into the filling funnels. (They planned eventually to feed the hopper by belt elevator conveyor direct from the mixers). The mixture temperature at this stage is 90°C.

A little of the mixture is dropped into the container through the funnel to form a preliminary footing, and then the tamper is adjusted. This tamper is a complicated piece of apparatus, electrically driven, working on the "lazy pile-driving" principle at about 60 strokes per minute with a travel of 6" to 8". It also rotates at about 4 r.p.m. The head of the tamper weighs about a ton, and the tool itself is composed of a ring with harrow teeth arranged radially, alternately in pairs and triplets.

The mixture is added continuously over about ten minutes, tamping being carried on all the while. When all the mixture is in, the tamping tool is lifted by an idle rope clear not only of the container but the filling funnel also, so as to allow the whole tamping gear to traverse and serve the opposite container.

The containers are worked at a temperature of 80° internally though temperature is gauged by outside thermometer. As soon as it is full, the container is swung to the horizontal and traversed to the axis of the press, with the pre-pressing plate down in front of the die. A pre-pressing pressure of about 100 tons is applied, and under the influence of this the container floats to bear hard against the pressure plate, and the pressure is held for a minute or so. This pressure is released and the main ram withdrawn. The container floats back and allows the pre-pressing plate to be swung up clear. All is then set for the extrusion operation.

The total extrusion pressure varies with the sections, the smallest taking up to 300/400 atmospheres. For the full-size section of 14" they use a pressure of the order of 300 Kg. per cm^2.

The die is electrically-heated to a temperature 10/20° above the container - again measured by outside thermometer. Generally speaking, no lubrication is used, although sometimes a little oil is added to the mixture when small and difficult sections have to be made.

As the section comes out of the mouth of the die, it picks up the moving plate and is carried on to the conveyor. The flying shears are operated to cut the lengths needed. We saw the extrusion of a small triangular section with a 3" side and a central hole, which was to be used for a tram bow collector. It was noted that normally this section would be made in a smaller press, but the advantage of this particular installation was its adaptability to a wide range of sections.

We were told that extrusion was carried to within 1 cm. of the end of the container, and that all mixture remaining in the ~~die~~ was left in place and pushed out by the next charge. Care was taken to cut the extrusion at the joint, and all the old mixture was "scrapped", i.e., removed and taken back for re-mixing.

They design their own dies, and have been doing so for twenty years. It was admitted to be a matter of experience rather than theory. They have the die rough cast by an outside Firm - usually Eumeco - in steel, and then dress it up themselves.

There was no wide departure in the preparation of a mixture from normal anode paste practice, but they have been trying to reduce porosity by the use of binders treated with organic chlorides. They also reduce porosity by impregnating the baked section in hot tar and then re-baking. They claim that by this means they can get down to 12/13%.

10. BAKING

Both extruded and pressed electrode blocks are baked in a sunk ring furnace in muffle cells measuring 5' x 2'9", with dome-shaped heat-resistant refractory lids covering each group of four cells. The furnace was fired by producer gas, derived from brown coal briquettes, to a temperature of 1250/1300°C. The firing cycle is three weeks. Petroleum oil coke was used as a packing powder and a suction apparatus was installed for moving powder out of the cells on discharge.

APPENDIX 1.

Testing Methods.

We were told that the following routine tests were used:-

On the Green Mixture

(a) Density; (b) examination of polished sections to ascertain the distribution and arrangement of the various grain fractions.

Samples for this test were polished under water with polishing powder.

On the Baked Product

(a) Density; (b) porosity; (c) crushing strength; (d) electric (d) electrical conductivity.

APPENDIX 2.

SCREEN ANALYSES OF PITCH COKE FINES FROM PENDULUM MILL

	Fraction No:	Size	Kgms. Percentage
1.	1 - 2	0.3	4.5
2.	2 - 5	2.15	32.0
3.	10 - 20	1.40	21.0
4.	30 - 40	0.90	13.5
5.	40 - 70	1.70	25.4
6.	60 - 90	0.10	1.5
7.	Circa 100	0.05	0.8
8.	150 - 250	0.085	1.3

Whilst elutriation apparatus was not available at Griesheim, investigations into the size distribution and particle shape of the combined pendulum mill and electrostatic precipitator products had been undertaken by microscopic examination.

49182/1450/11.3.46/P.S.C/27.59.2.

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FINAL REPORT NO. 337
ITEM NOS. 21, 22, 31

GERMAN GRAPHITISING FURNACES AT MEITINGEN

(Siemens Plania)

Perrycoste, W. B. C.

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. JUL - 1946
TIIC L.F. & L. S-C.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON — H.M. STATIONERY OFFICE

GERMAN GRAPHITISING FURNACES AT MEITINGEN (SIEMENS PLANIA).

Reported by

W.B.C. Perrycoste, M.A.P.

16 February, 1946.

Metallurgy

BIOS Target Numbers
C21/794, C31/808, C22/2866

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

10 p. diagr.

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PERSONNEL OF TEAM.

F.N. Goss, M.A.P.
W.B.C. Perrycoste, M.A.P.

1. OBJECT OF VISIT.

The Siemens Plania Graphitising Factory at Meitingen. (Bavaria), which is 18 Km. North of Augsburg on the road to Donauwörth, was visited on 18th September, 1945. It is normally concerned solely with the graphitising of amorphous carbons from Siemens Plania's Carbon Factories (and on occasions from Griesheim I.G.F.), and the subsequent machining operations.

2. INTRODUCTION.

The target was included in the list for the Team inspecting Aluminium Reduction Factories, in the belief that amorphous carbons used in that industry were made there. It was found that, in fact, Meitingen only graphitised, and that their sole connection with the aluminium industry lay in the supply of the circular cathodes used for the super-purity aluminium furnaces operating on the three-layer process, and on rare occasions also of some rectangular blocks for the ordinary reduction furnace cathodes.

The members of this Team did not feel themselves qualified to undertake a critical investigation of the graphitising process, but as they were on the spot they took the opportunity to make a fairly brief inspection of the Factory and to obtain some details of furnace construction and operation. We did not inspect the machining shop.

No graphitising was being carried out at the time of the visit, but a start had just been made, on instructions from the Occupying Authorities, with some jobbing work in their machine shops.

3. PERSONNEL INTERVIEWED.

Dr. Minstring (Manager); Herr Gerhard (Production Superintendent); Dr. Hubmann (Electrical Engineer).

4. BOMB DAMAGE.

There was no damage whatever from bombing. (It may be worth mentioning here that this was the only Factory we had seen where foreign workers had not at the time of the collapse broken out into an orgy of petty damage and looting. There had been no damage either by military operations or personnel).

5. GENERAL DESCRIPTION OF FACTORY.

Meitingen was chosen for its proximity to the new Lech Hydro-electric Station. At that time power development was apparently ahead of consumption, and tariffs described as "favourable" were being offered to attract orders. It appeared that later, when the demands for power grew, the tariffs hardened considerably, and the Management complained about the prices they had to pay for power for their latest extensions.

The Works were first built in 1926 with small furnaces of 12-ton capacity, giving an annual production of 6,000 tons. Progressive additions were made, so that by 1939 the output was 10,000 tons. During the war there were further extensions, though the full programme was not completed at the time of the collapse. The output planned was 25,000 tons per annum; the peak rate reached was 15,000 tons per annum. The latest developments used furnaces with a capacity of 60 tons, taking up to 7,500 KW. each.

The great bulk of their production went to the steel industry, which explains their expansion in recent years. The largest size of carbon which they graphitise was given as 500 mm. square, i.e. about 20", but we cannot see why there should be this limit, and this may refer to their capacity for machining operations afterwards.

We did not study the lay-out of the Works, but there is plenty of room, with good access. In addition to the Furnace Houses, there was a Machine Shop for turning and threading finished electrodes. We did not visit this, nor did we visit the Laboratory.

6. POWER SUPPLY.

Power comes in at 11,000 volts from the Lech Power Station. There is also a connection to the Grid. The total consumption at the Factory was given as 9,000,000 KWH. per month. There are a number of individual transformers, and each of the large furnaces has one to itself. These operate from a single phase, to deliver up to 50,000 amps at 50/150 volts, with 32 tappings for regulation. The nature of the process calls for careful juggling to balance the demand on the three phases, which can only be done by operating several furnaces simultaneously.

7. FURNACE DETAILS.

(a). General Construction. The details of their latest furnaces are indicated in the attached diagrammatic sketch. They are installed in a building about 200' long x 90' wide, composed of one main central Bay and an Annexe at either side. The furnaces are arranged at right angles to the length of the building, off-centre, so that one end of a furnace is close to the wall of an Annexe, and there is a wide gangway down past the other end. They are served by a heavy overhead crane. There are about 12 furnaces.

The furnace proper consists of two end walls, and a floor built up in a pit to the level of the shop floor.

The end walls are built of fire-brick 7' high, 12' wide, and about 3' thick. There is a clear space between them of about 60', which is the effective length of the furnace. These end walls are reinforced with buck-stays. They are pierced by six square graphite conductors of 300 mm. (say, 12") side, which project into the furnace for a distance measured at 32 cm. (12"), and outwards a somewhat smaller distance. These six conductors are arranged in two columns of three at a distance between centres of about 7', though this was not measured exactly.

Contact at the outside is made through side plates of copper held by hollow water-cooled clamp plates, with a hollow bolt through each electrode to pull up the connections. These bolts are water-cooled. Water connections are by rubber tubing, the three electrodes at each side being in series.

This arrangement is repeated at the other end of the furnace, so that there are six carbons leading in and six leading out.

The current is supplied through aluminium conductors feeding the carbons at either end. At one end the lead out to the transformers is short, but that from the other has to traverse the length of the furnace. The traverse is made through aluminium conductors made in channel section. There are nine for the lead each side, supported on insulated stands, and the whole can readily be dismantled when the furnace is being charged or discharged. These conductors are arranged to cross each other so as to ensure even distribution of the current between them.

As an experiment, they have varied the construction of some of their end walls and incorporated for the greater part of the inner face graphite slabs instead of fire-brick.

These graphite slabs have a depth of about 1' each. We were told that there was a backing of graphite powder for another foot, leaving a foot of the ordinary outside fire-brick. We were told that this experiment was very successful.

A lot of emphasis was laid on the construction of the floor of the furnace. This was made by excavating a pit, about 4' deep and 15' wide for the full length of 60' between walls, in the Furnace Room floor. This pit is built up with fire-bricks to a depth of about ten courses and also lined with about 18" of fire-brick, so that at this stage of construction there is a "bath" in the floor about 18" deep and of the same width as the end walls. A layer of about 2" of sawdust is laid on this. They use this material quite a lot, and say that it has the virtue of minimising sticking. By this we take it that the charcoal formed and left by coking forms a useful physical separation between the fire-brick and the packing powder which follows. Above the sawdust there is a layer of about 12" of pulverised carborundum (q.v.), and on this again about 8" of their packing powder (q.v.).

The bed thus formed is, after settlement and the first heating, roughly level with the floor of the building, but after several rounds growth and distortion affect it. The bottom needs partial or full renewal every two or three years.

This bottom and the end walls really constitute the only permanent parts of the furnace.

The charge of carbons to be graphitised is built up in layers on this prepared bottom for the full length between the walls, with fillings of packing powder. When the greater part of the charge has been built, side walls formed of heavy buttresses of a special concrete carborundum heat-resisting mixture, which they make themselves, are placed along both sides. These buttresses have cast-in eyes at the top to facilitate cranage. It was pointed out that at the temperatures reached in the furnaces, given as 3,000°C., the packing flows like water, but that when cooling starts, after power has been switched off, it binds again so that the furnace side walls can be removed to increase cooling.

When the charge has been built up to the top of the side walls, the furnace is covered with slabs of rough carborundum. (Reference to this material is made later in this Report).

The above describes the construction of their large 60-ton furnaces. The older, smaller ones are built in a generally similar fashion. They were described as having a capacity of 10 to 15 tons.

(b). <u>Packing Powder</u>. Their special packing powder is a prominent feature in the construction and operation of their furnaces. It consists of coke, sawdust, quartz-sand, and graphite.

Gas coke is used - ash content immaterial. It is ground to about 15/20 mm. maximum size in a jaw-crusher; very roughly dried, when necessary, in a coal-fired "Didier" vertical furnace; further crushed in a roll-crusher to 5 mm. maximum; and then bunkered. Other bunkers contain an ordinary quartz-sand, and sawdust, whose anti-sticking virtues were again emphasised when the packing-powder plant was being inspected. These three ingredients are mixed in a simple "Draise" mixer consisting of a horizontal pan with a vertical axis, in the proportion, by weight, of about 90% coke; 5% sand; and 5% sawdust. We were told that if too much sand is used the mixture binds; if too little is used the "walls collapse", i.e. presumably, the mix does not bind at all when heated.

To secure conductivity at the start of each cycle, graphite is added to the packing powder. This graphite is obtained from scrap, turnings, etc. The proportion added varies from 1:3 up to 1:1 according to the size of the articles to be graphitised. They told us that small articles need more graphite in their packing powder than large ones, and that for very small articles indeed they use 100% graphite dust for their packing powder. This graphite is mixed with the other three ingredients in the same "Draise" mixer.

In the Furnace Room the packing powder is at present handled by grab. There was a suction plant, which, they say, had worked well, but during the war they were unable to obtain spare parts and had had to abandon its use.

(c). <u>Carborundum</u>. Mention has already been made of carborundum. This we understand as a rather loose description of the product that is obtained when the packing powder has been through the furnace cycle two or three times. There will obviously be pretty heavy oxidation of the carbon, and the presence of the silica will explain the formation of an impure carborundum.

In effect, it can be said that the silicon in the packing powder remains as the coke is being consumed. The actual consumption of coke seems to be fairly heavy, as their formal Return to the Military Government shows the need of about 500 tons of "mine coke" to match 1,500 tons of raw electrodes, i.e. a consumption of about 33%.

Big lumps of carborundum, when they cannot be used for the covers to the furnaces already mentioned, are broken up and re-ground in a special hammer mill to bean size, for use in rebuilding the furnace bottoms.

8. OPERATION OF FURNACE.

(a). Load characteristics. We were told that the cycle from cold to cold - i.e. empty to empty - is about ten days.

When the furnace charge has been built up and covered, as already described, and the bus-bar connections made good, a load of 1,200 KW. is applied. During the first nine hours this load is increased to 2,000 KW., and then from hour to hour in steps of 200/300 KW. to build up to a total of 7,500 KW.

The total time under power was given as from 40/70 hours, depending on the size and quality of the carbons to be graphitised. (This is for the large furnace. The graphitising time for the small ones was given as 12/20 hours).

We were told also that the total energy consumption was as follows:-

For the old small furnaces pre-war, working
on "good material" ... ... 3.5 KWH per Kg.
-do- -do- -do- using
"poor material" ... ...6.5 KWH per Kg.
For the new modern furnaces, working, of
course, on present-day "poor
material" ... ... 5.0 KWH per Kg.

We were not able to ascertain how they determine when graphitising is complete, but, in view of the temperatures reached and the impossibility of getting samples, it must be an empirical question decided by experience. The main concern, of course, when power is switched off, is to cool the furnace down as quickly as possible without undue oxidation. (They do not appear to have any particular cooling fans, but allow for natural convection through the roof, assisted by the earliest possible removal of the side walls of the furnaces).

Frequent reference was made to "good material" and "poor material". By this was implied material which graphitised easily, and therefore did not take an undue amount of power, as opposed to material which took a lot of power to graphitise it. It was clear that during the war the electrodes which they received had been made from raw materials which were less easy to graphitise. We did not hear of any scientific expert at Meitingen with whom to discuss this question, and we have an idea that the science of the process was concentrated at the Siemens Plania Head Office, and that the Management at Meitingen were the practical people. During a conversation with Dr. Hubmann we mentioned the effect of iron or other catalyst in minute quantities on speeding up graphitisation. He agreed to that, but implied that it was not a matter on which they had much knowledge. They just had to do the best they could with the carbons which they received.

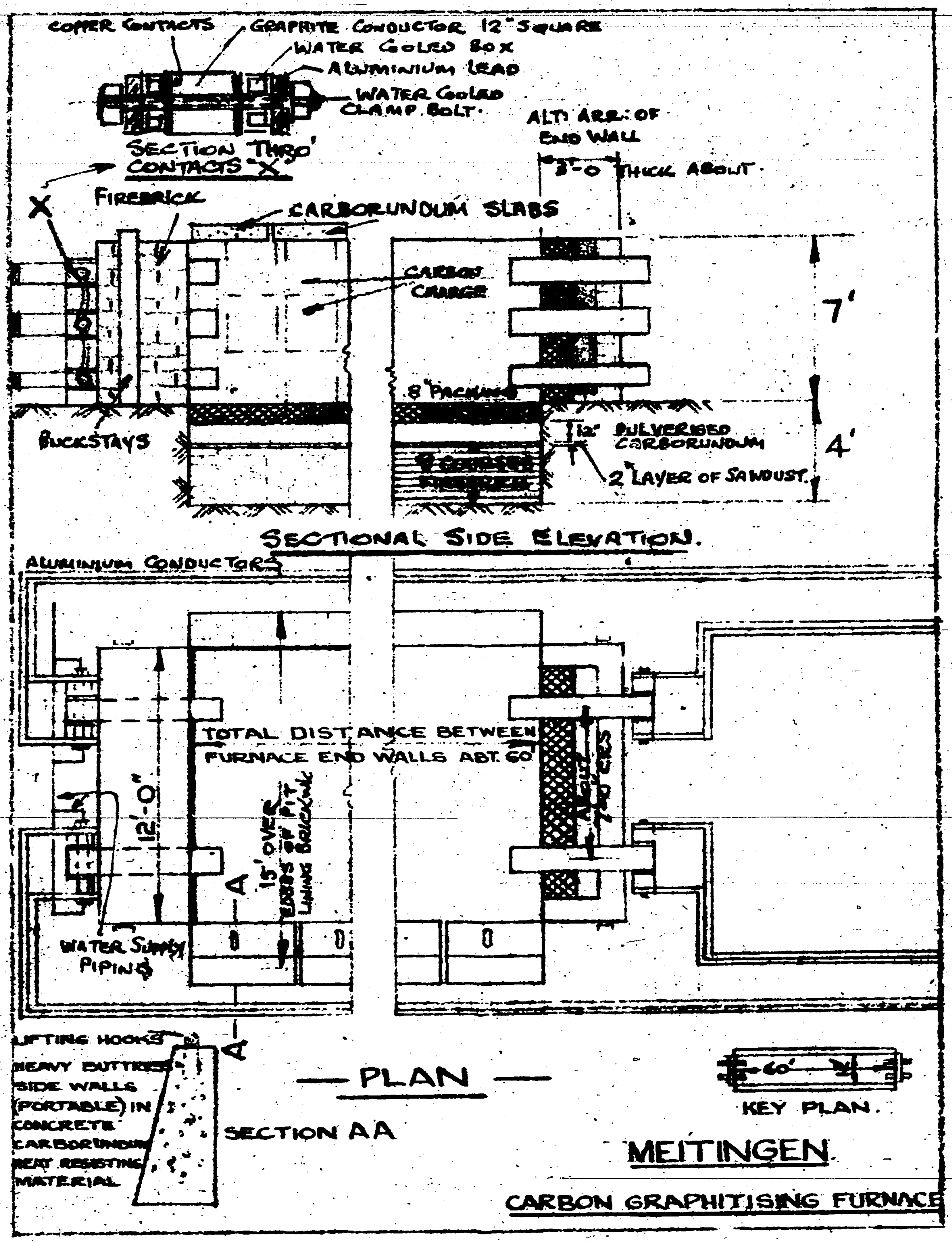
(b). Labour. The total labour employed at the Works, including administration, was 350. The great majority of these were paid on piece-work.

Basic wages had not altered since before the war, the prices of materials having been controlled by the Reich to prevent justification for wage increases. At the beginning of the war continuous shift work, which had previously called for 48 hours per week, was put up to 56, the change-overs being achieved on Sundays by 12-hour shifts for two Sundays out of three.

As far as Meitingen was concerned, this applied only to Power House Attendants and the like, since the bulk of the work was done during the day under piece-work conditions. The average earnings of piece-workers were given as 50 M. per week. At Meitingen, as at other places, there seems to have been far less of a differential for specialised jobs, and the chief attraction to people engaged on heavy and hot jobs seems to have been the privilege of buying increased rations. It was freely admitted that the work of charging and discharging furnaces was extremely hot, arduous, and dirty. They had about 100 Russian P.O.W.'s on this work. They were all Officers from a nearby camp.

(c). Costs. We were told that the cost of graphitising was 25/40 M. per 100 Kg., depending upon the size. This excluded machining costs and covered only the graphitising.

When the Factory was first built power was charged at 1.5 Pf. per KWH., which they considered good. Although they had long-term contracts for this, these did not cover the extensions, for which the tariff was progressively increased, and at the time of the shut-down the average cost for power over the Factory had risen to "between 2.5 and 2.8 Pf. per KWH". On the power consumption already calculated, the cost of power per 100 Kg. would come to 10/14 M.



MEITINGEN.

CARBON GRAPHITISING FURNACE

FINAL REPORT No. 258.
ITEM No. 22.

Copy 1

CARBON ELECTRODES, I.G. FARBEN, GRIESHEIM.

Purdon, F.F.

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BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H M. STATIONERY OFFICE.

10 JUL 1946

CARBON ELECTRODES. I. G. FARBEN

GRIESHEIM.

Reported by

F. F. Purdon.

CIOS Black =List Item 22
Miscellaneous Chemicals

BIOS Target No. 22/1(t)

(1946)

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

8 p.

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Report: I.G. Farbenindustrie, Griesheim, near Frankfurt am Main.

Personnel of Team.

F. F. Purdon.
P. E. Gagnon.
Otto Whitson (Interpreter)

CARBON ELECTRODES.

I.G. Farbenindustrie, Griesheim, near Frankfurt am Main.

The factory was visited on September 12th, 1945.

OBJECT OF VISIT.

To see the carbon electrode plant, and to obtain preliminary information about raw materials, plant, process, labour, and costs.

To find out what chemicals were manufactured for the fire-proofing of timber.

To find out whether work was being done on the bleaching of bast fibre.

SUMMARY.

Until March, 1945, some 2000 tons a month of carbon electrodes were manufactured from petroleum pitch coke, coal tar pitch coke, and other cokes, for a large variety of industries.

No graphitizing of the burnt electrodes was carried out at Griesheim.

Chemicals for the fire-proofing of timber were not made at Griesheim.

It was admitted that work was being done on the bleaching of bast, but no information was available, and a special permit was required for a visit to the plant. As the author was not specially qualified to study this problem, no further action was taken.

GENERAL.

The manufacture of carbon electrodes was only one of many activities at Griesheim.

The carbon electrodes were made by the well known method of mixing powdered cokes of suitable grists with pitch, compressing the hot mixture, and then "burning" the electrodes in kilns under conditions which prevented the furnace gases having contact with the heated electrodes.

For some purposes, such as electro-chemical processes, the electrodes have to be graphitized, and electrodes requiring such treatment were sent to another factory for finishing.

PERSONNEL.

We were received by the Control Officer, Col. Colt, who gave us every assistance, and introduced us to Capt. M. J. Smith, the Sub-Control Officer, and to Capt. W. P. Quantz.

The plant was visited with Dr. Ernst Engelbertz, in attendance, who supplied all the information which was obtained.

PRODUCTION.

The normal production until March 1945, was 2000 tons a month of carbon electrodes of a great variety of sizes and forms. The maximum capacity of the plant was 2500 to 3000 tons a month.

STAFF.

The plant was controlled by 1 engineer, 1 chemist, and 4 foremen.

LABOUR. (output about 2000 tons a month.)

Process workers - 200 men, and most of them on 3 - 8 hour shifts.
Repair workers - 30 to 50 men.

The skilled repair labour was made up approximately as follows:-

Bricklayers	4 to 5
Millwrights	15 to 20
Electricians	2

RAW MATERIALS.

The raw materials used were petroleum pitch coke which came from Deurg, Miesburg, Hanover, coal tar pitch coke from the Ruhr, anthracite coal from Aachen and the Ruhr, and finally coke from coal, chemically treated to lower its ash content. This coal came from the Mine Alexander in the Ruhr. The ash in these cokes is about 0.8%, mainly Si, Fe, Al, and a trace of vanadium. Other raw materials were pitches of various degrees of softness used as binders.

PROCESS OF MANUFACTURE.

The coke is elevated to the top of a bank of vertical retorts, similar to those used in a modern works for towns gas. The coke passes down the retorts, which are heated by the gas obtained from the volatile matter distilled from the coke, assisted by some towns gas.

The retorts are of fire brick, but the bottom portion is of steel and is water cooled. The temperature in the hot zone was said to be 1200°C.

The coke leaving the retorts is elevated and conveyed to another building, where it passes through a pair of crushing rolls, and is elevated to a screening plant to remove the fines.

The coarser material is ground in mills which have three rolls working within a bull ring and the fines removed from the mill by air separation. There was some doubt as to the fineness to which the coke was ground, as this varies for the different types of electrodes.

The ground material is delivered to storage bins which feed a number of mixers and blenders and is then mixed with about 25% of binding material. The binding material is pitch which varies in consistency from almost liquid to hard pitch which could be powdered and mixed in the dry state.

The binding material is thoroughly incorporated with the coke in electrically heated mixers which can be inverted for emptying and the hot material is conveyed to a variety of hydraulic presses. The presses used varied from 500 to 1000 kilos per cm^2.

In general, the presses were of two types, block presses and extrusion presses. The only press working was a small extrusion press providing carbons urgently required for locomotive repairs.

The "green" carbons leaving the presses are fired at 1200°C. in ring furnaces to remove the volatile matter from the pitch and to bind the material together. There are six ring furnaces, two old ones in a bad state of repair and four new furnaces one of which has never been used. The newer ring furnaces consist of 18 kilns each divided into eight compartments. Silics brick enters largely into the construction of the furnaces.

The material to be burnt is loaded directly into the compartments and packed with powdered petroleum pitch coke to exclude the action of the furnace gases.

The top of each kiln is level with the surrounding floor and as each eight compartments are filled, a travelling crane replaces a fire brick lined iron cover, the valves and dampers changed over, and the kiln is put on to heat. The furnaces are heated by producer gas which is made from briquetted brown coal. The cycle of operations from charging to removing the electrodes is about three weeks. The passages in the various flues within each kiln and between the compartments are kept free from dust and ash by means of a large "vacuum cleaner" each time the cover is removed.

REPAIRS.

It was stated that the life of a ring-furnace was 2 years before extensive repairs were needed. The life of the retorts was given as 5 years.

The life of the grinding mill rolls was given as 6 months, and of the bull ring, about 1.5 years.

STORAGE CAPACITY.

The normal storage capacity, under cover, for cokes is about 2000 tons.

STOCKS.

The stocks at the present time (September, 1945) are as follows:-

Cokes of various kinds.

About 4500 tons, and much of this is stored in the open.

Electrodes.

For aluminium, 1150 tons, and some 164 tons in the furnaces.

Burnt electrodes ready for graphitizing, 355 tons, and 500 tons loaded in a boat on the Main.

In the furnaces, 670 tons partly burnt electrodes.

Green pressings, 82 tons.

COST. (Normal times.)

The following cost figures were given as an average of all types of burnt electrodes ready for graphitizing:-

Raw Materials	226.9	R.M. per 100 kilos
Wages	27.3	
Salaries	6.8	
Welfare	17.8	
S.W.S.	1.9	
Power	4.5	
Steam	3.1	
Water	1.6	
Towns gas	3.5	
Fuel		Unfortunately this figure was not given.
Repairs	38.1	
Equipment (gloves, etc)	7.2	

COST. (Normal times) Cont.

Transportation	0.6
Fire service	2.8
Overheads	1.5
Depreciation	28.1
Interest on capital	5.7
Taxes	5.9
Sundries	6.4
	389.8

Dr. Engelbertz had given the average cost as approximately 400 M. total. The above analysis was provided by the cost clerk.

FINAL REPORT No. 334.
ITEM No. 30.

Copy 1

DEVELOPMENTS OF GEOPHYSICAL PROSPECTING IN GERMANY DURING THE WAR

Rankine, A. O.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H. M. STATIONERY OFFICE.

DEVELOPMENTS OF GEOPHYSICAL PROSPECTING IN GERMANY DURING THE WAR

Reported by
Prof. A.O.Rankine
On behalf of
Ministry of Fuel and Power

BIOS Target No.C30/107
Fuels and Lubricants

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

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Personnel of Team

Prof. A.O.Rankine, Ministry of Fuel & Power
Mr. A. van Weelden do.
Mr. R.Davies do.

Developments of Geophysical Prospecting in Germany
During the War

Object of Visit:

We have regarded the purpose of our visit to Germany from 27th September to 10th October, 1945, as primarily to discover what improvements and developments have been made there during the war in the apparatus used in geophysical prospecting for oil. We have not examined in any detail the results obtained in the field, to which brief reference is made later. The records of these are in the hands of Major Gunther at Celle, and he, we understand, will communicate them in full in due course.

Our aim, therefore, was to locate examples of the most recent geophysical instruments, and to find and interrogate the inventors, makers and users respecting the design, operation and performance of the said instruments. Our investigation was confined, as will be seen from the attached itinerary, to the British zone of Occupation, for local enquiries showed that projected visits to Berlin and Munich would be unlikely to be fruitful, for reasons which will appear. Nevertheless, we believe that the information we have collected enables us to assess with confidence the progress which has been made by Germany in relation to that in other parts of the world.

1) The Measurement of Gravity - Gravimeters:

It was well known before the war that the instrument preferred in Germany for gravity surveying was the Thyssen gravimeter, made by Seismos G.m.b.H. in Hanover. This instrument had been used extensively outside as well as within Germany, and its structure and performance were of common knowledge. Whatever its merits at the time of its invention, the Thyssen instrument is now definitely inferior to some, at least, of the gravimeters which have since been developed in the United States. But there was information also to show that a new gravimeter, due to Dr.Graf, was coming into use, and an early model of this instrument was, in fact, exhibited in the United States in the summer of 1939. We therefore concentrated our efforts on finding and interrogating Dr. Graf and in discovering and examining any Graf instruments that might be accessible. Enquiries at Helmstedt had indicated that Dr.Graf was in Munich but we were fortunate in finding him in the Nienhagen

Office of Dr.Brinkmeyer, whom he was visiting. An example of the most modern type of Graf gravimeter was also found to be in the custody of Dr.Brinkmeyer, and it was therefore possible to arrange for an examination in Celle in the presence of Dr. Graf, the inventor, and Dr. Brinkmeyer, a user.

The interrogation revealed that there had been about 20 of these gravimeters in a state of incomplete adjustment in the Askania factory in Berlin at the time of the Russian occupation, and that these, together with all the other Askania apparatus having been removed, would not be available for inspection. But with the fully adjusted instrument before us in Celle, and with the opportunity of examining it there with the verbal explanations of Dr.Graf, we feel justified in expressing already the following opinions:-

(i) The Graf gravimeter is a better instrument than the Thyssen gravimeter, which it has recently superseded in the extensive gravity surveys carried out in Germany and neighbouring countries during the war.

(ii) It is, however, very definitely inferior to the best of the American gravimeters, such as the Gulf and the La Coste, both in speed of operation and in the reliability of the results.

(iii) Even if an organisation could be re-established for the manufacture of Graf gravimeters, it is unlikely that they could be improved to the extent necessary to compete with the products of the United States.

We obtained from Dr. Graf a number of details of the construction of his gravimeter, of which there have been two types described as large and small, the latter being the more recent. Both depend on the use of springs to balance gravity, as has been customary in most gravimeters, and the special steel of which the springs are made is an important matter. We accordingly obtained a specification of this steel from Krupps, who supplied it to Dr. Graf. The composition given for the metal, called WT8T, was:-

0.15	- 0.20%	C
0.30	- 0.50	Si
0.70	- 0.80	Mn
7.7	- 8.3	Cr
33.0	- 35.0	Ni
0.6	- 0.9	Mo
Rest		Fe

the higher Cr. percentage apparently giving the better results.

The novel feature of the gravimeter appears to be the use of a photo-electric method of exhibiting the deflections caused by changes of gravity. This, particularly, seemed to be worthy of closer examination, and we therefore arranged with Major Gunther to have the instrument sent to England for this purpose. We propose thereafter to submit a detailed report on it.

We saw one other example of the Graf gravimeter in Barbis, in the laboratories of Seismos G.m.b.H., who have been employing it in their gravity surveys. Our conversations there with Dr. Schander and Dr. Schleusener confirmed us in the views we have expressed above. Mr. van Weelden, in his subsequent discussions at The Hague, Holland, with members of the staff of Messrs. Bataafsche Petroleum Maatschappij, on the claims made by Dr.Graf and German users, obtained additional confirmation of our statements herein.

2) Seismic Investigations - Apparatus for Refraction and Reflection Shooting:

In relation to seismic operations our investigation shows that no great progress has been made. As regards refraction work it appears that the apparatus still employed is quite antiquated, the seismometers used being of the Mintrop mechanical type developed 25 years ago. With these, however, a large part of Germany has been mapped seismically in the manner indicated later.

New equipment has, however, been developed and constructed for reflection shooting. We examined this in the Seismos laboratories, and interrogated Dr. Schander and his colleagues concerning it. There appears to be in this apparatus no special feature of importance. We also examined in Dr. Brinkmeyer's offices at Nienhagen comparison records as between the Seismos reflection outfit and an American Magnolia outfit imported into Germany before the war, and found little by which one could be preferred as against the other.

We learned that two other reflection outfits had been produced in Germany during the war, but we had no opportunity of examining the actual apparatus. We did, however, see records from one of these, made by Siemens, and novel in its reported use of carbon microphones as tremor receivers. These records were of a quality about on a par with those of the Seismos and Magnolia equipment mentioned above. The other recording unit, made by Askania in collaboration with Dr. Graf, is now in his custody in Munich. It is in the early stages of development, and has so far undergone no operational tests.

We consider it safe, therefore, to conclude that, in reflection work, German equipment has only now reached a state of approximate equality with that of the United States pre-war, and has yet to overtake the many improvements made in the United States since then.

3) Instruments for Electrical Prospecting:

We interrogated in Hanover Dr. Paul, the German representative of the Schlumberger organisation. He had carried out a number of surveys during the war, the results of some of which we saw without finding them convincing. No contribution had been made on the instrumental side, the apparatus having been supplied from Paris and contact having been maintained with the Schlumberger office there up to the time of liberation.

4) Magnetic Measurements - Magnetometers:

Our enquiries showed that the instruments used for magnetic surveying were the well-known Schmidt vertical and horizontal magnetic variometers, made by Askania in Berlin. We had no opportunity of inspecting any of these, but were informed that considerable improvements had been achieved in rendering the performance independent of fluctuations of temperature. The same is true of the magnetometers, based on the same general principles, by Messrs. E. & R. Watts in London, and it is reasonable to assume that the modern German instruments are not greatly, if at all, superior to the British.

5) <u>The Compilation of Geophysical Data in Germany</u>:

Although, as indicated at the beginning, we have confined our attention to geophysical instruments, we feel bound to express our admiration of what we saw of the comprehensive and systematic way in which the Germans have carried out and put on record the results of their geophysical work. Practically the whole country and some of the neighbouring countries during occupation have been surveyed in great detail gravitationally by various forms of gravimeter, and seismically by means of refraction fan shooting on radii about 4 kilometers in length. Moreover, the results are in the course of compilation by continuation of the work of the Reichsamt für Boden Forschung, and complete maps of these two types will before long be available. Major Gunther, under whose direction this work is proceeding in Celle, feels strongly, and we support him in this, that a similar system might, with great advantage, be adopted in Britain.

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FINAL REPORT No. 352.
ITEM No. 22.

CYCLOPOLYOLEFINES

Miscellaneous Report compiled from interviews with
Dr. Reppe, Dr. Schlichting and Dr. Kröper.
(I. G. Farben, Ludwigshafen.)

Rose, J. D.

REC'D. JUL - 1946
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BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H. M. STATIONERY OFFICE.

CYCLOPOLYOLEFINES

Miscellaneous report compiled from interviews
with Dr. Reppe, Dr. Schlichting and Dr. Kröper
(I.G.Farben, Ludwigshafen.)

Reported by

J. D. ROSE, M.O.S.

BIOS Target Nos.22/1f, 22/1

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

32, Bryanston Square, W.1.

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PERSONNEL OF TEAM

*J.D.Rose	M.O.S. (Team Leader)
*C.J.S.Appleyard	M.O.S.
*J.F.C.Gartshore	M.O.S.
*J.W.Fisher	M.O.S.
P.W.Blaylock)	Canadian Department
A.H.Andersen)	of Reconstruction

Those marked with an asterisk took part in the interrogation.

CYCLOPOLYOLEFINES

Introduction

The subject of *cyclo*octatetraene and higher acetylene polymers has been almost completely reported in the lecture "Uber Cyclopolyolefine" by Dr. Reppe, translations of which are in B.I.O.S. files. This report [*] is dated 28.4.44 and an investigation was carried out to determine whether further work had been done since it was written. Dr. Reppe, Dr. Kröper and Dr. Schlichting were interviewed on the subject - the first named in Frankfurt and Mainkur, the second in Gendorf and the third in Ludwigshafen. On factual matters, essentially the same story was obtained from each, the greater detail and accuracy being obtained (as would be expected) from Dr. Schlichting who actually did the laboratory work. On non-factual matters (i.e. interpretation of results) there was divergence of opinion between, e.g. Drs. Reppe and Schlichting. The information contained in this miscellaneous report should be regarded as complementary to that contained in the report "Cyclopolyolefines - Translation of a lecture by Dr. Reppe". [*]

Preparation of *cyclo*Polyolefines

A 2 litre autoclave of stainless (V_2A or V_4A) steel (see Note 1) is charged with 1 litre of carefully dried tetrahydrofuran, 20 g. nickel cyanide added and 50 g. of ethylene oxide (see Note 2). The autoclave is sealed, and nitrogen repeatedly pressed in and released, a residual pressure of 5 atmospheres of nitrogen being finally left. The autoclave is warmed to 50° (see Note 3) and then acetylene (15 ats.) is pressed in (total pressure 20 ats.). The autoclave is stirred and heated at 80° (see Note 4) until the pressure drops, when more acetylene is added, and the process repeated until absorption ceases. This usually requires 24-36 hours.

The contents of the autoclave are filtered from catalyst and cuprene and the tetrahydrofuran removed at ordinary pressure by distillation. The residual liquid is then distilled in vacuo. Crude *cyclo*octatetraene is rather unstable on distillation at ordinary pressure, but after one vacuum distillation can be refractionated at ordinary pressure. The higher polymers are fractionated under reduced pressure.

[*] B.I.O.S. Final Report No. 137.

Constants of the cycloPolyolefines

The four products isolated have the following constants:-

C_8H_8	- cyclooctatetraene,	b.p. 142-143°/760 mm,	- golden yellow
$C_{10}H_{10}$	- b.p. 48-50°/2 m.m.,	b.p. 190-195°/760 mm.	- deep yellow
$C_{12}H_{12}$	- b.p. 60-65°/0.5 m.m.,	b.p. 230-235°/760 mm.	- light yellow
$C_{10}H_8$	- Azulene,	m.p. 99.5°	- deep blue

Yield: At 80°C., the hydrocarbon mixture is formed in 90% yield on the acetylene consumed. The mixture contains about 80% cyclooctatetraene and 15-20% of Azulene, $C_{10}H_{10}$ and $C_{12}H_{12}$.

Notes on Preparation

Note 1 - Constructional Material

The reaction is extremely sensitive to catalytic impurity. Dr. Schlichting pointed out that although there were numerous autoclaves available, all of the same structural material (i.e., V_2A or V_4Asteel), many of these gave widely varying results. In some autoclaves no reaction whatever could be induced, and finally it had been necessary to keep a list of the serial numbers of the autoclaves in which the polymerisation was successful. It was considered that this behaviour was bound up with the previous history of the autoclave, but Dr. Schlichting's opinion was that a new V_2A or V_4A autoclave should be satisfactory, or that a porcelain or glass liner would solve any difficulties.

Note 2

cycloPolyolefines were accidentally discovered during an attempt to synthesise 1:6-dihydroxyhexine-3 from ethylene oxide (2 mols.) and acetylene (1 mol.) in the presence of a nickel cyanide catalyst. The product was found, surprisingly, to be the mixture of hydrocarbons C_8H_8, $C_{10}H_{10}$, $C_{12}H_{12}$ and $C_{10}H_8$. The function of the ethylene oxide is not well understood. Dr. Reppe's view is that it forms intermediate products with nickel cyanide which, with acetylene, give nickel acetylide in very active form. Dr. Schlichting is of the opinion that it is merely a dehydrating agent, and supports this by the experimental facts that (a) finely powdered calcium carbide can replace the ethylene oxide and (b) if all reagents are rigorously dried, the ethylene oxide can be omitted entirely. However, the ethylene oxide procedure is the best, and gives the highest yields.

Note 3.

It is especially dangerous to add acetylene to the cold autoclave and then heat it. Too much acetylene dissolves in the cold tetrahydrofuran and is expelled from the solution on heating, setting up a dangerously high acetylene pressure.

Note 4.

Within certain limits, the ratios of C_8H_8:$C_{10}H_{10}$:$C_{12}H_{12}$ can be varied. In general, the higher polymers are favoured by a higher temperature.

The most favourable condition for $C_{10}H_{10}$ formation is a temperature of about 90-100°C., and for $C_{12}H_{12}$, 130-140°. No data could be obtained on the proportions of the higher polymers formed at these elevated temperatures beyond the qualitative statement that the yields were best at the temperatures given. There was no data on the variation of the Azulene content of the mixture with temperature variation.

Azulene - Isolation

Azulene occurs in the high boiling fraction, b.p. 60-110°/1.5 of the hydrocarbons resulting from acetylene polymerisation. It can be separated by chromatography and distilled (b.p. 80-84°/0.8 mm.) or sublimed. Alternatively, it may be purified (after chromatography) by dissolving the crude material in petroleum ether and extracting the Azulene with 80% phosphoric acid. The Azulene passes into the acid layer, from which it is precipitated by dilution with water, and may then be extracted with ether.

Structure, Properties and Utilisation of Acetylene Polymers

The chemical properties of cyclooctatetraene are fully described in the earlier report "Cyclopolyolefines". The work described there establishes beyond doubt that the hydrocarbon C_8H_8 is, in fact, 1:3:5:7-*cyclo*octatetraene. Similarly, Azulene $C_{10}H_8$ can be considered as completely identified.

$C_{10}H_{10}$ and $C_{12}H_{12}$, however, must be regarded as hydrocarbons of unknown structure. The evidence in favour of the *cyclo*decapentaene and *cyclo*dodecahexaene structures is not good. Thus, $C_{10}H_{10}$ on hydrogenation yields a hydrocarbon $C_{10}H_{20}$ which is not identical with the *cyclo*decane described in the literature, and this $C_{10}H_{20}$ hydrocarbon on oxidation gives no trace of sebacic acid (the oxidation products had not been identified, but the absence of sebacic acid was established). Dr. Reppe, the chief supporter of the *cyclo*decapentaene structure, explains this on the basis that $C_{10}H_{20}$ obtained from his hydrocarbon is stereoisomeric with the $C_{10}H_{20}$ described in the literature (corresponding to the hypothetical "boat" and "armchair" forms of cyclohexane). This explanation appears unsatisfactory to the author, and Dr. Schlichting (who did the work) stated bluntly that he did not believe it.

There is practically no data on $C_{12}H_{12}$. On complete hydrogenation, followed by dehydrogenation, it gives 1:2-dimethylnaphthalene, but this cannot be allowed to infer a naphthalene structure for $C_{12}H_{12}$, as Ruzicka has shown, for example, that *cyclo*octane on dehydrogenation gives *p*-xylene.

Little attempt had been made to utilise the *cyclo*polyolefines. *cyclo*Octatetraene offers a good route to suberic acid, the best method being partial hydrogenation to *cyclo*octene and oxidation (permanganate or nitric acid) which gives 80% yields. *cyco*-Octane, on oxidation, gives only 40% of suberic acid. The maleic anhydride adduct of *cyclo*octatetraene had been investigated as a component in alkyd type resins, but nothing of interest had emerged. *cyclo*Octenyl*cyclo*octane and *cyclo*octatetraene dimer had been investigated as lubricating oil additives but were not of interest.

*cyclo*Octatetraene and Azulene had been investigated pharmacologically (in what direction was not stated) and shown to have no activity, but Professor Kuher had established that the $C_{12}H_{12}$ fraction completely inhibited the growth of certain pathogenic bacteria in a concentration of 1:100000.

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FINAL REPORT No. 353.
ITEM No. 22.

PREPARATION OF 5-DIETHYLAMINOPENTANOL-2 BY THE REPPE PROCESS.

Rose, J. D.

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

PREPARATION OF 5-DIETHYLAMINOPENTANOL-2
BY THE REPPE PROCESS.

Translation of a report by

Dr. Hecht and Dr. Gassenmeier, Ludwigshafen.

Reported by

J. D. ROSE M.O.S.

BIOS Target No. 22/1(f)

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32, Bryanston Square, W.1.

