulphuric acid (kg.)	0.40	3.05	0.01	
Methanol (Yield 96%)	3.00	18.00	0.54	
			1.54	1.54
(b) Intermediates.				
Acetylene (m^3) (Yield 96%)	56.00	43.38	24.25	
			24.25	25.79
(c) Services.				
Wages (10 men/shift)	0.11	1.00	0.14	
Salaries			0.05	
Steam (kg.)	535.00	2.50	1.34	
Water (m^3)	30.00	1.80	0.54	
Electricity (k.w.h.)	15.00	1.51	0.23	
Nitrogen (m^3)	1.00	2.15	0.12	
			1.00	
(d) Maintenance, etc. (7% capital cost).				
Materials, etc.			0.12	
Offices and laboratory.			0.06	
Welfare, etc.			0.02	
Amortisation (8% capital cost).			1.14	
			4.76	30.55

Sale of impure C_2H_2 was expected to realise 42.68 R.M. per 100 m^3. This would reduce cost, per 100 kg. CH_3CHO, to 30.20 R.M.

Comparison of Product Costs.

	Schkopau Mercury Process.	Via Vinyl Methyl Ether. (Schkopau prices).
Raw Materials.	0.50	1.54
Acetylene.	24.81	23.90 (corr.)
Charges.	5.18	4.76
	30.49 R.M.	30.20 R.M.

Installation Costs.

(1) Vinylation (264 tons V.M.E./day).

Item.	Cost.(R.M.)
1 Converter (60 ats. construction)	200,000
1 Pressure boiler (70 ats.)	75,000
1 Degassing column (60 ats.)	200,000
Expansion vessels.	50,000
Condensers, dephlegmators.	200,000
Measuring equipment.	50,000
Pipework.	500,000
Compressors with Motors(4030 m^3 C_2H_2/hr.)	1,500,000
Gas circulating pumps (1000 m^3/hr.)	1,000,000
Tank storage.	500,000
	4,275,000

(2) Hydrolysis section.

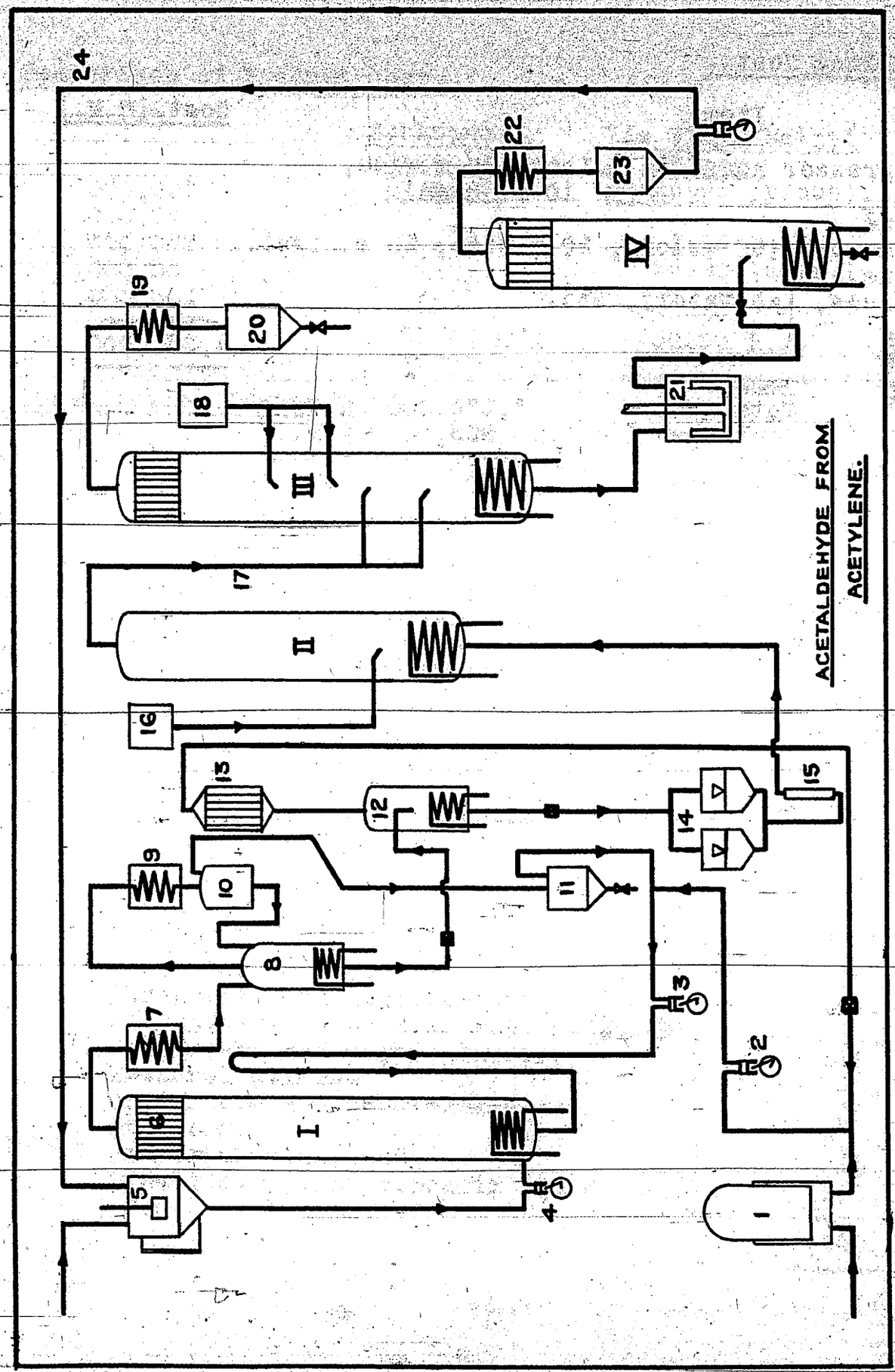
1 Converter (3 ats. construction).	200,000
Condensers and dephlegmators.	100,000
Aldehyde-methanol distillation column.	250,000
Condensers and dephlegmators.	150,000
Methanol column.	50,000
Condensers and dephlegmators.	50,000
Pipework.	500,000
Measuring equipment.	50,000
Electrical power circuits (3000 k.w.h.)	300,000
	1,650,000