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PERSONNEL OF TEAM

*J.D.Rose	M.O.S. (Team Leader)
C.J.S.Appleyard	M.O.S.
J.F.C.Gartshore	M.O.S.
J.W.Fisher	M.O.S.
P.W.Blaylock	Canadian Department of Reconstruction
A.H.Andersen	

Only those marked with an asterisk took part in this investigation.

TRANSLATOR'S NOTE.

It is known from the investigations of teams working specifically on medicinal manufacturing targets that the route to 5-Diethylaminopentanol-2 described in the attached report is not the one used by I.G. in their manufacture of Atebrin and Plasmoquin. Nevertheless it was considered to be of sufficient interest to report, as it illustrates the versatility of the acetylene work done by Dr. Reppe's team at Ludwigshafen, and includes many small practical points of potential value to anyone undertaking work in the acetylene field.

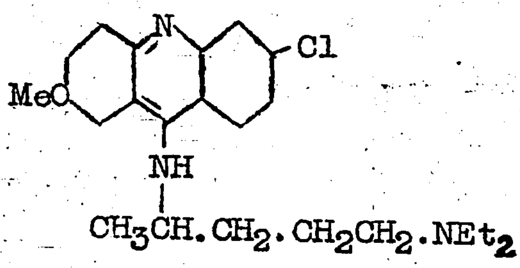
Appended to the report is a short addendum which was found in period summary reports issued from the laboratory of Anorgana G.m.b.H., Gendorf, to which the acetylene team moved after the devastation of Ludwigshafen.

PREPARATION OF 5-DIETHYLAMINOPENTANOL-2

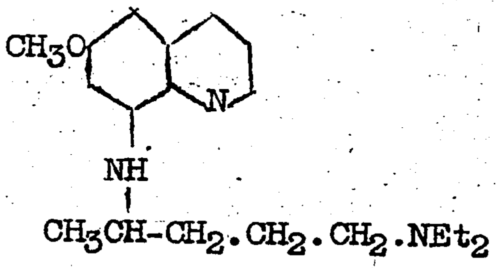
BY THE REPPE PROCESS.

Report by Dr. Hecht and Dr. Gassenmeier, Ludwigshafen, 24.2.43.

5-Diethylamino 2-pentanol and 5-diethylamino 2-pentylamine are necessary intermediates for the synthesis of the antimalarial drugs Atebrin and Plasmoquin.



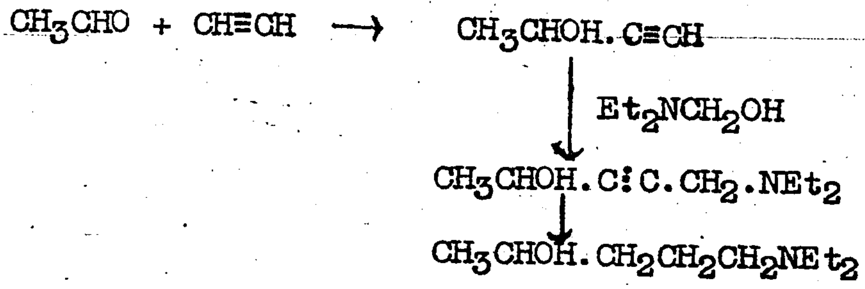
Atebrin



Plasmoquin

5-Diethylamino 2-pentanol is at present made in Elberfeld by a rather laborious process starting with acetoacetic ester and ethylene oxide; the synthesis presented here is a combination of the Reppe synthesis of alkinols from acetylene and aldehydes, with the interaction of alkylol amines with acetylenic hydrocarbons.

The outline of the synthesis is as follows:



$$CH_3CHO + CH\equiv CH \longrightarrow CH_3CHOH.C\equiv CH$$
$$\downarrow Et_2NCH_2OH$$
$$CH_3CHOH.C\equiv C.CH_2.NEt_2$$
$$\downarrow$$
$$CH_3CHOH.CH_2CH_2CH_2NEt_2$$

Interaction of the diethylaminopentanol with ammonia gives diethylaminopentylamine.

The best method of preparation is as follows:

730 g. Diethylamine (10 mol.) is added slowly to an ice-cooled paste of paraformaldehyde (300 g.; 10 mol.) in dry dioxan (1 litre; see Note 1). This paste is made by a short heating of the dioxanparaform slurry, followed by cooling. The addition of the diethylamine should be done slowly and carefully, as in spite of ice cooling the temperature may rise to 60-70°. Alternatively, diethylamine acetate (formed from 730 g. diethylamine and 600 g. glacial acetic acid) may be treated slowly with the cold suspension of dioxan-paraformaldehyde.

710 g. (10.2 mol.) of anhydrous butin 3-ol-2 (see Note 2) and a paste of copper acetylide (see Note 3) are added and the mixture agitated and immediately charged to a stainless steel autoclave. The air is removed by repeated flushing with nitrogen, and the autoclave is then heated at 100-120°/12 hours.

The contents of the autoclave are filtered, and 100 g. of Raney nickel paste (30% Ni content) are added and the mixture hydrogenated at 50°/200 atmospheres hydrogen pressure until absorption of hydrogen ceases.

On fractionation, the crude product, b.p. 100-115°/10 min., is obtained. The amino alcohol is purified by dissolving in dilute sulphuric acid, removal of non-basic constituents by vacuum distillation, basification with caustic soda, extraction of the amine with ether, and distillation.

This gives 1,250 g. pure diethylaminopentanol.

NOTE 1.

Dioxan is purified by freezing, and the frozen out, separated product is distilled, m.p. 12°, b.p. 101°/760.

NOTE 2.

Anhydrous butinol. The crude butinol from the acetaldehyde acetylene synthesis contains 50-60% butinol and 2% acetaldehyde. It is purified by dehydration over potassium carbonate and distillation, b.p. 108-110°/750.

NOTE 3.

Copper acetylide. Crystalline copper sulphate ($CuSO_4, 5H_2O$) (17 g.) is powdered and dissolved in 685 cc. water and 69 cc. of 20% ammonia and 51 g. hydroxylamine hydrochloride are added. The solution, which decolourises rapidly with evolution of nitrogen, is filtered and stored with exclusion of air. To prepare copper acetylide from this solution, nitrogen is led through, followed by acetylene for 30 minutes. After settling, the supernatant liquor is decanted and the solid washed with distilled water until free of electrolyte, the water removed by successive washes with alcohol, and then with dioxan to give a dioxan-copper acetylide paste.

ADDENDUM.

(The following additional information on the above process was found in a summary research report published at Gendorf covering the period 20th September, 1944 - 4th May, 1945.)

The continuous preparation of 1-Diethylamino 2-pentine 3-ol, $\mathrm{Et_2N.CH_2.C\vdots C.CH(OH).CH_3}$, was carried out without difficulty by interaction of butinol and methylol diethylamine over a catalyst of either copper acetylide or the copper salt of butinol supported on silica. The product, after hydrogenation, was satisfactory to Elberfeld for the manufacture of Atebrin.

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FINAL REPORT No. 359.
ITEM No. 22.

PRODUCTS FORMED BY INTERACTION OF ACETYLENE AND AMINES.

Rose, J. D.

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BRITISH INTELLIGENCE OBJECTIVES
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PRODUCTS FORMED BY INTERACTION OF ACETYLENE AND AMINES

Reported by

J. D. ROSE, M.O.S.

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32, Bryanston Square, W.1.

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PERSONNEL OF TEAM

* J. D. Rose	M.O.S. (Team Leader)
C. J. S. Appleyard	M.O.S.
J. F. C. Gartshore	M.O.S.
J. W. Fisher	M.O.S.
P. W. Blaylock	Canadian Department of Reconstruction
A. H. Andersen	Canadian Department of Reconstruction

Only those marked with an asterisk took part in the investigation.

SUMMARY

Acetylene and ammonia in presence of complex salts of cobalt at 100°, or vinyl alkyl ethers heated with ammonia and copper phosphate yield 2-methyl 5-ethylpyridine. Heated with primary or secondary aliphatic amines and a copper catlyst, acetylene yields 2-amino 3-butines of the general formula $R_2N.CH(CH_3).C:CH$. Tertiary aliphatic or heterocyclic amines (pyridine, trimethylamine), heated with acetylene and water yield vinyl ammonium hydroxides; if the amine salt is used the corresponding ammonium salt is formed.

INTRODUCTORY NOTE

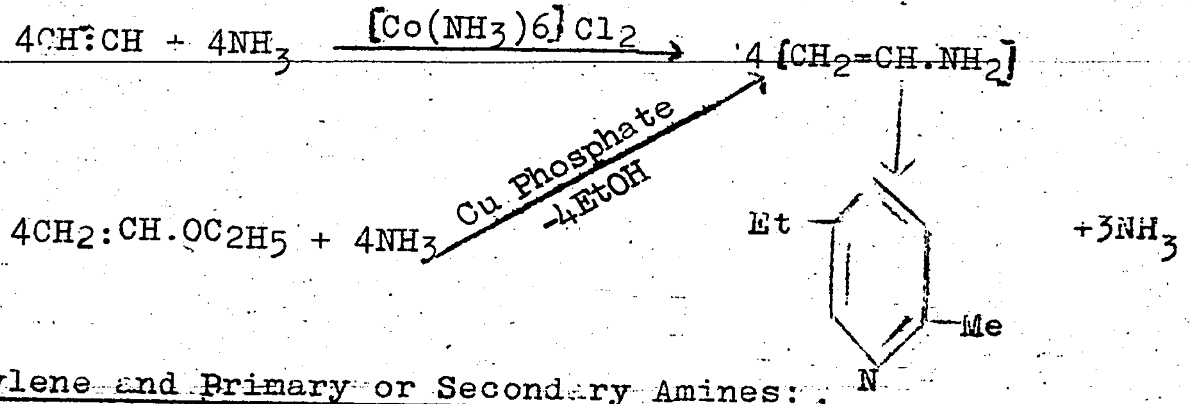
The following report is a compilation of information from various sources. Part of the data was obtained in conversations with Dr. Reppe at Mainkur (26th - 30th November), and some was collected as isolated jottings in period research reports, drafts of patent examples and short memoranda found among Dr. Reppe's papers in the library at I. G. Casella Works, Mainkur, Near Frankfurt.

INTERACTION OF ACETYLENE WITH AMMONIA AMINES

(a) Acetylene and Ammonia: Formation of Pyridine Bases.

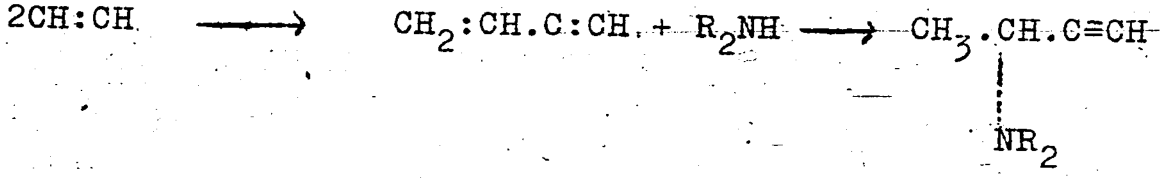
Attempts made at Ludwigshafen to synthesise ethyleneimine or vinylamine by interaction of acetylene and ammonia led to the formation of complex mixtures of pyridine bases. It was found that by using as catalysts certain complex salts of copper and nickel, using water as a solvent, temperatures up to 100°, and acetylene under pressure, the product was predominantly 2-methyl 5-ethylpyridine with small quantities of higher molecular weight basic resins. Vinylamine is assumed as a hypothetical intermediate, as shown in the scheme below.

Vinyl ethers heated in the liquid phase with ammonia using copper phosphate on titanium phosphate give quantitative yields of 2-methyl 5-ethylpyridine.



(b) Acetylene and Primary or Secondary Amines: Formation of Aminobutines

Interaction of a primary or secondary aliphatic amine with acetylene under pressure in the presence of a copper catalyst results in the formation of 2-amino 3-butines. The first stage is (presumably) dimerisation of acetylene to vinylacetylene, which then adds the amine across the ethylenic linkage, thus:



$$2CH:CH \longrightarrow CH_2:CH.C:CH + R_2NH \longrightarrow CH_3.\underset{NR_2}{CH}.C\equiv CH$$

To the amine (500 g.) is added cuprous chloride (50 g.); the salt goes partly into solution giving an intensively coloured complex salt. The reaction mixture is charged to an autoclave (18:8:1:1 steel), and after repeated flushing with nitrogen is heated to 100 - 110°, and 20 - 25 atm. of 2:1 acetylene-nitrogen mixture are pressed in. Fresh acetylene is added as absorbed until no further absorption occurs. The mixture is filtered and distilled. The following have been prepared. 2-Dimethylamino 3-butine, b.p. 96°; 2-Diethylamino 3-butine, b.p. 128°, m.p. 10°; 2-Butylamino 3-butine, b.p. 148°, 49°10 mm.;2-Benzylamino 3-butine b.p. 98°/9 mm.; 2-*cyclo*Hexylamino 3-butine, b.p. 60°/5 mm., m.p. 44°; and 2-N-Piperidino 3-butine, b.p. 58°/12 mm.

(c) Acetylene and Tertiary Amines: Formation of Vinyl ammonium Compounds

It has been shown that acetylene or acetylenic compounds interact with tertiary amines under pressure in the presence of water (60° and no catalyst) to give quaternary ammonium compounds. The simplest case is the formation of neurin (trimethylvinylammonium hydroxide) from trimethylamine and acetylene at 60°. The salts of tertiary bases give the corresponding vinyl trialkyl ammonium salts. Hydrogenation saturates the vinyl group giving the appropriate ethyl trialkyl ammonium salts.

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FINAL REPORT NO. 357
ITEM NO. 22

PROPARGYL ALCOHOL DEHYDRATION AND OXIDATION TO HEXADIINEDIOL

Interview with Dr. Von Kutepow, Haupt laboratorium, I. G. Farben, Ludwigshafen - 19th November, 1945

Rose, J. D.

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PROPARGYL ALCOHOL

DEHYDRATION AND OXIDATION TO HEXADIINEDIOL

Interview with Dr. von Kütepow. Haupt laboratorium, I.G. Farben, Ludwigshafen - 19th November, 1945

Reported by

J.D. ROSE M.O.S.

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

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7p. diagrs.

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PERSONNEL OF TEAM

*J.D.Rose	M.O.S. (Team Leader)
C.J.S.Appleyard	M.O.S.
J.F.C.Gartshore	M.O.S.
*J.W.Fisher	M.O.S.
P.W.Blaylock	Canadian Department of Reconstruction
A.H.Andersen	Canadian Department of Reconstruction

Only those marked with an asterisk took part in this investigation

Summary

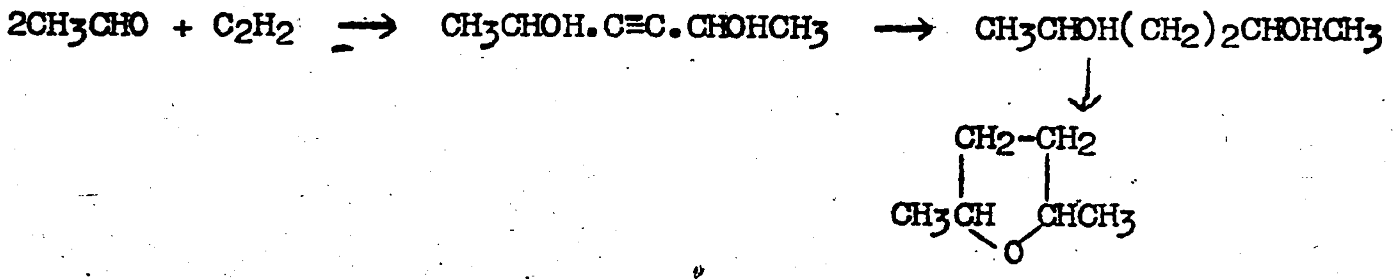
Aqueous propargyl alcohol recovered from the butinediol plant can be dehydrated by azeotropic distillation with 2:5-dimethyltetrahydrofuran. Experiments now in progress at Ludwigshafen indicate that benzene can be used in place of dimethyltetrahydrofuran. Air oxidation of propargyl alcohol in presence of ammonium chloride-cuprous chloride catalysts gives excellent yields of hexadiinediol. A flow sheet of a projected pilot plant for continuous oxidation is given.

Introduction

Dr. von Kütepow, of the Haupt laboratorium at Ludwigshafen, was interrogated on 19th November, 1945 on the oxidation of propargyl alcohol to hexadiinediol.

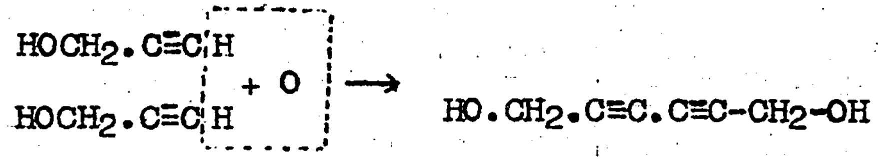
Dehydration of Propargyl Alcohol with Dimethyltetrahydrofuran

Aqueous dimethyltetrahydrofuran on distillation gives an azeotrope with 13% water content. Propargyl alcohol recovered from the fore-runnings of butinediol distillation is obtained as an aqueous solution. Aqueous propargyl alcohol is distilled with dimethyltetrahydrofuran, and the water layer removed from the distillate in a Dean and Stark type separator, the dimethyltetrahydrofuran being continuously returned to the still. When no more water separates the anhydrous mixture of propargyl alcohol and dimethyltetrahydrofuran is fractionated. This was being carried out in a small-scale laboratory apparatus in which the dimethyltetrahydrofuran dissolved in the water was neglected, but a large-scale apparatus had been designed in which this dimethyltetrahydrofuran was recovered. The flow diagram of this projected plant is attached (Figure 1) but detailed description is not considered necessary as it appeared to the author unlikely that it would ever be erected. Experiments were in progress on the use of benzene as an entraining liquid, and these appeared to be extremely promising. Dimethyltetrahydrofuran was a small-scale product of the acetylene lab. at Ludwigshafen, being produced from acetaldehyde and acetylene by the following outline synthesis:



$$2CH_3CHO + C_2H_2 \longrightarrow CH_3CHOH.C\equiv C.CHOHCH_3 \longrightarrow CH_3CHOH(CH_2)_2CHOHCH_3$$

Propargyl Alcohol: Oxidation to Hexadiinediol



$$\left.\begin{array}{l} HOCH_2.C{\equiv}C\,H \\ HOCH_2.C{\equiv}C\,H \end{array}\right\} + O \longrightarrow HO.CH_2.C{\equiv}C.C{\equiv}C\text{-}CH_2\text{-}OH$$

Laboratory Experiments

These were carried out in the following manner. An aqueous solution is prepared containing approximately (by weight) 6% cuprous chloride, 20% ammonium chloride, 14% propargyl alcohol and 20% of water. The ammonium chloride is first dissolved, followed by the cuprous chloride. The molar ratio of Cu_2Cl_2:propargyl alcohol is about 4:1 (cuprous chloride calculated as CuCl). The solution is contained in a suitable glass flask fitted with rapid stirring, and air is led in. The temperature is adjusted to 32-35°C.; if a higher temperature is reached resins and other by-products are produced. After 2-3 hours, the first crystals of the diol appear, and the addition of further propargyl alcohol is then started. This is added at a rate determined by the amount of oxygen taken up, which in turn is determined by measuring the volume of air entering and leaving the system. The crystalline diol is continuously removed by running some of the slurry from the bottom of the flask and centrifuging, the liquors from the centrifuge being pumped back into the reaction flask. The crystalline diol is washed with water free from inorganic matter, and dried.

The oxidation of propargyl alcohol by this method proceeds more rapidly if carried out under pressure; initial trials showed the rate to be 5-6 times more rapid. Batch procedure was initially carried out as follows, and it will be noted that in this case all the alcohol is present in the pressure vessel from the beginning of the oxidation. The mixture (250 cc. made up as before) in a 1 litre rotating autoclave was heated to 32°, and air pressed in to 20 ats. When the pressure had fallen to a point (approx. 16 ats.) indicating the absorption of all the oxygen, the nitrogen was blown off and air pressed in again to 20 ats. This procedure was repeated until all the propargyl alcohol was oxidised.

This method of working was unsatisfactory since the long time required for the process caused resinification and formation of polymeric material. Combination of the use of pressure with continuous working was therefore attempted, and the process amended as follows. In seeking a suitable constructional material it was found that the acidic mixture (NH_4Cl) caused no corrosion of stainless (V_4A) steel, but copper was badly attacked.

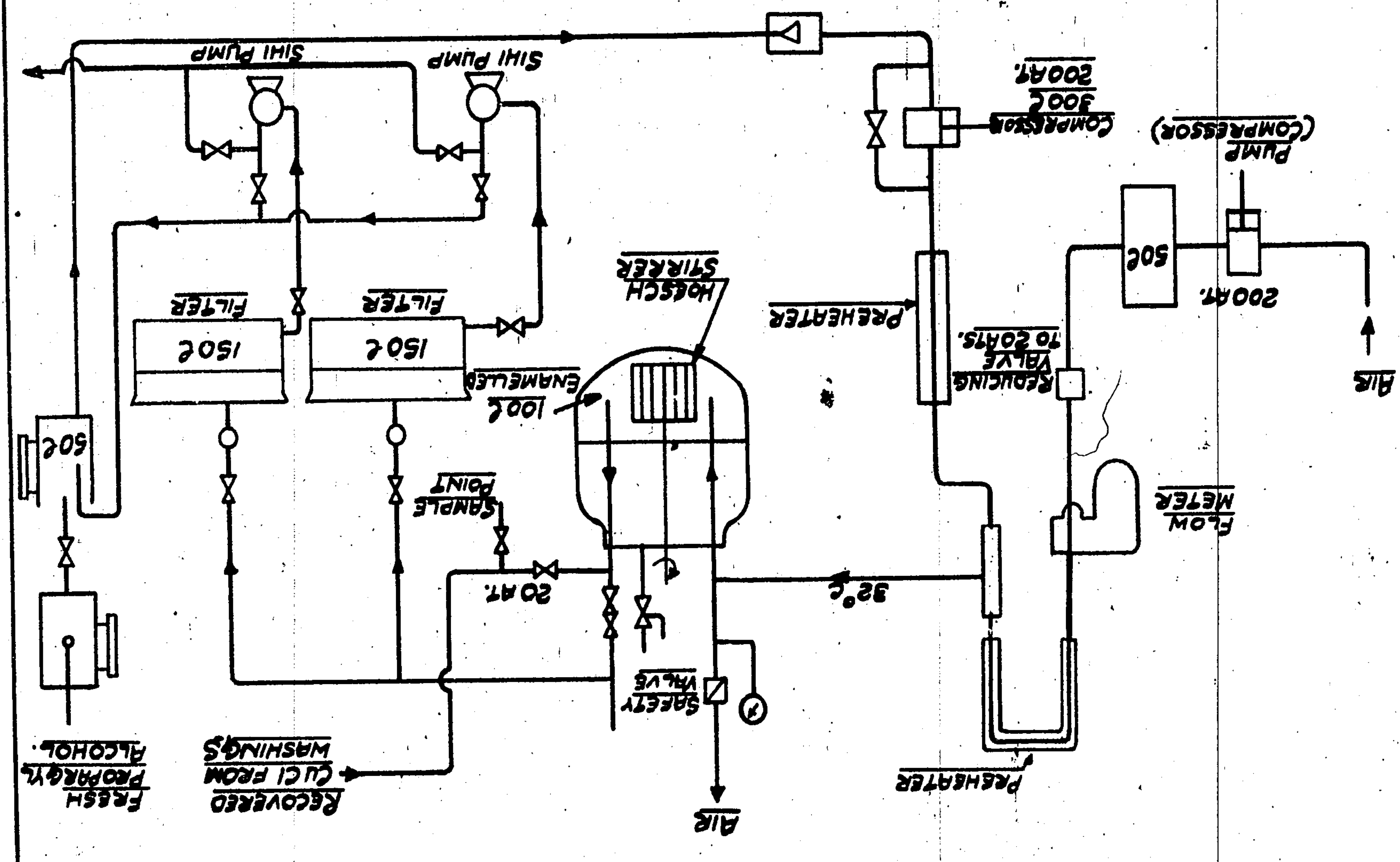
A 93 litre autoclave of stainless steel (V_4A) was charged with 1,800 g. cuprous chloride, 5,760 g. ammonium chloride, 18,440 g. water and 4,250 g. propargyl alcohol. The autoclave was rotated at ordinary temperature and air pressed in at 20 atmospheres; the temperature rose 26°, and the pressure dropped to 18.5 atmospheres. The pressure was blown off, air repressed to 20 atmospheres and rotating continued until the pressure had again dropped to 18.5. The process was repeated until a total pressure drop of 4.5 atmospheres had been recorded, corresponding on the free space in the autoclave to air absorption of 300 l. of oxygen at 20 ats. and to the oxidation of 3,030 g. propargyl alcohol. A further 2,055 g. propargyl alcohol was then added, and the process repeated. The following table sets out the additions made and the relevant calculations:

Propargyl Alcohol (100%) Added	Oxygen Absorption		Oxidised Propargyl Alcohol
	in Ats.	in l. at 20 Ats.	
4,035 g.	4.5	300	3,030 g.
2,055 g.	2.4	153	1,330 g.
700 g.	2.3	144	1,440 g.
2,020 g.	(1.6	97)	970 g.
	(1.7	103)	1,030 g.
3,000 g.	(1.8	103)	1,030 g.
	(1.1	63)	630 g.
	(2.4	137.5)	1,375 g.
3,000 g.	(1.7	92)	920 g.
	(1.6	86.5)	865 g.
	(1.7	92)	920 g.
3,000 g.	(2.0	101.4	1,014 g.
	(1.6	81	810 g.
	(2.4	121.4	1,215 g.

The contents of the autoclave are filtered, the solid dissolved in the minimum of water at 60° and cooled to 0°. The aqueous mother liquor on extraction with ether gives more diol, and the total yield is 15.45 kg. hexadiinediol from 18.045 kg. propargyl alcohol, i.e. 89%, or, including recovered propargyl alcohol, 93%. The heat of the reaction is 83 k cal/mol., and in the oxidation of large batches it is necessary to use ice water cooling on the autoclave in the initial stages to maintain the temperature below 32°.

General

No commercial outlets had been found for hexadiinediol. Its chief importance lay in its use as a source of 1:6-hexanediol, which was being investigated as an intermediate for polyurethane type polymers. A continuous pressure oxidation unit had been designed, but not erected, and a flow sheet of this projected plant is presented in Figure 2.



OXIDATION OF PROPARGYL ALCOHOL : FLOWSHEET OF PROJECTED SEMI-SCALE PLANT AT LUDWIGSHAFEN.

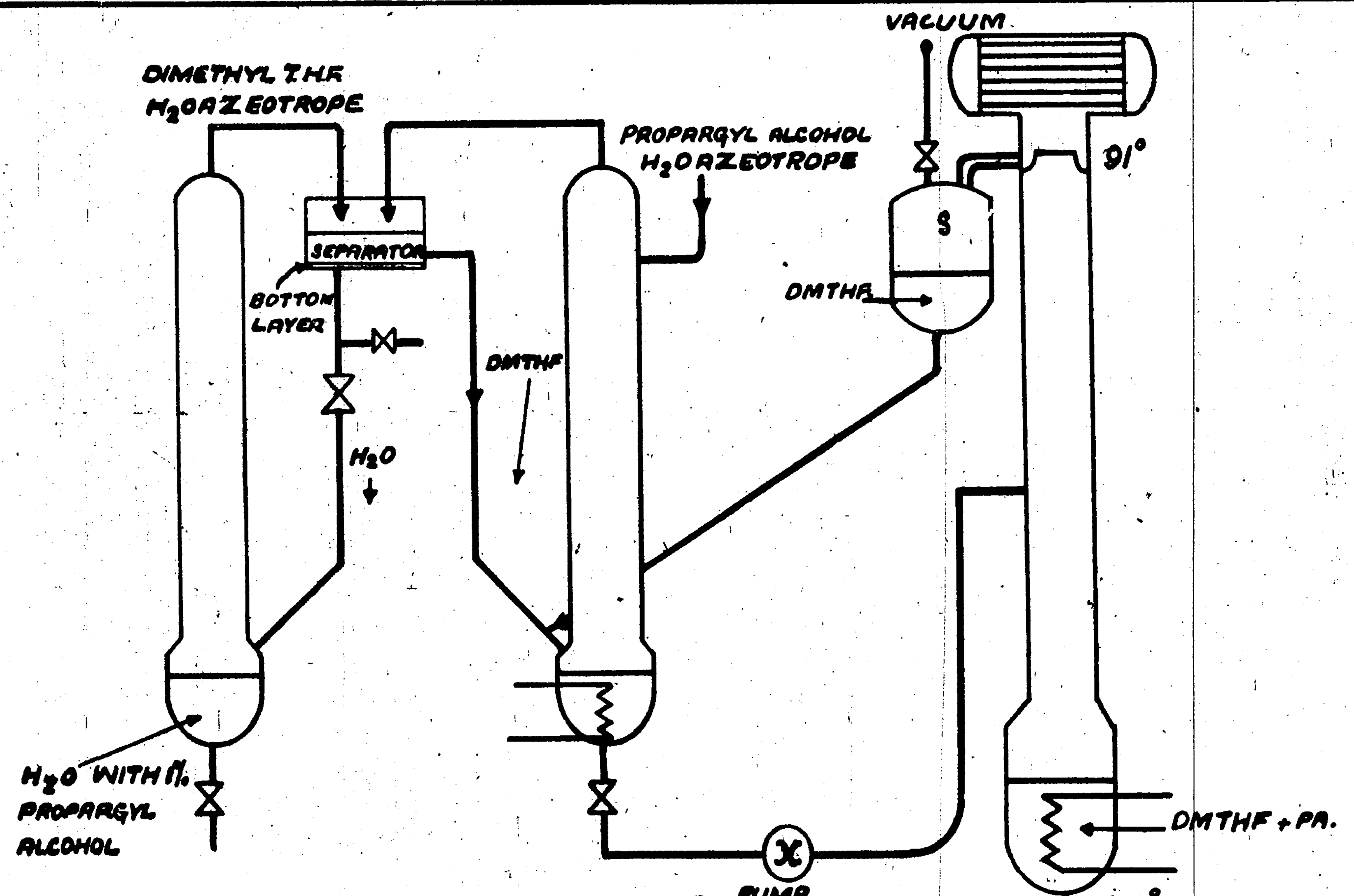


FIG. 1.

DEHYDRATION OF AQUEOUS PROPARGYL ALCOHOL (PA) WITH DIMETHYLTETRAHYDRO FURAN (DMTHF)

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RECENT ADVANCES IN THE CHEMISTRY OF CARBON MONOXIDE.

Rose, J. D.

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BRITISH INTELLIGENCE OBJECTIVES
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RECENT ADVANCES IN THE CHEMISTRY OF CARBON MONOXIDE

Translation of lecture by
Dr. W. Reppe, Ludwigshafen

Reported by
J.D.ROSE M.O.S.

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PERSONNEL OF TEAM

*J.D.ROSE	M.O.S.(Team Leader)
C.F.S.APPLEYARD	M.O.S.
J.F.C.GARTSHORE	M.O.S.
J.W.FISHER	M.O.S.
P.W.BLAYLOCK)	(Canadian Department
A.H.ANDERSEN)	of Reconstruction)

Only those marked with an asterisk took part in this investigation.

RECENT ADVANCES IN THE CHEMISTRY OF CARBON MONOXIDE

Lecture by Dr.W.Reppe, Ludwigshafen, 26.4.45.

INTRODUCTION

Carbon monoxide has for many years been a substance of extraordinary interest to chemical industry. As examples of its large scale utilisation may be cited the synthesis of methanol from CO and hydrogen, of formic acid, of acetic acid from methanol and CO, the Fischer-Tropsch synthesis and the Mond nickel process. More recently American patent literature has shown an increasing interest in the addition of CO and water to olefines, and of CO to alcohols and ethers; these syntheses, however, are normally carried out at extremely high pressures and temperatures.

The great reactivity of carbon monoxide can be attributed to the free valencies (two lone electron pairs) and it was considered that CO should be capable of participating in many more reactions than had hitherto been reported. For example, reaction with acetylene could be expected, and this, if successful, would be doubly interesting as carbon monoxide and acetylene are formed in equimolecular proportions in the formation and utilisation of carbide, as shown in the following equation.

$$\begin{tikzcd} CaO + 3C \arrow[r] & CaC_2 + CO \arrow[d, "2H_2O"] \\ & C_2H_2 \end{tikzcd}$$

Normally, the carbon monoxide from a carbide oven is burnt, and its only value is that of a fuel.

It was thought that CO and acetylene should give a mono- or dialdehyde, and in the preliminary experiments in which nickel was used as catalyst, it became clear that the reaction which occurred was between acetylene and nickel carbonyl, and that the products of the reaction were not aldehydes but derivatives of acrylic esters.

1. SYNTHESIS OF ACRYLIC ACID AND ITS DERIVATIVES

The first experiments carried out used mixtures of acetylene and carbon monoxide with either nickel or nickel carbonyl as catalysts. When water was present, acrylic acid was formed and it was rapidly found that other substances containing active hydrogen atoms could be used in place of water with formation of corresponding derivatives of acrylic acid, thus

Alcohols : $R.OH + C_2H_2 + CO \longrightarrow CH_2{:}CH.COOR$ (Esters)

Amines : $R.NH_2 + C_2H_2 + CO \longrightarrow CH_2{:}CH.CONHR$ (Amides)

Mercaptans : $R.SH + C_2H_2 + CO \longrightarrow CH_2{:}CH.COSR$ (Thioesters)

Acids : $R.COOH + C_2H_2 + CO \longrightarrow CH_2{:}CH.CO.O.COR$ (Anhydrides)

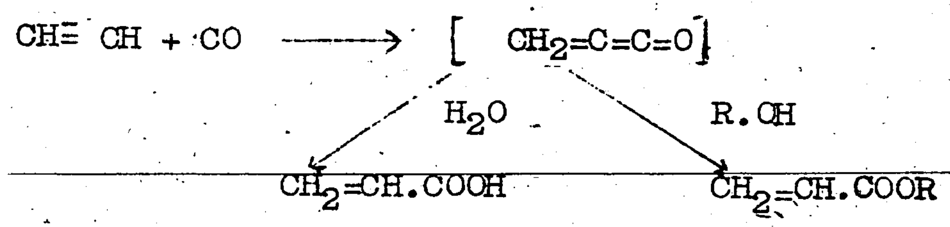
The formation of acids, esters and amides from water, alcohols and amines, respectively, shows the following thermodynamics

$C_2H_2 + CO + H_2O \longrightarrow CH_2 = CH.COOH$ - 39.6 k cal/mol.

$C_2H_2 + CO + ROH \longrightarrow CH_2 = CH.CO.OR$ + 50.7 k cal/mol. ($R = CH_3$)

$C_2H_2 + CO + RNH_2 \longrightarrow CH_2 = CH.CONHR$ + 87.1 k cal/mol. ($R = Ph$)

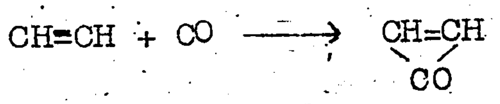
A tentative hypothesis put forward during the earlier work to account for the above reactions postulated the combination of acetylene and carbon monoxide with the formation of methylene ketene as an unstable intermediate product. The reactivity of ketene is well known, and it was thought that the fission of methylene ketene by water or alcohols would satisfactorily account for the formation of acrylic acid and esters.

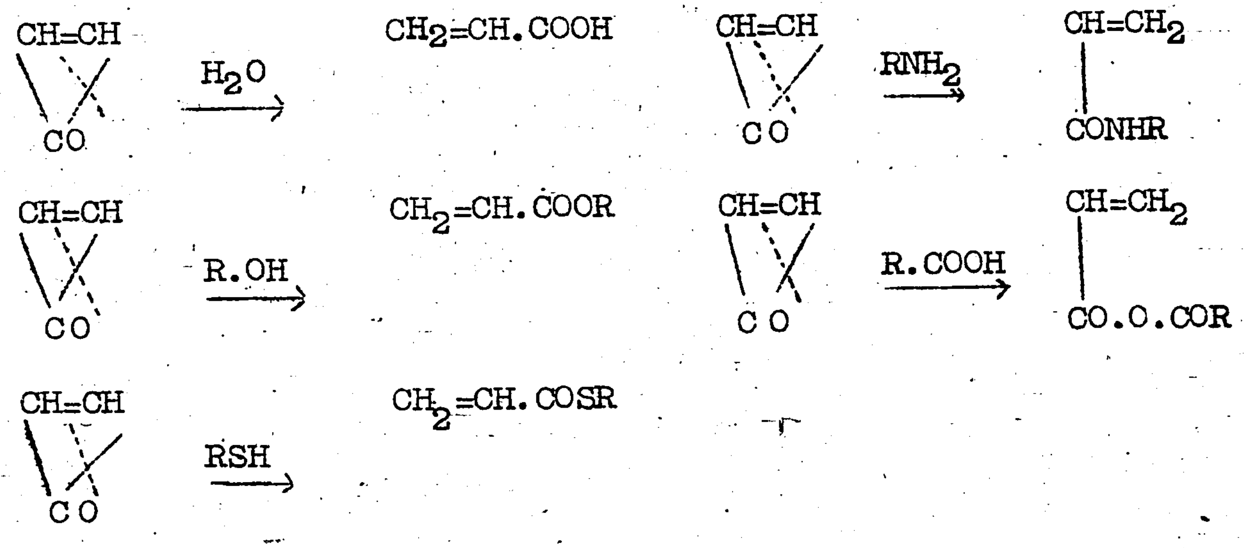


This explanation is entirely unsatisfactory; it will not account for the activity of mono- and di-substituted acetylenes. Thus

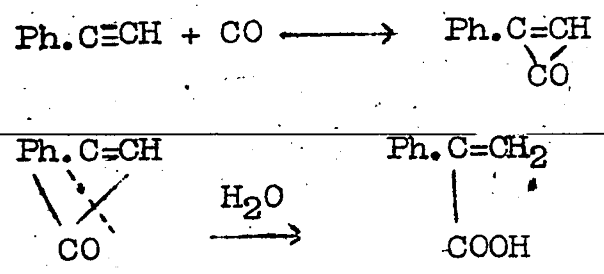
phenylacetylene with CO gives a-phenylacrylic acid, $CH_2{:}CPh.COOH$, and not cinnamic acid, whilst on the above hypothesis disubstituted acetylenes should be incapable of reaction.

It is therefore postulated that the intermediate product in this type of reaction is cyclopropenone and that acrylic acid derivatives are formed by fission of this unstable ring system, as follows:

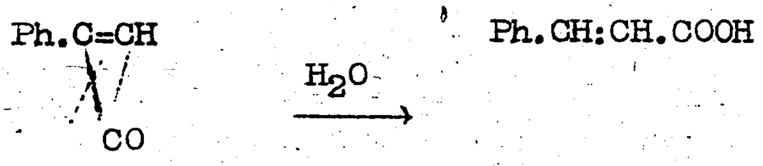




Similarly, using phenylacetylene, phenylcyclopropenone is postulated as an intermediate and this might be expected to open in two ways giving a-phenylacrylic acid (I) and cinnamic acid (II).

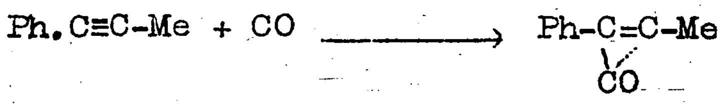


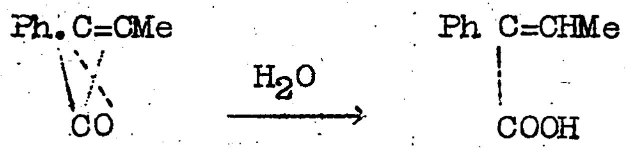
(I)



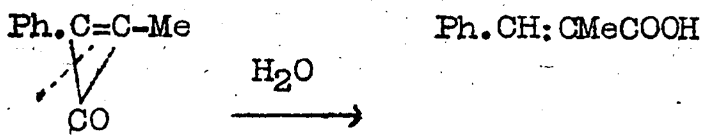
(II)

In fact only a-phenylacrylic acid is formed; with phenylmethylacetylene, fission of the hypothetical phenylmethylcyclopropenone can occur in both directions and both a-phenylcrotonic acid (III) and a-methylcinnamic acid (IV) are obtained.





(III)



(IV)

The reactions of acetylene and carbon monoxide with compounds containing active hydrogen atoms are applicable to all acetylenic compounds, and can be carried out using $Ni(CO)_4$ in stoichiometric quantities, or catalytically using carbon monoxide and metals capable of forming carbonyls, or derivatives of such metals.

Stoichiometric method

Using metal carbonyls, it is necessary to use an acid to remove the metal, and the equation of the reaction is as follows:-

$H_2O + C_2H_2 + \frac{1}{4}Ni(CO)_4 + \frac{1}{2}HCl\ aq. = CH_2{:}CH.COOH + \frac{1}{4}NiCl_2\ aq. + \frac{1}{4}H_2$

$ROH + C_2H_2 + \frac{1}{4}Ni(CO)_4 + \frac{1}{2}HCl\ aq. = CH_2{=}CH.COOR + \frac{1}{4}NiCl_2\ aq. + \frac{1}{4}H_2$

$RNH + C_2H_2 + \frac{1}{4}Ni(CO) + \frac{1}{2}HCl\ aq. = CH_2{:}CH.CONHR + \frac{1}{4}NiCl_2\ aq. + \frac{1}{4}H_2$, etc.

Nickel carbonyl is the most generally useful carbonyl compound; similar results can be obtained from cobalt carbonyl but this is less accessible; the reaction does not work with iron carbonyl, and mixtures of nickel and iron carbonyls give only poor yields. The usual acids are hydrochloric, hydrobromic, phosphoric or acetic acids, and these are best used in aqueous solution. If the acid (e.g. acetic) is used in the anhydrous condition, then the hydrogen liberated (see above equation) adds to the double bond of the acrylic acid and a 25% yield of propionic acid is obtained. In the presence of water the hydrogen reduces part of the carbon monoxide liberated from the nickel carbonyl. Using technical 36% hydrochloric acid, a vigorous reaction occurs at temperatures as low as 40°C., and quantitative yields of acrylic acid derivatives are obtained.

The formation of ethyl acrylate serves as an illustration of this reaction.

A three-necked flask contains ethanol and hydrochloric acid (36%) in the quantities calculated from the equation given. The contents are stirred vigorously and the air removed by an acetylene stream whilst the flask is warmed to 40-42°C. Nickel carbonyl (calculated amount) is added from a burette while the acetylene stream is passed in, and it should be noted that if the acetylene stream is not sufficiently vigorous, the flask can collapse due to the rapid absorption creating a vacuum. After absorption is complete, the ester-alcohol mixture is distilled from the aqueous nickel chloride and purified in the usual way.

The regeneration of nickel carbonyl from nickel chloride is a relatively simple process. The nickel chloride solution is treated with rather more ammonia than is necessary for the formation of hexammino nickel chloride and then with carbon monoxide at 80°C. and 50-100 atmospheres pressure. The solution now contains nickel carbonyl, excess ammonia, ammonium chloride and ammonium carbonate. After removal of the nickel carbonyl the ammonia can be recovered by liming the aqueous phase.

The regeneration of nickel carbonyl can be done continuously in a specially designed tower, and is completely novel. It is considered to be a great advance over normal metallurgical practice, in which an aqueous nickel solution is precipitated with sodium carbonate, the nickel carbonate filtered, dried, ignited and the dry oxide treated batchwise with carbon monoxide. The equation of the regeneration from aqueous solutions is as follows:

$$\boxed{4CO + Ni}Cl_2 + 2NH_3 + H_2\boxed{O + CO} \longrightarrow Ni(CO)_4 + 2NH_4Cl + CO_2$$

or, overall

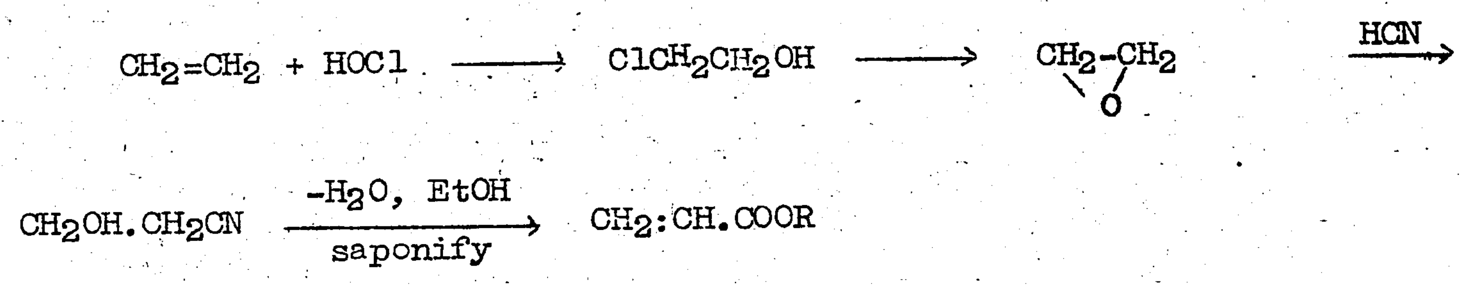
$$[Ni(NH_3)_6]Cl_2 + 5CO + 2H_2O \longrightarrow Ni(CO)_4 + 2(NH_4)Cl + (NH_4)_2CO_3 + 2NH_3$$

The synthesis of acrylic esters from nickel carbonyl, hydrochloric acid, alcohol and water can be carried out continuously and at atmospheric pressure. The facility of the reaction combined with the ease of regenerating nickel carbonyl makes this a cheaper and technically more attractive process than the normal one. The synthesis is also applicable to substituted acetylenes - methy-, ethyl-, phenyl-, vinyl- or divinyl-acetylene, to diacetylene, to alkinols and alkindiols their ethers and esters, and to acetylenes, carrying amine or mercaptan groups.

Catalytic process

Following the success of the "stoichiometric process" it was a natural consequence that a continuous catalytic process should be sought. This has been successful. Nickel is the most favourable metal catalyst and is best used as a halide. The reaction has to be carried out under pressure as it is under these conditions only that nickel carbonyl is formed from nickel salts. In the case of ethyl acrylate the alcohol is passed at 120-180° over catalysts contained in a pressure tower, and a counter stream of acetylene and carbon monoxide is circulated. A crude liquor containing a high percentage of ethyl acrylate is continuously removed from the foot of the tower.

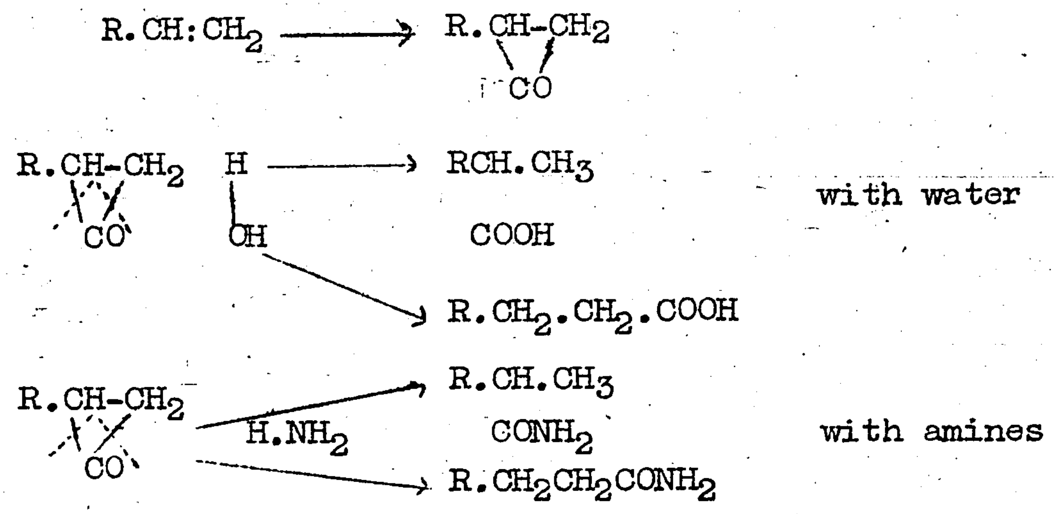
This contrasts with the normal commercial process for ethyl acrylate which is as follows:-



II. SYNTHESIS OF CARBOXYLIC ACIDS AND DERIVATIVES

(a) From olefines and olefinic compounds

It was thought that if the process described in Section I using acetylene could be applied to olefines, the cyclopropanone ring would be formed as an intermediate product which should undergo hydrolytic fission with compounds containing active hydrogen atoms, thus:-



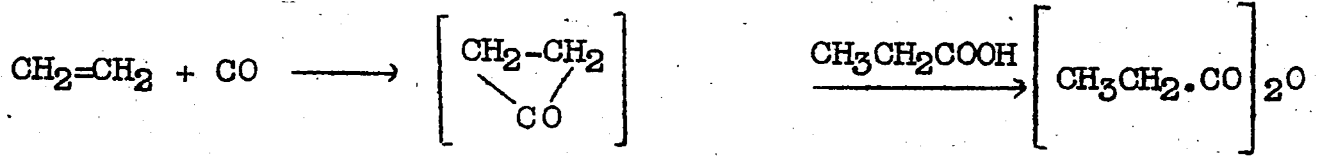
These expectations were realised, and it was in fact found that by interaction of olefines and carbon monoxide, both straight chain and a-methylated carboxylic acids were formed.

During the early part of this work information on the work of Ruhrchemie A-G (so called "Oxo process") became available. This firm following up observations made on the Fischer-Tropsch process, showed that carbon monoxide and hydrogen added to olefines to give aldehydes which could subsequently be reduced to alcohols. Work in the I.G.

demonstrated that nickel carbonyl was an intermediate product in this process.

The interaction of olefines with carbon monoxide proceeds easily at 200-300° and 150-300 atmospheres, and works equally well for the higher and the lower olefines, e.g., ethylene, propylene, butylene and C_5-C_{25} olefines. The C_{12}-C_{18} olefines prepared by cracking or by Fizcher-Tropsch synthesis are suitable starting materials. The acids formed can be hydrogenated to alcohols for use as detergents. An interesting application of the synthesis is the use of the acid originally formed as the agent for the fission of the cyclopropanone ring, giving anhydrides. Thus from ethylene, propionic anhydride, important for the manufacture of cellulose propionate, can be prepared.

$$CH_2{=}CH_2 + CO + H_2O \longrightarrow CH_3.CH_2.COOH$$



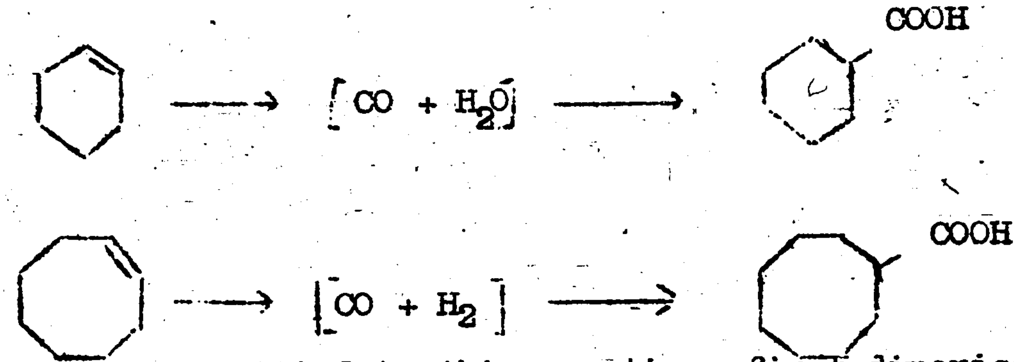
$$CH_2{=}CH_2 + CO \longrightarrow \left[\begin{array}{c} CH_2-CH_2 \\ \diagdown \quad \diagup \\ CO \end{array}\right] \xrightarrow{CH_3CH_2COOH} \left[CH_3CH_2.CO\right]_2O$$

In this connection, it is interesting to note that Mailhe (Bull.Soc.Chim.,(4),5,1909,815-819) showed that anhydrides could be split over a nickel catalyst into olefines, carbon monoxide and carboxylic acids.

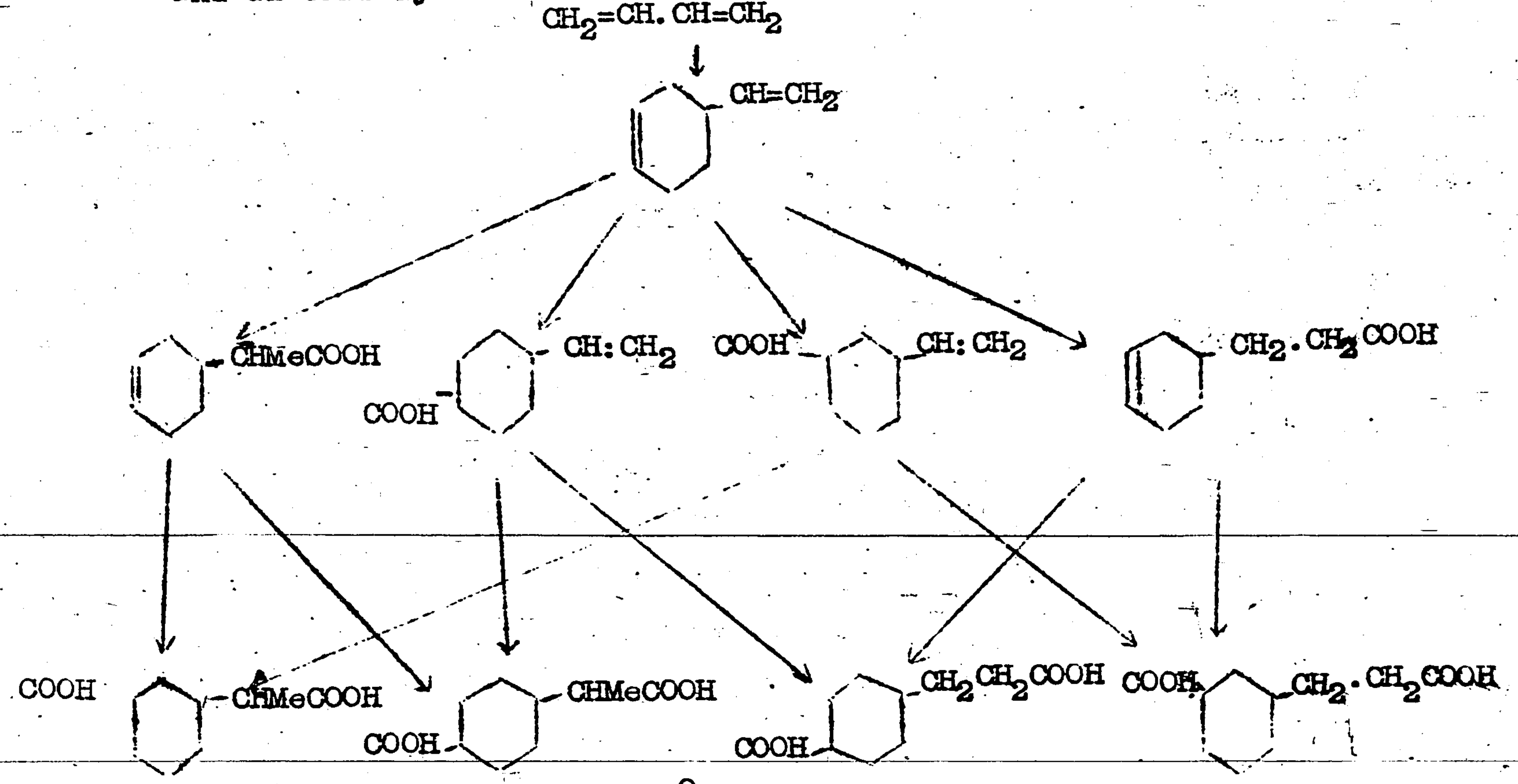
The mixed straight chain and a-methylated acids formed from the higher olefines have advantages over those obtained from natural fats inasmuch as they have higher solubility and dispersing power for lime soaps, and the same holds for the sulphates of the alcohols formed by catalytic reduction of the acids. Since higher olefines are cheap only as low percentage mixtures with paraffins, the above synthesis of acids from carbon monoxide and water is especially favourable since the separation of unreacted paraffin from the soaps of the acids formed is simple, and the regenerated fatty acids can easily be separated into fractions either as such, or after reduction to the corresponding alcohols.

It is clear from patent literature that American workers are interested in this synthesis but the conditions they use (high pressures) are on the borderline of technical possibility. It is not known how far American work has gone, but our experience is that yields are almost quantitative.

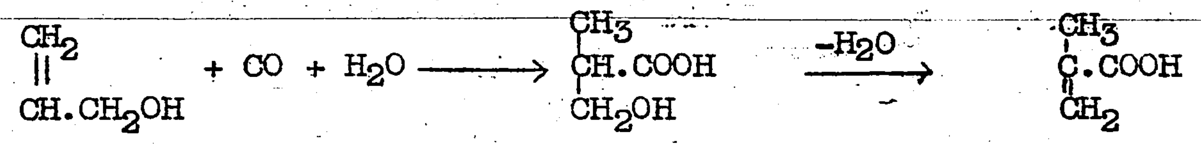
Cyclic olefines with carbon monoxide and water behave in the normal manner, thus cyclooctene gives cyclooctane carboxylic acid and cyclohexene gives cyclohexane carboxylic acid.



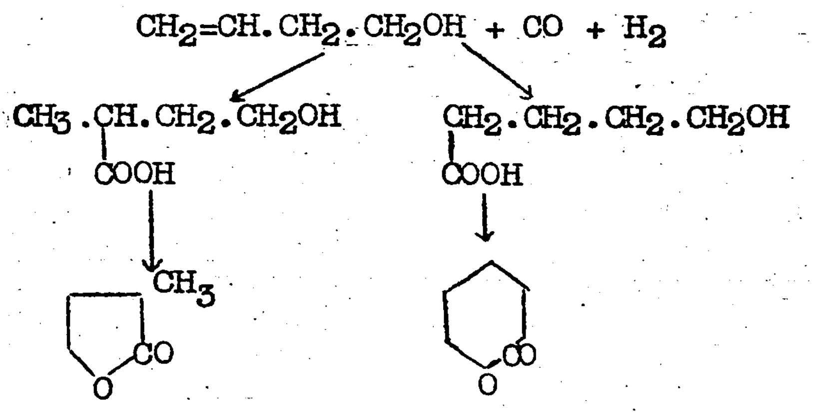
Butadiene, submitted to this reaction, first dimerises to vinyl cyclohexene, and from this a mixture of the following mono- and di-carboxylic acids are formed:



Similar reactions are shown by derivatives of olefines. Thus, allyl alcohol gives β-hydroxy isobutyric acid which on dehydration affords methacrylic acid.



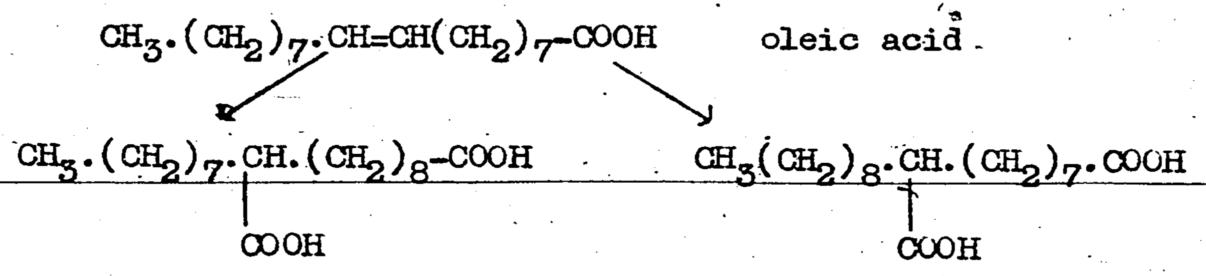
Buten-1-ol-4 yields, via the unstable hydroxy acids, a mixture of δ-valerolactone and methylbutyrolactone.

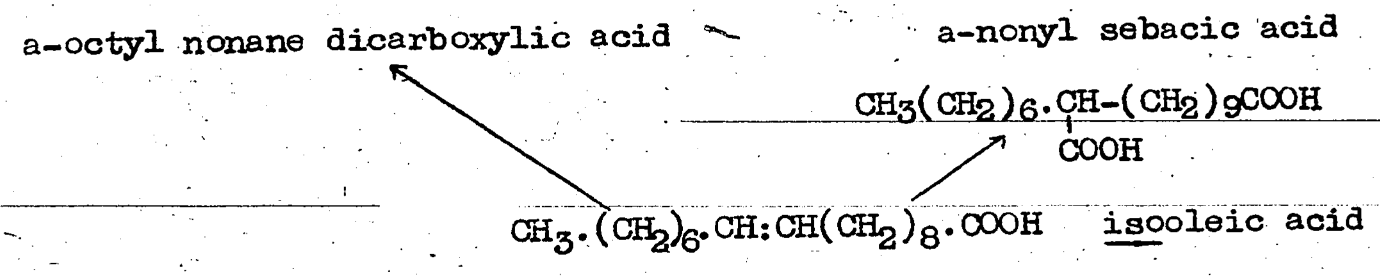


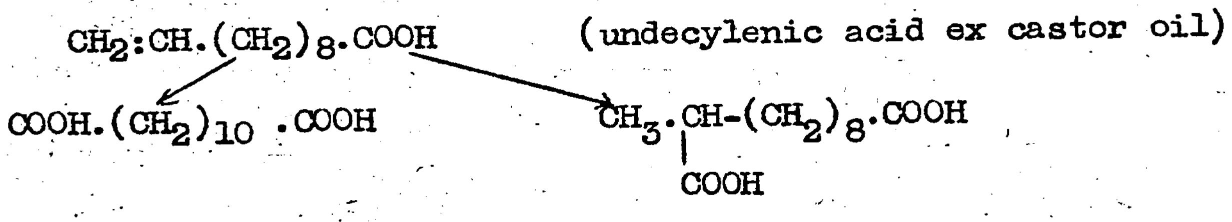
methylbutyrolactone δ-valerolactone

Olefinic carboxylic acids

Oleic and undecylenic acids react with water and carbon monoxide yielding dicarboxylic acids suitable for use as intermediates for polyamides, alkyd resins, plasticisers, etc.

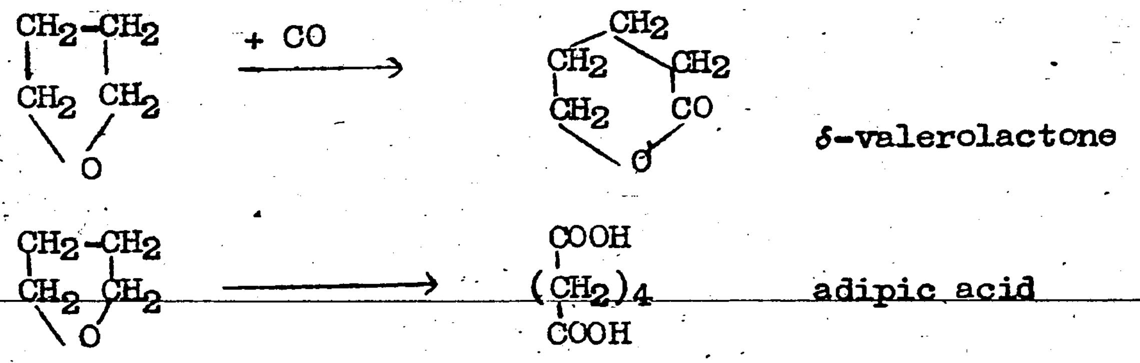






Ethers and alcohols

Aliphatic and cyclic ethers react with metal carbonyls giving carboxylic acids, but, in contrast to the reaction with olefines in which nickel carbonyl acts alone as catalyst; with ethers the simultaneous addition of a halogen is necessary. By this method tetrahydrofuran gives adipic acid, and this is visualised as the cheapest and simplest route to adipic acid. Normally small quantities of valeric acid are formed as a by-product, and by the use of special conditions, the addition can be restricted to equimols of tetrahydrofuran and carbon monoxide, the product being δ-valerolactone (which can be converted into caprolactam).



Tetrahydropyran, similarly treated, yields pimelic acid. The diols corresponding to these cyclic ethers can be used with equal efficiency; 1:4-butanediol gives adipic acid, 1:5-pentanediol pimelic acid, and 1:6-hexanediol suberic acid.

III. REACTIONS WITH HYDROCARBONYLS

The hydrocarbonyls were prepared according to Hieber's method by the action of solutions of alkalies or alkaline earths on metal carbonyls, especially iron pentacarbonyl. Later, experiments were conducted using sodium phosphate, sodium silicate, zinc aluminate and chromium aluminate. It was found that iron hydrocarbonyl, $Fe(CO)_4H_2$, in alkaline solution reacts quantitatively with carbon monoxide giving iron pentacarbonyl and hydrogen. The pentacarbonyl then reacts further with alkali, giving the hydrocarbonyl and CO_2, thus setting up a continuous reaction which ceases only when all the alkali present is converted into carbonate.

$$Fe(CO)_5 + H_2O \longrightarrow Fe(CO)_4H_2 + CO_2$$

$$Fe(CO)_4H_2 + CO \longrightarrow Fe(CO)_5 + H_2$$

i.e., the overall reaction is:-

$$CO + H_2O \longrightarrow CO_2 + H_2$$

To convert the process from a discontinuous to a truly continuous one it was necessary to find some base which would fill the role played by caustic alkali in the discontinuous process. Such a base must have the following properties:-

(1) Sufficiently basic to catalyse the reaction $Fe(CO)_5 + H_2O \longrightarrow Fe(CO)_4H_2 + CO_2$, and to combine with the CO_2.

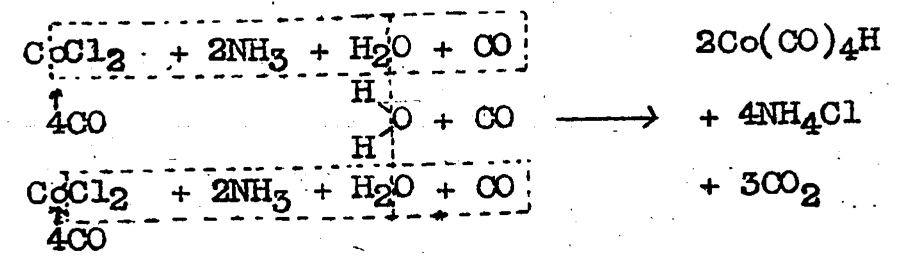
(2) The carbonate so formed should be thermally unstable and evolve CO_2 at higher temperatures.

(3) It should be water-soluble and non-volatile.

(4) It should be inert to the reactants (caustic soda forms formates with carbon monoxide).

Another method of preparation of hydrocarbonyls consists of an application of the process which has already been mentioned for the regeneration of nickel carbonyl from nickel salts. If this process is applied to ferrous or cobalt salts (e.g. ammoniacal Mohr salt), iron hydrocarbonyl, $Fe(CO_4)H_2$, can be prepared by regulating the rate of CO addition and stopping the addition at the right point. Using ammoniacal cobalt chloride the reaction stops automatically with the formation of $Co(CO)_4H$ which, in contrast to the iron compound, is stable to carbon monoxide. Pure cobalt hydrocarbonyl can be formed from such a solution by treatment with phosphoric acid.

The reaction can be represented as follows:



$$\begin{array}{lcl} CoCl_2 + 2NH_3 + H_2O + CO & & 2Co(CO)_4H \\ \uparrow 4CO \qquad\qquad\qquad {}^{H}_{H}{>}O + CO & \longrightarrow & + 4NH_4Cl \\ CoCl_2 + 2NH_3 + H_2O + CO & & + 3CO_2 \\ \uparrow 4CO & & \end{array}$$

or, including excess ammonia to interact with the CO_2,

$$2[Co(NH_3)_6]Cl_2 + 11CO + 6\,H_2O \longrightarrow 2Co(CO)_4H + 4NH_4Cl + 3(NH_4)_2CO_3 + 2NH_3$$

Cobalt hydrocarbonyl $[Co(CO)_4H]$ is a stable compound. Its alkaline solution can be heated to 200° for long periods without decomposition. Iron hydrocarbonyl on the other hand can be obtained pure only with difficulty and is decomposed rapidly by alkali at 100°. Cobalt hydrocarbonyl is a strong inorganic acid; it can be titrated with caustic soda using methyl orange indicator, and the end-point can be approached from either the acid or the alkaline side. It can be titrated with methylene blue in acetic acid solution, giving a reduction value corresponding to the content determined alkimetrically; iron hydrocarbonyl, however, can be titrated with methylene blue only on the alkaline side. Iron hydrocarbonyl is a much weaker acid than cobalt hydrocarbonyl.

Reaction of hydrocarbonyl with olefines

Interaction of alkaline iron hydrocarbonyl, $Fe(CO)_4H_2$, with ethylene gave, as main product, *n*-propanol; higher alcohols and organic acids (formic, propionic, etc.) were also formed. The same results were obtained if iron carbonyl, $Fe(CO)_5$, and ethylene were used in alkaline solution.

$$Fe(CO)_4H_2 + 2CH_2{:}CH_2 + 4H_2O \longrightarrow 2CH_3CH_2CH_2OH + Fe(HCO_3)_2$$
$$(\text{or } FeCO_3 + H_2O + CO_2)$$

It was hoped to carry out the reaction using iron carbonyl itself as catalyst, witn continuous addition of CO; the expected sequence of reactions was as follows:

$$2Fe(CO)_5 + [\text{base}] + 2H_2O \longrightarrow 2Fe(CO)_4H_2 + [\text{base}] + 2CO_2$$
$$2Fe(CO)_4H_2 + 2CO \longrightarrow 2Fe(CO_5) + 2H_2$$

$$\text{or, in total}\quad \begin{array}{l} \underline{CH_2{:}CH_2 + CO + 2H_2 \longrightarrow CH_3.CH_2CH_2OH} \\ CH_2{:}CH_2 + 3CO + 2H_2O \longrightarrow CH_3.CH_2.\,CH_2OH + 2CO_2 \end{array}$$

The actual reaction scheme, however, is much more complicated than the above, and has not been fully elucidated.

From what has been said, it is clear that the nature of the products to be obtained from identical reactants is entirely dependent on the nature of the catalyst used. Thus, ethylene, CO and water give propionic acid in presence of nickel carbonyl, and *n*-propanol in presence of iron hydrocarbonyl.

$$CH_2{=}CH_2 + CO + H_2O \longrightarrow CH_3CH_2COOH \quad (Ni(CO)_4 \text{ catalyst})$$
$$CH_2{:}\,CH_2 + 3CO + 2H_2O \longrightarrow CH_3CH_2CH_2OH \quad (Fe(CO)_4H_2 \text{ catalyst})$$

Further work showed that the formation of alcohols from olefines could be effectively accomplished only if the base were properly chosen, and that only tertiary bases would fulfil the necessary conditions of water solubility, non-volatility, and non-participation in side-reactions. Ammonia, primary and secondary amines, in these ethylene reactions are ineffective until they have been completely alkylated, thus:

$$CH_2{:}CH_2 + 3CO + H_2O + NH_3 \longrightarrow NH_2.CH_2CH_2CH_3 + 2CO_2$$
$$CH_2{:}CH_2 + 3CO + H_2O + NH_2C_3H_7 \longrightarrow NH(C_3H_7)_2 + 2CO_2$$
$$CH_2{:}CH_2 + 3CO + H_2O + NH(C_3H_7)_2 \longrightarrow N(C_3H_7)_3 + 2CO_2$$

The most effective bases are those containing a tertiary amino group, and a COOH or SO_3H group. The selected base was sodium dimethylamino acetate, $(CH_3)_2N.CH_2.\,COONa$.

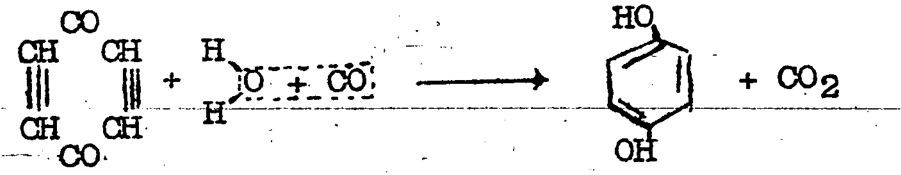
IV. SYNTHESIS OF HYDROQUINONE FROM ACETYLENE, CARBON MONOXIDE AND WATER

An attempt was made to synthesise unsaturated alcohols by submitting acetylene to the carbon monoxide-water reaction in presence of hydrocarbonyls. Surprisingly hydroquinone was formed, the conditions of the reaction being the same as those used for olefines, but at a rather lower temperature. A base (monoethanolamine) may be used, but is not essential; hydroxylic compounds (water or alcohol) must be present. The reaction is formulated as follows:

$$Fe(CO)_4H_2 + 4C_2H_2 + 2H_2O \longrightarrow 2C_6H_6O_2 + Fe(OH)_2$$

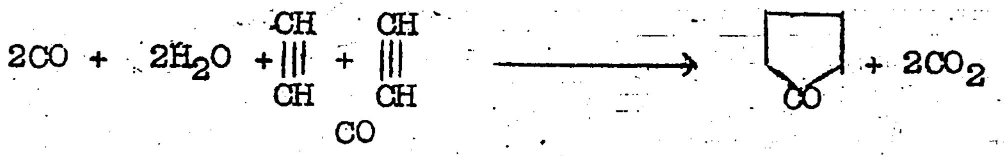
$$Fe(CO)_5 + 4C_2H_2 + 2H_2O + [\text{base}] \longrightarrow 2C_6H_6O_2 + FeCO_3 + [\text{base}]$$

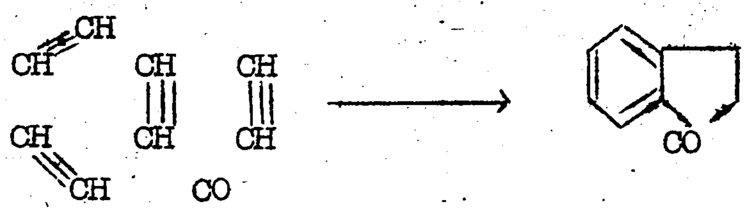
The yield at the moment is 20-30% of hydroquinone based on the hydrocarbonyl used.



This reaction is also applicable to methyl, phenyl and dimethylacetylenes, to ethers of propargyl alcohol, butinol, butindiol, hexindiol and dimethylamino derivatives of acetylene, e.g. $Me_2N.CH_2.C\equiv CH$ and $Me_2N.CH_2.C\equiv C.CH_2.NMe_2$.

There is some preliminary evidence that the possibilities of acetylene in this connection are by no means exhausted. For example, the formation of cyclopentanone and hydrindone have been observed in certain cases, although these reactions have not yet been investigated further.





Aldehydes and ketones also react with acetylene in the presence of nickel carbonyl, but the course of the reaction is, at the moment unknown.

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FINAL REPORT NO. 350
ITEM NO. 22

The SYNTHESIS of INTERMEDIATES for POLYAMIDES on an ACETYLENE BASIS

(Translation of a report by Dr. W. Reppe, Ludwigshafen)

Rose, J. D.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON — H.M. STATIONERY OFFICE

THE SYNTHESIS OF INTERMEDIATES FOR POLYAMIDES ON AN ACETYLENE BASIS

(Translation of a report by Dr.W.Reppe, Ludwigshafen)

Reported By

J.D.ROSE M.O.S.

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British Intelligence Objectives Sub-Committee,
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(1946?)

19 p., diagrs. (part fold.)

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PERSONNEL OF TEAM

*J.D.Rose	M.O.S. (Team Leader)
O.J.S.Appleyard	M.O.S.
J.F.C.Gartshore	M.O.S.
J.W.Fisher	M.O.S.
P.W.Blaylock	(Canadian Department
A.H.Andersen	(of Reconstruction

Only those marked with an asterisk took part in this investigation

TRANSLATOR'S NOTE

The report, a translation of which follows, appears to be a summary written by Dr.Reppe in 1941 of the application of his acetylene work to the particular problem of the synthesis of intermediates for polyamides. One section of the report, on cyclopolyolefines, was omitted as it gave a very brief, and at that time immature, picture of a subject which has since been reported much more fully.

There is no indication in the original report of whether the flow sheets enclosed are those of actual working plants, or merely proposed flow sheets for plants to be erected later. The subject matter should be regarded as suspect, particularly on the grounds of premature optimism. As an example the synthesis of adipic acid from carbon monoxide and tetrahydrofuran is presented here in a very simplified form; later work showed that there were difficulties, particularly in structural materials, which were probably not known, and were certainly not indicated, when the report translated here was written.

THE SYNTHESIS OF INTERMEDIATES FOR POLYAMIDES ON AN ACETYLENE BASIS

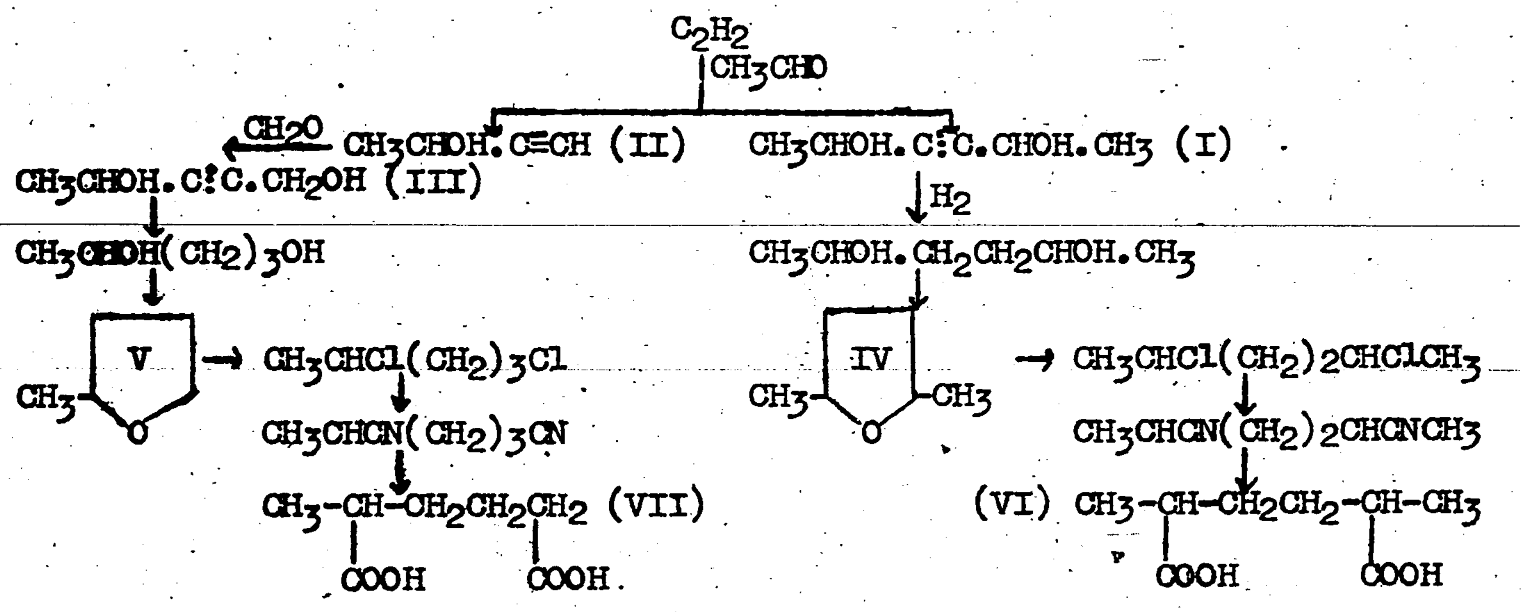
Summary Report by Dr. W. Reppe, Ludwigshafen, 18.10.41.

A. DICARBOXYLIC ACIDS AND AMINO ACIDS

Tetrahydrofuran and hydrochloric acid in presence of 50% sulphuric acid give dichlorobutane. This process has been worked in Ludwigshafen on the 5 ton/day scale; 1:4-dichlorobutane costs 0.65 RM/kg. with tetrahydrofuran at 0.60 RM/kg. The yield is 95% of theory.

The reaction with cyanide is carried out in methanol solution, best under pressure, and gives yields of over 90%. The reaction is exothermic, evolving 73.5 k cal/mol. Since no pressure apparatus was available for this step, the reaction had been carried out in an iron pan at atmospheric pressure. Corrosion was severe in early experiments but had been got over by working in anhydrous methanol, by rigidly excluding moisture, and by adding amphoteric salts of lead or aluminium. After trial of the process on the 500 l. and 1,500 l. scale, manufacture was undertaken in a pilot plant at Schkopau, with a capacity of 100 tons/month. With tetrahydrofuran at 0.60 RM/kg., adiponitrile by this route costs 1.60 RM/kg.

Methyl analogues of adiponitrile can be prepared by a similar reaction. Acetaldehyde and acetylene yield hexine-3-diol-2:5(I) and butin-3-ol(II); with formaldehyde, butinol(II) gives pentin-3-diol-2:5(III). By hydrogenation and cyclisation, (I) and (III) yield 2:5-dimethylfuran(IV) and 2-methylfuran(V), respectively, which yield the corresponding adipic acids, 2:5-dimethyl adipic acid(VI) and 2-methyl adipic(VII) by interaction with HCl, followed by treatment with cyanide, and hydrolysis.



Adipic acid from tetrahydrofuran and carbon monoxide

By far the most elegant synthesis of adipic acid is that from tetrahydrofuran, carbon monoxide and water. In batchwise operations, 80% yields have been obtained, the by products being valeric acid and valerolactone. The reaction is exothermic, 72 k cal/mol. being evolved.

The apparatus designed for continuous operation is shown in Figure I.

A high pressure tower is charged with a nickel catalyst and a solution of nickel iodide in aqueous tetrahydrofuran is added from the top. Simultaneously a stream of carbon monoxide at 200 ats. and 250° is circulated through the tower. At the foot of the tower the reaction mixture flows through a heat exchanger at 180°, and the carbon monoxide passes via a cooler and separator to a circulating pump which recycles it to the top of the reaction tower.

From the main separator the adipic acid passes to a cooled secondary separator and thence, via a let-down valve, to a continuous centrifuge in which it is washed with fresh aqueous tetrahydrofuran. The wash liquors, which contain nickel iodide, valerolactone, water and tetrahydrofuran, are circulated to the reaction tower with a pump. The crude adipic acid from the centrifuge is then recrystallised.

The small amount of nickel carbonyl contained in the off gases decomposes to nickel and CO in a separator. After nickel has built up in this separator, the gas is switched through a second separator, in parallel with the first, and the first treated with CO at 200 atmospheres to regenerate nickel carbonyl which is recycled.

With yields of 70-90%, expenses of 0.08-0.24 RM/kg. and a tetrahydrofuran price of 0.50-0.60 RM/kg., the price of adipic acid by this process should be RM 0.40-0.70/kg. This should give adiponitrile (by the ammonia process) at RM 1.05-1.55/kg. This implies a reduction in the cost of Igamide A of from 28-46% (based on a price of Igamide A from adipic acid at 1.25 RM/kg. made by the normal process from phenol).

Present prices are:-

Phenol	0.77 RM/kg.
Cyclohexanol	0.895 RM/kg.
Adipic acid	0.37 RM/kg.

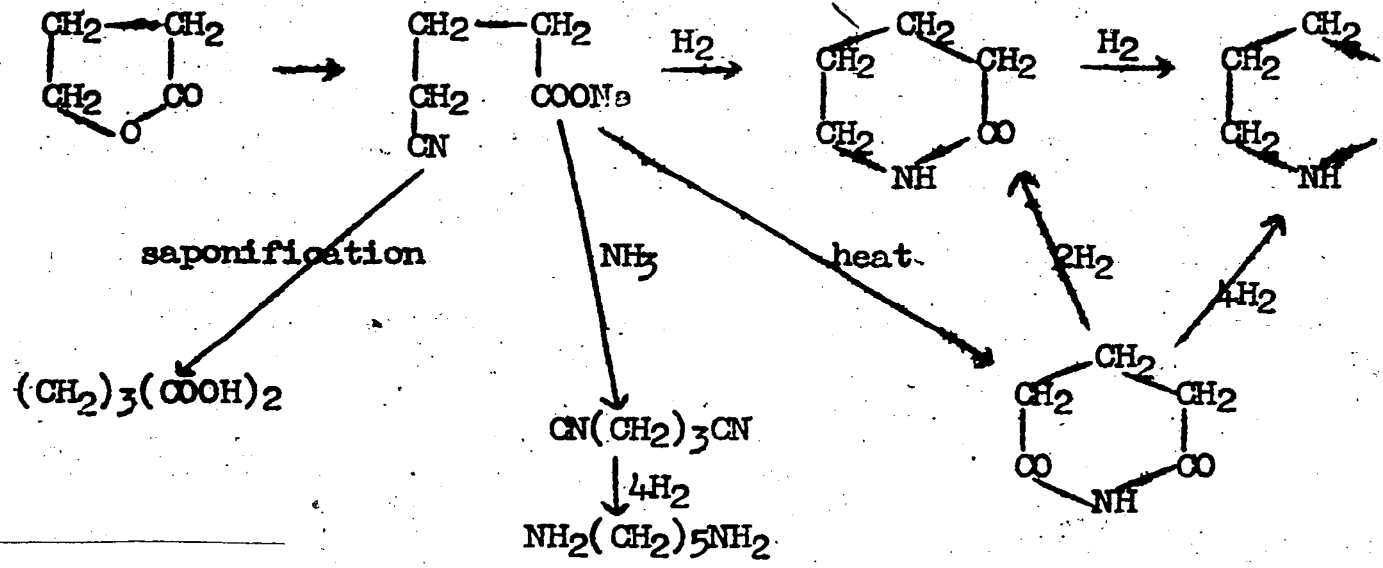
Pimelic acid

The synthesis of adipic acid from tetrahydrofuran, CO and H_2O described above can be applied to higher homologues, such as tetrahydropyran. Alternatively, tetrahydropyran can be converted into 1:5-dichloropentane and thence via pimelonitrile to pimelic acid.

Glutaric acid

Glutaric acid can be obtained easily by alkinol synthesis. Butyrolactone can be prepared in quantitative yield by dehydrogenation of 1:4-butanediol, and can be converted to cyanobutyric acid in high yield by heating with sodium or potassium cyanide. Saponification of cyanobutyric acid gives glutaric acid. Butyrolactone is at present made on the 20 tons/month scale, but a plant for 100 tons/month is being planned at the moment.

The formation of cyanobutyric acid from butyrolactone and cyanide is a very exothermic reaction, and it is necessary to interact small quantities at a time of a mixture of finely powdered lactone and cyanide. The resulting product is the alkali salt, which is treated with hydrochloric acid and the solution so formed is evaporated to a syrup from which cyanobutyric acid crystallises. On heating, cyanobutyric acid isomerises to glutarimide of which 500 kg. have so far been manufactured.



Succinic acid

Succinic acid is manufactured by oxidation of tetrahydrofuran with nitric acid at 20-30°. The NO produced is re-oxidised with air to nitric acid and used again; only small quantities of make-up nitric acid are therefore needed. The yield is over 96% of theory and a continuous plant of capacity 10 tons/month is being erected. At present 5 tons/month are being made by batchwise operation.

Succinic anhydride

The conversion of succinic acid to maleic anhydride and ketopimelic acid is best done via the anhydride. Succinic acid is evaporated in vacuo at 100 mm.Hg. and the vapour led over an aluminium catalyst at 300°. The yield is 95%, and a 2-3 tons/month plant is being designed. See Figure II.

Maleic anhydride

If chlorine is led at 170-200° into molten succinic anhydride, maleic anhydride distils off with about 5% of chloromaleic anhydride which can be separated by pressing from the maleic anhydride. Any unchanged succinic anhydride in the product can be removed by vacuum distillation. The yield is 88-90% of theory. See Figure III.

Ketopimelic acid

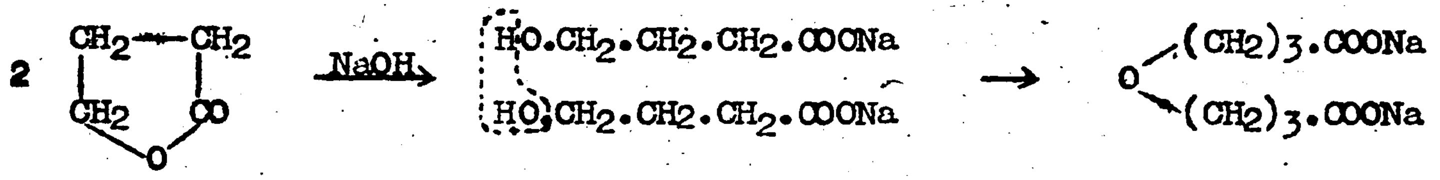
The dilactone of ketopimelic acid, an important intermediate for polyamide syntheses, can be made continuously by decarboxylation of succinic anhydride or succinic acid at 240-250°. The process is carried out at a conversion of 50-60%, so that the excess of starting material acts as a diluent. The molten acid (or anhydride) is led through a series of reactors at 230-250°, in which the time of contact is 5-7 hours. It is then distilled under reduced pressure, when unreacted succinic anhydride is separated from the dilactone or the ketopimelic acid. It is better to use succinic anhydride; if the acid is used, partial sublimation occurs.

A plant for continuous production of 2 tons/month is now being erected. The flow sheet is shown in Figure IV.

Oxydibutyric acid

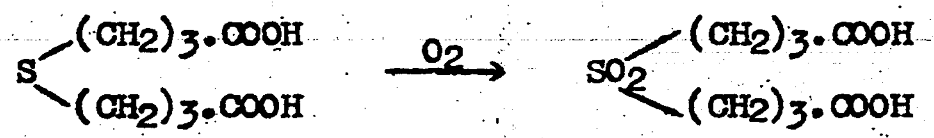
Both oxydibutyric acid, $O[(CH_2)_3.COOH]_2$, and thiodibutyric acid, $S[(CH_2)_3.COOH]_2$, can be made from butinediol via butyrolactone.