(3) Building Costs.

Item.	Cost.(R.M.)
Compressor house(50 m.long, 30 m.wide, 10 m. high).	300,000
Crane.	50,000
Framework (60 m.long, 20 m.wide, 25 m.high).	750,000
Crane.	50,000
Offices, laboratory, etc.	100,000
	1,250,000

Total -	7,175,000	R.M.
Contingencies -	825,000	R.M.
Total Cost -	8,000,000	R.M.

Note. For the same production capacity, a plant based on the mercury-catalysed process was reckoned to cost R.M. 7,400,000.


ACETALDEHYDE FROM ACETYLENE.
I
II
III
IV
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

Copy 1

Final Report No. 368.
ITEM No. 22

MANUFACTURE OF ADIPIC DINITRILE AND HEXAMETHYLENE DIAMINE.

Fisher, J. W.

"This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement"

LIBRARY
of the
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION
Bureau of Mines
AUG - - 1946

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE
LONDON - H.M. STATIONERY OFFICE

MANUFACTURE
OF
ADIPIC DINITRILE
AND
HEXAMETHYLENE DIAMINE.

Reported by:

J.W.Fisher, M.of S.

BIOS Target No. 22/1(f)

British Intelligence Objectives Sub-committee,
32, Bryanston Square, W.1.

(1945?)

10 p. diagrs.

TABLE OF CONTENTS.

Subject.	Page No.
Part I. Adipic Dinitrile.	
Object of Visit.	2.
Personnel Interrogated.	2.
Description of Process.	2.
Yield.	5.
Part II. Hexamethylene Diamine.	
General.	5.
Description of Process.	6.
Yield.	7.
Condition of Plants.	7.

—

Personnel of Team.

J.D. Rose, M.of S.
J.W. Fisher, "
J.F.C. Gartshore, "
C.J.S. Appleyard, "
A.H.Andersen, "
P.W.Blaylock, "

—

Firm's Name and Location.

I.G.Farbenindustrie A.G.,
Ludwigshafen.

Object of Visit.

The general object of the visits paid to the above factory during November 1945 being to study certain large-scale applications of the Reppe acetylene chemistry, interest extended nevertheless to various intermediates which could be considered to stem from the products of the main reactions. In this way, attention was given to the preparation of adipic dinitrile from adipic acid, and to the manufacture of hexamethylene diamine by reduction of the adiponitrile.

Personnel interrogated.