Butyrolactone, treated with alkali hydroxide at 180-200°, gives sodium γ-hydroxy butyrate, which loses water intermolecularly under the influence of dehydrating catalysts such as alumina giving the disodium salt of oxydibutyric acid. Alkaline earth hydroxides also promote the dehydration; the yield is 80-90%, the m.p. of oxydibutyric acid is 81°.



Quantities of 10-20 kg. have been made for use in mixed polyamides. By a similar series of reactions, δ-valerolactone gives oxydivaleric acid.

If alkali or alkali earth sulphides are used in place of the hydroxides, thiodibutyric acid and thiodivaleric acids can be obtained. Thiodibutyric acid can be made in Ludwigshafen at the rate of 7-8 tons/month. Its use as a component of polyamides is at present under investigation; its esters give plasticisers for rubber and it is also useful as an intermediate in synthetic resin manufacture. Thiodibutyric acid, on treatment with chlorine in water, gives quantitatively the sulphone, di(δ-carboxypropyl)sulphone, m.p.197°.



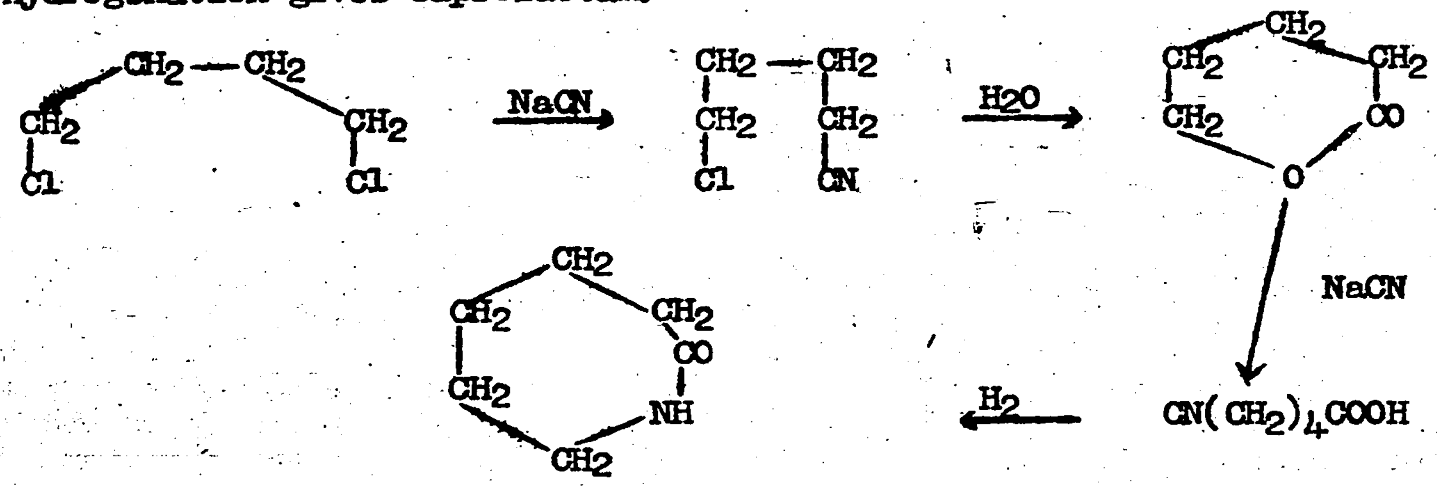
$$S\begin{matrix}(CH_2)_3.COOH\\(CH_2)_3.COOH\end{matrix} \xrightarrow{O_2} SO_2\begin{matrix}(CH_2)_3.COOH\\(CH_2)_3.COOH\end{matrix}$$

Aminocarboxylic acids

Caprolactam, the important intermediate for polyamide syntheses, can be manufactured by the alkinol process by methods which are independent of benzene as a raw material. The following possibilities exist.

(a) Valerolactone from chlorovaleronitrile

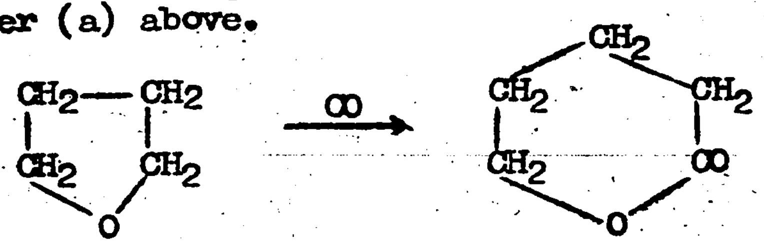
Interaction of 1:4-dichlorobutane with an insufficient quantity of sodium cyanide gives (besides some adiponitrile) quantities of δ-chlorovaleronitrile. This, on simple heating with water under pressure at 180°, yields δ-valerolactone and ammonium chloride. By heating δ-valerolactone with cyanide, δ-cyanovaleric acid is obtained which on hydrogenation gives caprolactam.



caprolactam

(b) From valerolactone, prepared from tetrahydrofuran and carbon monoxide

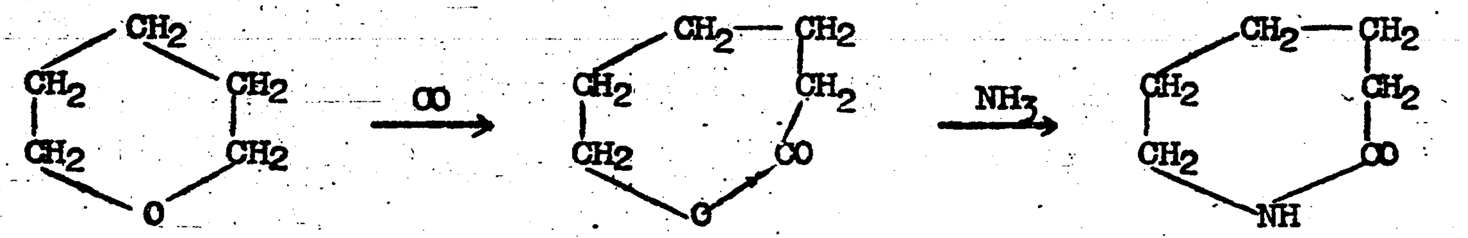
This can be done by interaction of tetrahydrofuran with one molecule carbon monoxide to give valerolactone, the synthesis then proceeding as under (a) above.



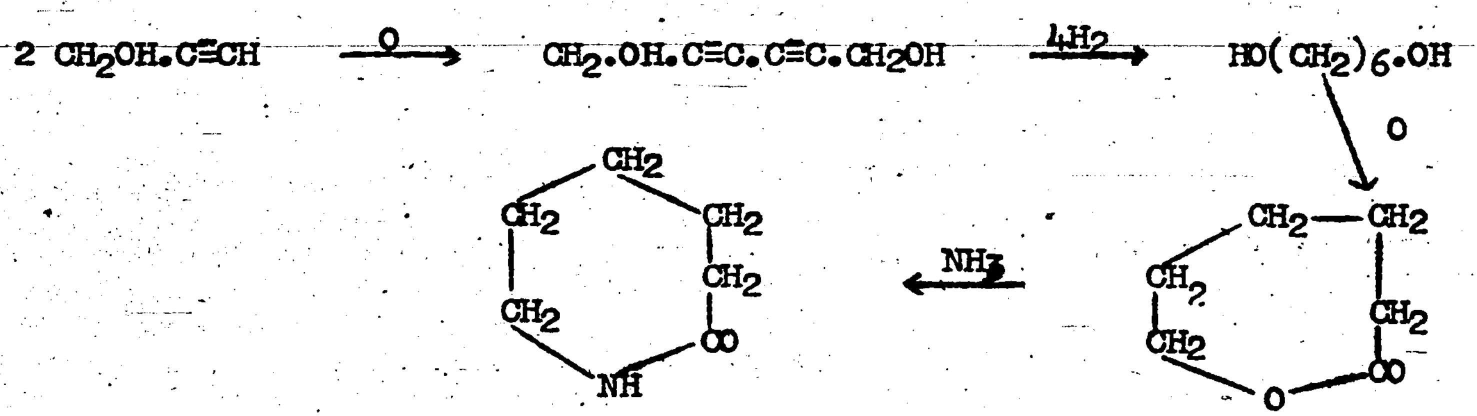
(c) A third possibility lies in the synthesis of caprolactone and its conversion to caprolactam with ammonia.

Caprolactone can be prepared by two methods:-

(i) by introduction of 1 mol. carbon monoxide into tetrahydropyran.



or (ii) by oxidation of propargyl alcohol to hexadiinediol, followed by hydrogenation to 1:6-hexanediol and dehydrogenation to caprolactone.



B. DIAMINES

Hexamethylenediamine - continuous process

A semi-scale laboratory unit has been in operation at the Main laboratory, Ludwigshafen, and has run for 68 days with an average yield of 89.6%, many individual tests giving over 90%. 1.8 kg. pure diamine per litre per day were produced, and catalyst usage was decreased from 0.3 kg. to 0.1 kg. per 100 kg. diamine. A flow sheet of the apparatus is given in Figure V.

Further improvements are visualised when a more even distribution of heat over the catalyst bed can be achieved. The life of the catalyst should be increased by dilution of the acrylonitrile feed with part of the reduced product. Preliminary experiments indicate that by this method yields of 93% (average) and 95% (peak) can be achieved.

Pentamethylenediamine

This is accessible via butyrolactone. As stated above, butyrolactone and cyanides give cyanobutyric acid, and this (or better, glutarimide made by isomerisation) with ammonia and dehydrating catalysts gives glutaronitrile. Batchwise reduction of glutaronitrile with Raney cobalt at 80-100° has given 62% yields of pentamethylenediamine and 34% yields of piperidine. Reduction in solvents gives 10% of diamine and 85% piperidine, and continuous hydrogenation gives 87% pentamethylenediamine and 8% piperidine.

C. POLYHYDRIC ALCOHOLS

1:4-Bis(4-hydroxybutoxy)butane $HO(CH_2)_4.O.(CH_2)_4.O(CH_2)_4OH$

This is prepared from 1:4-dichlorobutane (1 mol.) and butanediol (2 mols.)

1:2:4-Butanetriol $HO.CH_2.CHOH.CH_2.CH_2OH$

A 35% aqueous solution of 1:4-butindiol adds water to the triple linkage in presence of mercury compounds at 45-60°.

$$HO.CH_2.C{\equiv}C.CH_2OH \longrightarrow HO.CH_2.CO.CH_2CH_2OH$$

As in the formation of acetaldehyde from acetylene, the mercury forms a water-soluble addition compound which, on treatment with acids, or on heating, splits into ketobutandiol and mercury salts, which latter then add to more butindiol. The addition of water to butindiol is strongly exothermic, about 18 k cal/mol. being evolved. This heat of reaction is removed by carrying out the hydration in a stirred autoclave which is maintained under vacuum, and the heat dissipated by boiling the autoclave contents under the reduced pressure. At the end of the hydration the mercury salt is normally recovered as metallic mercury.

Ketobutandiol (hydroxymethyl-β-hydroxyethylketone) is an unstable substance, which dehydrates readily to hydroxymethylvinylketone; this is an easily polymerisable substance, and it is therefore necessary to proceed with the synthesis of butantriol without attempting to isolate the ketobutandiol in pure form. The solution of crude hydration product is therefore separated from metallic mercury, neutralised with calcium carbonate, filtered from calcium sulphate and the calcium ions remaining are removed with a "Wolfatite" filter. The aqueous solution is then hydrogenated in presence of a nickel or cobalt catalyst to 1:2:4-trihydroxybutane. The reduction is carried out at 40-80°. At higher temperatures (100° and over) 1:2-butylene glycol is formed. Using less active catalysts which hydrogenate only at 100-150°, as much as 70% of 1:2-butylene glycol can be obtained. A pilot plant producing 100-200 kg./day of 1:2:4-butanetriol is in operation; the flow sheet of this plant is given in Figure VI.

Butanetriol is similar in chemical properties to glycerol, and can be used as a glycerol substitute. On dehydration it yields 3-hydroxytetrahydrofuran, which can be oxidised to 3-ketotetrahydrofuran.

The addition of water to the majority of acetylenic compounds is easier than is the case with butinediol. Propargyl alcohol, for example, can yield acetol and (by reduction) 1:2-propylene glycol. The pilot plant for butanetriol manufacture can be used equally well for the hydration and reduction of propargyl alcohol to propylene glycol.

Pentandiol, hexandiol and 2:3-butylene glycol

By the use of acetaldehyde as the aldehydic component in the alkinol synthesis, a series of glycols can be obtained which were formerly accessible only in small quantities.

The reactions are as follows.

$$CH_3CHO + CH{\equiv}CH \longrightarrow CH_3CHOH.C{\equiv}CH + 24 \text{ k cal/mol.}$$
$$2CH_3CHO + CH{\equiv}CH \longrightarrow CH_3CHOH.C{\equiv}C.CHOH.CH_3 + 9 \text{ k cal/mol.}$$

By suitable adjustment of the experimental conditions either butinol or hexindiol can be obtained as the major product. On hydrogenation, butinol gives 2-butanol and hexin-3-diol-2:5 gives hexandiol-2:5.

Hydration of butinol in presence of mercury salts gives acetoin in good yield, and hydrogenation of the crude hydration solution gives 2:3-butylene glycol, b.p. 178-179°, in good yield.

$$CH_3.CHOH.C{\equiv}CH \longrightarrow CH_3CHOH.CO.CH_3 \longrightarrow CH_3CHOH.CHOH.CH_3$$

Butindiol, like acetylene, has an active hydrogen atom and can react with aldehydes. With formaldehyde, pentin-3-diol-2:5 is formed, as follows.

$$CH_3.CHOH.C{\equiv}CH + CH_2O \longrightarrow CH_3CHOH.C{\equiv}C.CH_2OH + 25 \text{ k cal}$$

This reaction, which can be carried out as a continuous process using a supported catalyst, gives good yields. The conversion is almost 100%, and 1 kg. pentindiol per litre catalyst per day can be produced. Hydrogenation of pentindiol to pentandiol-1:4 is an extremely easy reaction, yields of 93-95% being obtained. By fission of water from hexandiol-2:5 or pentandiol-1:4, 2:5-dimethyltetrahydrofuran or 2-methyltetrahydrofuran, respectively, can be obtained. These can be converted via the dichlorides into the dinitriles, and thence to the substituted methyl adipic acids.

The work referred to so briefly in this lecture illustrates the wide possibilities of the synthesis, from acetylene, of a series of important raw materials for polyamides which are entirely independent of benzene as a starting material.

FIG. I.

ADIPIC ACID FROM TETRAHYDROFURAN AND CARBON MONOXIDE.

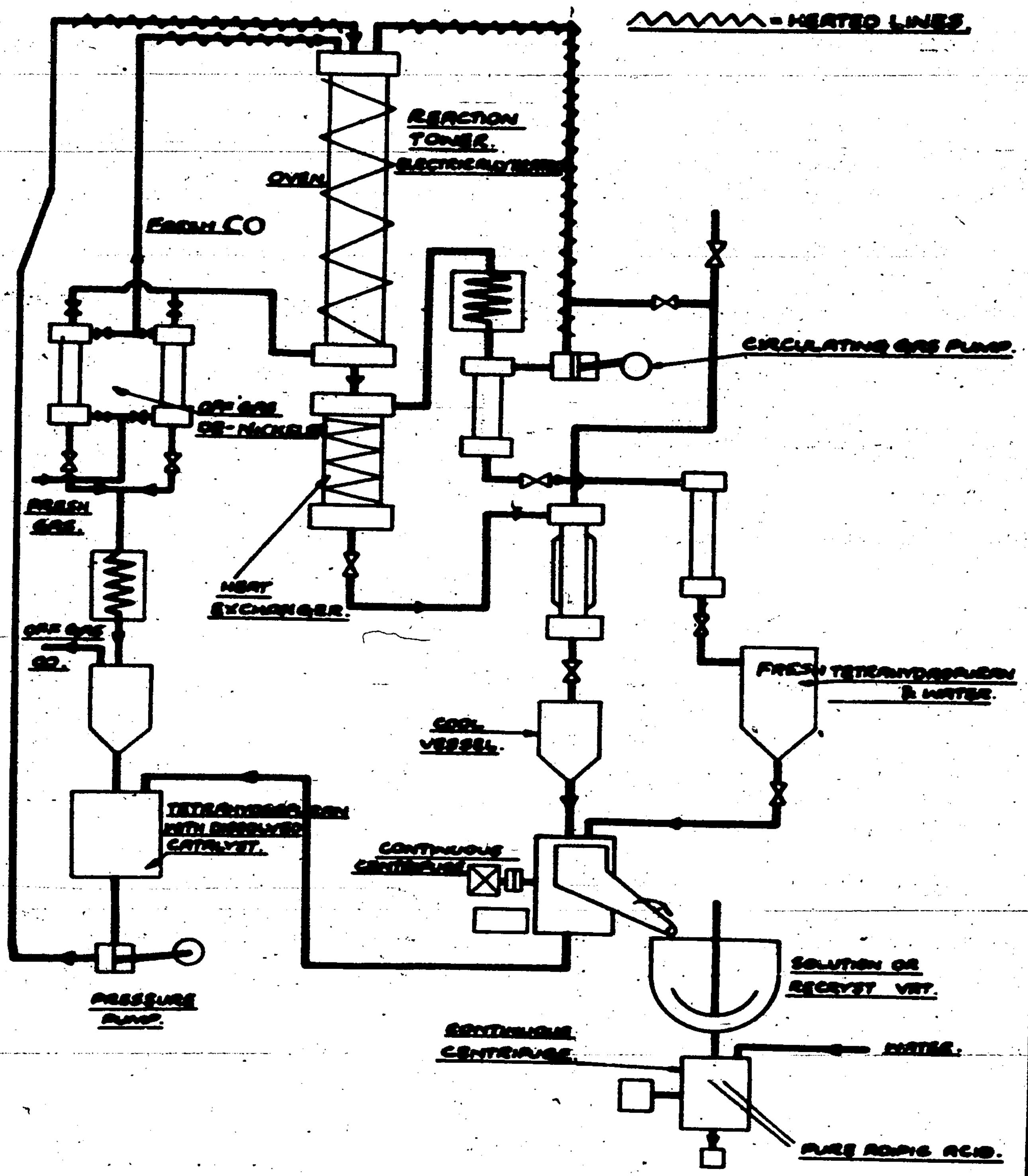


FIG. II.

SUCCINNIC ANHYDRIDE.

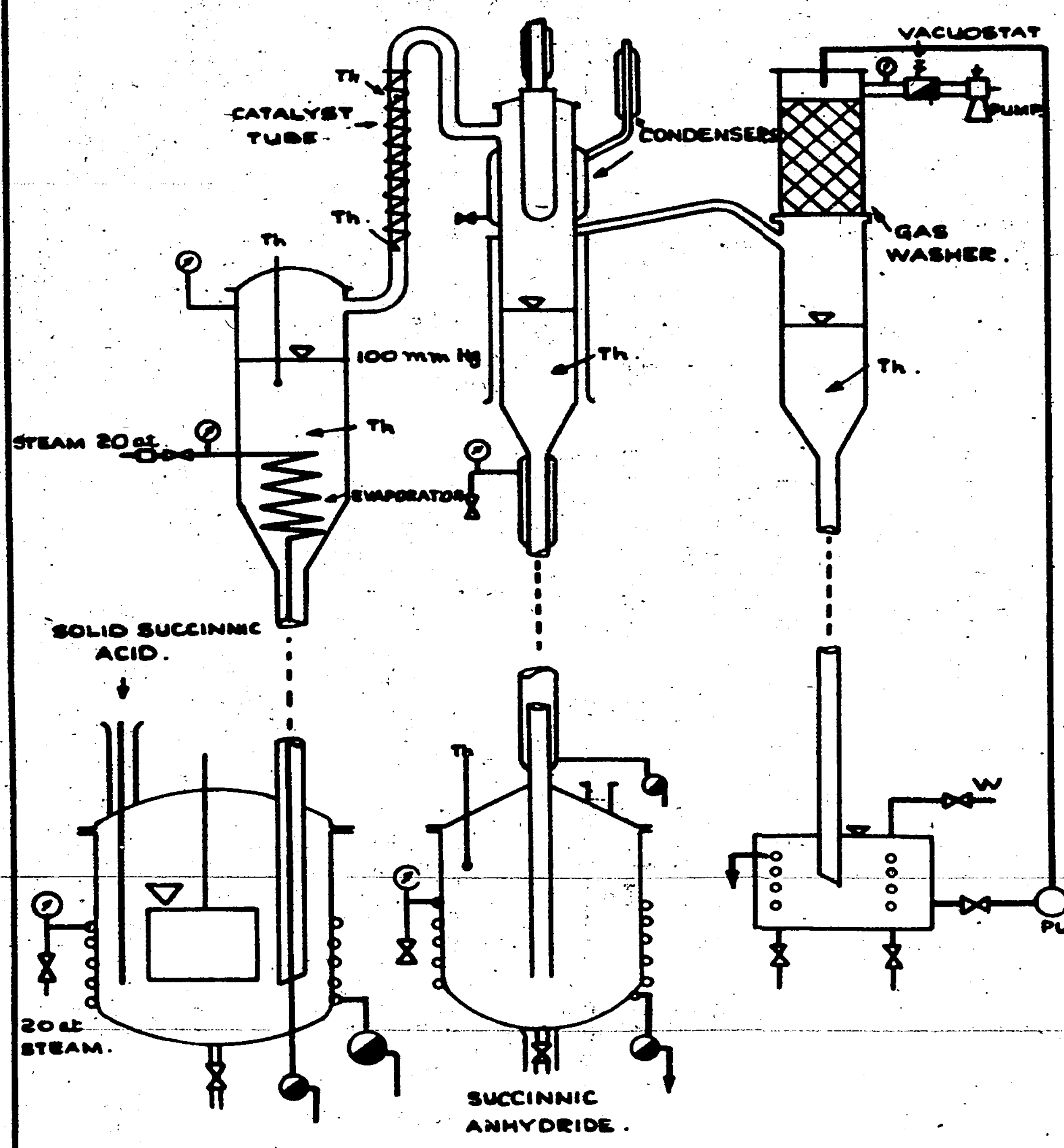
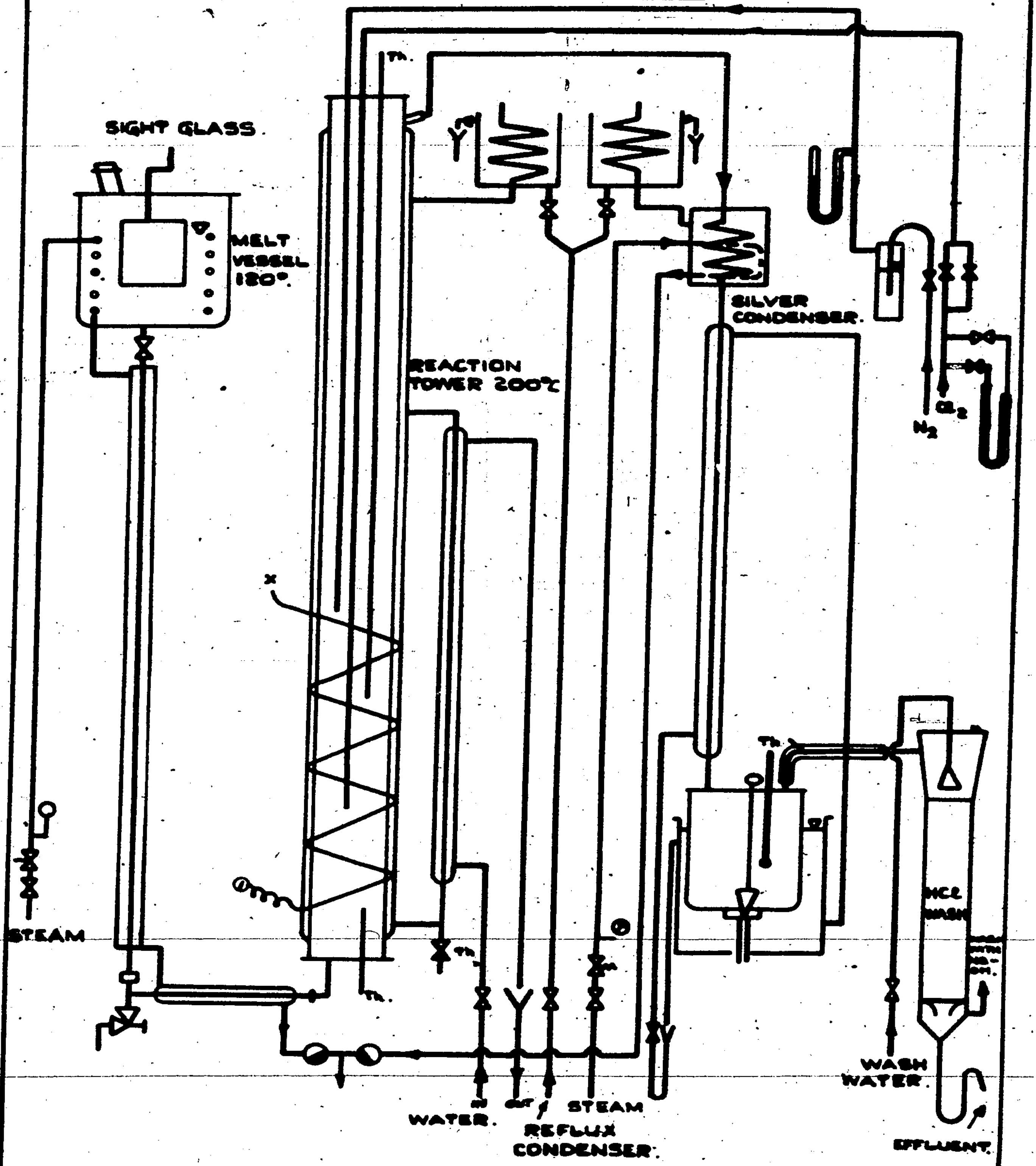
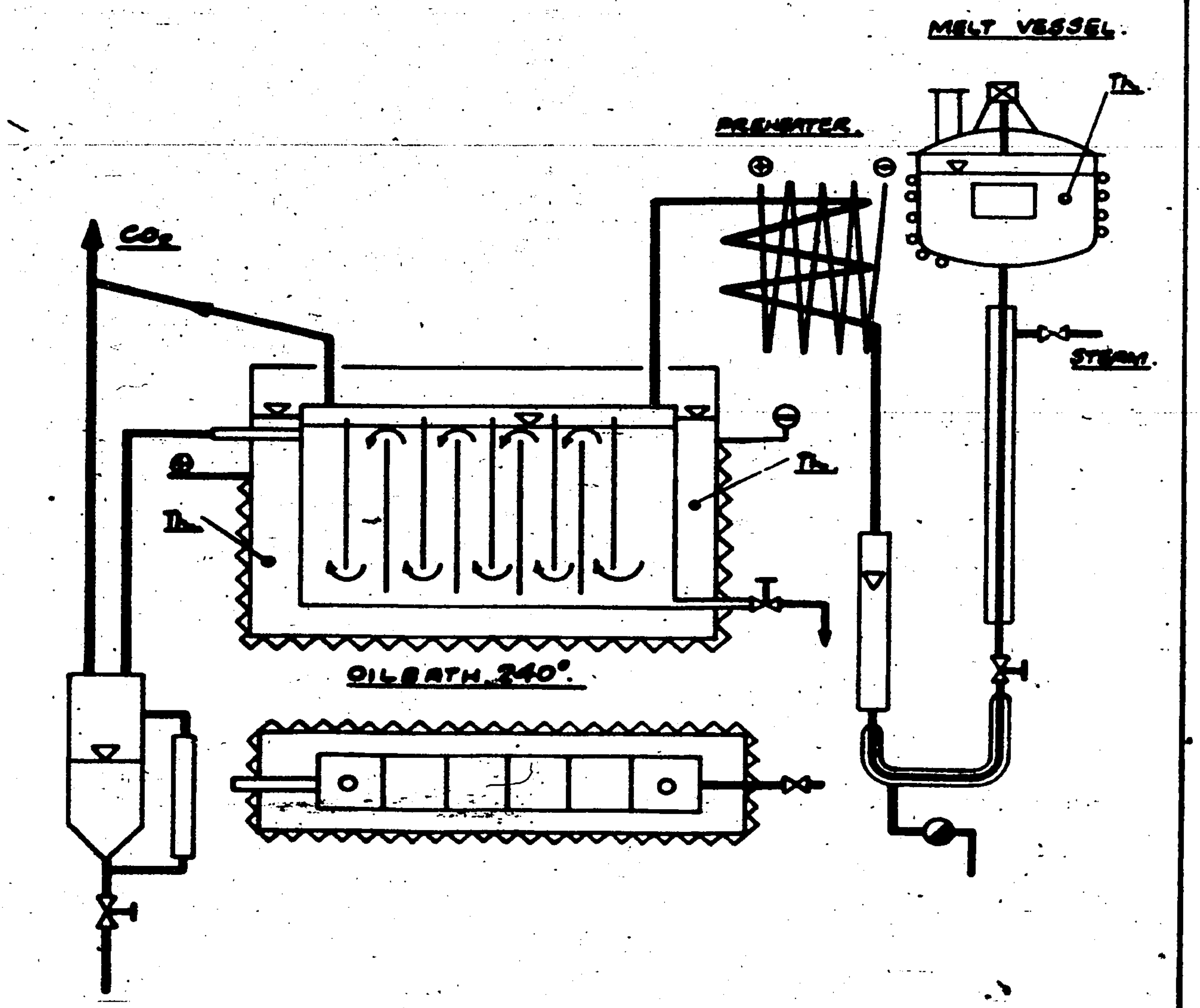


FIG. III.
MALEIC ANHYDRIDE.





APPARATUS FOR MANUFACTURE OF KETOPIMELIC ACID.

FIG. IV.

FIG. V

CONTINUOUS HYDROGENATION OF ADIPONITRILE.

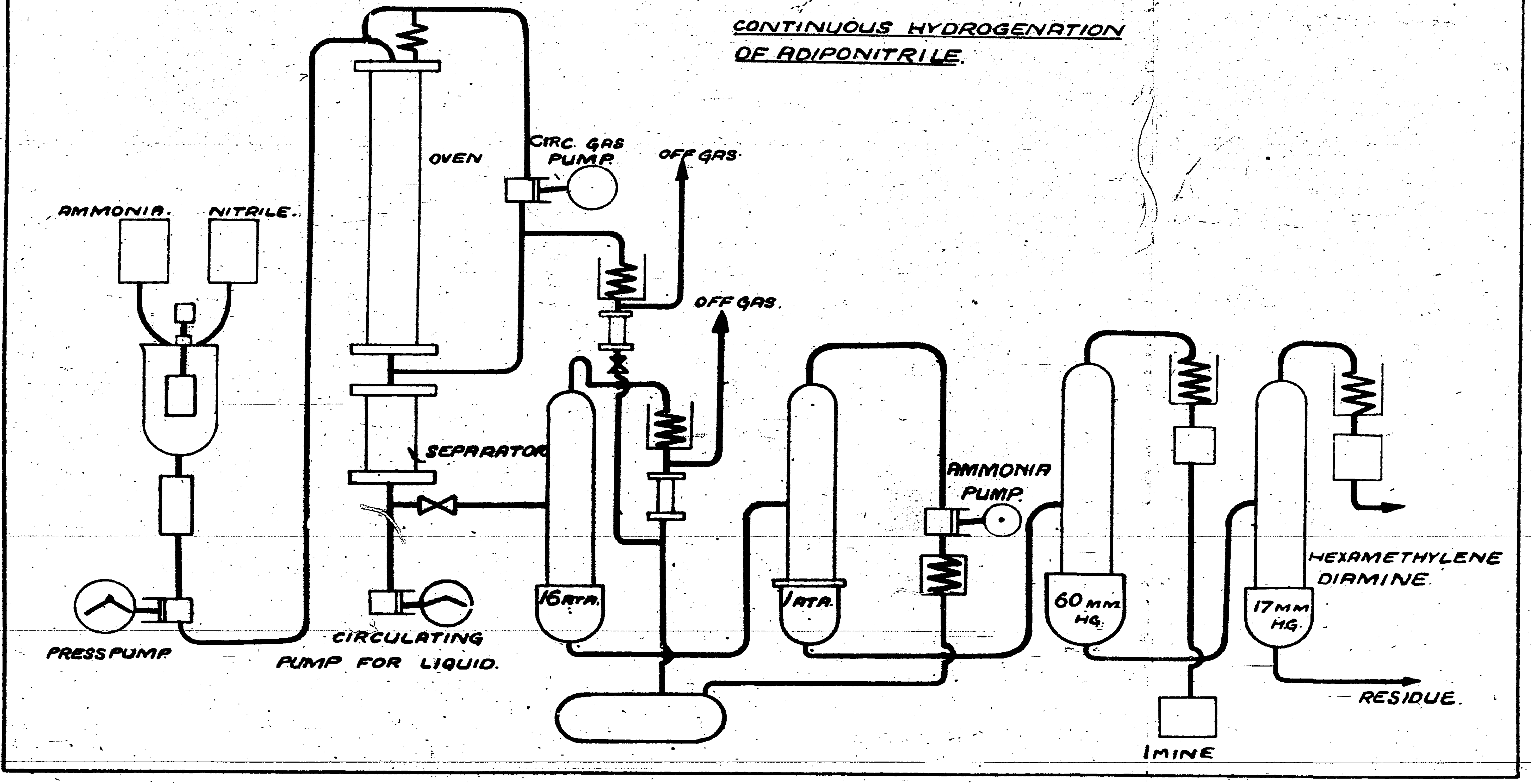
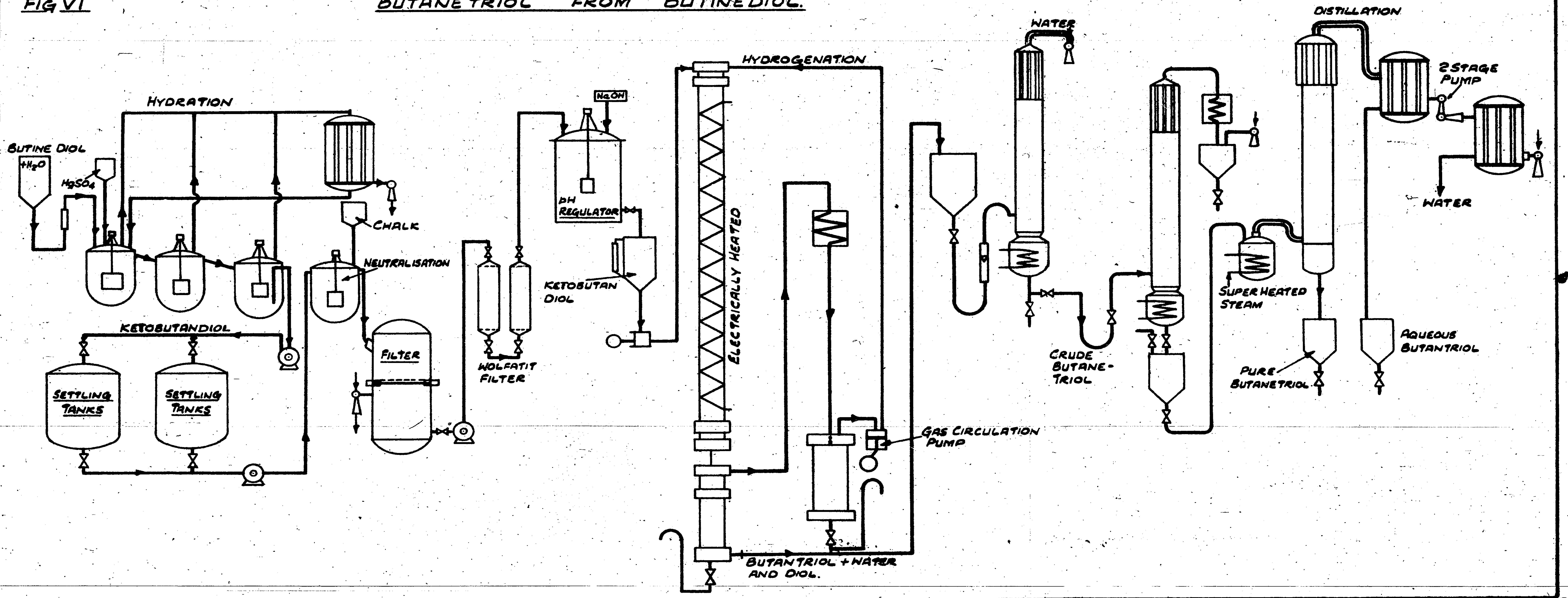


FIG VI

BUTANETRIOL FROM BUTINEDIOL.



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FINAL REPORT No. 199
ITEM No. 30

"TEN YEARS OF OXYGEN-GASIFICATION AT LEUNA"

BY

OBERINGENIEUR SABEL

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"TEN YEARS OF OXYGEN - GASIFICATION AT LEUNA"

by OBERINGENIEUR SABEL

TRANSLATED BY D.G.FRASER AND R.J.MORLEY ✓

ON BEHALF OF

BRITISH MINISTRY OF FUEL AND POWER

NOVEMBER 1945

BIOS Target No. 30/4.02

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

36 p. diagrs.

Translator's Notes

The existence of this document became known in May 1945 to one of us (RJM) during a visit to the I.G. factory at Leuna on behalf of the British Ministry of Fuel and Power; the I.G. were told to have a photostat prepared and this was collected and brought back to England in June, by a member of a British Ministry of Supply Mission. The original should have come to London as a C.I.O.S. document in the normal way, but at the time of writing it has not been traced.

The report, which in effect summarizes the experiences and opinions of the leading I.G. expert on this subject, has been considered worthy of full translation. Such a translation has been made, with the addition of the minimum of notes by the translators, intended to clear up a few expressions, peculiar to Leuna. The subject matter will be critically reviewed in later subject reports.

Below is a short glossary of translations used here:

Hüttenkoks :	hard coke (≡ metallurgical or oven coke).
Steinkohle :	bituminous coal.
Schwelkoks = Halbkoks :	semi-coke (≡ low temperature coke).
Grude or Grudekoks :	grude (= brown coal low temperature coke).
Hartgrude :	hard grude (see note on p 3).
Rohschlacke :	"semi-ash" (see note on p 2).
Feinkörnig :	particulate (= fine-grained)
Körnig :	grained
Stückig :	lump
Generator :	generator [The German word is used both for the English "generator" and "producer", although occasionally and indiscriminately the German word "Erzeuger" is used for "producer". When using oxygen and steam the usual definitions break down and the term "generator" is used throughout this translation].
Brassert and Pintsch :	Proprietary names for manufacturers of ordinary make and blow water gas generators, operating normally on hard coke.
Drehrostgenerator :	The term "Drehrost" has been retained in the translation: if translated as "rotary-grate type" it is less distinguishable from the Pintsch-Brassert generators.
Abstichgenerator :	Slagging generator.
Schachtgenerator :	Shaft Generator.
Schwelgenerator :	Carbonisation generator, in which coal is carbonised in the upper portions and sinks down into the generator proper.
Schwelvergasung :	Carbonisation-gasification, where the two processes occur in the same vessel.
Schwelgas :	Carbonisation gas.

Figures - All figures in the text have been replotted, using data from tables where available.

Gas Measurement - Throughout gas quantities written as M^3 are measured dry at 15°C and 735.5 mms Hg (i.e. 1 kg/cm2), which is standard at Leuna. Gas quantities written as NM^3 are measured dry at 0°C and 760 mms Hg.

D.G.Fraser.
R.J.Morley.

TEN YEARS OF OXYGEN-GASIFICATION AT LEUNA

Leuna Works, September 15th, 1942.

SABEL
OBERINGENIEUR.

TEN YEARS OF OXYGEN-GASIFICATION AT LEUNA

On the 7th December 1932 a Linde air-separation plant, which was to be used exclusively to make oxygen for water gas production by oxygen-gasification, was put into operation at Leuna for the first time. In the past ten years oxygen-gasification has been tried out in numerous processes with both lump and particulate fuels. The following is a summary of the most important of these processes.

Start-up and Development of Oxygen-gasification at Leuna

Prior to 1929 about 3,000 M³/hr of impure oxygen, containing about 55% oxygen and 45% nitrogen, was available at Leuna from four Linde air-separation plants, used for producing pure nitrogen for ammonia synthesis. Until 1928 this impure oxygen went to waste into the atmosphere. From 1/6/28 it was partly used in the gas plant, by adding it to the blast of the slagging generators, manufacturing power gas, but this ceased in 1931. The oxygen content of the blast was increased to 24%.

We then suggested this oxygen should be utilized for synthesis gas production, since the Winkler "make and blow process"* for the gasification of particulate dry brown coal had not come up to expectation.

No useful information had then been published on the gasification with oxygen of particulate or lump material. The experiments of Vandeveer and Parr 1) with a laboratory furnace producing 2-3 M³ gas were a failure; the single large-scale test of Drawe 1) could not be repeated and, like the very first experiment of Hempel 1) in Dresden in 1899, is of no practical significance.

Apart from these three attempts, in which large-size fuel had been used, published material was purely theoretical, and this, partly due to lack of actual experience, led to mistaken ideas, particularly the apprehension felt about the effect of high temperatures on the danger of slagging and on damage to the materials of construction of the generator.

The experiments on oxygen-gasification in the Winkler generator, which were started in February 1929, were limited at first to the production of ammonia synthesis gas, using mixtures of oxygen and air, because the use of pure oxygen then appeared to be too dangerous. From February 1929 to April 1930 the groundwork on gasification of grude and dry coal was done in a small experimental generator with a shaft area of 2 M², and this led to the continuous production from June 1930 of about 10,000 M³/hr of mixed gas for ammonia synthesis in No.1 generator in building Me 278.

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*"Blase-Gase-Verfahren" - an early Winkler process operating a boiling-bed on a make and blow cycle, using air and not oxygen. Trans. note.

1) See literature references on p 32.

After this first success it soon became possible, on the basis of the information so obtained, to use mixtures of pure oxygen and steam to make a nitrogen-free water gas, suitable for hydrogenation. In June 1930 nitrogen-free water gas was produced experimentally from grude and in April 1933 on the full-scale from dry brown coal. It was shown that slagging, which was so much feared with pure oxygen, could be controlled just as well as when running with air, and further, that the methane content of synthesis gas could also be kept sufficiently low in large scale operation, in spite of using uncarbonised dry brown coal, so that this new water gas could be used for synthesis.

Today there are seven Linde-Fränkl air-separation plants at Leuna making 98-99% oxygen, which is used in Winkler generators for the continuous production of 50-55,000 M³/hr of nitrogen-free H_2 + CO.

When in 1936 oxygen-gasification in Winkler generators was considered at Böhlen by the Braunkohle-Benzin-A.G. for the production of hydrogen from particulate grude, we were able to give exact guarantee figures, based on actual experience, for the consumption of fuel and oxygen and for the purity of hydrogen, using a fuel not tested for the quality of its ash. On acceptance the guarantee figures were maintained without difficulty, just as they are today in the works built subsequently at Magdeburg and Zeitz.

After solving the problem of oxygen-water gas production in Winkler generators, oxygen-gasification of grained and lump material in a fixed bed was studied. From July to December 1931 the first experiments were made in a small slagging generator, using oxygen and hard coke with the result that since October 1935 two Linde-Fränkl air separation plants, specially installed for the purpose, have made pure oxygen continuously for the production of 20,000 M³/hr nitrogen-free water gas in slagging generators. The fuel used in this case is "semi-ash" from the Pintsch generators of the water gas plant, containing about 50% carbon.

Experiments on the production of water gas with oxygen in a fixed bed were then extended in 1936 to brown coal briquettes and lump grude. Many variations of oxygen-gasification were carried out systematically in an experimental apparatus with complete tar condensation e.g. carbonisation-gasification with a common outlet for carbonisation gas and water gas, or with a separate outlet for water gas, free from carbonisation gas, and also preheating the steam-oxygen mixture to temperatures of 200-900°. The experiments were then extended to the full scale generators of the water gas plant, using hard coke and lump grude, thereby obtaining full scale experience for larger units.

When about 1938 hard grude[*] came on to the market as a new and improved product of the brown coal industry, a further Linde air separation plant was ordered, so as to make water gas in the Pintsch generators of the gas plant, using oxygen to gasify hard grude obtained at Deuben from "Ringwalzen" briquettes. So begins oxygen-gasification of a new fuel, which is conceivably a suitable substitute for Westfälischen hard coke at Leuna, but one which cannot be used for water gas manufacture - at least as yet - by the old make and blow process.

When this new Linde plant is put into operation at the beginning of 1943, 26% of the hydrogen needed in the works at Leuna will be obtained by oxygen gasification, partly of dry brown coal and grude in Winkler generators, partly of "semi-ash" in the slagging generator and partly of hard grude in Brassert generators.

Meanwhile as a consequence of the varied nature of the oxygen-gasification experiments and of the oxygen-gasification processes at Leuna, our experience of using oxygen, and of the necessary safety precautions, had progressed so far that in May 1941 useful suggestions and performance figures could be given, when bituminous coal semi-coke was being considered for hydrogen production at the Auschwitz factory; this semi-coke could only with difficulty be used for water gas manufacture by methods other than oxygen-gasification.

---

[*] Probably "Hartgrude" is the name given to carbonised briquettes made by the "Ringwalzen" or "ring-roll" process, whilst "Grude" is the name given to carbonised briquettes made by the older "Strangpressen" or "extrusion" or "plunger-press" process. It is known [see C.I.O.S. Report, Item 30 File No.XXXII-14 "Deutsche Erdöl A.G. Regis] that the former process yields a much harder product, described as a high class fuel for domestic use, whilst the latter process yields a weaker product, used for power production and general industrial use. [Trans. Note].

The Reaction Mechanism of Oxygen-Gasification

Firstly we have the following well-known water gas reactions.

$$C + H_2O = CO + H_2 \quad - 1393 \text{ kcal per } 2 \text{ NM}^3 \ (CO + H_2)$$
$$C + 2H_2O = CO_2 + 2H_2 \quad - 963 \text{ " " } 3 \text{ NM}^3 \ (CO_2 + 2H_2)$$

As in almost all technical processes for making water gas the first equation, with its greater heat requirements, preponderates in oxygen-gasification, on account of the high temperatures used, viz. over 900°.

The heat required by the water gas process must be balanced by external sources of heat; apart from chemical heat requirements in forming water gas, the other heat losses of the process must also be balanced, e.g., the sensible heats of the gases made, of the undecomposed steam, of the solid residue, radiation and, for slagging producers, the heat of fusion of the slag as well. The heat required for the reaction between carbon and steam and the other heat losses are balanced in oxygen-gasification by the heat liberated in the simultaneous combustion of a corresponding amount of oxygen. Oxygen can be burnt to either CO or CO_2:

$$C + O = CO + 1190 \text{ kcal for } 1 \text{ NM}^3 \ CO$$
$$C + O_2 = CO_2 + 4235 \text{ " " } 1 \text{ NM}^3 \ CO_2$$

As an example of how oxygen can react, two practical oxygen water gas analyses have been mathematically split into the above four equations; the split of the analysis of 1 NM³ water gas is arranged, so that the components of the equations are subtracted in steps. 1)

a) Hard Coke with Oxygen and Steam in the Brassert Generator

	CO_2 NM³	CO NM³	H_2 NM³	N_2 NM³	H_2O NM³	O_2 NM³	Heat Change kcal
1 NM³ water gas	0.227	0.347	0.403	0.009			
disp. H_2 & N_2 from coke			0.005	0.002			
	0.227	0.347	0.398	0.007			
from $C + H_2O = CO + H_2$		0.347	0.347		0.347		- 484
	0.227	-	0.051	0.007			
from $C+2H_2O = CO_2+2H_2$	0.0255	-	0.051		0.051		- 24
	0.2015	-	-	0.007	-		
from $C+O_2 = CO_2$	0.2015	-	-	-	-	0.2015	+ 852
	-	-	-	0.007	0.398	0.2015	+ 343

---

1) This calculation is a form of the normal H_2-O_2 balance, giving a clear overall picture, since the amount of the various reactions can be followed simultaneously. For simplicity CH_4 has been ignored, but for accurate calculation must of course be taken into account, along with carbonisation gases obtained by gasification of bituminous fuel.

Accordingly for 1 NM³ water gas, 0.2015 NM³ O_2 + 0.007 NM³ N_2 (oxygen about 97% pure) is converted to CO_2 and 0.398 NM³ steam is decomposed; the gasification liberates 343 kcals, which balance external losses!

b) Hard Coke with Oxygen and Steam in the Slagging Generator.

	CO_2 NM³	CO NM³	H_2 NM³	N_2 NM³	H_2O NM³	O_2 NM³	Heat Change kcal
1 NM³ water gas	0.057	0.640	0.287	0.009			
disp. H_2 & N_2 from coke			0.005	0.002			
	0.057	0.640	0.282	0.007			
from $C+H_2O = CO+H_2$		0.282	0.282		0.282		- 380
	0.057	0.358	-	0.007			
from $C + O = CO$		0.358				0.179	+ 425
	0.057	-	-	0.007			
from $C+O_2 = CO_2$	0.057					0.057	+ 242
	-	-	-	0.007	0.282	0.236	+ 287

Accordingly of 0.236 O_2 + 0.007 N_2 (oxygen about 97% pure) about $\frac{1}{4}$ is converted to CO_2 and $\frac{3}{4}$ to CO. 0.282 NM³ steam is decomposed, 287 kcal are available to cover external heat losses.

In both examples the sequence of reactions is taken arbitrarily. One could also first calculate the reaction $C + 2H_2O = CO_2 + 2H_2$ or $C + O = CO$ and finally $CO + H_2O = CO_2 + H_2$. The final result, with respect to steam decomposed, oxygen used and heat liberated, would always be the same. The practical man will always welcome the simplest and clearest split of the analysis, because, in spite of extensive research work and a large technical literature, there is still no certainty about the actual order, in which the various reactions occur.

In the Brassert generator (Case (a) more oxygen is burnt to CO_2 than in the slagging generator. This is because of the greater internal heat requirement of the larger quantity of undecomposed steam in the Brassert generator.

Instead of steam CO_2 can also be made to react with carbon, given the necessary heat of reaction by combustion of oxygen, according to the equation:

$$C + CO_2 = 2\,CO \quad - 1841 \text{ kcal per } 2 \text{ NM}^3 \ CO.$$

For example:

c) Hard Coke with Oxygen and CO_2 in the Slagging Generator

	CO_2 NM^3	CO NM^3	H_2 NM^3	N_2 NM^3	CO_2 used NM^3	O_2 NM^3	Heat Change
1 NM^3 water gas	0.061	0.902	0.027	0.01			-
disp. H_2 & N_2 from coke			0.005	0.002			
	0.061	0.902	0.022	0.008			
from CO_2 used			0.022	0.001	0.023		
	0.061	0.902	-	0.007			
" " "	0.061				0.061		
	-	0.902	-	0.007			
from C + CO_2 = 2CO		0.442			0.221		- 390
	-	0.460	-	0.007			
from C + O = CO		0.460				0.230	+ 550
	-	-	-	0.007	0.305 1)	0.230	+ 160

Thus for 1 NM^3 water gas 0.230 NM^3 O_2 + 0.007 NM^3 N_2 (O_2 = 97%) are used. Oxygen is wholly burnt to CO; 0.305 NM^3 92% CO_2 is about 75% decomposed, and 160 kcal are liberated to cover external heat losses. The overall picture of the simple theory of oxygen-gasification can be seen by imagining a shaft generator divided into two chambers by a vertical wall; on one side of the wall occurs the strongly endothermic reaction of steam with hot carbon, whilst on the other side the heat necessary for this is produced by burning oxygen to CO_2 or CO. The wall is not there in reality and all reactions proceed side by side, so that the actual sequence of the various reactions is in practice of secondary importance.

---

1) 92% CO_2, about 7% H_2, 0.3% N_2.

The Technical Principles of Oxygen-Gasification.

The first big difficulty in using pure oxygen for water gas production is slagging of the fuel, and this will happen very quickly at the high temperatures used, if fluctuations occur in the oxygen-steam mixture. A second unpleasant difficulty is the effect on grates, tuyères, oxygen supply pipes, generator brickwork and metal walls resulting from changes in the oxygen-steam mixture or from strong local slagging, which has previously occurred. At first we met considerable difficulty from both effects until we found that the usual methods for mixing steam and air under the grate could not be used for mixing steam and oxygen. The resultant poor mixing led to stratification and the formation of regions of higher oxygen concentration, and this caused severe slagging and burning of the grate and tuyères.

There were similar failures later in 1935, when, neglecting this previous experience, we tried introducing steam and oxygen separately through the tuyères of the slagging generator in Me 240.

The first basic principle for oxygen-gasification is: "mix oxygen and steam or oxygen and CO_2 at some distance from the generator and use only a homogeneous mixture under the grate or in the tuyères." In practice a distance of 10-15 m, if possible incorporating a bend or restriction plate, has proved adequate for good mixing. This makes it unnecessary to use copper tuyères or delivery lines of copper or any other special material to prevent attack.

In the light of this it is interesting to note that leakage of water from the stirrer of a Winkler generator or from the water-cooled ash discharge could result in severe slagging. This can only be explained by assuming that locally, through condensation of water vapour from the steam-oxygen mixture, strong oxygen-enrichment occurs directly over the grate. A similar phenomenon was also met in the Pintsch-Brassert generator with oxygen-gasification through a leaking stirrer.

Careful mixing of oxygen and steam is thus essential for oxygen-gasification, but this is not always recognised, although it appears so simple and obvious. It is well-known, that Lurgi still get a lot of slagging in their pressure-oxygen generator probably because oxygen and steam are not sufficiently well mixed, and at the only place in Germany, where besides us oxygen-gasification is used in slagging generators (Thyssen, Mülheim-Ruhr, after the patent of Galoscy, DRP 573,112), they have changed over to building pre-combustion chambers before the slagging generators, in which oxygen and gas are pre-combusted, giving a highly superheated steam-gas mixture, which is then introduced into the fuel bed, so that in effect only endothermic reactions occur inside the generator. These elaborate precautions, which also reduce the output of the producer, are completely superfluous if there is early intimate mixing of oxygen and steam.

The high concentration of oxygen, e.g. 30-40% on the Winkler generator and up to 55% on the slagging generator, involves certain operational dangers. If in the slagging generator, owing to irregularity in fuel or flux, lumps of slag build up in front of the tuyēres then such lumps of slag can so obstruct the path of the oxygen that the oxygen immediately strikes on the hot fuel, leading to attack of the brickwork and metal wall of the generator; e.g. it happened in one oxygen slagging generator that the oxygen leaving the tuyēre was deflected by a lump of slag and burnt a hole in the wall of the water jacket. The escaping water quenched the generator; the process, which may have taken only a few seconds, was noticed but the danger was not immediately appreciated, with the result that oxygen entered the water gas main and together with water gas from a neighbouring generator caused a destructive explosion in the coolers and gas mains. /_ See Fig. 1_/

Similar burning through of the wall often happened earlier in the Winkler generator, only there the consequences were not so unfortunate, because this had no water jacket.

Oxygen can of course also get into the upper part of the generator and thence into the water gas mains, gasholder, etc., if the fuel bed level in the generator is lost. Two serious explosions in outside factories ("Lizenzwerken") were caused in this way.

The <u>second basic principle</u> of oxygen-gasification is, therefore, the most careful supervision of operations.

In order to study the course of an oxygen break-through, the fuel supply to a small Winkler generator with 2 M^2 shaft area was shut off, whilst maintaining the full flow of oxygen and steam. The course of the oxygen break-through, as shown by CO_2, is illustrated in Fig. 2. Therefore, all oxygen-generators at Leuna have a small flame, working with a selenium cell. When the flame goes out an alarm sounds, and the operator must immediately turn off the oxygen supply.

As well as this precaution, each Winkler oxygen generator has duplicate pressure gauges, fitted with alarms, showing the height of fuel.

If by any chance [1] steam is omitted from the oxygen-steam mixture, the grate naturally begins to burn in the undiluted, dry oxygen. This has happened twice on our water gas plant, through the carelessness of the operator on the Drehrost generator; the damage can be considerable. There is also a possibility of the hot fuel bed discharging into the atmosphere. Therefore an independent steam connection, the so-called "emergency steam", is provided under the grate.

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[1] e.g. in an outside factory the spindle of a vertical steam valve on the main steam line broke, and there was danger of the valve closing.

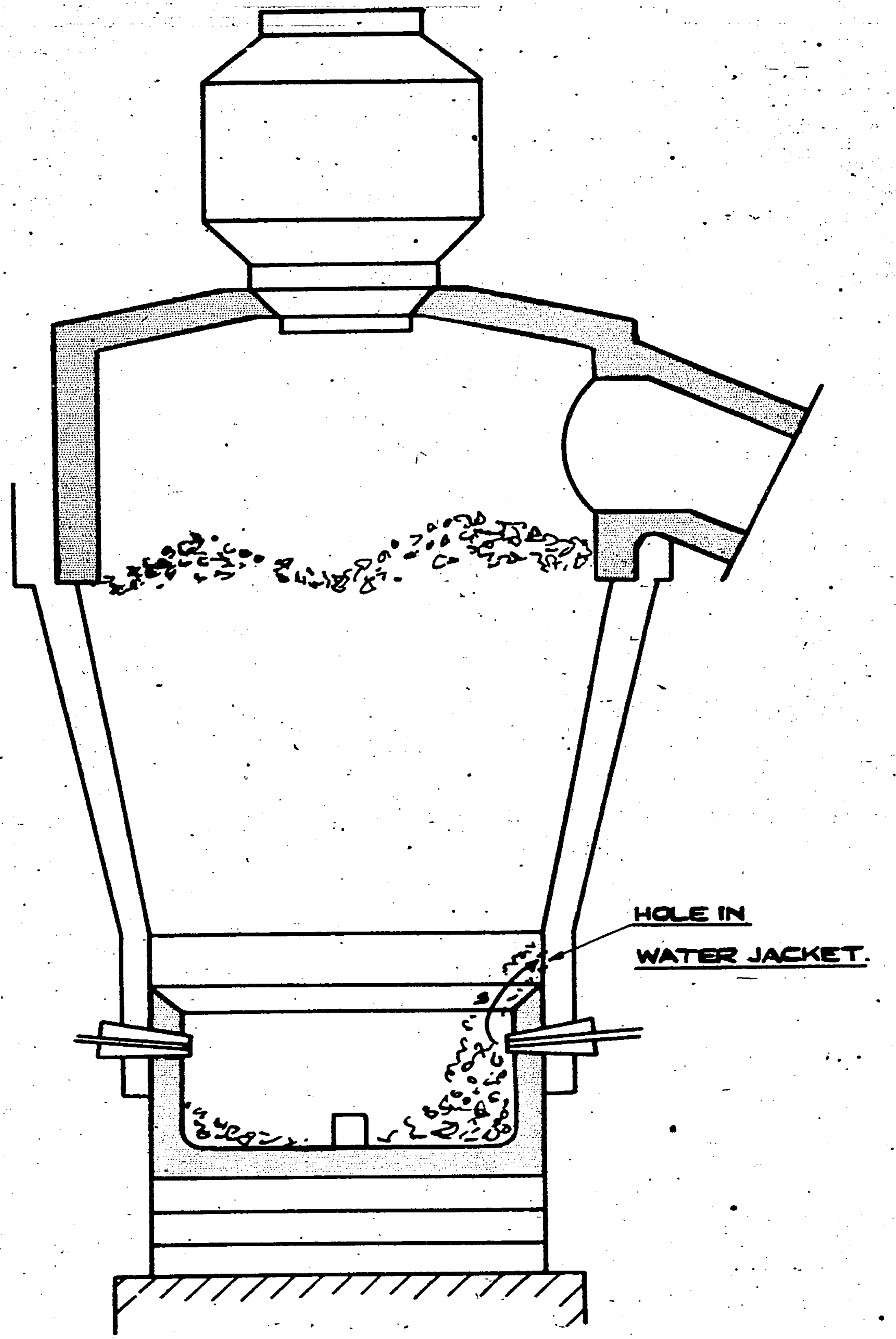

FIG. I.

Each time an oxygen generator is started up or shut down the grate is purged with CO_2 or N_2.

Besides the generator the oxygen blowers, which compress dry oxygen to 5 m water column, can also be a source of danger. In the course of the development of oxygen-gasification at Leuna and the outside factories some oxygen blowers have actually fired. Such fires, apart from the destruction of the blower, are dangerous, since large clouds of iron oxide make access difficult and the very hot oxygen-iron flames can easily cause the fire to spread. Such fires started either by oil running from a bearing when the sealing water was left off, or else by the rotor........

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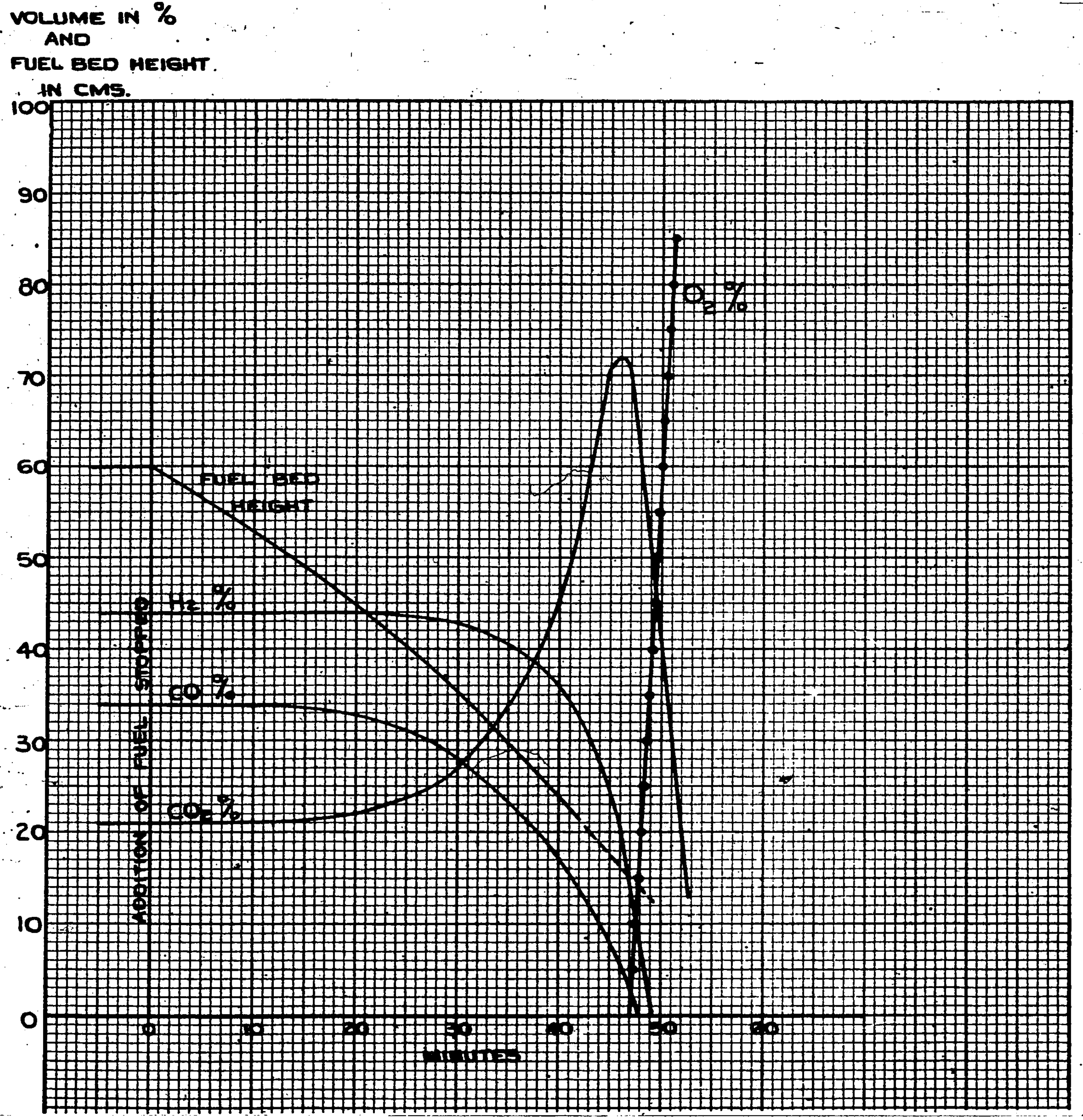
FIG. 2.

CHANGE OF GAS COMPOSITION WITH AN OXYGEN BREAK-THROUGH



Fuels for Oxygen-Gasification and Comparison with the "Make and Blow" Process

The price of 1 NM^3 $CO + H_2$ from hard coke is about 10% higher using oxygen-gasification than when using the normal make and blow process. The saving of coke by using oxygen and the simpler plant for continuous gasification does not - with the present-day price of oxygen at 1.7 to 2.0 Pfg./NM^3 - balance the cost of the extra oxygen. In the subsequent usage of water gas a further charge against oxygen-gasification of hard coke is incurred, because the quantity of catalysed gas ("Kontaktgas") and consequently the gas in the first three stages of compression and the gas to be scrubbed with water at pressure are increased by an amount of CO_2 corresponding to the oxygen used.

In practice 1) the comparison is as follows for hard coke gasified in various ways.

Test Number	-	3	1	5	-
Process	Make and Blow in Brassert with steam	O_2-Gasification in slagging generator with steam	O_2 gasification in Brassert with Steam	O_2 gasification in slagging generator with CO_2	Make and Blow in Brassert with CO_2 2)
Analysis CO_2 %	5.0	6.8	22.7	6.1	24.6
CO %	42.0	61.4	34.7	90.2	68.8
H_2 %	49.0	31.0	40.3	2.7	5.1
N_2 %	4.0	0.8	2.3	1.0	1.5
per 1 NM^3H_2(97% pure) are needed:					
Hard Coke kg	0.620	0.530	0.560	0.590	0.70
Oxygen NM^3	-	0.261	0.290	0.269	-
Steam to generator kg	0.763	0.370	1.06	-	-
" to CO conversion plant kg	0.600	0.710	1.09	1.24	1.38
Total Steam "	1.363	1.080	2.15	1.24	1.38
per 1 NM^3 pure H_2 is used:					
Moist Catalysed gas at exit of system NM^3	2.44	3.18	3.25	4.05	4.72
Dry catalysed gas before compressor"	1.68	1.88	1.95	2.22	2.37

---

1) For the calculation a gas with 6% CO and 1.5% CO_2 before hydrogen purification is assumed; CO regeneration gases have not been considered, but assumed to be used for another synthesis (at Leuna for NH_3 sysnthesis); 5% H_2-losses have been assumed.

2) In the comparison the substitution of steam by CO_2 as gasification (continued at foot of page 11.)

In test (1) using hard coke with O_2 and steam in the Brassert, the generator was very cold; if the test had been longer it is quite possible that steam could have been saved.

It can be seen at once from the above efficiencies, that the amount of oxygen needed is not small, that the savings in coke and steam are not great and that the additional load on the compressors, in terms of quantity of gas compressed, is correspondingly great. Theoretically the extra amount of compressed gas should correspond exactly with the oxygen used. That this is numerically not the case here is due to the fact that for the comparison with "Make and Blow" a water gas with 4% N_2 has been taken, which therefore contains a small quantity of oxygen derived from the air.

A calculation in Reichmarks shows that the cost of pure hydrogen by gasification of hard coke with oxygen, costing 1.7 Pfg/NM^3, is about 8-15% higher than by the old "Make and Blow" process.

Oxygen-gasification is not yet competitive for good hard coke; its proper use is for the production of hydrogen from fuels, not suitable for "Make and Blow" but which are cheaper than hard coke. Fortunately there is a whole series of such suitable fuels:-

particulate dry brown coal	in the Winkler generator
particulate grude	in the Winkler generator
lump grude and hard grude	in Drehrost, Brassert, slagging
brown coal briquettes (carbonisation-gasification)	in shaft generator with carbonisation superimposed
non-caking bituminous coal nuts (carbonisation-gasification)	- ditto -
bituminous coal semi-coke	in Drehrost, Brassert & slagging
poor quality hard coke, e.g. upper Silesian hard coke waste, and fines from hard coke and semi-coke, 5-10mm.	- ditto -

Both brown and bituminous coal dust can be utilized quite well with oxygen-gasification, although these consume more oxygen than the above fuels and methods of gasification, because gas exit temperatures are essentially higher when gasifying dust. The increase in oxygen consumption is however not too great that it could not be compensated for by a low price for coal dust.

Cont'd.from p.10

2) medium which has often been suggested, is included. It may be seen from the figures that the amount of gasification steam used, by which is meant the steam consumed by generator + CO conversion plant is not any less, and that the CO_2 to be recirculated would enormously overload the CO conversion plant and the compressors and also of course the pressure water scrubbing process. This addition of CO_2 to the generator, unless it is desired to produce CO, is fundamentally wrong.

All the fuels named have been systematically tested at Leuna since the development of the Winkler process for gasifying dry brown coal with oxygen; information on the most important results is given in the accompanying tables. At Leuna it is out of the question to increase gasification of dry brown coal in the Winklers, because the coal requirements of the factory make big demands on the mines in the neighbourhood. Also Winkler oxygen-gasification needs considerably larger oxygen plants than gasification in shaft generators.

In these circumstances hard grude is the ideal fuel for replacing Westphalian hard coke for oxygen-gasification at Leuna. This would be certain to lead to a considerable cheapening of hydrogen. Although the present day selling price of hard grude is higher than for industrial grude [normal Lurgi grude from "Strangpressenbriketts"] it is known that the production costs for hard grude are not only no higher then for industrial grude but are even somewhat lower.

The conversion of our coke water gas plant to hard grude does not involve any great changes. Fortunately the output, in $H_2 + CO$, of a generator using hard grude is the same, and probably even somewhat greater than that with the "make and blow" process. Adjustments have to be made only to the water services because the sulphur content of water gas is higher than with hard coke. What adjustments will have to be made for the higher H_2S and CO_2 content of water gas made from hard grude, during sulphur purification, CO conversion and in the first three stages of compression, cannot be assessed until the Linde air-separation plant, due to start up in 1943 making oxygen for gasification of hard grude, has been running for some time. It is certain, however, that these adjustments, after allowing for the lower production cost of hard grude, will still result in a considerable cheapening of hydrogen.

Besides the low production cost of hard grude, which permits transportation from more distant Central German mines, there is the pleasantness of handling, which is scarcely less than that of hard coke. Loading and unloading do not cause a dust nuisance, whilst rightly handled hard grude is not liable to spontaneous combustion, and like hard coke it is easily stored. It has been stored at Leuna on the open ground for months without difficulty. Breakage during transport and handling is not serious. Fines and dust can be screened out immediately before the water gas generators, and can, like dry fly dust ("Flugstaub"), be fed to the Winkler generators, where the hard grude "breeze" can be turned to good account; in this it is unlike hard coke breeze, which cannot be gasified.

In a few months time oxygen-gasification of hard grude at Leuna will commence by making about 9,000 M^3 $CO + H_2$/hr, and one hopes and expects, that with the return of normal conditions, the process will make great progress.

Besides oxygen-gasification of hard grude in Central Germany, it is to be expected that this type of gasification, with its simple technique will also have a good future in Upper Silesia. Moreover non-caking bituminous coal can be used for manufacturing hydrogen by carbonisation-gasification, and particularly, Upper Silesian semi-coke; the latter has already been chosen for Auschwitz.

The Results of Tests and Large Scale Operation

In the following tables the analyses and consumptions, with several check calculations, are summarised for the oxygen-gasification of:

Hard Coke
Bituminous Coal semi-coke
Brown Coal Grude
Dry Brown Coal and
Brown Coal Briquettes

Oxygen-Gasification of Hard Coke with Steam

Table I

Test Number	(1)	(6)	(3)	(4)	(7)	(8)
Process	in the Pintsch Brassert	in the Pintsch Drehrost	in the slagging generator	in the slagging generator	in the slagging generator using "semi-ash"	in the Pintsch Brassert "Waschkoks"
Record note of	9.5.41.	2.9.37.	29.5.41.	1.6.42.	17.5.39.	17.11.41.
Gas analysis CO_2 %	22.7	22.4	6.8	5.7	9.7	23.6
CO %	34.7	35.5	61.4	64.6	66.5	35.7
H_2 %	40.3	40.7	31.0	28.7	22.9	39.7
CH_4 %	1.4	0.5	0.0	0.1	0.0	0.5
N_2 %	0.9	0.9	0.8	0.9	0.9	0.5
Sulphur in Gas H_2S g/NM^3	3.8	- 3)	4.3	- 3)	2.7	- 3)
organ.S "	0.31	- 3)	0.380	- 3)	0.380	- 3)
Consumptions: measured						
Oxygen (98-99%) $NM^3/NM^3 CO+H_2$	0.267	0.252	0.262	0.260	0.347	0.324
L.P.Steam kg/ " "	0.985	0.802	0.346	0.294	0.207	1.21
C incl. losses " " "	0.454	0.452	0.424	0.436	- 3)4)	0.486
Coke " " " " "	0.518 1)	0.51	0.490 2)	0.496	- 3)4)	- 3)
Gas output NM^3dry/M^2 shaft	690	890	920	2100	1100 5)	710
Gas exit Temperature °C	500°	- 3)	400°	390°	200°	- 3)
Check Calculations						
Oxygen $NM^3/NM^3 CO+H_2$ from analysis	0.268	0.260	0.242	0.256	0.350	0.290
undecomposed steam kg/NM^3 dry gas	0.420	0.284	0.075	0.047	0.002	0.592
%age steam decomposition	43 %	53 %	76.5%	83 %	98 %	35 %
% Oxygen in steam-oxygen mixture	18 %	21 %	35.5%	41.5%	58 %	16.5 %
C in gas as % of used C	93 %	91 %	93 %	93 %	-	89 %
Heat change per 1 NM^3 dry gas, kcals	+ 343	+ 321	+ 232	+ 280	+ 611	+ 394
Residue from heat balance for radiation and sensible + heat of fusion of the ash, as % of heat throughput of fuel	3 %	- 3)	2.7 %	4.4 %	12 % 6)	- 3)
"Gas formation temperature" water gas °C	1060°	920°	1250°	1150°	1350° 7)	[1240°]
- do - producer gas °C	651°	660°	777°	794°	765°	648°

1) 87.2 % C, 7.9 % ash, 3.9 % H_2O
2) 86.8 % C, 9.1 % ash, 1.8 % H_2O
3) not determined

continued on page 15.

4) 45-50% C, remainder - slag
5) Limited by charging and removal of the large quantity of ash, but higher outputs possible.
6) High heat of fusion of the large quantity of molten ash.
7) With 0.002 kg undecomposed steam, cannot be calculated.

Oxygen-Gasification of Bituminous Coal Semi-Coke with Steam

TABLE II

Test Number	(9)	(10)	(10a)	(12)	(13)	(14)
Process	in the Pintsch Brassert	in the slagging generator	in the slagging generator 1.4m ID	in the slagging generator "Karsten-Centrum"	in the shaft generator 1.1m ID "Weber briquettes"	in the slagging generator 0.4m ID "Königin Luise"
	Fürsten Mine					
Record note of:	4.11.41.	25.5.42.	31.7.42.	25.5.42.	19.11.40	19.11.40.
Gas analysis CO_2%	21.1	2.9	2.5	3.2	24.0	6.2
CO %	32.8	66.3	67.0	67.0	21.5	57.3
H_2 %	44.6	30.1	29.6	29.4	52.5	35.4
CH_4%	1.1	0.0	0.2	0.0	1.9	0.8
N_2 %	0.4	0.7	0.7	0.4	0.1	0.3
Sulphur in gas H_2S g/NM^3	1.8	5.4	2.6	2.5	- 9)	- 9)
organic.S "	0.130	0.7	0.56	0.425	- 9)	- 9)
Consumptions - measured						
Oxygen (98-99%) $NM^3/NM^3 CO+H_2$	0.255	0.262	0.263	0.243	0.188 6)	0.220
L.P.Steam kg/ "	0.813	0.232	0.243	0.215	1.200 6)	0.300
C.incl.losses "	0.427	0.539	0.445	0.542	0.352	0.415
Semi-coke incl. losses kg/$NM^3 CO+H_2$	0.545 1)	0.670 3)	0.605 5)	0.667 4)	0.460 7)	0.540 7)
Gas output NM^3dry/M^2 shaft	720 2)	890 3)	1380	920 4)	400	1600
Gas exit temp. °C	400°	345°	350°	345°	650°	- 9)
Check Calculations						
Oxygen $NM^3/NM^3 CO+H_2$ from analysis	0.238	0.256	0.255	0.267	0.174	0.235
undecomposed steam kg/NM^3dry gas	0.325	0.039	0.050	0.030	0.536	0.070
%age steam decomp.	48 %	83 %	79 %	86 %	40 %	75 %
% Oxygen in steam-oxygen mixture	19.2 %	47 %	46 %	50 %	10 %	38 %
C in gas as % of used C	89 %	71 % 8)	87 % 11)	72 % 8)	98 % 10)	90 % 11)
Heat change per 1 NM^3 dry gas, k.cals.	+ 302	+ 324	+ 312	+ 361	+ 136	+ 277

continued on page 16

TABLE II (Cont'd)

Test Number	(9)	(10)	(10a)	(12)	(13)	(14)
Process	in the Pintsch Brassert	in the slagging generator	in the slagging generator 1.4m ID	in the slagging generator "Karsten-Centrum"	in the shaft generator 1.1m ID "Weber briquettes"	in the slagging generator 0.4m ID "Königin Luise"
	Fürsten Mine					
	4.11.41.	25.5.42.	31.7.42.	25.5.42.	19.11.40.	19.11.40.
Residue from heat balance for radiation and sensible + heat of fusion of the ash, as % of heat throughput of fuel	3%	3.8%	4.7%	0.5%	2%	– 9)
"Gas formation temp." water gas °C	930°	1475°	[2050°]	1250°	840°	1130°
" producer gas	655	835°	930°	834°	604°	774°

1) 7% ash, 9.5% H_2O
2) 5 - 30mm. grain size
3) 11% ash, 1% H_2O. 10-40mm. grain size
4) 8% ash, 1% H_2O, 5-40mm. grain size
5) 74.1%C, 9.6% ash, 9.8% water, grain size 6-13mm under 5%
6) Steam-oxygen mixture preheated to 600°C
7) Weber briquettes with 9.2% ash and 5.4% H_2O, 77%C
8) First test, high losses at the slagging hole and measurements not wholly reliable
9) not determined or not determinable
10) briquette pieces sieved from ash and used again.
11) high rate, therefore, much fly dust.

Oxygen-Gasification of Grude with Steam

TABLE III

Test Number	(15)	(16)	(17)	(18)	(20)
Process	in the shaft generator 1.1m ID, grude from Bitterfeld briquettes 1)	in the slagging generator Deuben lump grude with "semi-ash" 1 : 1	in the Drehrost	in the Brassert	in the slagging generator
			Deuben hard grude		
Record note of :	18.9.39.	27.10.39.	15.11.40.	9.5.41.	27.10.39.
Gas analysis CO_2%	22.9	7.5	32.0	25.0	5.4
CO %	25.4	62.2	6.4	26.0	62.4
H_2 %	49.7	29.3	60.0	46.9	31.2
CH_4%	1.2	0.0	1.1	1.5	0.0
N_2 %	1.0	1.0	0.5	~~0.6~~	1.0
Sulphur in gas H_2S g/NM³	1.6	– 10)	10.1	26	13
organic.S "	0.3	– 10)	0.18	0.74	0.87
Consumptions - measured					
Oxygen (98-99%) NM³/NM³ CO+H_2	0.160 5)	0.269	[illegible]087 2)	0.159	0.276
L.P.Steam kg/ " " "	0.0 1)	0.286	2.65	0.750 12)	0.266
C.incl.losses " " " "	0.390	0.392	– 10)	0.395	0.482
Grude incl." " " " "	0.530 1)	– 10)	0.77 4)	0.72 7)	0.80 8)
Gas output NM³dry/M² shaft	680	1000	540	1120	930
Gas exit temp. °C	–	200°	410°	326°	240°
Check Calculations					
Oxygen NM³/NM³ CO+H_2 from analysis	0.160	0.258	0.073	0.176	0.220
Undecomposed Steam kg/NM³ dry gas	0.135	0.046	1.310	0.185	0.04
%age steam decomp.	72 %	83 %	26 %	66 %	84 %
% Oxygen in steam-oxygen mixture	15.5 %	42 %	2.3 %	16 %	39.5 %
C in gas as % of used C	91 %	104 %	–	98 %	80 %
Heat change per 1 NM³ dry gas kcals	[+ 67]	+ 314	- 112 2)	- 120	+ 230
Residue from heat balance for radiation and sensible + heat of fusion of the ash, as % of heat throughput of fuel	[± 0]	8 % 11)	~10 % 9)	~ 2 %	3.7 %
"Gas formation temp." water gas °C	600°	970°	660°	650°	1030°
" " producer gas	635°	730°	504°	630°	795°

TABLE III (Cont'd)

1) Grude from carbonisation shaft at 550-600°, steam-oxygen mixture 220°; 73.6% C, 10.3% ash.
2) Steam-oxygen preheated to 625°
4) 19% ash, 6% H_2O
5) calculated
7) 54% C, 16.9% ash, 22% H_2O
8) 60% C, 17.4% ash, 18.0 - % H_2O
9) high radiation losses due to steam preheating
10) not determined
11) large quantities of slag
12) high pressure steam

Oxygen-Gasification with CO_2 as Gasification Medium

TABLE IV

Test Number	(5a)	(5)	(11)	(19)
Process	Hard coke in the slagging generator	Hard coke in the slagging generator	Semi-coke from "Fursten Mine" in the slagging generator 0.4m ID.	Hard Grude from Deuben in the Pintsch Brassert
Record note of:	13.11.39.	29.5.41.	27.5.41.	17.1.42.
Gas analysis CO_2%	3.0	6.1	4.0	25.3
CO %	92.5	90.2	86.0	65.7
H_2 %	3.0	2.7	8.2	8.0
CH_4 %	0.0	0.0	0.8	0.4
N_2 %	1.5	1.0	1.0	0.6
Sulphur in gas H_2S g/NM³	2.2	3.1	4.3	12.5
organ. "	2.7	1.5	0.67	3.6
Consumptions - measured				
Oxygen (98-99%) NM³/NM³ CO + H_2	0.310	0.318 1)	0.238 4)	0.265
CO_2 (90-93%) " " "	0.258	0.328	0.286	0.600
C.incl.losses kg/ " "	0.460	0.473	0.54	0.454
Fuel incl. losses - do -	0.530 6)	0.545 2)	0.620 4)	0.735 5)
Gas output NM³dry/M²shaft	930	720 3)	1700	1100
Gas exit temp. °C	400°	420°	325°	260°
Check Calculations				
Oxygen NM3/NM3 CO + H_2 from analys.	0.266 1)	0.256 1)	0.238	0.223
Undecomp. CO_2 as % of gas made	3.- %	6,1 %	4,0 %	25,3 %
%age decomposition of CO_2	86.- %	78,- %	83,0 %	39.0 %
% Oxygen in CO_2/O_2 mixture	49.5 %	43.5%	45.5 %	29.5 %
C in gas as % of used C	87.- %	84.-%	70.- % 7)	84.- %
Heat change per 1 NM³ dry gas kcals	+ 220	+ 180	+ 157	+ 114

(Continued on Page 19)

Oxygen-Gasification with CO_2 as Gasification Medium (Cont'd) TABLE IV

Test Number	(5a)	(5)	(11)	(19)
Process	Hard coke in the slagging generator	Hard coke in the slagging generator	Semi-Coke from "Fursten Mine" in the Slagg-ing generator 0.4m I.D.	Hard Grude from Deuben in the Pintsch Brassert
	13.11.49.	29.5.41.	27.5.41.	17.1.42.
Residue from heat balance for radiation and sensible + heat of fusion of the ash, as % of heat throughput of fuel	2.5%	1.2%	1.2%	1 %
"Gas formation temperature" producer gas	860°	832°	850°	723°

---

1) Calculated quantity, more accurate than the measured quantity, apparently in error.
2) 86.3% C, 9.1% ash, 1.8% H_2O.
3) Still capable of being increased.
4) 88.5% C, 5.6% ash, 0.4% H_2O, quantity not determined.
5) Grain size: hazelnut to walnut; 61.8%, C, 20.5% ash, 13.2% H_2O.
6) 87.2% C, 11.8% ash, 1.0% H_2O.
7) Very Small Generator.

Oxygen-Gasification of Brown Coal in the Winkler Generator

In the record note "water gas with oxygen in the Winkler Generator" of 2/2/34 a preliminary estimate of consumptions, made when justifying the new Linde-Fränkl plant, is compared with the achieved figures.

TABLE V

Referred to 1 M³ $CO + H_2$ 1)

	Requirement of dry brown coal, 6% H_2O kg estimated	Requirement of dry brown coal, 6% H_2O kg actual	O_2 - Requirement, 98% M³ estimated	O_2 - Requirement, 98% M³ actual
Mixed Gas	0.805	0.825	0.278	0.280
Water Gas	0.840	0.800	0.350	0.330

Gas Composition :	Mixed Gas	Water Gas
CO_2	17.0 %	19 %
CO	33.0 %	38 %
H_2	33.0 %	40 %
CH_4	1.5 %	2 %
N_2	15.5 %	1 %

The results were obtained with dry brown coal from the mine Elise II; present day consumptions are somewhat higher, with higher CO_2 content of water gas, since in general poorer coal, e.g. Tannenberg mixed with Deuben grude, has to be used.

In the report mentioned it is stated : "Severe slagging at first caused a good deal of maintenance. The grate of No.1 generator was renewed at least three times between June and October 1933; in addition it underwent 5 major repairs." Today slaggings are quite unknown.

The latest improvement to the Winkler generator is a full-scale grateless generator of the simplest construction, which entirely avoids even the very infrequent repairs to the grate, and which in addition uses about 10% less fuel and oxygen.

Oxygen-gasification in the Winkler generator at Leuna and at the outside factories of Böhlen, Magdeburg and Zeitz has proved to be the safest water gas process using particulate brown coal or grude.

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1) Gas quantities at 15°C and 735.5 mms Hg.

TABLE VI

Oxygen-Carbonisation-Gasification of Brown Coal Briquettes

(Theissen 14% H_2O) in the shaft generator with alternating steam-oxygen mixtures (without preheating), and steam-oxygen mixture at 220°C.

Test Number		21	22	23	24	25
Record note of:		20/4/37				
Gas analysis	CO_2 %	26.5	28.0	35.5	40.8	43.8
	CO %	21.4	18.0	5.4	3.2	2.4
	H_2 %	44.6	46.0	51.5	51.4	45.4
	CH_4 %	5.6	7.0	6.0	4.4	6.2
	N_2 %	1.6	1.0	1.7	0.2	2.2
S in Gas H_2S g/NM³ dry organ. S " "		not determined				
Consumptions per NM³ $CO + H_2$						
Oxygen (98-99%)	NM³	0.194	0.194	0.200	0.238	0.260
L.P.Steam	kg	0.825	0.92	1.92	3.00	4.00
C incl. losses Brown coal briquettes including losses	"	Average 0.62 2) kg brown coal briquettes per NM³ gas including tar production1)				
Gas output NM³ dry/M² shaft		640	600	320	210	185
Gas exit temp.(carbonisation zone) °C		180°	200°	230°	270°	-
Check Calculations :						
Oxygen requirement (100%) per NM³ H_2 + CO(calculated)		0.150	0.133	0.127	0.225	0.350
Undecomposed steam kg/NM³ gas		0.216	0.230	0.700	1.258	1.576
%age steam decomposition		60%	61%	36%	23%	18%
% oxygen in steam-oxygen mixture		16%	14.4%	7.8%	6.1%	5%
"Gas formation temperature" water gas °C		640°	600°	530°	520°	515°
"Gas formation temperature" producer gas °C		610°	595°	510°	460°	435°

1) Briquette with 14% H_2O, 10% ash, 55% C and 16% Fischer-tar

2) With 20% C in the ash.

Observations on the Tables

All data refer to 0° and 760 mm Hg, unless otherwise stated.

The results (unless otherwise stated at the head of the column) have been obtained with Pintsch-Drehrost generators and Pintsch-Brassert generators of 3 - 3.2 m I.D. and with slagging generators of 2.1 m I.D. at the bottom and 3.4 m I.D. at the top.

Shaft outputs refer to the highest cross section still filled with fuel.

The check calculations given show mostly, but not always, satisfactory agreement with the measured values; with practically gas-free fuel, such as coke, the agreement is of course better than with fuels containing hydrogen or with bituminous fuels, with which it is notoriously difficult to obtain good balances from experimental data. Where there are obvious errors, the calculated values are put in parenthesis.

In order to illustrate the fundamental course of oxygen-gasification of lump fuel in a stationary bed as a function of the operating temperature of the generator, all dry gas analysis in Tables I - III, i.e. covering the results for hard coke, bituminous coal semi-coke and grude, have been plotted in Fig.3 against the per-cent content of O_2 in the oxygen-steam mixture.