The description of the processes given in this Report is based on information supplied by Drs. Hüttner and Freytag during a visit to the Works on 20th November, 1945.

PART 1.

Adipic Dinitrile from Adipic Acid.

Description of Process.

By a process of simultaneous ammoniation and dehydration, adipic acid can be converted at temperatures above 250°C. to adipic dinitrile.

$$\begin{matrix}COOH\\|\\(CH_2)_4\\|\\COOH\end{matrix} + 2NH_3 \rightarrow \begin{matrix}CN\\|\\(CH_2)_4\\|\\CN\end{matrix} + 4H_2O.$$

The operation as conducted at Ludwigshafen was carried out in the vapour phase, the catalyst being phosphoric acid on silica gel. (1 part H_3PO_4 to 4 parts silica).

The plant had a rated capacity of 30 tons/month, but was producing almost twice this amount. The building of a larger unit for 100 tons per month had been begun, but had never been completed.

The operation of the process may be followed by reference to the diagram on page 8.

Molten adipic acid is held in the heated vessel (1) at a temperature of 200°C. and is forced, at a rate of 130 kgrms. per hour, and with rotameter control (2), into a vaporiser (3).

Ammonia gas is circulated by the blowers (4) through a heat-exchanger (5), whence it comes at 150°C., and passes on through an electric heater (6) which delivers it to the vaporiser at a temperature of 450°C.

From the vaporiser, ammonia and adipic acid (or its diamide) pass at a temperature of approx. 390°C. to a cylindrical vessel (7) packed with the silica gel-phosphoric acid catalyst. This chamber is not heated other than by the inflowing gases, which pass out at 320°C., and flow via pipe-line (8), through heat-exchanger (5), and so to the condensing system (9,10,11), where adiponitrile and water are condensed out. The ammonia gas then circulates to the suction side of the blowers, fresh gas being introduced into the system as required.

Adipic acid container (1). This vessel, with coil (10 ats. steam) for melting and heating the adipic acid, and the pipework leading to the vaporiser (3), are of aluminium construction. The pipework is steam-jacketted, as is also the rotameter (2), which is made of glass and V2A steel.

Gas circulation. The blowers (4) which are of the Root's compressor type, and of 2000 m^3/hr. capacity, force ammonia round the system at a rate of 1000 m^3 per hour. Measurement is made by means of orifice plate meters. This large gas volume, which has to carry all the heat necessary for the vaporisation of the adipic acid and maintenance of reaction temperature, is passed through a heat-exchanger (5). In this it runs counter to the hot gases coming from the reaction chamber, the temperatures established being -

Ammonia in - Room Temp.

" out - 150°C.

Product gas in - 240°C.

" " out - 40°C.

Preheater (6). The gas enters the preheater and passes down and up through four rows of six tubes, each tube containing an electric heating element. The gas is thus heated, in four passes, to 450°C., and moves with a linear velocity of 30 metres/sec., the height of the heating-tubes being 1.5 metres.

Vaporiser (3). This consists of an aluminium tube, 0.7 m. diam., and 2.6 m. high, packed with porcelain or stoneware Raschig rings supported on a bottom grid. The molten adipic acid enters centrally at the top, while the ammonia comes in tangentially at 450°C. The hot gas vaporises the acid, and the mixture passes out at the bottom at approx. 395°C., via an iron pipe, to the catalyst chamber. The vaporiser has a capacity of 130 kgrms. per hour of adipic acid, and runs five days before tarry deposits begin to appear. The rings are changed every 8 - 10 days, and the vessel is furnished with a bottom outlet through which tarry residues etc. may be dropped.

Catalyst Chamber (7). The catalyst vessel has a capacity of 3.85 m^3 when empty, and contains 3500 litres of the silica gel-phosphoric acid catalyst. The vessel is of aluminium throughout and is fitted with a grid which supports the catalyst. The hot mixture of ammonia and adipic acid enters the bottom of the chamber, passes up through the catalyst, and the products emerge from the top at a temperature of approx. 320°C. The average temperature throughout the catalyst bed is 360°C. The vessel has no independant heating or cooling system, all the heat being carried in by the ammonia.

The 3500 litres of catalyst, which fill the vessel completely, are stated to handle 3120 kgrms. adipic acid per day, or 0.89 kgrm. adipic/litre/day. The time of contact is approx. 6 secs.

The life of the catalyst is about 6 weeks. When