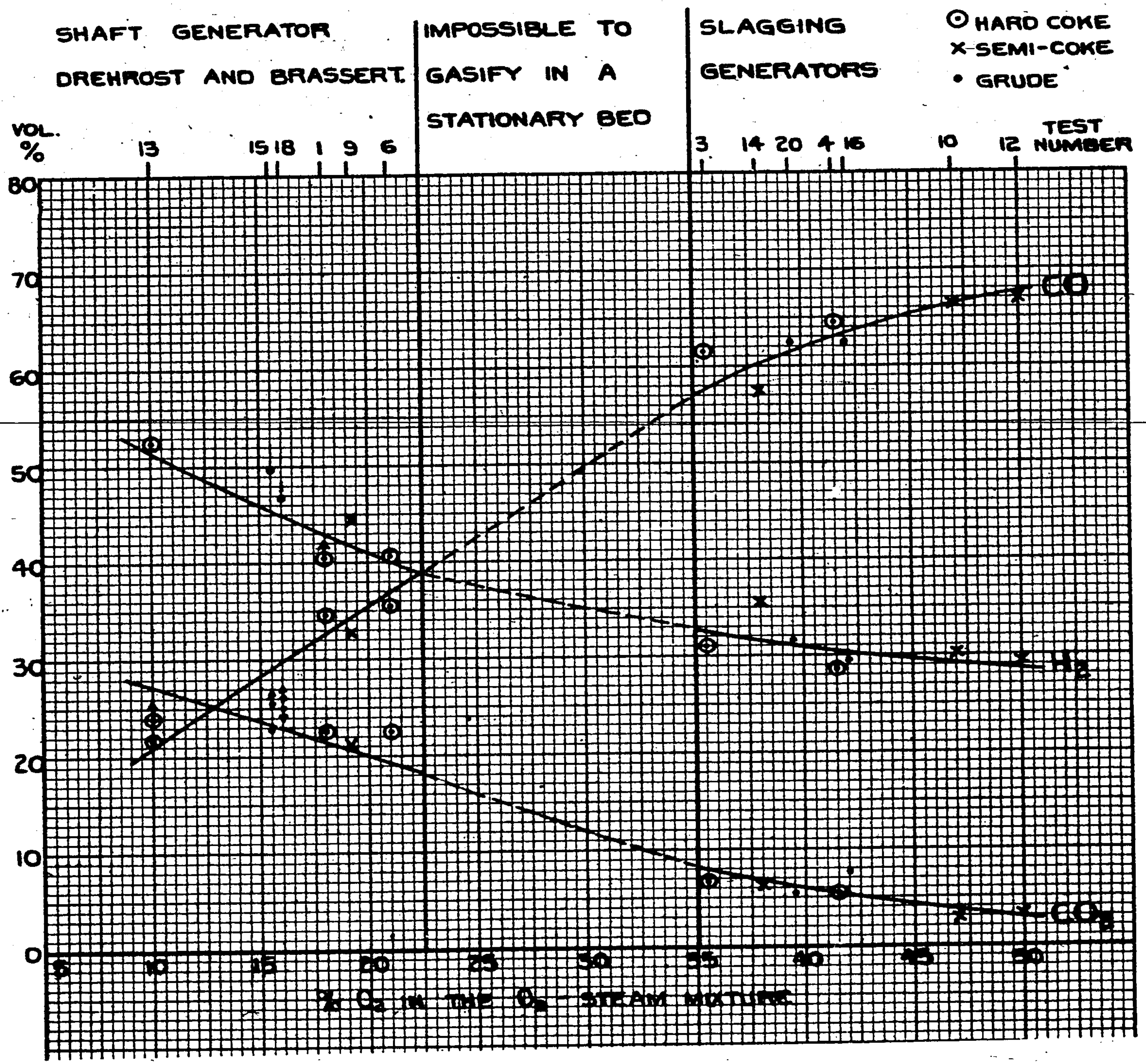
It is seen that it is possible to vary the ratio CO : H_2 over the whole range from 1 : 2 to 2 : 1. The region of the colder method of working extends to about 22% O_2 in the mixture; for this purpose simple shafts generators, Drehrost generators or Pintsch-Brassert generators are used. The last are particularly useful if one wishes to obtain low carbon in ash ("guter Ausbrand") by using a hot generator, where slag is already beginning to soften. In the range of about 22 to 35% O_2 in the mixture there is no gasification method available; above 35% O_2 in the mixture we enter the region of the slagging generator; the extreme limit for normal cokes and "semi-ash" is reached with 55-60% O_2 in the mixture, and at that point the materials of construction of the generator begin to be severely attacked as a result of the high working temperatures.

In our record note of 7/3/33, using the few data then available, we attempted to represent the correlation between dry gas analysis and the operating temperature of the generator. The earlier diagram* shows the same characteristics as the new one, based on curves drawn up for all the numerous tests carried out.

* not reproduced here, because it uses only a few data and is less accurate than Fig.3 - Trans. note.

FIG. 3.

GAS ANALYSIS AS FUNCTION OF % O_2 IN BLAST



Steam consumption and percentage steam decomposition, corresponding to Fig.3, are shown in Fig.4.

Almost pure CO can be produced by oxygen-gasification with CO_2 as gasification medium, if coke is used as fuel. In other respects Table IV and Fig.5 show a similar picture to gasification with steam.

CO gas made from coke contains about 3% H_2. About 2% of it is added along with the CO_2 used as gasification medium, as our CO_2 contains 5-6% H_2, about 0.5% comes from residual hydrogen in the coke and 0.5% from moisture in oxygen and CO_2. By using pure dry CO_2 and "semi-ash" or very well degassed coke, the hydrogen content of the CO made would be reduced to less than 0.5%.

The partial addition of CO_2 to the normal steam-oxygen mixture allows the CO : H_2 ratio to be varied in a convenient manner.

When CO_2 is used for gasification in the Brassert generator it is very interesting that the ash of Deuben hard grude behaves quite differently than when oxygen and steam are used. When using steam and a steam-oxygen mixture of 16% O_2, which according to all other evidence should not result in slagging, ash removal causes great difficulty. On the other hand when using CO_2 an oxygen content of 30% can be used. The difference is much too great to be explained solely by the larger heat requirements, of CO_2 decomposition, for the same amount of CO + H_2 produced. At present we are still working on this subject. In the laboratory it has so far been established, that by ashing the coal in a stream of CO_2, the softening point of the ashes from Deuben grude, Hermine-Henriette coal and Fürsten mine coal, is raised by about 200-300°, without really raising the melting point and without altering the chemical composition of the ashes, Mixtures of CO_2 and steam gave intermediate values.

A further interesting fact is that when using CO_2 in the Brassert generator the water gas made contains no more CO_2 than water gas made with steam and oxygen.

It can further be concluded from the tables that steam consumption decreases the hotter the generator can be run, without increasing the oxygen consumed per NM^3 CO + H_2; it is also well known that the carbon content of ash is lower the hotter the generator. With the slagging generator practically the only carbon loss is in fly dust. As steam decomposition improves with hotter running, the output of useful gas per unit of shaft area also becomes greater; this is particularly striking if the output of useful gas per M^2 shaft area is expressed in CO + H_2.

FIG. 4.

% O_2 IN BLAST VERSUS STEAM USAGE AND DECOMPOSITION

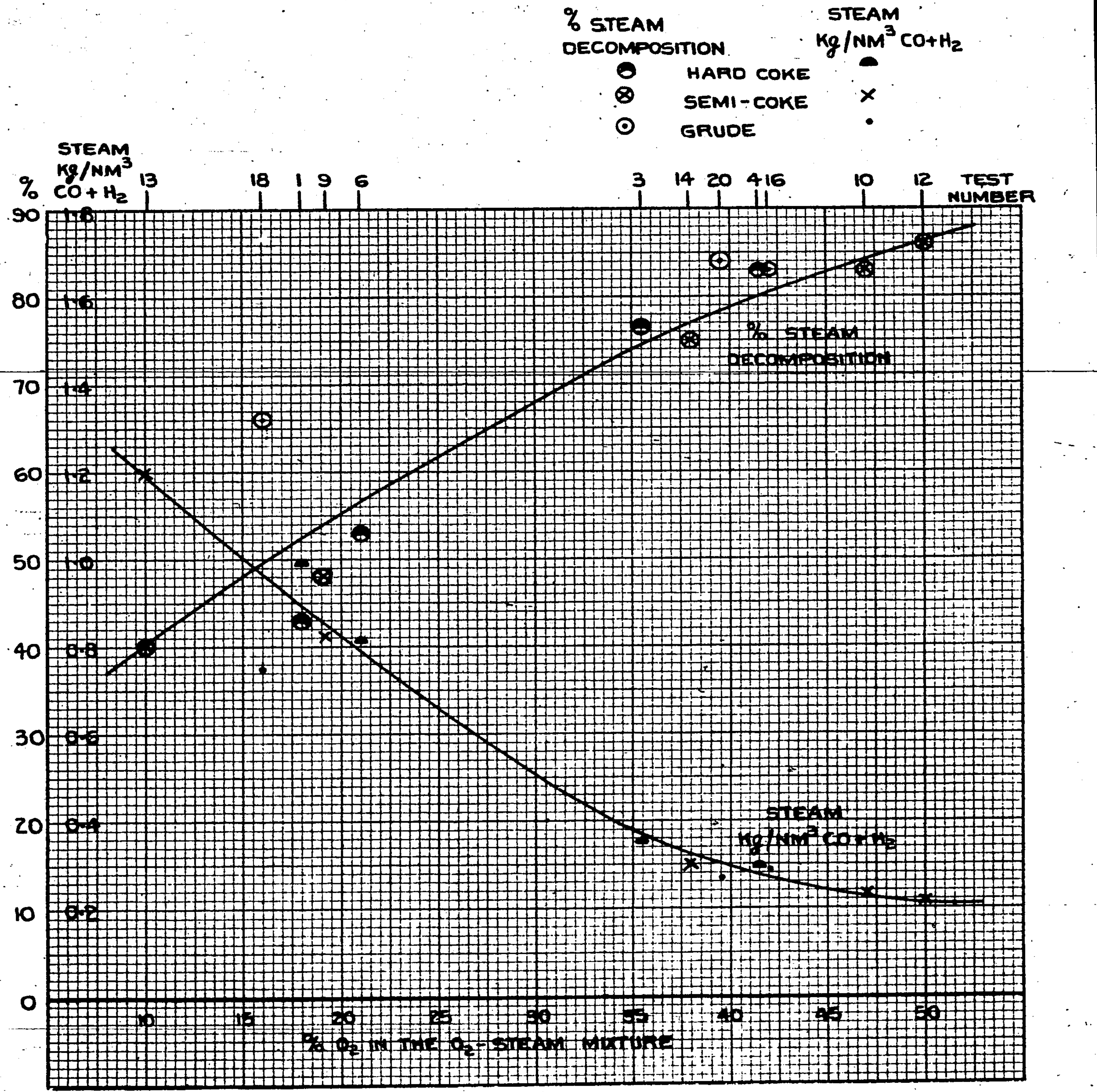
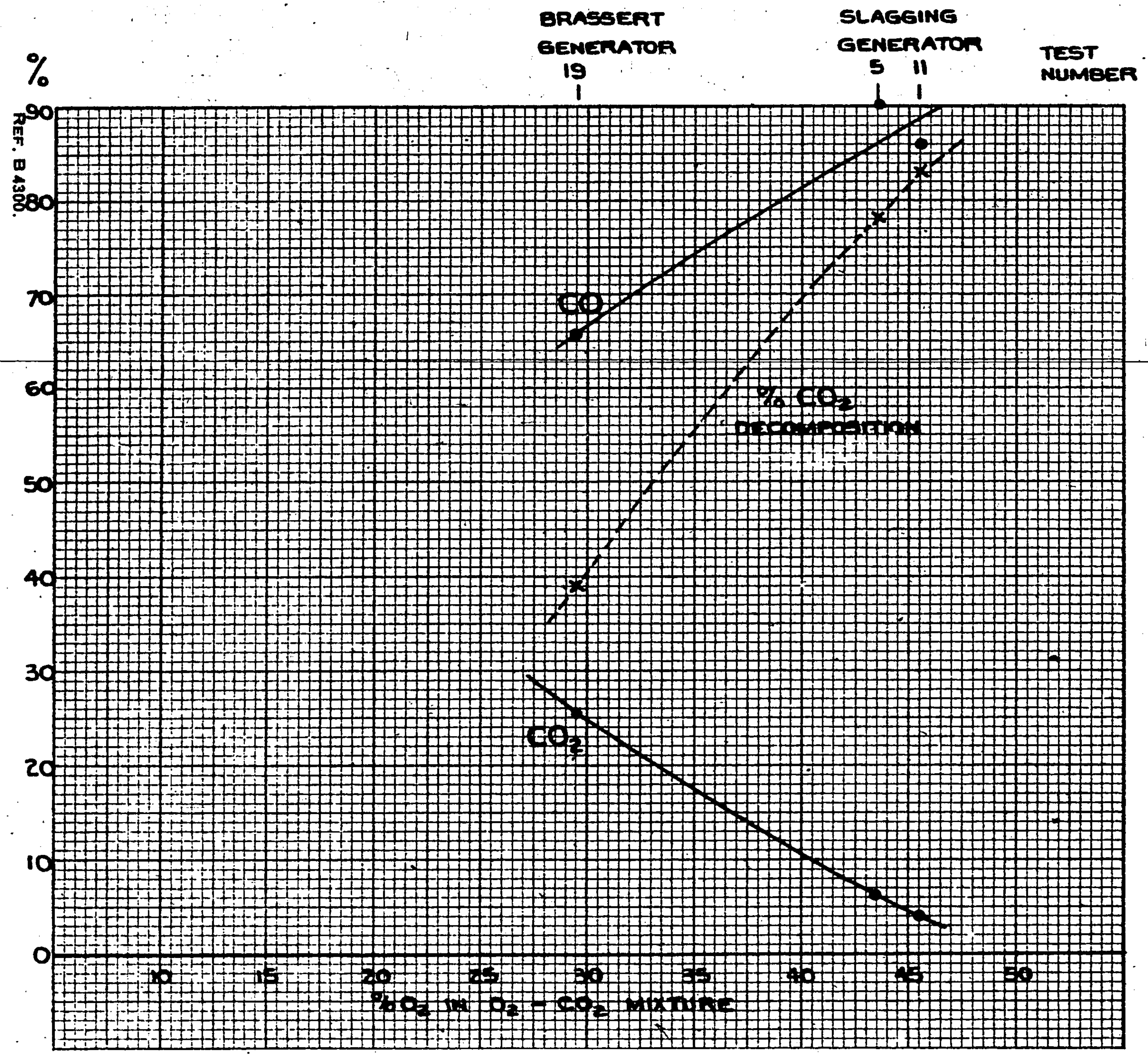


FIG. 5.

GASIFICATION WITH CO_2



The tables also confirm the well-known fact that it is advantageous to run the generator hot so as to favour as much as possible the reaction $C + H_2O = CO + H_2$ rather than the formation of CO_2 and the CO formed should not be converted before the CO- conversion plant. The extreme case, represented by Test Number 17, Table III, shows how much steam must be used at the lowest outputs in order to make catalysed gas ("Kontaktgas") directly in the generator. What is found to be wrong in the extreme case also holds for intermediate cases; running the generator hot is normally the correct method.

According to these considerations the slagging generator ought to be superior to all other generators for oxygen-gasification. The consumptions in the Tables and the summary on Page 10 show that this is actually the case, judged from a purely efficiency point of view. Whether slagging generators are built in individual cases depends of course not only on efficiency, but also on technical considerations and especially on the suitability of the fuel concerned.

With most fuels one can use steam-oxygen mixtures containing up to 16-17 % O_2 in the Drehrost or Brassert generators. This is the limit beyond which there is a serious danger of slagging. From about 30-55% oxygen in the mixture one can operate with liquid slag removal.

Although we know that the shaft generator should be run as hot as possible, several series of experiments were carried out, in order to find out the effect of running the generator colder, in order to make "catalysed gas" (Kontaktgas) in the generator itself; this is not unlike the Pattenhausen water gas process . Table VI gives the results of such an experiment for carbonisation-gasification of brown coal briquettes.

Figures 6 and 7 show the results of the experiment for Theissen briquettes, gasified with oxygen in the carbonisation generator.

The experiment was actually carried out by starting with a constant introduction of 400 kg steam and the maximum addition of O_2, 16%, at which point slagging became imminent. The oxygen-steam mixture was not preheated. Then the amount of oxygen was slowly cut down. Corresponding to the increase in undecomposed steam the gas output, calculated as dry gas, of course fell.

It is seen that the generator with 5% oxygen in the mixture still works very well (with a reaction zone temperature of 600°) and produces directly an acceptable "catalysed gas". Unfortunately the amount of steam used and the reduction in output render this method of working quite out of the question.

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[x] In which steam and gas is preheated and recirculated to gasify the fuel completely, without internal use of air or oxygen. Trans.note.

FIGS. 6 AND 7. (SEE TABLE VI)

CARBONISATION-GASIFICATION OF BROWN COAL BRIQUETTES EFFECT OF VARIOUS O_2 RATES AND OUTPUTS WITH CONSTANT STEAM RATE.

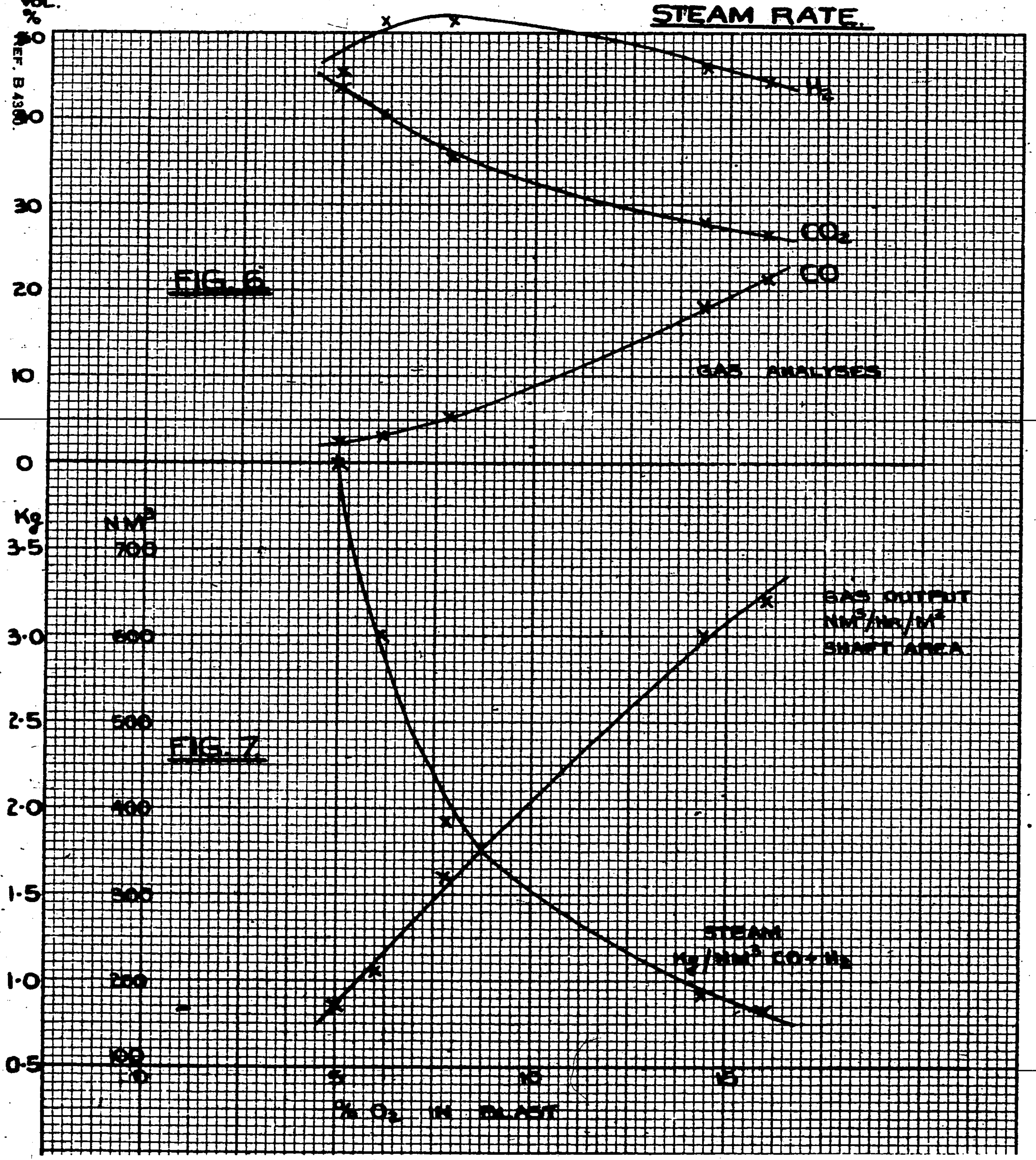
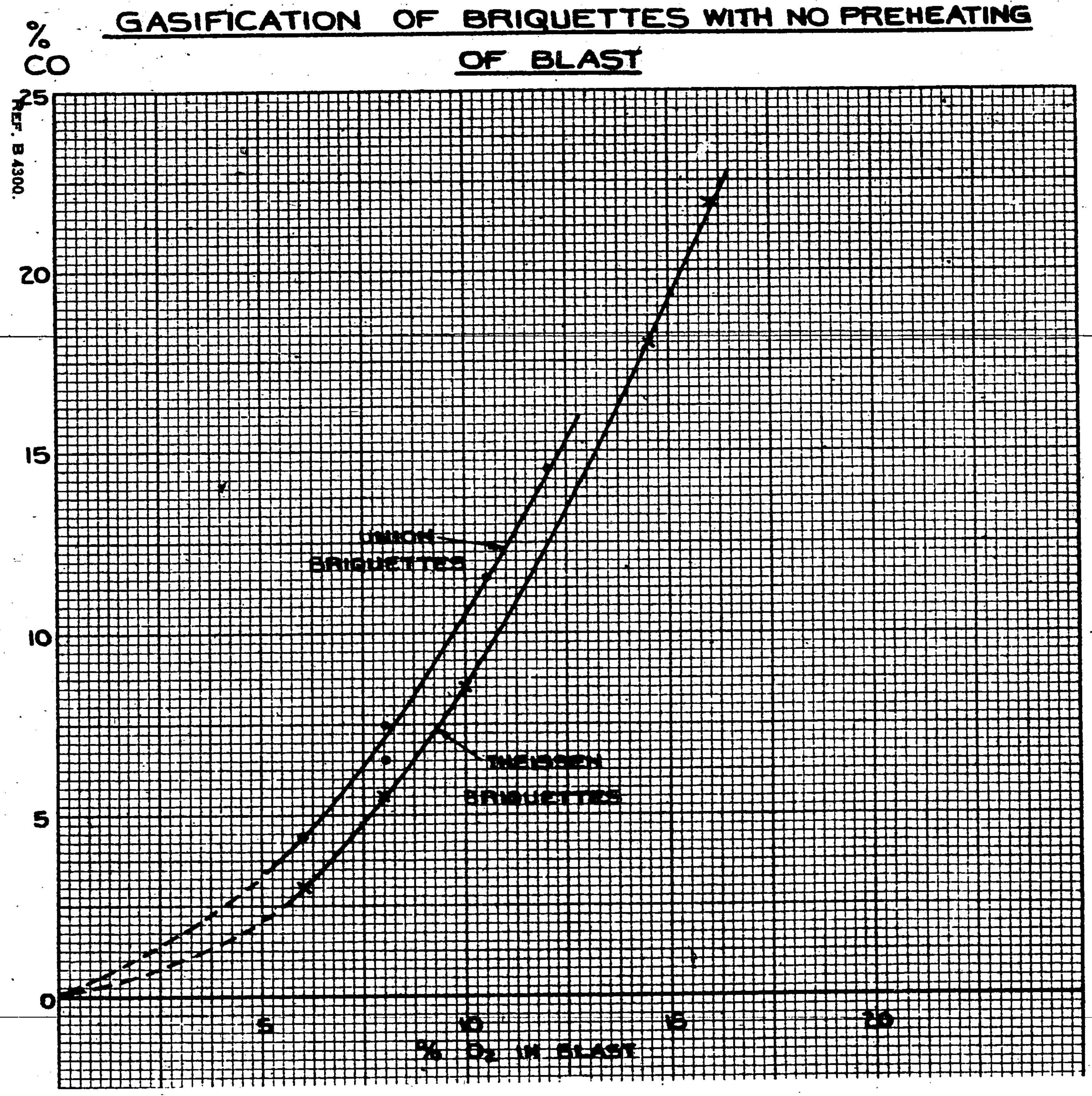


FIG. 8.

GASIFICATION OF BRIQUETTES WITH NO PREHEATING OF BLAST



When the experiment was repeated with Rhine "Union" briquettes the same picture was obtained, although with the same conditions somewhat more CO was formed than with Central German "Theissen" briquettes.

In general it is true for oxygen-gasification that preheating of the gasification medium results in a saving of oxygen. Calculated from the heat change this saving must amount to 0.03 - 0.01 parts of oxygen per NM^3 CO + H_2, depending on whether the oxygen burns to CO_2 or to CO and how much steam is used in the generator.

The experiment was actually made with grude from Bitterfeld briquettes (report of 18/9/39) in a shaft generator surmounted by a carbonisation chamber, so that the carbonised grude entered the lower part of the generator at a temperature of 550 - 600°C. The graph shown in Fig.9 was obtained, showing the oxygen consumption per NM3 CO + H_2 as a function of the preheat temperature, for about the same steam decomposition and about the same shaft output.

On the average it is estimated that for the above case about 0.018 parts of oxygen are saved per NM^3 CO + H_2 for every 100° of preheat temperature.

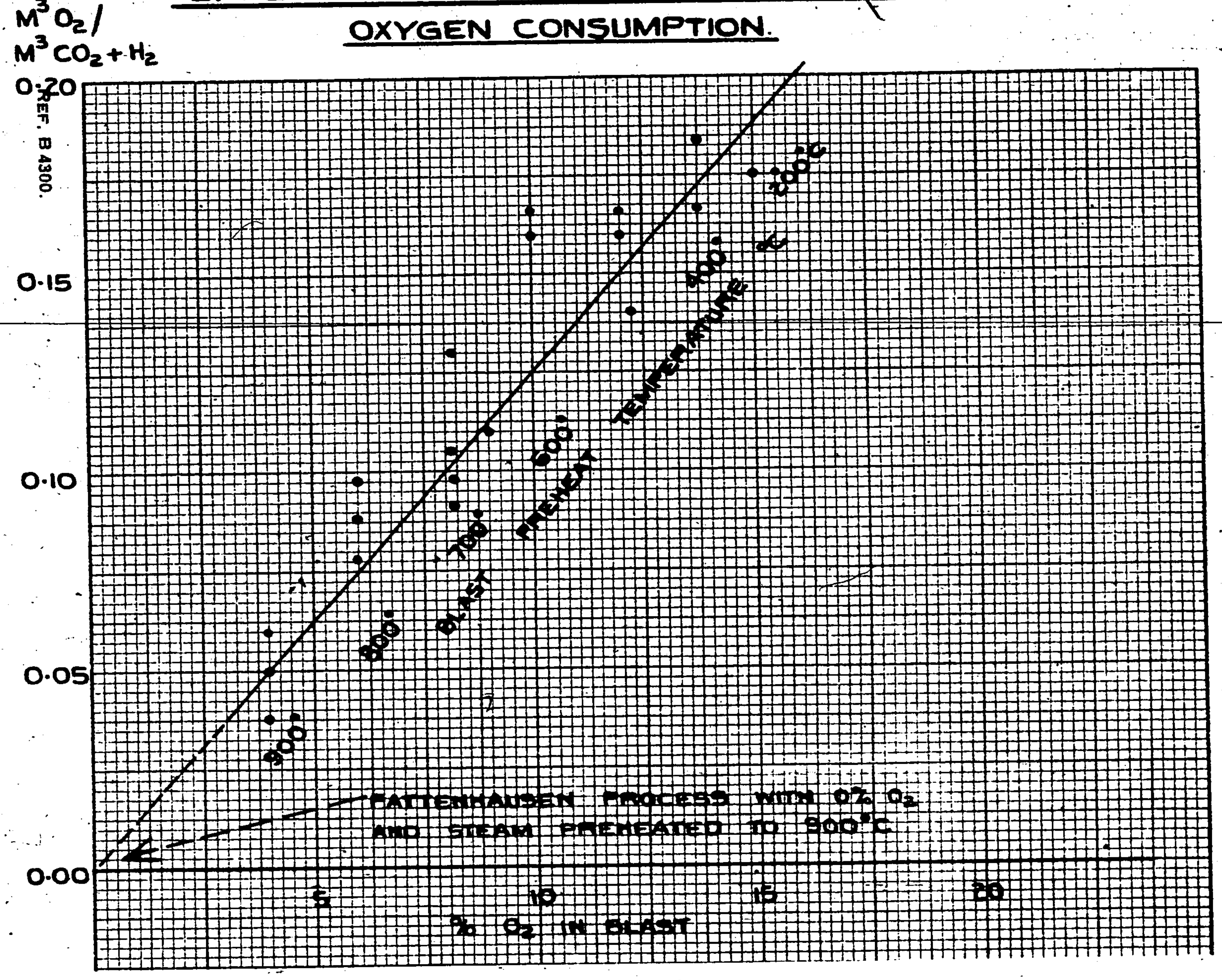
The savings compared with a normal consumption of 0.25 M^3 O_2/M^3 CO + H_2 are, therefore, not insignificant and would, e.g. by preheating to 400°, amount to 25% of the oxygen requirement without preheating. Whether it would be worth while complicating the gasification plant by installing preheaters is a matter for investigation in each particular case. In those cases of oxygen-gasification where the gas exit temperature is low there is not much waste heat available; moreover at lower preheat temperatures the oxygen saving is still small, whilst the preheaters are no simpler. High preheat temperatures require external heating, and Brassert grates, as an example are not very suitable for operation with preheated blast. Moreover preheating introduces certain dangers of its own, when not confined to preheating of the steam only. Therefore, we recommended for the oxygen-water gas plant at Auschwitz the initial omission of preheaters for the sake of simplicity of plant and operation, but leaving room for installing preheaters later on.

In Tables I - IV are shown the amounts of heat liberated, which leave as sensible heat of exit gases, undecomposed steam, ash and slag and as radiation, as deduced from check calculations, based on the corresponding analyses. If the sensible heat of the exit gases and undecomposed steam is deducted, there is still a residue. This residual heat is lost as radiation and sensible heat of slag, and is expressed in the table as %age of the total throughput of heat in the fuel. It is seen that these losses are mostly similar to those usually experienced in generators; where they tend to zero the measurements for fuel consumption are apparently somewhat too favourable.

The Tables are so arranged as to provide quick reference to the behaviour of fuels actually gasified. They also enable trials with other fuels to be started along the right lines.

FIG. 9.

EFFECT OF PREHEATING BLAST ON OXYGEN CONSUMPTION.



Oxygen-Gasification of Dust

Oxygen-gasification of fuel dust is of little interest to operation at Leuna. The cost price of brown coal dust is only slightly below that of lump dry brown coal. Grinding costs and the cost of special arrangements for bunkering and transport make it less advantageous to use dry brown coal dust, considering the convenience of handling brown coal briquettes. Moreover the oxygen requirements - if oxygen-gasification of briquettes and brown coal dust is being considered - is essentially less for briquettes than for dust. This is particularly true for gasification of dust with liquid slag removal; it is quite obvious that the high exit gas temperatures in this kind of gasification result in high oxygen consumptions.

It may be a different case with hard coal dust, in particular for caking coal, which is difficult to gasify in any other way. Here the high cost for oxygen might be offset by the low fuel price. But at Leuna we have no hard coal dust at our disposal for experimental purposes.

In order to get an idea of the possibilities of gasifying fuel dust, we have carried out several series of experiments, in which dry brown coal dust was gasified with oxygen with liquid slag removal in a small experimental generator of 400 mm. internal diameter. The experiments were varied between complete combination of the dust and optimum gasification to water gas. The fuel dust used was dry brown coal from Tannenberg, with about 10% H_2O, 54% C and 14% ash. The dust came from the electro-filters of the steam drying plant and consisted of 80% below 0.5 mm and 20% below 0.1 mm, and was thus fairly coarse.

The results are shown in Figs.10 and 11.

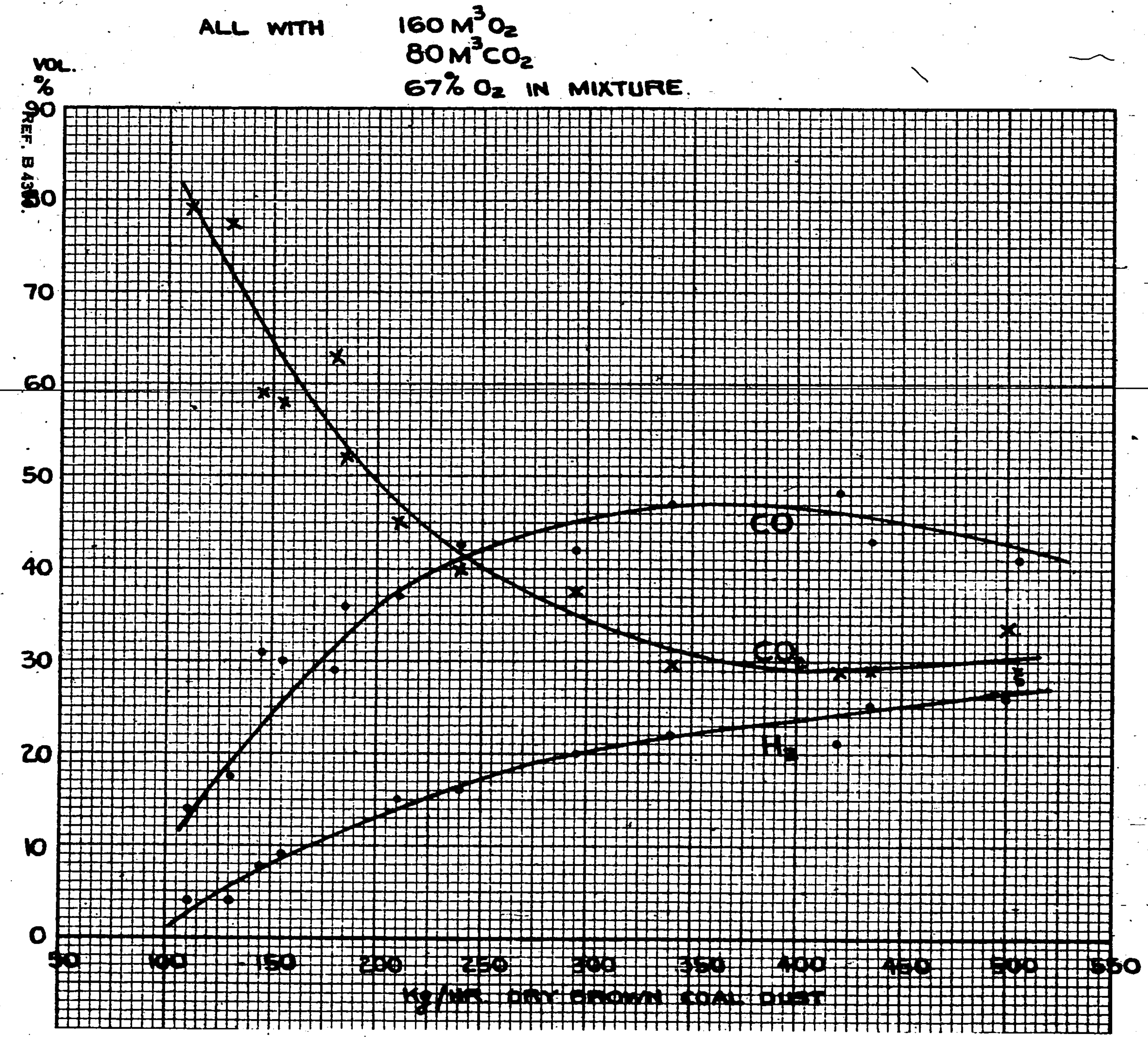
CO_2 was used for blowing in the fuel dust; one could also of course have added steam and thus obtained a gas richer in H_2. Removal of liquid slag caused no particular difficulty.

One can see the high consumption of oxygen per NM^3 $CO + H_2$ in that part of the series of experiments which were run to make water gas; the high gas temperatures, required to permit fusion of the ash, necessitated an overall reaction, which was strongly exothermic, i.e. a lot of oxygen had to be consumed. In a larger generator, with relatively lower radiation losses, the oxygen consumption would be appreciably less, but it would always remain above that of the Winkler generator or even of the shaft generator, in which the fuel in passing down the shaft returns a large part of the sensible heat of the exit gases to the reaction zone.

The poor carbon efficiency, in that part of the series of experiments, run to make water gas, is due to the formation of fly ash. Analysis at various heights in the generator showed that this was due solely to the smallness of the generator[1]. Likewise when making water gas from oxygen and dust in a larger generator with lower outputs/shaft area, there should be no practical difficulty in ensuring complete combustion of the ash and the removal of all the ash as liquid slag.

FIG. 10.

OXYGEN GASIFICATION OF BROWN COAL DUST



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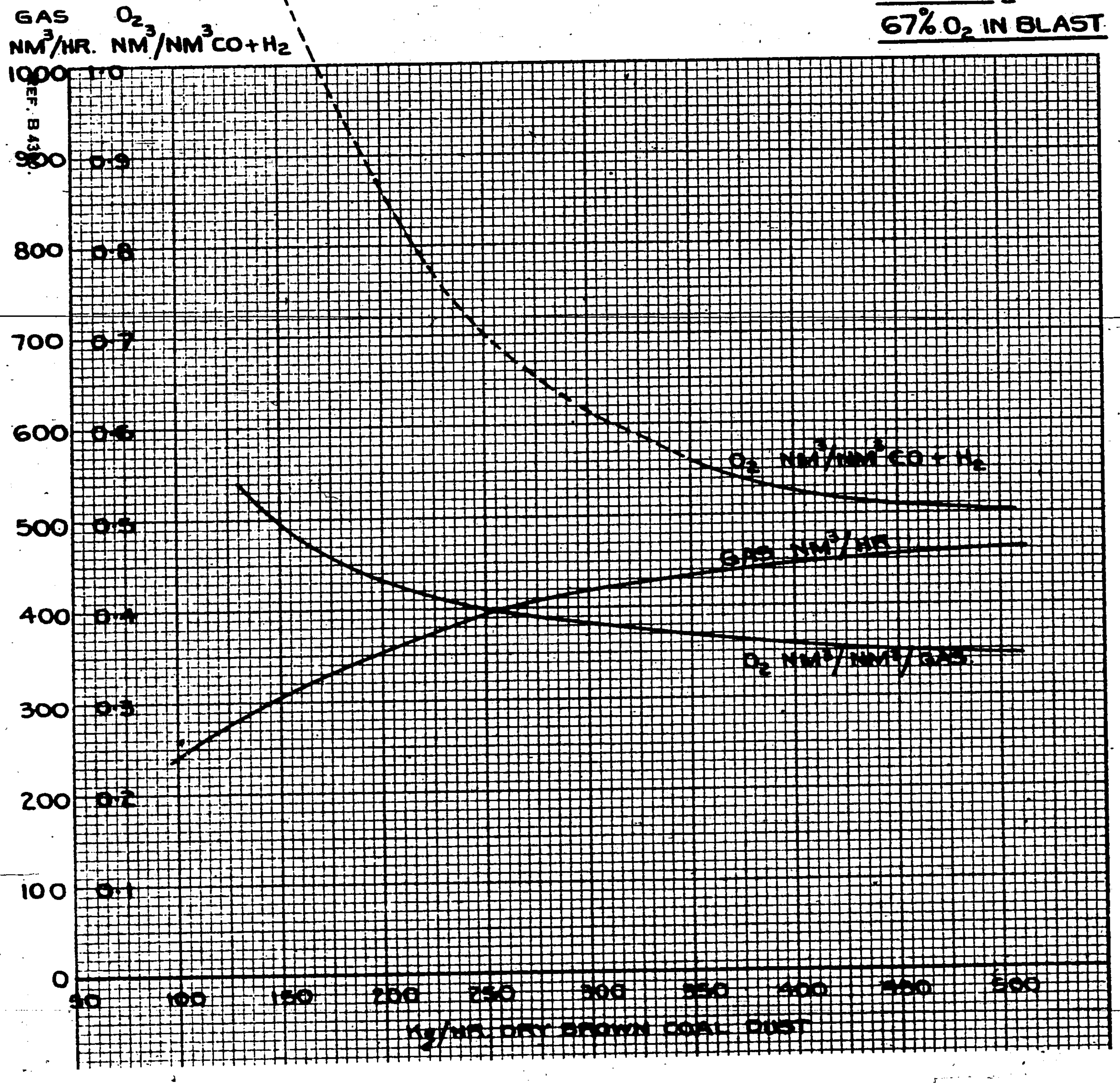
[1] At 300 kg/hr dry brown coal the generator made over 3000 M^3/hr gas per M^2 shaft area!

FIG. 11.

OXYGEN GASIFICATION OF BROWN COAL DUST

BASED ON PERFORMANCE WITH 160 M³ O_2
80 M³ CO_2
67% O_2 IN BLAST



If oxygen-gasification is not operated with removal of liquid slag, oxygen is certainly saved, but the high carbon content of ash must be taken into consideration. It does not pay in this type of gasification to grind the dry brown coal, because such material can be very well gasified in Winkler generators. In a Winkler generator dust is gasified with oxygen above the fuel bed; there dust originally contained in the fuel, as well as the dust which is continuously formed by attrition in the lower, boiling fuel bed, is gasified to water gas at temperatures below the fusion point of slag.

Unfortunately the amount of dust coming in with the fuel naturally fluctuates somewhat; but the appropriate addition of oxygen above the fuel bed cannot be continuously adjusted to suit, because there is no measurement of the amount of fine dust contained in the fuel. Certain inefficiencies in fuel utilisation must, therefore, be accepted as inevitable. When there is a strongly fluctuating dust content of the fuel, a preliminary screening into dust and coarse material and an exact estimation of dust and of oxygen to be added above the bed, will ensure constant and satisfactorily complete combustion, a procedure which will be tried out on one of the Winkler generators at Leuna, when the opportunity arises.

Preheating of the gasification mixture, if possible by utilizing waste heat in the water gas made, is particularly advantageous for gasification of dust with its high oxygen consumption. This is just as true for water gas generators, operating on dust with liquid slag removal, as for Winkler generators. To try out on a Winkler generator the effect of preheating the blast with its own waste heat, an apparatus has been prepared on No.1 Winkler generator on Me 278, which will be connected up at a suitable opportunity. This producer is particularly suited for running with preheated blast, because it has no grate.

Thermal Considerations of Oxygen-Gasification

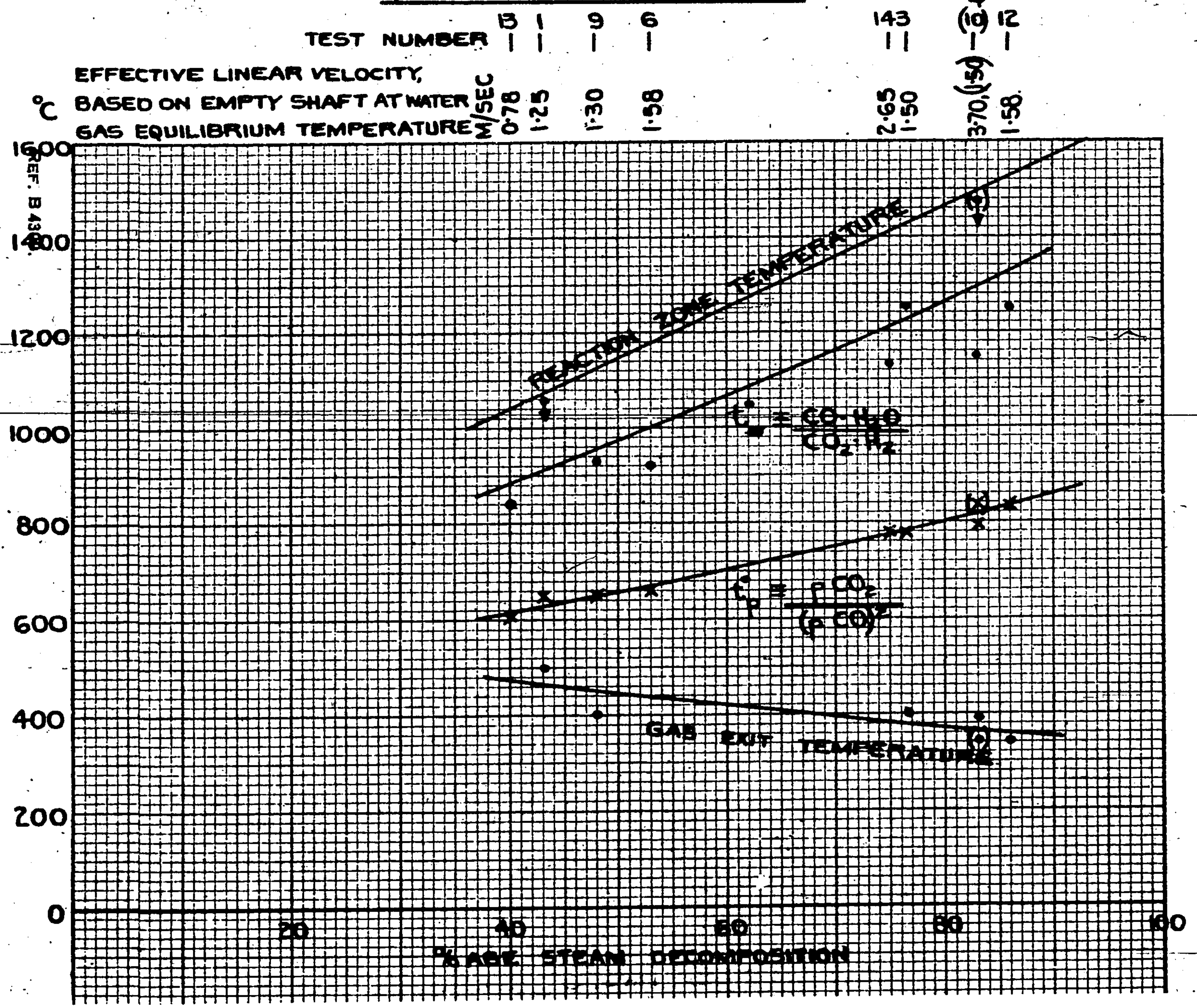
If the components of the gas analysis are inserted in the water gas equilibrium formula $\frac{CO.\ H_2O}{CO_2.\ H_2} = K$, one finds for each of the analysis in Tables I & II, i.e. with coke as fuel, a characteristic temperature which can be called "the apparent water gas equilibrium temperature" or the "gas-formation temperature". Similarly one can calculate the "apparent producer gas equilibrium temperature". If the points for single analyses are plotted together with the temperature of the hottest reaction zone, Fig.12 is obtained.

The apparent water gas equilibrium temperatures are scattered on account of inaccuracies in measurement and calculation, the latter particularly at high temperatures, where the amount of undecomposed steam present is quite small. But there is no doubt that the apparent water gas equilibrium temperature is higher with hotter generator operation than with colder.

FIG. 12.

HARD COKE AND SEMI-COKE, APPARENT EQUILIBRIUM TEMPS.

(SEE TABLES I AND II)



At first sight this appears contrary to expectation, if it is assumed that with the same fuel the water gas reaction in the fuel bed always proceeds to approximately the same temperature.

An explanation of the form of the water gas equilibrium curve cannot be made on the basis of observations published in the literature on the conditions governing the water gas equilibrium in water gas generators.

But one can assume the following, which is not in the least at variance with the achieved curves shown.

When a mixture of oxygen and steam is introduced into the reaction zone, one cannot talk about attainment of water gas equilibrium so long as any oxygen is still present. Inside the hottest reaction zone of the generator, however, the products of combustion rapidly tend to reach equilibrium with the steam or with the hydrogen formed from it. Equilibrium is not reached at the highest temperature prevailing in the reaction zone, but the reaction approaches nearer to equilibrium the hotter the reaction zone. Hence the observed curve for the water gas equilibrium temperature shown in Fig.12 slopes up to the right, and the apparent equilibrium temperature for hot generators is higher than for cold generators.

Besides the tendency to reach equilibrium in the reaction zone at the temperature prevailing there, a secondary reaction occurs in the layer above the reaction zone, where hot gases coming from the reaction zone meet the hot fuel, which however has not yet begun to react; here the hot fuel acts as a catalyst. It is obvious that this secondary tendency of the gas to reach an equilibrium, corresponding to this temperature, is favoured by the higher temperatures of hotter generators. But this mean, that the curve of the water gas equilibrium temperature rising steeply to the right in the diagram, is again forced downward.

The net result of both processes is characterised by the form of the "apparent water gas equilibrium" curve.

According to general ideas the producer gas equilibrium, i.e. the ratio carbon dioxide to carbon monoxide plays no part in the water gas generator. But plotting the calculated values for the producer gas equilibrium temperatures in Fig.12 gives essentially the same form of curve, showing a dependence on the temperature at which the generator is run.

If one supposes, therefore, that the producer gas equilibrium is attained essentially more slowly, and is to some extent hindered by the water gas equilibrium in its attainment, the form of the producer gas equilibrium curve in Fig.12 does not conflict with the conception that the apparent equilibrium temperatures, for the ratio $\frac{pCO_2}{p(CO)_2}$, just as for water gas, are higher with hotter than with colder generators.

If the same calculations and diagrams are made for Table III, i.e. for grude, an appreciably more reactive fuel, curves are obtained, which are similar in character to those for coke, except that the "equilibrium temperatures" are lower than with coke. (See Fig.13).

Corresponding plots (Fig.14) for carbonisation-gasification of brown coal briquettes yield curves of a similar character. Of course owing to water gas containing some carbonisation gas, the curves are not strictly correct and only in a general way are they comparable with the other curves. In spite of the presence of carbonisation gas the character of the curves is the same, i.e. higher equilibrium temperatures with higher generator temperatures.

The curves for "apparent producer gas equilibrium temperature" for oxygen-gasification with CO_2 are also comparable. (see Fig.15).

The "equilibrium curves" for oxygen-gasification are of particular interest, because it is not possible with any other kind of gasification to cover so wide a range in the various possible ways of running a generator on the same fuel.

The curves show clearly that the reaction zone temperature is the factor governing the apparent equilibrium obtained. That the linear velocity is of secondary importance can be deduced from Fig.12 where the calculated linear velocities (based on an empty shaft at the equilibrium temperature) are given. It should be noted, from tests 3 and 4, that doubling the effective linear velocity had no influence on the apparent equilibrium.

In practice it is not possible to make any direct use of these conclusions, but they assist in the critical examinations of gasification processes; so experiments are at present being carried out to make clearer the relationship between the various reactions.

Patents Position In The Field Of Gasification Of Solid Fuels With Oxygen.

Gasification with oxygen had reached the industrial stage and was already very fully described in D.R.P. 108,158 as early as 21/5/1898. Likewise the Swiss Patent 75,030 of 28/2/17 claimed the production of high grade mixed gases by using a mixture of technical oxygen with steam. Further the English Patent 142,874 of 28/11/17 described a generator for making raw gas for ammonia synthesis with the use of oxygen. These patents have now completely expired, so that there is no patent restriction on gasification of solid fuels with oxygen.

FIG. 14. FIG. 13.

GRUDE AND BRIQUETTES: APPARENT EQUILIBRIUM TEMPS.

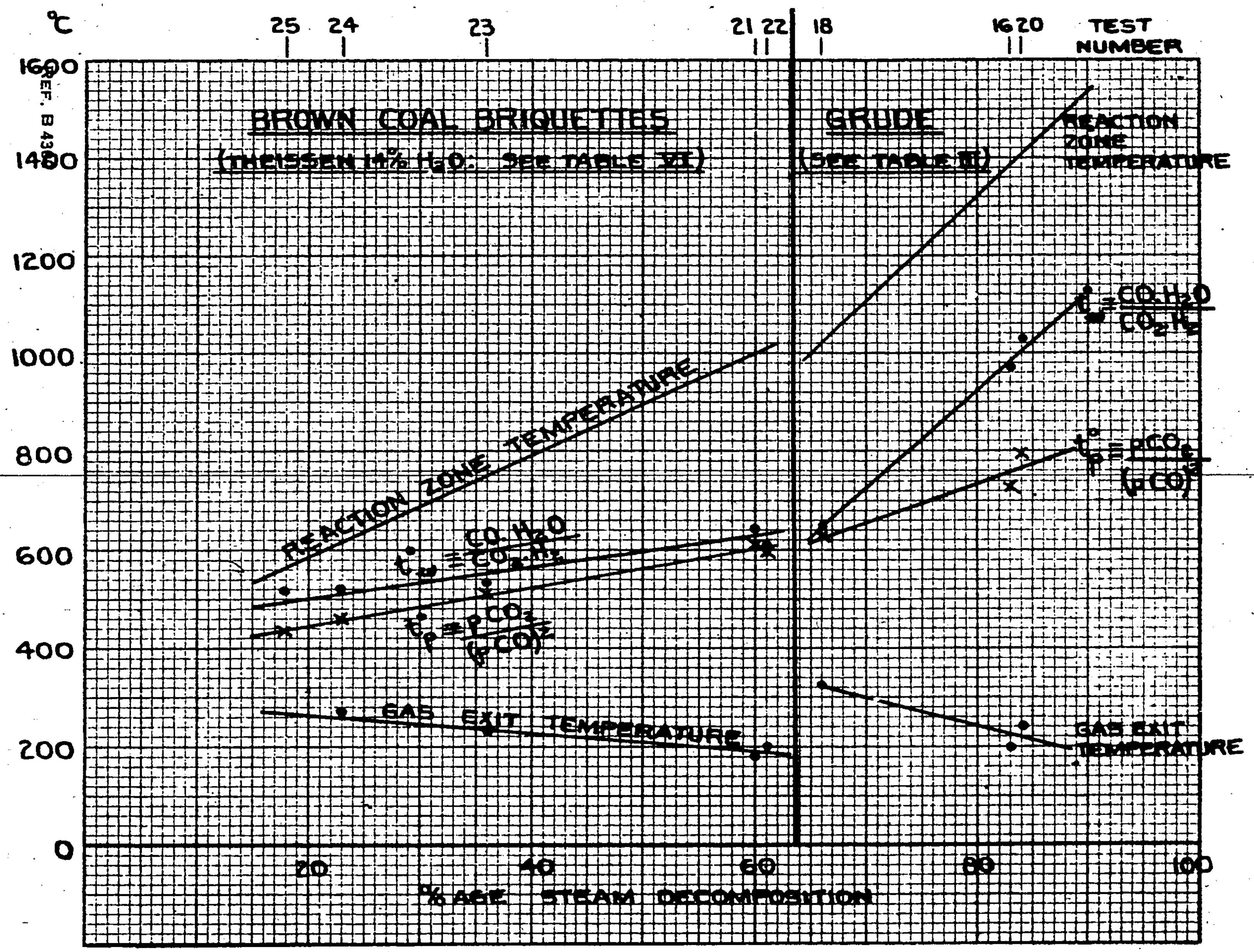
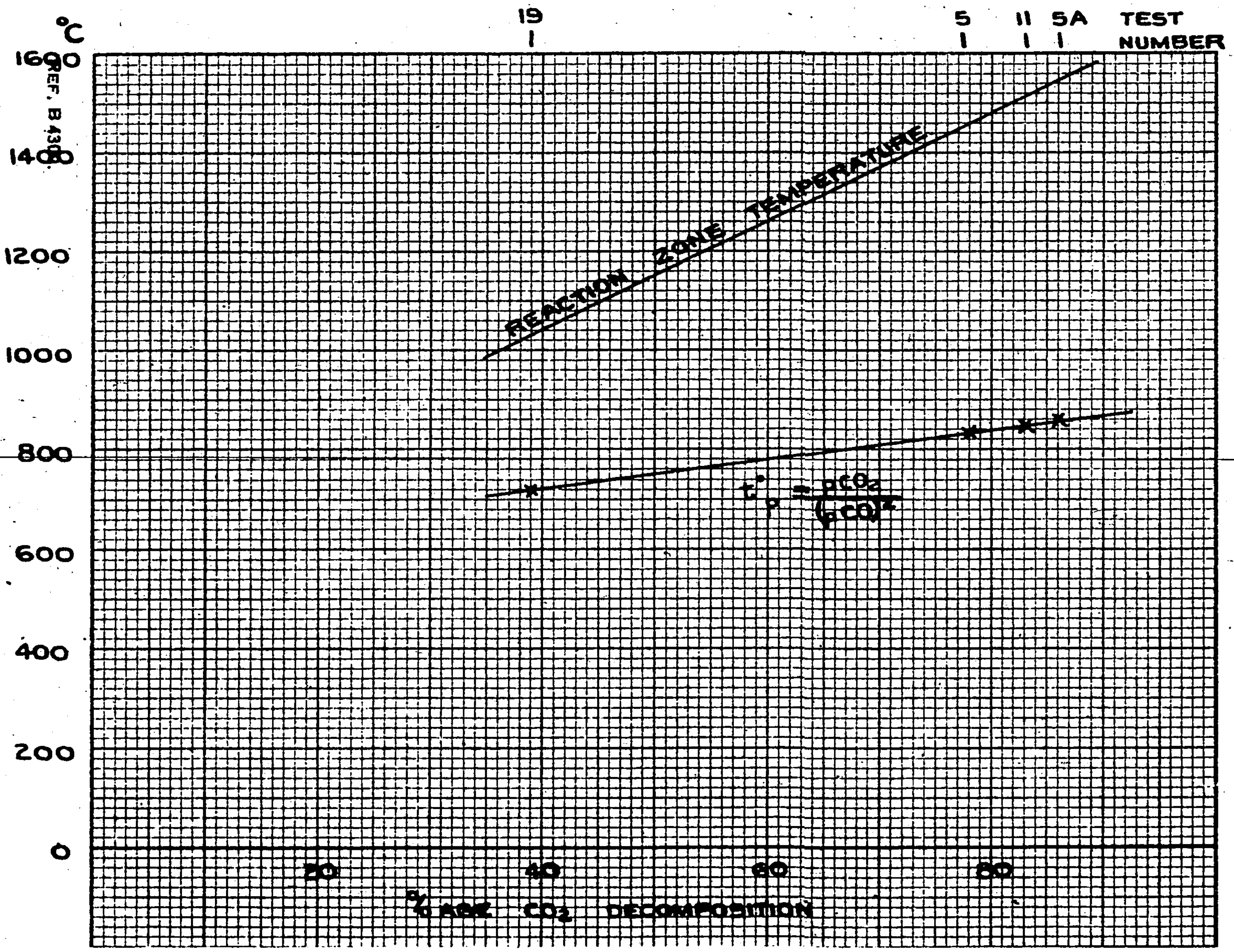


FIG. 15.

APPARENT EQUILIBRIUM TEMPERATURES WITH CO_2 AS GASIFICATION MEDIUM. (SEE TABLE VI)



Therefore, the patents now valid cover only special ways of operating the process. Here we may refer to the summaries of the Merseburg Patent Office, dated 22/6/32 and 3/7/42. The following additional processes are worthy of mention:

D.R.P. 573,112. Dipl.-Ing. Zsigmond v. Galocsy and Karl Koller. In this process a solid, liquid or gaseous fuel is burnt with oxygen in a chamber separated from the gas producer, the oxygen being saturated with the amount of steam required by the gasification process, and the flue gases are introduced into the producer, with the addition of more oxygen if so required.

A further process for the gasification of fuel dust with oxygen appears to have been developed recently by the firm of Heinrich Koppers, Essen. Details are not yet available.

Our own patents or applications are the following:

D.R.P. 701,232 (O.Z.9,622)

Carbonisation-gasification with special recirculation of carbonisation gas, from which a part of the gas is drawn off and together with oxygen is blown through a specially shaped domed grate in the generator.

O.Z. 11,545.

Process for the gasification of particulate waste fuel in a slagging generator, whereby the fuel in a damp condition is fed, together with lump fuel, into the top of the generator, and the dry flue dust, after separation from the gases produced, is blown back pneumatically into the generator. The application has been published.

O.Z. 12,375.

Process for the production of water gas in the slagging generator with oxygen, with simultaneous decomposition of hydrocarbon-containing gas, whereby the hydrocarbon-containing gas is preheated by indirect heat exchange with the gases made, and the preheating temperature is regulated by returning a certain amount of slag to the generator. This application has likewise been preheated.

An addition to this was made recently, according to which control of the preheating temperature was done by introducing water or cold gas into the top of the generator.

O.Z. 12,695.

Oxygen-gasification in the Pintsch-Brassert generator, whereby a layer of slag is maintained on the grate, of such a height that the stirrer moves practically only in the slag.

O.Z. 13,090.

Gasification of solid fuel, whilst maintaining a deep layer of slag on the grate, at the same time using a grate, whose width of slot is at least as great as the average grain size of the fuel.

O.Z. 13,147.

Gasification of solid fuel with oxygen and carbon dioxide, wherein the oxygen-carbon dioxide mixture under the grate should contain 25-40% oxygen.

In addition work on the following applications is going on :

(1) Nozzles for introducing gasifying agents and hydrocarbon containing gases into the oxygen-slagging generators, wherein the tube for introducing hydrocarbons is so attached to the inner wall of the water-cooled nozzles, that it is in this way cooled by them.

(2) A slagging generator, the base of which consists of a sort of brick-lined sheet metal stuffing box, which is so designed that the generator shell, suspended from above, can expand through the bottom.

(3) A tapping hole for discharge of liquid slag from the slagging generator, consisting of a sheet-metal box, lined with its own slag.

(4) Nozzles with special liners for oxygen gasification in slagging generators.

We also possess D.R.P. 577,725 (O.Z. 7377).

Process for operating slagging generators, whereby the fire zone is only maintained periodically at such temperatures as to cause liquefaction of the slag, the fire zone being run during the remaining time at appreciably lower temperatures,

---

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B.I.O.S. FINAL REPORT No. 524.
ITEM No. 30.

DEUTSCHE GASOLIN A.G.
HAMBURG · GERMANY

LUBRICANTS

Thomas, W. H.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H. M. STATIONERY OFFICE

V

DEUTSCHE GASOLIN A.G.

HAMBURG - GERMANY

LUBRICANTS

October 2nd - 10th 1945. ✓

Reported by:

W. H. Thomas, British, Ministry of Fuel and Power.
J. G. Withers, British, Ministry of Fuel and Power.

BIOS Target Numbers
C30/410, C30/410a, C30/410b,
C30/410c.

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

(1946)

50 p.

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PERSONNEL OF TEAM.

Mr. J. G. Allen	(U.S.)
Dr. W. F. Faragher	(U.S.)
Maj. W. H. Thomas	(Br.)
Mr. J. G. Withers	(Br.)

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ACKNOWLEDGEMENT.

The German Translations involved in the production of this report were made by Mr. K. G. C. Kirkpatrick.

1. SUMMARY.

The Deutsche Gasolin A.G.'s three refineries at Dollbergen, Emmerich and Korneuburg were operated to produce a wide range of products ranging from motor fuel to bitumen. The plant employed apparently possessed no unusual features and the methods of refining were in the main of conventional type.

It is of interest to note that engine oils were produced directly as a blend of refined distillate and refined residue (bright stock) and that hard paraffin wax was removed in an initial stage, leaving the softer waxes to be removed together with the acid resins derived from refining treatments.

The acid resins were processed to yield low-grade engine oils, a dark waxy oil for crude types of lubrication and a waxy bitumen. A neutral refinery fuel oil and recovered (85%) sulphuric acid were also obtained from the same source.

This report gives details of the various processes involved, summarises the yields of products and provides answers to a comprehensive questionnaire on lubricants.

2. INTRODUCTION.

The information given in this report was obtained from Herr G. Madeyski in the course of a visit (B.I.O.S. Trip No. 1248) to the Hamburg area during the period October 1st to 31st 1945. Herr. Madeyski was a senior technical employee of the Deutsche Gasolin A.G. and also one of the directorate of the Zentralbüro für Mineralöl (Z.B.).

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He gave details of the production, refining and quality of a wide range of petroleum products and provided answers to a series of questions on lubricants.

The report which follows is therefore divided into two main sections, the first of which deals with the Dollbergen, Emmerich and Korneuburg refineries while the second gives the answers to the questionnaire.

3. GENERAL INFORMATION.

The Deutsche Gasolin A.G. with its head office in Berlin had a capital of 16½ million Reichmarks allocated as follows:

Standard Oil Co. of New Jersey	25%
I.G. Farbenindustrie A.G.	41%
Royal Dutch - Shell Co.	25%
Rhenania - Oassag and others	9%

It possessed three refineries, Dollbergen, Emmerich-on-Rhine and Korneuburg near Vienna, the products of which were sold either direct to consumers or to jobbers.

At present the products from the Dollbergen refinery are being disposed of in the following manner:-

Light Distillates	to the Civilian Pool.
Asphalt	to the Military Government.
Lubricants	to the Civilian Pool - these are of high

pour point because the dewaxing plant was destroyed by bombing.

The Emmerich refinery, north of Düsseldorf, was destroyed but its tankage is being operated by the Military Government.

The Korneuburg plant was undamaged but is in Russian hands.

Dollbergen Refinery.

The Dollbergen works were planned and operated in peacetime for the purpose of preparing the necessary amount of motor oil to cover the needs of those purchasing fuel from the firm. In addition, large amounts of oils for axle-lubrication were manufactured for supply to the Reichsbahn. Other lubricants and fuels were originally produced at Dollbergen solely in so far as they occurred as unavoidable by-products in processing crude oil.

From the beginning of 1934 onwards, a special method which had been evolved in the Dollbergen works laboratory between 1930 and 1933 was used for processing the crude. The considerable technical problems involved in handling the refining residues obtained were overcome during the war namely in April 1943, so that the yield figures given herein can only be regarded as applying as from that date.

A. Throughputs.

Up to the beginning of the war, the quantity of crude oil available at Dollbergen was about 4500 - 4700 tons (metric) per month from the Nienhagen field. During the war, the works obtained, in addition to fluctuating quantities of the same oil as in peace time, smaller amounts of topped Heide crude and untopped paraffinic crude from the Vienna basin. The yield data given in the subsequent description of the process refer to the working-up of Nienhagen crude oils.

3800 tons of paraffinic Nienhagen crude per month represented the main bulk processed and about 1000 tons of engine oil was obtained therefrom. A further 400 tons of paraffin-deficient Nienhagen crude together with 500 tons of paraffinic crude provided a somewhat dark residual oil used for gear lubrication and as a railway axle oil. Dollbergen received a monthly delivery, both in peace time and during the war, of about 400 tons of light spindle oil distillate with a good cold test. This oil was used as a blending component for the manufacture of the axle oil and was delivered from the gasoline refinery at Emmerich.

During the war, further quantities of finished lubricating oils were drawn from Emmerich to serve as a base oil for the subsequent incorporation of additives at Dollbergen to render them suitable for every kind of metal working. Finally, Dollbergen obtained about 200 tons/month of an aromatised gas oil from the Deurag refinery at Misburg. This oil was found to be especially suitable for working-up with a by-product of the Dollbergen refining processing, namely part of the acid resin.

B. Refining Procedures.

The process used at Dollbergen is characterised by four features which may be considered usual in the mineral oil industry:

1. Engine oils were produced directly as a blend of refined distillate, lubricating oils and refined residual oil (bright-stock).

2. A crude paraffin wax was isolated which consisted only of hard wax, while the lighter portion was removed from the lubricating oil together with the acid resin.

3. It produced primarily an engine oil with a viscosity of about 8°E./50°C. This oil was concentrated to give a summer-grade oil of higher viscosity whereby a light raffinate-like distillate of viscosity ca. 3°E./50°C. was obtained. The latter oil could be used as a blending component to convert part of the original 8°E./50°C. oil into a winter-grade oil having a viscosity of about 6°E./50°C.

4. By processing the considerable quantities of acid resins formed, the following products could be made:-

(a) A moderate quantity of lower grade engine oil.

(b). A wax containing dark oil for crude types of lubrication.

(c) Bitumen containing a considerable amount of soft wax.

(d) A neutral fuel oil for use at the refinery itself.

(e) About 85% regenerated sulphuric acid.

The process was as follows:-

For an input of 3800 tons/month of paraffinic Nienhagen crude into the atmospheric-pressure side of the two-stage pipe still distillation plant there resulted:-

Yield - about	200 tons/month	of straight run benzine boiling between 45° - 170°C. This was disposed of to benzine works for making test benzine.
- "	250 " "	Kerosene distillate.
- "	250 " "	Solvent A, boiling between 170°-280°C. for use in the refining process.
- "	650 " "	Diesel fuel.
- "	2400 " "	Paraffin wax containing topped residue with a flash point of 190°C. and viscosity of approximately 45°E./50°C.

900 tons/month of the 2400 tons of topped residue were passed direct to the de-waxing and raffination stages as raw material for the bright stock component of the engine oils. The remaining 1500 tons/month alternating about 500 tons/month of a by-product from acid resin processing (the so-called "acid oil residue"), were distilled in the vacuum stage of the pipe still to give:-

900 tons/month	of paraffin wax containing primary lubricating oil distillate (from 1500 tons/month of topping residue).
300 " "	of waxy secondary lubricating oil distillate (from 500 tons/month of "acid oil residue").
760 " "	of waxy bitumen with a melting point of 28° "K.S." About 180 tons/month of this was used as fuel oil in the pipe still, while 580 tons/month were airblown to give a melting point of 50°-120° K.S. and then sold.

The dewaxing process handled alternately:-

900 tons of primary lubricating oil distillate, mixed with 680 tons of topping residue and
300 tons of secondary lubricating oil distillate mixed with 220 tons of topping residue.

To the total of 2100 tons of unrefined lubricating oil was added 1900 tons of solvent A and the mixture was cooled to +5°C. for dewaxing in two neumann system brine coolers (Brünn-Kravolo Factory) each with 40 m² of cooling surface. 4% of kieselguhr was then stirred into the cooled oil to aid filtration and the mixture subsequently separated, using a Moore filter press, into partly dewaxed filtrate and crude, kieselguhr containing paraffin wax.

The latter, after addition of sufficient solvent A, was passed hot through a rotating filter (Imperial Meissen system) yielding kieselguhr, which was returned to the filtration cycle and a crude wax solution, which when distilled, gave a residue of black, oily crude wax and solvent A as distillate.

The partly dewaxed filtrate from the presses was chilled in three Borsig-Berlin type coolers (each with 40 m² cooling area) by direct ammonia evaporation to -30°C. and fed to 4 heat insulated agitators in turn, which were charged with 28 m³ of chilled oil. The agitators, which had a total capacity of 30 m³., were fitted with low speed stirring operators and in the course of about one hour, 1200 litres of 97-98% sulphuric acid were stirred into each agitator. As a result of the heat of reaction, the oil temperature rose to -20°C. As soon as the agitator had received the full charge of sulphuric acid, a smooth separation into an upper raffinate layer of about 19.5-20 m^3 and a lower acid resin layer of about 9-9.5 m^3 took place with great rapidity. After a short settling period, those two layers were separated by running off the lower one.

The upper raffinate layer was neutralised at 80°C. by adding 2.5% of used, oily, fullers earth (from the final refining of the finished engine oil) and about 1% of powdered lime and then the earth and lime were removed in the filter presses.

The filtrate was transferred to a pipe still operated at atmospheric pressure, to give 850 tons/month of first quality and 150 tons of second quality engine oil, solvent A being also recovered as distillate (150 tons spindle oil, 50 tons cleaning oil raffinate).

The pipe still was so arranged that in addition to the distillate mentioned, a further concentration of the engine oil residue could be effected to give a light lubricating oil distillate of raffinate type, leaving the engine oil with the desired viscosity.

The spindle oil distillate, light lubricating oil distillate and the remaining engine oil were finally bleached with 3 - 4% of fresh fullers earth (supplied by the Tannenberg Co., Stassfurt Leopoldshall) at 80 - 100°C. to give the finished product.

A very difficult problem was presented in working up the acid resin drawn off from the agitators because of the corrosion of the equipment employed. the solution finally reached was as follows :-

The acid resin was mixed in lead lined stirring vessels of 20 m^3 capacity with 800 litres of condensate water and 2600 litres of a solvent B (derived from the acid resin itself) per vessel and heated to about 100°C. After the mixture had stood for over five hours, a fairly good separation into three layers had taken place, namely an upper layer of sulphuric acid free oil containing sulphonic acids, a resinous middle layer (ca. 600 litres) containing some dilute sulphuric acid and a lower layer of about 50% residual sulphuric acid. The layers were separated by drawing off the "acid oil" upwards through a tube dipping into the liquid and by running out the residual sulphuric acid from below. The resinous middle layer was stirred in the same vessel with 1000 litres of aromatised gas oil from the Deurag-Misburg refinery, transferred (using vacuum) into a leaded pressure vessel and there heated by live steam under 3 atmospheres pressure. This generally gave a clean separation into a residual sulphuric acid layer and one of resin solution ("resin oil") free from sulphuric acid but containing a considerable amount of sulphonic acids.

The two acid resin solutions containing sulphonic acids ("acid oil" and "resin oil") were finally distilled in special apparatus to give a distillate of SO_2-containing solvent B and a completely neutral residue of "acid oil residue". This special equipment consisted of 2 tubular retorts and two cast iron bladder shaped vessels (Blasen) each of 6 m^3 capacity provided with leaded condensors to condense the SO_2-containing solvent B. By means of two hot oil pumps, the contents of each of the vessels were re-cycled through the corresponding tubular retorts where its temperature was raised to 360°C. The hot (90°-100°C.) "acid oil" was pumped into the first of the two vessels by means of a lead lined centrifugal pump. The quantity of oil recycling through the retorts was so adjusted, that a steady distillation temperature of 320°C. was maintained on the circulating oil mixing with the "acid oil" pumped into the bladder shaped vessel. Using only a little heating by live steam, SO_2-containing solvent B was distilled out of this kettle, with complete break down of the sulphonic acids, while completely neutral oil residue accumulated, the excess of which was continually led into the second vessel. By maintaining a continual re-cycling of the contents of the second vessel through the tubular retort and pumping "resin oil" into this second vessel, complete breaking down of the sulphonic acids in the "resin oil" was achieved in a way similar to that in the first vessel and retort. Thus the product from the second vessel was a finished, completely neutral "acid oil residue", while the distillate consisted of more SO_2-containing solvent B.

Dollbergen prepared a total of about 850 tons of neutral acid oil residue per month from the acid resins. This product was used as follows :-

1. About 500 tons as feed stock for the vacuum stage of the pipe still, for distillation to give a secondary lubricating oil distillate and bitumen.

2. About 200 tons as fuel oil for the tubular retorts and acid concentration plants.

3. About 150 tons sold as black oil with a viscosity of 40°E./50°C. and a flash point of 190°C.

The greater part of the SO_2-containing distillate was used while still acid, for re-cycling in the acid resin plant (as solvent B). The excess was neutralised with caustic soda lye and sold as diesel fuel.

The 50% sulphuric acid from the processing of the acid resin was concentrated in a Bamag type plant to give a 95% regenerated acid which replaced 85% of the sulphuric acid used in the refining process. The 15% loss was covered by the purchase of 20% oleum, which was mixed with the regenerated acid (95%) to give a 97-98% acid.

C. Yields.

In addition to the special apparatus and normal pipe still described, Dollbergen had a simple distillation plant consisting of four vessels which processed about 500 tons of paraffinic- and 400 tons of paraffin-deficient Nienhagen crude into light distillates and residual oils. The 500 tons of paraffinic crude yielded:-

70 tons of a blend of benzine and petroleum distillate.
70 tons of diesel fuel.
350 tons of residual oil of flash point 170°C. and of a viscosity of 30°E./50°C. (a blending component in summer-grade Reichsbahn axle oil).

The 400 tons of paraffin-deficient crude yielded:-

10 tons of benzine petrol,
30 tons of diesel fuel,
50 tons of residual oil of flash point 175°C. of a viscosity of 3.3°E./100°C. and pour point -15°C.
300 tons of residual oil of flash point 155°C., of a viscosity of 19°E./50°C. (a blending component in winter-grade Reichsbahn axle oil).

For the manufacture of Reichsbahn axle oils, Dollbergen took delivery of 400 tons/month of light spindle oil distillate (flash point 135°C., pour point <-30°C.) from the gasoline plant at Emmerich. Of this quantity, 180 tons were directly blended with 300 tons of residue oil from the paraffinic Nienhagen crude to give the finished Reichsbahn winter-grade axle oil. The remainder of the spindle oil, (220 tons/month) was concentrated to give 150 tons of spindle oil, distillate with a flash point of 158 °C. and as distillate 70 tons of diesel fuel. The 150 tons of concentrated spindle oil with a flash point of 158°C. gave, when blended with the 350 tons of residue oil from Nienhagen paraffinic crude, 500 tons of Reichsbahn summer grade axle oil.

When excess axle oil (of both grades) was available it was disposed of to other purchasers as black lubricating oil. Thus the total production at Dollbergen in peace time and up to August 1944 was:-

Straight run benzine	220	tons/month
Kerosene	300	"
Diesel fuel	1050	"
Cleaning oil raffinate	50	"
Spindle oil raffinate	150	"
Engine oils	1000	"
Black oil	200	"

Reichsbahn axle oil winter-grade	480	tons/month.
" " " summer-grade	500	"
Blown bitumen	580	"
Dark, crude paraffin wax	140	"
Fuel oil (for own consumption)	380	"
Total losses	250	" = 4.7% by wt.
	5300	tons/month

This was derived from the following feed stocks:-

Nienhagen crude	4700	tons/month
Light spindle oil dist. ex Emmerich	400	"
Deurag gas oil	200	"
	5300	tons/month

The analytical data for the engine oils prepared at Dollbergen were as follows:-

Flash point - 205 to 225°C. according to viscosity.
1st Grade - Viscosity Index 77.78 (Dean and Davis) corresponding to a pole height of about 2.2
2nd Grade - Viscosity Index ca.70 (Dean and Davis) pole height about 2.3
Pour point - -12 to -14°C.
Conradson carbon residue - 0.7 to 1.5% according to viscosity
Ageing test (M.A.N., involving the maintaining of 50 gm. of oil in a 100 ml. beaker at 150°C. for 144 hours in the drying oven) - free from asphalt
Acid value - below 0,1
Saponification value - ca. 0.2
Ash - Traces.

As the war went on, separation of the engine oils produced into the two grades was dropped, so that in the vacuum stage, the pipe still topping residue and acid oil residue were distilled together to give a uniform lubricating oil distillate. 1000 tons (approx.) of engine oil were produced in this way, with a viscosity index of about 76 (Dean and Davis) and a pole height of 2.25

On 5.8.44 the Dollbergen refinery was extensively damaged by air attacks and further dewaxing and low temperature acid treatment was impossible. for the rest of the war the sole refining activity at Dollbergen was the topping of crude oil to produce light distillate.

A blending plant installed at Dollbergen made possible the manufacture of a series of special lubricating oils from their own oils together with those from other makers as well as with chemical additives. These special products are dealt with in the answers to Questionnaires 2 and 3.

Emmerich Refinery.

The plant at Emmerich-on-Rhine was erected specially for the processing of asphaltic base crude oils. Thus it produced mainly bitumens with a range of melting points down to 70° "K.S." The plant was originally constructed in the years 1922 - 1924 and was of the Bormann type, working at atmospheric pressure and solely with steam. Over a period of years it was improved and adapted so as to handle the particular crudes in use at the time. Originally, topped Panuco crude was ~~processed~~ giving a yield of 60% bitumen and later, topped Venezuelan oil (thick fuel) with a yield of 35 - 50% bitumen according to the melting point. From 1937 onwards, untopped Venezuelan crude was handled after a modern Heckmann topping column with a capacity of 200-220 tons/day had been installed. During the war, the plant was converted to work first with German asphaltic or mixed base crudes from the Reitbrook and Rodewald fields, then with Rumanian paraffin-deficient Pacura or untopped Rumanian crude and finally with asphaltic base oils from the Vienna basin (van Sickle-Sarmat).

Since lubricating oils with a high naphthonic acid content were produced by simple distillation of asphaltic crudes, Emmerich ran a distillation plant where these primary lubricating oil distillates were redistilled with lime to give naphthenic-acid-free oils and a residue (containing lime) used as a works fuel oil.

Further processing of the light oils and of the light and heavy lubricating oils produced followed the usual lines, refining being carried out with sulphuric acid, caustic soda solution or fullers earth and lime being used as neutralisers. The acid resins produced were made pumpable by mixing with hard coal tar oils and burned as fuel oil in burners of normal design.

Besides the bitumen production mentioned, the Emmerich works made lubricating oil distillates and raffinates of the normal type, some with low pour points (especially spindle oils). All the oils had low viscosity indexes and high pole heights corresponding to their aromatic nature. The manufacture of a few special oils is dealt with in answers to Questionnaires 2 and 3. Emmerich possessed a modern grease plant, the products of which are described in the answers to Questionnaires 2 and 3 as far as possible in the absence of the appropriate documents (now mostly at Mieste/Altmark in the Russian zone). The works were badly damaged during fighting in the neighbourhood.

Korneuburg Refinery.

The Korneuburg works (near Vienna) consisted of a distillation plant working at atmospheric pressure and in peace time prepared auto fuels, kerosene and recovered

Pacura from a so-called "Kunstöl" of Rumanian origin. This was an artificial mixture of straight run benzine, petroleum distilate and paraffin-deficient Pacura, all of Rumanian origin. The composition of this blend was such as to avoid difficulties as regards duty.

There was also a discontinuous, vacuum distillation plant, rather smaller in size, for processing the Pacura to give lubricating oil distillates and a certain amount of residual bitumen. Further, Korneuburg possessed a simple chemical refining plant for treating the lubricating oil distillates by means of acid, alkali or fullers earth to produce normal lubricating oil raffinates. No details of capacity or performance are available at present.

ANSWERS TO QUESTIONNAIRES

LUBRICANTS

A. Aviation.

Aviation oils were not made in the Deutsche Gasoline works.

B. Automotive.

These were made principally at the Dollbergen works.

Question 1. To what specifications are lubricants for petrol engines and high speed diesel engines produced, and what relative importance is assigned to the various properties?

2. What are the chief sources of motor oils? What crudes are used, what refining methods and to what extent are synthetic oils incorporated?

Answer. These questions have already been answered in part in the previous section of this report.

The method evolved for the Dollbergen plant for processing Nienhagen paraffinic crude combined two basic conclusions reached by the Deutsche Gasoline both in dealing with purchasers and in numerous observations on its own vehicles. These were :-

(a) Every automotive oil should have a minimum content of typical bright stock, i.e. should contain a refined crude oil residue. Raffinates of the same viscosity obtained from lubricating oil distillates have not the same effect in the engine.

(b) It is of minor importance if a small residue of soft wax is left after dewaxing a paraffinic crude. On the other hand, to avoid starting trouble it is absolutely essential to remove all the crystalline hard wax.

Both requirements were fulfilled concurrently by the refining process in use at the Dollbergen works and coincided with the production of a maximum amount of automotive lubricating oil.

The viscosity index attained by the process is sufficient for engine lubrication, provided that climatic conditions and demands made on the engine were not too severe. The introduction of a typical solvent extraction process to obtain engine oils of higher viscosity index thus did not appear necessary at the time of the Gasolin A.G.

Synthetic oils were not generally blended with engine oils, except when producing especially low cold test and easy starting winter oils for the Army, corresponding to their requirements. By order of the Army a "Wehrmacht Winterol" was produced after the winter of 1941-2, consisting of 40% synthetic oil delivered from Ruhrchemie Holten, 40% of Dollbergen engine oil 20% of neutral oil from Deurag-Nerag Misburg. This oil had such a flat viscosity/temperature curve, that while the viscosity was about 5°E./50°, it was still 1.71°E./100°, corresponding to a pole height of 1.85-1.88. According to army sources, it had satisfactory starting behaviour in the extreme cold of subsequent winter campaigns.

Question 3. Are engine tests carried out before approval, and if so, what are they?

Answer. We did not engine test our own products.

Question 4. What laboratory oxidation tests, or sludge tests are used and how do they Corrrelate with performance in an engine?

Answer We used solely the so-called M.A.N. test in our laboratories as a regular oxidation test. This consists of heating for 144 test hours, 50 g. of the oil in a 100 mls. beaker which is placed in a drying oven heated to 155°C. After the test period, the sample must be free from sludge and on dilution with 20 times its volume of normal benzine must show, at the most, only traces of asphaltic compounds. All Dollbergen produced engine oils passed this test satisfactorily. Other oxidation tests mentioned in the literature were tried out in the Laboratory but no positive correlation between results and running behaviour in our own vehicles could be obtained.

Question 5. To what extent is Voltol used in motor oils? Is it more commonly used in motor oils that aviation oils and if so why? what particular advantages in engine cleanliness, viscosity index, etc., have been found with Voltol?

Question 6.	Are detergents other than Voltol used in (a) Petrol Engines? (b) Diesel Engines?
Answer.	No additions of Voltol or detergents were made by the Gasolin A.G.
Question 7.	Is trouble experienced with ring sticking in diesel engines and if so what palliatives are used?
Answer.	Ring sticking trouble in diesel engines was rarely experienced with the auto oils of Dollbergen manufacture.
Question 8.	What type of filters are used in mechanically propelled vehicles? If chemical type filters are used, is any trouble experienced with them?
Answer.	No information is available.
Question 9.	What mileage is normally recommended between sump drainings?
Answer.	Oil change was generally recommended after a running time of 2500 km. This was because it was thought that the oils would not stand up to longer running and also because experience had shown that after this running time, an appreciable amount of contamination of the engine oil occurred due to fuel soot, oil dilution and mechanical impurities.
Question 10.	What inspections are carried out on used oils and how do the various types of oil compare on used oil condition?

Answer.	Samples of used oil were tested in our laboratories with respect to change of viscosity; contamination by soot and ageing compounds as well as by dust and metallic particles; change in acid and saponification values.
Question 11.	What additives are used as pour point depressors, V.I. improvers, anti-oxidants, anti-wear additives, anti-corrosion additives and film strength improvers?
Answer	Paraflow, supplied by D.A.P.G. and made by I.G. Ludwigshafen, was used in all Gasolin A.G. engine oils as a cold test improver. To improve viscosity index, the only additive used was up to 0.7% (corresponding to 3.5% Oppanol B.15) of pure Oppanol and this was blended with summer engine oils delivered to the army in accordance with service requirements. Other additives were not used.
Question 12.	To what extent are fatty oils used in m motor lubricants? What kind of fatty oils are used and what advantages have they?
Answer.	In peace time, Deutsche Gasolin manufactured small quantities of a two stroke oil and blended with fatty oil the so-called "Motanol R". The fatty oil used was 2.5% of acid-free tea seed oil. This oil was satisfactory in D.K.W. engines and no significant complaints were received from users.
Question 13.	Were any lubrication difficulties experienced with producer gas equipment (both wood and coal type), bottled gas or acetylene driven vehicles?

Answer. During the development of the numerous generator vehicles using wood-charcoal, wood and coke generators, trouble was caused at first by a considerable degree of engine oil contamination. This was due to the unsatisfactory nature of the gas scrubbing apparatus between the generator and the engine, which did not completely remove pulverised ash. As design improved, such difficulties were so far overcome, that engine oils used with these vehicles had the same life period of 2500 running km. without excessive contamination. Vehicles driven by bottled gas gave more especially good results as regards contamination of and change of the oil charge. It is not known to what extent acetylene powered vehicles used Deutsche Gasolin lubricating oils.

C. Marine.

Question 1. What lubricating oils were specified for use with marine diesel equipment.

Answer. The navy was supplied both before and during the war with Dollbergen engine oils for use with diesel engines. Because of the special requirements of the naval centres, these oils contained two additives as follows:-

(a) 0.03% of Dismulgen 8 to increase emulsion resistance. Whereas all engine oils prepared at Dollbergen were very stable towards distilled water in this respect, slight emulsification occurred with sea water. The addition mentioned above removed this trouble to the satisfaction of the naval authorities.

(b) As a result of the Dollbergen refining process, the engine oil contained traces of sulphonic acids, the quantity being too small to demonstrate analytically. The corrosion test used by the navy consisted of spraying the sample at 80°C. with a small addition of distilled water for several hours against a polished steel plate of ordinary carbon steel. A normal oil delivery pump was used for spraying. In this test the Dollbergen engine oils made in the usual way, caused a minute amount of corrosion of the steel plate. This was avoided by dissolving 0.03% of triethanolamine in the oil.

Question 2. What oils are used in steam turbine driven vessels? Are additives of any kind incorporated (anti-corrosion etc.)?

Answer. The Deutsche Gasolin A.G. manufactured small amounts of an ordinary lubricating oil for turbine lubrication, to which had been added 0.03% Dismulgen and 0.03% triethanolamine as is usual with marine oils. This oil was used for small auxiliary steam turbines with an output up to about 100 KW. The running time before oil change is not known in this case but the same oil was used for years in a 650 KW turbine supplying electricity to the Dollbergen works, with a running time of 2000-3000 working hours without any observable ill-effects. At the end of this period it was noticed that the formation of an oil water emulsion would commence, combined with an appreciable increase in saponification value. The oil was therefore changed regularly at the end of this period.

Question 3. To what extent are compounded cylinder oils used and what are the compounding agents employed?

4. To what specifications are stern tube greases manufactured, and what compounding agents employed?

5. For what uses are aqueous emulsions of oil, with the addition of montan wax employed?

Answer. Such oils were not delivered to the Navy by the Deutsche Gasolim A.G.

D. Transmission.

Question 1. What lubricants are recommended and specified for tank gear boxes and car and truck gear boxes of normal and synchromesh types?

2. To what extent are Voltolised oils and compounded oils used for tank gear boxes? What compounding agents are employed?

3. To what extent are additives of the nitrogen type, chlorine type, etc., used in oils for gear boxes?

4. In what proportion are straight tooth, spiral bevel, Hypoid and worm gears used in rear axles and what oils are specified in each type?

Question 5. What additives are used in extreme pressure oils?

6. To what extent are compounded oils (fatty oil compounded) used for rear axle lubrication?

7. What type of oil seals are used?

8. What temperature extremes are encountered in the different types of axle?

Answer. In peace time the Deutsche Gasolin A.G. prepared 3 types of gear oil :-

(a) "Motanol" gear oil (Winter) with a viscosity of 16°E./50° and 2.8°E./100°C.

(b) "Motanol" gear oil (Summer) with a viscosity of 4.2°E./100°C.

(c) A dark gear oil with a viscosity of 3.3°E./100°C.

While the two varieties of Motanol gear oil were based on correspondingly viscous Dollbergen engine oils the dark gear oil consisted simply of a residual oil obtained by topping Nienhagen crude of low paraffinic content. All three types contained 2% sulphurized rape oil to give E.P. properties (10% of sulphur was incorporated in the rape oil at 150°C.). In the four ball machine developed by the Shell Company, the pressure value shown by all these types was about 220 kg.

During the war, a special gear oil was manufactured at the request of the Army. This oil had a specially good cold test and an increased four-ball machine value of 240 kg. It was based on a blend of 10% Ruhrchemie Holten synthetic oil, 10% of a light, low cold test spindle oil raffinate prepared in our own works at Emmerich, 30% of Dollbergen engine oil with a viscosity of 6.5°E./50°C. and 50% of neutral oil delivered from Nerag, Misburg.

By blending this mixture with 5% Oppanol B.15 an oil with a viscosity of 8°E. and improved viscosity index resulted. 0.4% Paraflow was next added, as well as 1% Etrol C (for E.P.performance) from the Vacuum Oil A.G. Later, the addition of Oppanol was dropped, since it was reported that it soon lost its activity when the oil was used in heavy tank gearing. The oil was then delivered with a viscosity of 6°E., but was otherwise of the same composition as before. The Army specification called for a viscosity curve which, on exterpolation (using the Walther formula), did not exceed 3500°E. at -40°. This requirement was amply covered with the formula cited. Samples of Gasolin A.G. oil were continually tested for pumpability at low temperatures in a special apparatus developed by Rhenania-Ossag for the "Heereswaffenamt" and used for testing in their Harburg laboratory.

We have no information as to the various kinds of gearing, etc., in which oils delivered by us were used.

E. Hydraulic, Recoil and Buffer Oils.

Question 1. To what extent are pure mineral oils used for this purpose? What specifications apply with particular reference to V.I. pour point, etc.? From what crudes are they made and by what refining methods?

Answer. We supplied pure, light, lubricating oil raffinates for hydraulic purposes. They had a good oxidation test and were prepared using spindle oil raffinates available at Dollbergen. To some extent, ordinary Dollbergen engine oil with a viscosity of 6.5°E. / 50° was used for the same purpose.

In plants using special metal working oils supplied by the Deutsche Gasolin A.G. machines needing hydraulic oil were filled with the same oils.

Question 2. To what extent are non-mineral oils used for this purpose? How much castor oil is used for this purpose?

3. What solvents such as diacetone alcohol methyl carbinol, etc, are used?

4. To what extent are water and glycerol used in hydraulic fluids.

5. What work has been done on non-inflammable hydraulic oils?

6. What oil seals are used and has any trouble been experienced as a result of interaction between seals and fluids.

7. To what extent are compounded mineral oils used and why?

Answer. No information is available.

F. Railroad Lubricants.

Question 1. What oils are used for steam cylinder lubrication (satd. and superheat) valves, axle boxes, etc., and what compounding agents are used and why?

Answer.	As a consequence of the type of process used at Dollbergen, hot steam cylinder oils were not manufactured. Saturated steam cylinder oils were supplied to a limited extent. They were made by concentrating Nienhagen north field oil to give a residue with a flash point above 260°C. This oil was also delivered in part, to the "Reichsbahn". The manifacture of Reichsbahn axle oils has already been described, it was an important branch of Dollbergen production.
Question.2.	What type of crudes are preferred for this purpose? What asphaltone content is usual in such oils?
Answer.	An asphalt content below 0.3% is required by the Reichsbahn. The difficulty of obtaining a sufficient quantity of low pour point spindle oil distillate as a blending component of axle oil led to a relaxation, towards the end of the war, in the Reichsbahn specifications as regards the cold test of winter axle oil. In peace time, flow was required at -20oC. in a 6 mm. U-tube, this was amended to -15°C. in the last winter of the war.
Question 3.	Are any special oils used in the lubrication of diesel locomotives and what additives if any, are employed?
Answer.	A special light lubricating oil raffinate was supplied with a viscosity of 4°E./20° and 1.7°E./50° for filling the fluid drives incorporated in Reichsbahn diesel engines.

G. Industrial Oils.

Question 1.	What types of oil are used in steam turbine lubrication? Are any troubles experienced with corrosion or emulsification and if so, how are they combatted? What additives are used, if any? What is the average life of a steam turbine oil?
Answer.	As regards steam turbine lubrication, see section C.2.
Question 2.	What types of oils are used for transformers? What electrical tests, if any, are carried out? Are any additives employed?
Answer.	Transformer oils were not made in our own works.
Question 3.	To what extent are mineral, non-mineral, compounded oils, and aqueous emulsions used in quenching? What types are preferred for small and large objects?
Answer.	Pure mineral oils were supplied with correspondingly graded viscosities for quenching small objects (low viscosity) and larger objects (higher viscosity) Corresponding to their viscosity, such oils had as high flash points as possible. When necessary, this was attained by blowing off small quantities of light ends in the blower distillation plant at the Emmerich works.
Question 4.	What types of cutting oils are used? To what extent are sulphurised and compounded oils used? Are corrosion inhibitors added and if so, what are they?

Answer. Mineral oils of various viscosities were prepared and blended with chemical additives to increase cutting performance, for use as cutting oils and metal working oils. They were delivered under the designation "K" series. The chemicals added were:-

(a) tricresylphosphate and
(b) carbon tetrachloride.

No anti corrosion additives were used.

Question 5. What types of slushing oils are used? What additives are employed to give anti-corrosion properties?

Answer. Gasolin A.G. Supplied a light spindle oil raffinate for this purpose.

Question 6. From what sources are textile oils refined? What research has been done on carcogenicity?

Answer. The Emmerich works prepared a textile oil consisting of about 95% of well refined, light spindle oil or light machine oil, blended with about 5% of liquid sodium soap. This oil could be washed out with soda solution.

No research was carried out on skin disease.

Question 7. What oils are used for clock and instrument lubrication, especially for aviation use? What compounding agents are used?

Answer. These were not manufactured.

Question 8. What is "Radiol" and for what uses is it employed?

Answer. This material is unknown.

Question 9. What is the composition of compounded light machine oils?

Answer. No information is available.

H. Greases.

Question 1. To what extent are barium lithium and aluminium soap greases used?

Answer. Sodium Aluminate was used to a small extent for saponification in the preparation of gear greases. Barium and lithium soaps were not used.

Question 2. In peace time, preferential use was made of fatty acids from the margarine industry as raw material at the Emmerich grease works. Thus fatty acids, from soya, coconut, pea-nut and sunflower oil, were used. Later, waxes were utilised.

Question 3. To what extent are waxes, especially montan wax used in grease manufacture?

Answer. As vegetable and animal fatty acids as well as those from the initial and final distillation in the wax oxidation process became scarcer, all formulae was altered so as to be based on the use of crude montan wax, refined montan was from the Reitbrook works and I.G. waxes. In particular a new standard army chassis grease formula was evolved using solely I.G. waxes, types O. and S. Special methods of mixing and incorporating (rollers and hydraulic grease presses) gave the product an extraordinary degree of smoothness and homogeneity. Saponification was by means of caustic soda lye; the sodium soaps of montan wax are especially water resistant, which was a special requirement for army service.

Question 4. What types of greases are used for high temperature applications?

Answer. Greases of the "Monsapol" and "Monsapol extra" were marketed for high temperature use by Gasolin A.G. Such products were also based on I.G. waxes. They had very good temperature stability together with good spreading power and water repellent properties.

Question 5. For what reason and to what extent are greases used in shock absorbers for aeroplane landing gear?

6. What material is employed for ship launching purposes?

Answer. No information is available.

I. General.

Question 1. To what extent are aqueous emulsions used in industrial lubrication?

2. Has this type of lubricant ever been employed in engines of any types?

3. By what processes is Voltol made?

Answer. No information is available.

SPECIAL PRODUCTS

A. Bitumens

Question 1. To what extent are bitumens of petroleum origin used in road construction and to what extent are hot application, cut-back and bituminous emulsion application used?

2. What advances, if any, have been made in bitumen emulsion manufacture, and what crude sources are preferred for this purpose?

3. Are emulsions of any other pitch residues used for any purpose?

4. What work has been done on soil stabilisation, and to what extent has this process been used for airfield runways, etc.? What types of emulsion had been found most suitable and how are they made?

5. To what extent are bitumens and other residues used for :-

(a) Paper impregnation?
(b) Roofing?
(c) Insulating?
(d) Paint applications?

What fillers if any are used?

Answer. The mineral oil bitumen produced at Emmerich was transferred to special bitumen works but it is not known how this material was processed for used in road construction, as 'hot' bitumen, cut-back and bitumen emulsions. For the same reasons answers to questions 2 to 5 are not available.

The paraffin wax containing bitumens (blown) made at Dollbergen were sent to works which converted them into building material cable filling mastic, accumulator mastic and tube insulation.

Varieties with the highest melting points (ca. 120° "K.S.") were also used in making printing colours.

No details of the processes used are available.

B. Extracts and Polymers

Question 1. Are lubricating oil extracts produced by either acid treatment or solvent extraction being used as substitutes for :-

(a) Linseed oil in paints and putties?
(b) Plasticisers in rubbers and P.V.C. compositions?

Are they being used for any other purposes? What are the user requirements?

2. To what use are the phenol extracts from solvent extraction or lubricating oils put?

3. How are olefine polymers such as those of ethylene, propylene and particularly of butenes and butadiene being utilised?

4. To what extent are polymers being used in the manufacture of lubricants?

Answer. These materials were not produced in the Deutsche Gasolin A.G. refineries.

C. Waxes

Question 1. To what uses are waxes produced from petroleum, brown coal oils and Fischer Tropsch processes, being applied, and what particular properties are demanded by the user?

2. What types of waxes (with specifications) are used in candle manufacture, paper impregnation, insulating, etc?

3. To what extent is slack wax from solvent dewaxing processed into a usable wax and how is this done? What proportion is used as a cracking stock?

4. What results have been obtained with the use of montan wax and synthetic substitutes in grease manufacture?

5. What work has been done on micro-crystalline waxes?

Answer. The crude paraffin made at Dollbergen was used to a ssmall extent in the unrefined black state as technical vasoline. The main bulk was shipped to Misburg for use in the Deurag cracking plant or to Leuna or the I.G. Ludwigshafen plant.

D. Rust Preventatives

Question 1. What rust preventatives of the solvent type, suitable for spray application are used and what is their composition, with particular reference to corrosion inhibitors?

Question 2. What corrosion preventatives of the petrolatum type for brush or swab application, of the transparent hard drying type and of the permanent aluminium paint type are used? Are any special additives used? What solvents are employed?

3. Are "fly-away" corrosion preventative oils used and what is their composition?

4. Have any special compounds been produced to combat cold corrosion in stored engines?

5. Are any corrosion preventative additives manufactured for addition to turbine oils, transformer oils etc.?

Answer. Such oils were not manufactured by Deutsche Gasolin A.G.

E. Coolants and De-icing Fluids

Question 1. What coolants are used in automotive engines, both for normal operation and low temperature and in aviation engines? Are corrosion inhibitors added? Are soluble oil emulsions ever employed?

2. What fluids or compounds have been developed for de-icing or aircraft and what additives are used? For what purposes are lithium and potassium soaps added to these compounds.

Answer. The Deutsche Gasolin A.G. marketed the anti-freeze liquid "Glysantin" made by I.G.

F. Miscellaneous

Question 1. Have detergents of the ester salts type been developed and how are they made?

2. What developments have been made in products used for pest control?

Answer. No information is available.

INDUSTRIAL LUBRICANTS

A. Turbine Oils.

Question 1. What type of oil has been used for this purpose and from what raw materials?

2. What changes have been made in this type of product during the War and for what reason?

3. What imhibitors and/or additives have been used in these oils?

4. What troubles have been experienced in their use?

5. What length of service has been common without oil change and what limits in deterioration are allowed before an oil change is considered necessary?

6. What specifications exist for these oils?

Answer. See section C. Marine. No war time changes were made.

B. Railway Oils

Steam Cylinder Oils.

Question 1. What oils have been used for this purpose?

2. What changes have been made in quality during the war and for what reason?

3. What troubles were experienced in the use of these oils?

4. What specifications exist covering these types of oil?

5. What inhibitors and/or additives have been used in these products?

Axle Oils or Greases

Question 1. What products have been used for this purpose?

2. What specifications have been used covering these products?

3. What changes have been made in these products during the war and for what reason?

4. What troubles were experienced in the use of these oils and greases?

5. What additives have been used in these products?

Railway Diesel Oils

Question 1. What oils and fuels have been used for this purpose?

Question 2. To what specifications were they manufactured?

3. What changes in quality have occurred during the war?

4. What troubles were experienced in their use?

5. Have additives been used in these products such as ignition promoters in the fuel and detergents in the oil?

6. What operating times were common between oil drainage periods? Were these influenced by the quality of the products?

Answer. See section F. Railway Lubricants.

C. Cutting Oils.

Neat Cutting Oils

Question 1. What types of products (with formulae) have been used for this work showing the different types used for different machining operations on different types of metal, including non-ferrous?

2. Were these made to specification and if so, what?

3. What changes have been made during the war either voluntarily or due to lack of the required raw materials?

4. Were these materials satisfactory or could they have been improved?

Question 5. Were sulphur, phosphorous and chlorine additives used in these products as well as fatty oils?.

6. Have substitutes been employed for fatty oils?

7. Were any troubles encountered in their use?

Answer. The following products were made as cutting oils in peace time as well as during the war.

(a) Special Oil K, 3.5/50° containing 1.75% tricresylphosphate.
(b) Special Oil KL, 3.5/50° containing 0.4% tricresylphosphate and 3.0% carbon totrachloride.
(c) Special Oil DK30S, 2.0/50° containing 3.25% tricresylphosphate.
(d) Special Oil KL20/50, 7/50° containing 3.5% tricresylphosphate and 5.5% carbon totrachloride.

The basic oils used in peace time and up to 1942 were fully extracted lubricating oil raffinates, predominantly from the Emmerich works. After 1942, orders were issued from the 'Reichstelle' concerned, that lubricating oil distillates were to be used for reasons of economy but this change had no effect from the viewpoint of metal working oil. It was no longer possible, however, simultaneously to use the 'K' series of oils for hydraulic purposes, as had been done in peace time.

The choice of cutting oil depends on the nature and tensile strength of the metal being worked (e.g. alloys) as well as on the speed of cutting desired. As the latter increases so must the oil viscosity decrease. Special mention should be made of soft (lubricating) metals, which behave better with KL independant of the speed of cutting. This is due to the additives in the KL. It may be added that special oil K is also suitable for working with Elektron.

D. Soluble Oils.

Question 1. Show, with formulae, the changes made in these products during the war?

2. Were they used to a greater extent than prewar as a measure of economy?

3. Did the shortage of petroleum sulphonate greatly affect the properties of these products?

4. What troubles were experienced in their use?

5. Were these products made to company or outside specifications, give details of these?

6. What additives were used to impart outstanding qualities such as E.P., anti-rust, anti-foaming etc.?

7. Indicate what operations they were used on and for what metals?

Answer. Before the war, various types of soluble cutting oils were made by the Deutsche Gasolin A. G. and comprised raffinates with soaps (olein, resin and tallow oil) as well as naphthenic and sulphonic soaps together with small quantities of spirit.

The saponifiable materials were purchased but in the course of the war naphthenic soaps were prepared from a refinery by-product. Except for oil containing resin and naphthenic soaps, the other types were discontinued during the war because of lack of raw saponifiable material. With war time products, the same guarantee as before for stability of emulsion and anti-rust properties could not be given.

In 1944 orders were given to manufacture the emulsifying cutting oil 10950 by adding Dollbergen spindle oil to the soluble oil "Mittel H8" produced by I.G.

The use of this soluble cutting oil was compulsory with all metals and with almost all methods of working. Consumers endeavoured to alter cutting speed or the cutting angle of the tools so as to suit the new properties of the oil.

E. Metal and Wire Drawing Oils

Question 1. What materials were used for this purpose?

2. To what specifications were they manufactured?

3. What changes have been made during the war and why have they been made?

Question 4. Were any special materials developed for deep drawing?

5. What troubles have been experienced?

6. What additives have been used and why?

7. What products were used for this purpose for the different types of wire?

8. What were the specifications?

9. What changes were made during the war?

10. What troubles were encountered in their use?

11. What additives were used in these products to impart special properties?

Answer. Whereas before the war, highly fatted mineral oils were used almost exclusively for metal drawing, towards the end of the war the "K" series of oils given above were also used for this purpose.

For wire drawing it was sufficient to use strong aqueous solutions of soluble oils.

F. Rolling Oils

Question 1. What products, with formulae, were used for metal rolling and for the different types of metal?

2. What specifications existed for this type of product?

Question 3. What changes have been made in these products during the war and for what reason?

4. Have these products always been satisfactory, and, if not, why not?

5. Have any additives been used in these products and for what purpose?

6. Were different products used according to the size of the part being quenched or was a different technique used?

Answer. No information is available.

G. Quenching Oils

Question 1. What were the types of product used and their mode of application?

2. To what specifications were they made?

3. What changes in their composition have been during the war and for what reason?

4. Have these products always been satisfactory, and, if not, why not?

5. Have any additives been used in these products and for what purpose?

6. Were different products used according to the size of the part being quenched or was a different technique used?

Answer. The change from raffinate to distillates was made with hardly any trouble. Raffinates were only supplied for particular polished hardening processes (Blankhärtevorgänge) when the minimum amount of ageing products was necessary in view of the subsequent method of processing.

H. Core Oils

Question 1. What products were used for this purpose?

2. To what specification were they made?

3. What changes have been made in their composition and the reason?

4. Was any trouble encountered in the use of substitute materials?

5. Were any additives used to impart special properties?

Answer. No information is available.

I. Rust Preventatives

Question 1. What products have been used for this purpose, indicating the application for each type of material?

2. Which of these were peculiar to your company?

3. To what specification were they made?

4. What changes have been made during the war giving the reason?

5. Did the use of substitute materials improve or degrade the properties?

Question 6. What troubles have been experienced in their use?

7. What special materials were added to give increased effectiveness?

Answer. No information is available.

J. Slushing Oils.

Question 1. To what extent were they used and what was the type of product?

2. What changes have been made during the war and for what reason?

3. What specification governed the type of product used?

4. What troubles were encountered in their use?

5. What additions were made to impart special properties?

Answers. No changes were made in slushing oils.

K. Ink Oils

Question 1. What products were used for this application and from what raw materials were they made?

2. What specifications existed governing this type of product?

3. What changes were made in their composition and for what reason?

Question 4. What troubles were experienced in their use?

5. What additions were made to give special properties, such as easy flow, easy wetting of the pigment, etc.?

6. To what extent were refining extracts such as those from solvent refining used and/or sludge from synthetic oil manufacture?

Textile Oils)
Leather Oils)
Cable Oils)
Marine Oils)
Refrigeration Oils)
Insulating Oils)

No information is available.

L. Specialities

Question 1. Have any <u>oils</u> been developed <u>for high temperature lubrication</u>? If so, describe them fully as outlined in the above question.

2. Describe the uses of <u>Wire Rope Lubricants</u>, their composition etc. Have refinery extracts found application in this field?

3. What oils have been used as <u>Mold Lubricants</u>? Describe their use, composition, etc., as outlined above.

4. What products have been used as <u>Air Tool Lubricants</u>? Describe their use, changes in composition as outlined in the above question.

Question 5. What type of products have been used as <u>General Machinery Oils</u> and <u>Black Oils</u>? Describe their use, composition, etc. To what extent have oils been replaced by emulsions in the former case and to what extent have solvent extracts been used in the latter?

Answer. 1 to 4 - No information is available.

5. "Black Oils" were based on mineral oil residues. They behaved well, as regards lubrication, in all cases except with directly heated bearings or those subjected to radiant heat. Such oils were also not used for circulation lubrication.

M. Greases

Question 1. What types of products have been used, with their compositions, for the following purposes?

(a) Ball and roller bearing greases, for high and low speed, high and low temperatures and for heavily loaded applications.
(b) General lubrication greases.
(c) Block greases for steel mills, paper machinery crushers, etc.
(d) Greases or oils for open gears.
(e) Greases for marine application.
(f) Any other types of greases.
(g) Extreme pressure greases.

2. With each of the above give the relevant specification.

Question 3. What changes have been made in composition during the war and for what reason?

4. What troubles have been experienced in their use?

5. What additions have been made for special purposes?

Answer. As already mentioned section H. Greases formulae for the manufacture of these materials are not available because documents relating thereto are in the Russian zone. Below are given the types used for the purposes mentioned :-

(a) Ball and roller bearings:- High and low velocities as well as high and low temperatures and heavy load - Motanol roller bearing grease.
(b) General Lubricating greases:- (see section H).
(c) Block greases:- were not made by the Deutsche Gasolin A.G.
(d) Greases or oils for open gears:- To give the necessary degree of adhesiveness with open spur gears a blend of topping residue was supplied and was thickened by the addition of soft bitumen and a lubricant of very high viscosity.

(e) Marine grease:- No information is available.
(f) E.P. greases:- No information is available.

N. Research and Development

No Fundamental research was carried out.

O. Control Tests

No methods were used other than the usual commercial ones, or those officially specified.

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BIOS Final Report No. 512
Item No. 30

SCHLAFHORST CHEMISCHE WERKE G.m.b.H.

HAMBURG - GERMANY

LUBRICANTS

Thomas, W. H., Withers, J.G.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H.M. STATIONERY OFFICE

SCHLAFHORST CHEMISCHE WERKE G.m.b.H.

HAMBURG - GERMANY

LUBRICANTS

October 2nd - 10th

Reported by:

W.H. Thomas, British, Ministry of Fuel and Power.

J.G. Withers, British, Ministry of Fuel and Power.

B.I.O.S. Target No.C30/408
Fuels and Lubricants

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

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Mr. J.G. Allen - U.S. Petroleum Administration for War.
Major W.H. Thomas - British, Ministry of Fuel and Power.
Mr. J.G. Withers - British, Ministry of Fuel and Power.

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ACKNOWLEDGEMENT

German translations involved in the preparation of this report were made by Mr. K.G.C. Kirkpatrick.

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1. SUMMARY.

The Schlafhorst Chemische Werke G.M.B.H. was a subsidiary of the Atlantic Refining Company of the United States with its factory (now destroyed) at Georgswärderdamm 1.-Hamburg.

Materials manufactured by this firm were mainly lubricants and included greases and metal working oils, nevertheless specialities such as anti-frothing agents and resin oils were also produced.

This report gives a limited amount of information on the preparation of the company's products, but accurate details are lacking owing to the destruction of technical records due to bombing attacks.

Most of the information obtained concerned cutting oils, soluble oils and greases and is presented in the form of answers to a questionnaire.

2. INTRODUCTION.

The information given in this report was obtained from Herr T. Nielsen, the Manager of Schlafhorst Chemische Werke, in the course of a visit (B.I.O.S. Trip No. 1248) to the Hamburg area during the period October 1st to 31st 1945. The purpose of the interrogation was to ascertain what were the war-time activities of this firm and to obtain production details of the various manufactured products.

3. GENERAL INFORMATION.

Eighty-six per cent of the capital of the Schlafhorst Chemische Werke (amounting to R.M. 150,000) is held by the Atlantic Refining Co. of Germany which in turn is owned entirely by the Atlantic Refining Co. of the United States (Philadelphia).

The firm was founded in 1889 for the manufacture of all kinds of lubricating greases, as well as metal working oils, anti-frothing media for the sugar and fermentation industries, oils for the ceramic industry and resin oils for the printing trade.

In July 1943 the factory at Georgswärderdamm 1 and 2 was completely destroyed by high explosive and incendiary bombs and in March 1945, the oil works belonging to the Schliemann Co. at Wilhelmsburg, 13 Kanalstrasse (which was being used as an alternative factory) were also totally destroyed. This led to the complete destruction of all documents, plans, notes, specifications, etc. on research work, etc., which had been carried out. Thus in answering the questionnaire reliance has had to be placed on the memory of the company's chemist Herr Zink. Production statistics are also no longer available.

With the exception of forming oils and anti-frothing media, none of the firm's products were delivered directly to the consumers but to factors and therefore there was no direct communication with the industries which utilised the products. For this reason no details are available of their behaviour with the various machines involved.

In general, materials were manufactured of consistent standard quality and were not required to conform to customers specifications. In the case of new products, wholesale firms would submit samples of competing greases whereupon the equivalents were prepared and delivered.

4. ANSWERS TO QUESTIONNAIRES.

A. Lubricating Oils

No lubricating oils were prepared or sold and thus no information is available with respect to :-

Marine Lubricants
Transmission Lubricants
Hydraulic Recoil and Buffer Oils
Railroad Lubricants.

B. Cutting Oils

Question.	What types of cutting oils are used? To what extent are sulphurised and compounded oils used? Are corrosion inhibitors added and if so, what are they?
Answer.	No observations were made with regard to the use of products delivered to buyers. Fatted and sulphurised cutting oils were prepared, without anti-rust additives.

C. Greases

Question 1. To what extent are barium, lithium and aluminium soap grease used?

Answer. Certain quantities of aluminium soap grease were prepared but there was only a very small demand for this material.

Question 2. What fats are used for greases and what substitutes have been employed?

Answer. The following is a list of greases and fatty acids which were prepared :-

- Train oil and train fatty acids
- Hard grease
- Ground nut fatty acids
- Rape oil fatty acids
- Soya fatty acids
- Wool grease and wool grease fatty acids
- Lanolin fatty acids
- Stearine, wool and oleo stearine
- Bone fatty acids
- Flaying grease
- Cracked fatty acids; mixed fatty acids
- Refined Montan Wax
- I.G. waxes
- Resin oils

and substitutes for the above were :-

- Synthetic fatty acids
- Crude montan wax
- Refined montan wax
- I.G. waxes.

Question 3. To what extent are waxes, especially montan wax used in grease manufacture?

Answer. As the natural fats became increasingly scarce, the use of the substitutes listed above increased. It is however impossible to give figures because of the destruction of all statistics.

Question 4. What types of grease are used for high temperature applications?

Answer. Hot bearing greases, sodium and potassium soap greases.

Question 5. For what reason and to what extent are greases used in shock absorbers for aeroplane landing gear?

Question 6. What material is employed for ship launching purposes?

Answer. Materials for these purposes were not prepared.

D. General

Question 1. To what extent are aqueous emulsions used in industrial lubricants?

Answer. Emulsifying greases were used on an increasing scale subsequent to 1943 but the extent thereof is not known.

Question 2. Has this type of lubricant ever been employed in an engine of any type?

Answer. It is unsuitable for pressure lubrication and since such materials were delivered direct to factors, no information on the use and behaviour of the greases is available.

Question 3. By what process is Voltol made?

Answer. Voltol was not manufactured.

E. Special Products

No information is available with respect to bitumen, extracts and polymers.

F. Waxes

Question. What results have been obtained with the use of montan wax and synthetic substitutes in grease manufacture?

Answer. Good quality greases were prepared using montan wax and its derivatives, typical of which were the standard Army chassis greases.

G. Industrial Lubricants

No information is available regarding turbine oils or railway oils.

Cutting Oils

Question 1. What types of products formerly have been used for this work showing the different types used for different machine operations on different types of metals including non-ferrous?

Answer. Fatted cutting oils, i.e. raffinates with a viscosity of 2-4.5°E. at 50°C. with additions of rape oil, lard oil and other fatty oils, from 1 - 30 per cent.

Sulphurised oils, i.e. raffinates of 2-4.5°E. at 50°C. with 1 - 2 per cent sulphur.

Fatted and sulphurised oils, i.e. raffinates of 2-4.5°E. at 50°C., with circa 1 per cent sulphur and 6 - 10 per cent fatted oils.

Question 2. Were these made to specification and if so, what?

Answer. No specification was employed.

Question 3. What changes have been made during the war either voluntarily or due to lack of required raw materials?

Answer. During the war, the availability of fatty oil was much reduced but the supply of sulphurised oils was increased.

Question 4. Were these materials satisfactory or could they have been improved?

Answer. Owing of lack of contact with consumers, this is not known.

Question 5. Were sulphur, phosphorous and chlorine additives used in these products as well as fatty oils?

Answer. No.

Question 6. Have substitutes been employed for fatty oils?

Answer. No.

Question 7. Were any troubles encountered in their use?

Answer. No information is available.

Soluble Oils

Question 1. Show, with formula, the changes made in these products during the war.

Answer. Naphthene sulphonic soaps were gradually replaced (up to about 75%) by ordinary naphthenic soaps as well as liquid resin, resin and fatty acids.

The quantities of saponifiable compounds were decreased, so that for example, instead of 20 per cent, only 9 per cent remained.

Boring oils were prepared from commercial emulsifying agents, the composition of which was similar to that given above. To a certain extent these emulsifying agents contained still greater quantities of naphthenic soaps. The following are forumulae for boring oils manufactured by Schlafhorst Chemische Werke.

No. 1613

ca.	50%	Naphthene sulphonic soap oil.
	48%	Spindle oil raffinate
	2%	Triethanolamine
	100%	and caustic potash solution up to an alkali number of 2.

The oil gives a colloidal solution and is capable of great dilution.

No. 2285

31%	Naphthene sulphonic soap oil.
60%	Spindle oil raffinate
6%	Resin
1.4%	Triethanolamine
1.4%	Caustic soda solution
1.2%	Water
100%	

Soluble to give a colloidal solution.

No. 2305

65%	No. 2285
35%	Spindle oil raffinate
100%	

Gives a white emulsion.

No. 2310

50%	No. 2285
50%	Water
100%	

Gives a colloidal solution.

V. II

720	parts spindle oil with 150 parts naphthene sulphonic soap
1225	parts spindle oil raffinate
25	parts Turkey Red oil
30	parts spirit

V. IIb

1454	parts spindle oil
130	parts liquid resin
280	parts spindle oil with 23% sulphonic soap
40	parts spirit
25	parts caustic potash solution 50°
ca. 30	parts water

Because of war conditions, naphthene sulphonic soap was replaced to an increasing extent by naphthenic acids and triethanolamine had to be omitted. In place of liquid resin, synthetic fatty acids were used.

Boring Oils from prepared emulsifying agents.

20 - 25%	emulsifying agent
1.5%	spirit

The remainder contains spindle oil, raffinate or distillate and caustic soda solution as required.

Question 2.	Whether used to greater extent than pre-war as a measure of economy?
Answer.	No numerical data on this point are available.

Question 3. Did the shortage of petroleum sulphonates greatly affect the properties of these products?

Answer. Yes, colloidal solubility became poorer and the amount of free alkali in the oil had to be decreased.

Question 4. What trouble is experienced in their use?

5. Were these products made to Company or outside specifications?- give details of these.

6. What additives were used to impart outstanding qualities, such as, E.P., anti-rust, anti-foaming etc?

7. Indicate what operations they were used on and for what metals.

Answer. No answer can be given.

Drawing Oils
Rolling Oils
Quenching Oils
Core Oils.

These products were not manufactured by us.

Rust Preventatives

Question 1. What products have been used for this purpose, indicating the application for each type of material?

Answer. Anti-rust vaselines

50% Crude paraffin
50% Spindle oil
or
15% Crude paraffin
15% Ozokerite
70% Spindle oil.

Question 2. Which of these were peculiar to your Company?

Answer. Both products were prepared in approximately equal quantities.

Question 3. To what specification were they made?

Answer. None in particular.

Question 4. What changes have been made during the war? Give the reason.

Answer. In place of Ozokerite, the hard wax produced in the Fischer synthesis was used.

Question 5. Did the use of substitute materials improve or degrade the properties?

6. What troubles have been experienced in their use?

7. What special materials were added to give increased effectiveness?

Answer. No answer can be given to these questions.

Slushing Oils
Ink Oils
Textile Oils
Leather Oils
Cable Oils
Marine Oils
Refrigeration Oils
Insulating Oils

These products were not made by Schlafhorst Chemische Werke.

Specialities

Question 1. Have any oils been developed for high temperature lubrication? If so, describe them fully as outlined in the above question.

Answer. Not manufactured by Schlafhorst Chemische Werke.

Question 2. Describe the uses of Wire Rope Lubricants, their composition etc. Have refinery extracts found application in this field?

Answer. Not manufactured by Schlafhorst Chemische Werke.

Question 3. What oils have been used as Mold Lubricants? Describe their use, composition etc., as outlined above.

Answer. Moulding oils for the manufacture of electro-porcelains, flower pots, etc.

Composition:
30 - 32% Gas oil
30 - 32% Petroleum
30 - 32% Paraffin oil
10 - 4% Fatty acid

Question 4. What products have been used as Air Tool Lubricants? Describe their use, changes in composition as outlined in the above question.

Answer. Not made by Schlafhorst Chemische Werke.

Question 5. What type of products have been used as General Machinery Oils and Black Oils? Describe their use, composition, etc. To what extent have oils been replaced by emulsions in the former case and to what extent have solvent extracts been used in the latter?

Answer. Not made by Schlafhorst Chemische Werke.

Greases

Question 1. What type of products have been used, with their compositions, for the following purposes?

(a) Ball and roller bearing greases, for high and low speed, high and low temperature and for heavily loaded applications.
(b) General lubrication greases.
(c) Block greases for steel mills, paper machinery crushers, etc.
(d) Greases or oils for open gears.
(e) Greases for marine applications.
(f) Any other types of greases.
(g) Extreme pressure greases.

Answer. Ball and Roller Bearing Greases

No. 2237

10% Stearine
6% Rape oil
84% Raffinate 4.5 - 6.5°E. at 50°C.
100%

Saponified with caustic soda.

No. 1651

10%	Stearine
6%	Soya fatty acid
4%	Wool wax
80%	Raffinate 6.5°E. at 50°C.
100%	

saponified with caustic soda.

No. 2674

11%	Wool Stearine
2%	I.G. wax S.
87%	Raffinate 6.5°E. at 50°C.
100%	

saponified with caustic soda.

No. 2850

6.87%	I.G. wax S.
1.8%	P.H. wax
1.25%	I.G. wax E.
90.08%	Raffinate 4.5°E. at 50°C.
100.00%	

saponified with caustic soda.

Standard Chassis Grease

No. 2200

878	parts	Raffinate 4.5-6.5°E. at 50°C.
106	"	Refined montan wax
6.6	"	Wool wax
14.6	"	Wool Stearine
13	"	Oleo Stearine
8	"	I.G. wax S.
2	"	Lime

saponified with caustic soda.

No. 2760

7%	Refined montan wax
6%	Stearine
87%	Raffinate 6.5°E. at 50°C.
100%	

saponified with caustic soda.

No. 2900

8% I.G. wax S.
92% Raffinate 4.5°E. at 50°C.
100%

saponified with caustic soda.

or 6% I.G. wax S.
3% " " E.
91% Raffinate 4.5°E. at 50°C.
100%

saponified with caustic soda.

or 5.4% I.G. wax S.
2.7% Refined montan wax
91.9% Raffinate 4.5°E. at 50°C.
100.0%

saponified with caustic soda.

Lime Greases

12-20% Fatty acid in mineral oil saponified with lime.

Aluminium Greases

15-20% Aluminium stearate dissolved in raffinate.

Truck Greases

12-15% Resin oil in oil saponified with lime.

Spraying Greases

Lime or truck greases diluted with mineral oil.

Emulsifying Greases

140 parts crude montan wax
80 " P.H. wax from I.G.
1500 " dark residue oil
saponified with caustic soda,
emulsified with
15-1600 parts of water.

Crude Montan Wax Greases

8-10% Crude montan wax in raffinate or distillate, saponified with caustic soda.

Block Greases

15% Stearine, later 15% synthetic fatty acid
12% Resin, 73% raffinate 6.5°E. at 50°C. saponified with caustic soda.

Gear Grease

20/30% Hot bearing grease with a sodium soap basis, thinned with cylinder oil or bright stock.

(c)
(f) Not manufactured by Schlafhorst Chemische Werke.
(g)

Question 2.	With each of the above give the relevant specification.
Answer.	Information is lacking for the reasons explained above.
Question 3.	What changes have been made in composition during the war and for what reson?
Answer.	The natural fatty acids in the lime greases were replaced by synthetic ones or a part of the fatty acids was replaced by crude montan wax.

Triumph 80

210	parts	crude montan wax
140	"	Wool stearine
42	"	Lime
22	"	Caustic soda lye
2400	"	Mineral oil

Aluminium greases, as well as truck greases saponified with resin oil, gradually fell out of use because of the lack of the corresponding saponifiable materials.

Question 4.	What troubles have been experienced in their use?
Answer.	Unknown.

Question 5. What additions have been made for special purposes?

Answer. None were made.

H. Research and Development

Question. Indicate any research or development work which has been carried out, particularly of a more fundamental nature to elucidate properties, etc.

Answer. There was a particular development of a Standard Chassis Grease. The delivery specifications were made known in February 1937.

The greatest difficulty occurred in attaining the necessary water stability at 50°C. while maintaining a drop point up to 130°C. This very problem was mentioned in Klemgard's book on lubricants, in the last chapter dealing with the production of future greases. By combining the results of several series of experiments we succeeded in solving this problem with Grease No. 2200, thereupon we were given a testing machine, fitted with interchangeable ball-bearings, by the Army authorities and were requested to examine the bearing temperature curves and general behaviour of greases from other firms, under a load of 600 kg. and at 3000 r.p.m., using our grease as a standard. It was nearly 9 months before the first useful greases were available. Because of war conditions, natural lubricants could not be used, so that all that was available were waxes of German origin. The synthetic fatty acids were completely unsuitable, since greases prepared with even a small addition hardened when warm. It is true that the Ruhr Chemie A.G. had produced experimentally a suitable fatty acid for such purposes, but it was not available in large quantities.

I. Control Tests

Question. Give details of the control tests carried out to ensure uniformity of manufacture. Were these of a special nature, give full information.

Answer. For routine control purposes during grease manufacture the principal tests were, first the drop point by Ubbelohde's method, then the ash content and the saponification value, as well as the acid or alkali value. With the standard grease, the consistency at 50° and at -10°, the water stability at 20° and at 30° by the grease strip method as well as by the stirring test at 50°, were measured. Further tests were made for heat stability at 75° and oil separation and behaviour when hot. These tests were all in addition to the drop point. Drop points lay between 130 and 145°, and the consistency at 50° was 0.4 - 0.7 kg. at -10°, 1.0 - 2.0 kg. In the water stability test at 20°, the grease strips often remained smooth for over 8 days; at 50° good grease showed hardly any clouding after 5 hours. In the stirring test the water remained absolutely clear for one hour. At 75° many greases, after 24 hours, gave hardly any oil separation and after the test were still quite soft and pliant.

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B.I.O.S.—FINAL REPORT No. 507
ITEM Nos. 22, 30

Dr. F. RASCHIG, G.m.b.H.
Chemische Fabrik, Ludwigshafen.

COAL TAR DISTILLATION
CHLORINATED PHENOLS
PHENOL-FORMALDEHYDE RESINS
SYNTHETIC PHENOLS

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.

Waller, C. J.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

DR. F. RASCHIG, G.m.b.H.
Chemische Fabrik, Ludwigshafen

COAL TAR DISTILLATION
CHLORINATED PHENOLS
PHENOL-FORMALDEHYDE RESINS
SYNTHETIC PHENOLS

Reported by

C.J. WALLER

BIOS Target Numbers
22/84, C30/396

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

INVESTIGATING TEAM

G.C. Clark, (Chlorinated Phenols)

H.C. Raine, (Phenol-Formaldehyde Resins)

H.D. Macmurrary, (Plant)

C.J. Waller, (Tar and Phenol)

INDEX OF CONTENTS

Appendix "A" Full list of Products
"B" Tar Distillation Scheme & Production of Derivatives
"C" "The Synthetic production of Phenol" by
Dr. W. Mathes

SUMMARY OF MANUFACTURING PROCESSES EXAMINED

(A) DISTILLATION OF CRUDE COAL GAS TAR

Throughput was approximately 50,000 tonnes per annum to which should be added a quantity of crude naphthalene and carbolic oil bought in

(B) CHLORINATED PHENOLIC PRODUCTS

(1) Para chlor meta cresol

(2) Chlor Thymol

(3) Para chlor meta xylenol

(C) PHENOL-FORMALDEHYDE RESINS

(1) Resol and Novolak types moulding powders (approximately 300 tonnes a month).

(2) Cast Resins (approximately 30 tonnes a month)

(3) Hot setting p.f. glues. (Wartime product).

(D) SYNTHETIC PHENOL

From Benzene via Chlor Benzene. Process and plant fully described.

PERSONNEL INTERVIEWED

Technical Directors	The Raschig Brothers.
Chemist (Chief research)	Herr Mathas.

Products The products made come under the following main categories but for full list see Appendix A.

Tar Oils such as benzole and naphthalene wash oil
Naphthalene, hot pressed and pure.
Tar Acids.
Pure Phenol and standard grades of Cresol, etc.
Various phenol derivatives particularly chlor and nitro compounds.
Various grades of disinfectants.
Metal preservatives.
Benzole, toluol and xylole etc., and chlorinated derivatives.
Other tar compounds including pitch, pyridine, coumarone resin, etc.
Road Tars, bitumen mixtures, etc.
Phenol formaldehyde resins, in various grades.
Synthetic perfumes.
Hydrazin derivatives.
Tarred felts and other tar products for the building trade.
Raschig rings.
Sand blasting powders, etc.

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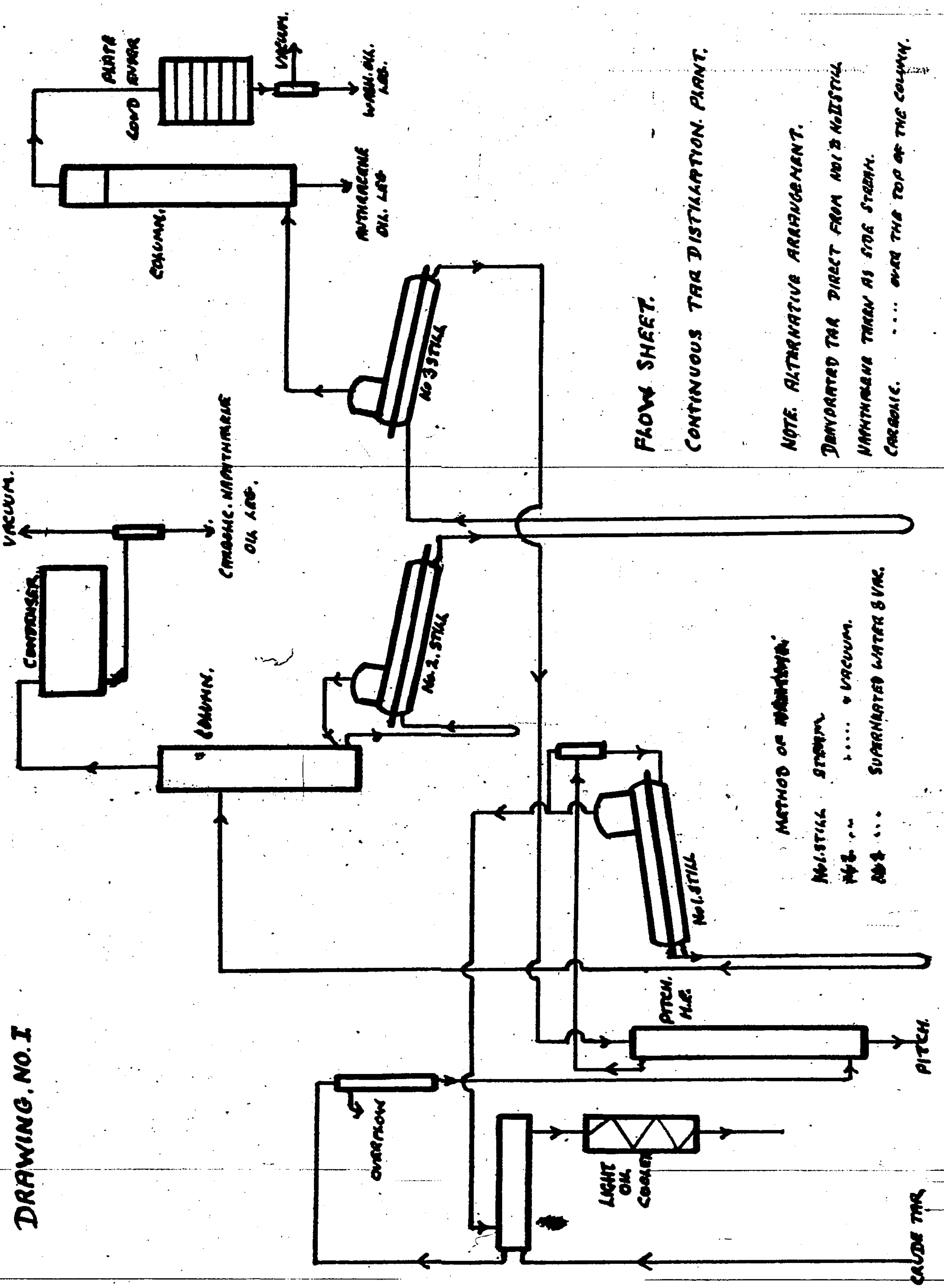


DRAWING. NO. I

FLOW SHEET.
CONTINUOUS TAR DISTILLATION. PLANT.

NOTE. ALTERNATIVE ARRANGEMENT.
DEHYDRATED TAR DIRECT FROM NO.1 TO NO.3 STILL
NAPHTHALENE THROWN AS SIDE STREAM.
CARBOLIC. .... OVER THE TOP OF THE COLUMN.

METHOD OF HEATING.
NO.1 STILL STEAM.
NO.2 ... . + VACUUM.
NO.3 ... SUPERHEATED WATER & VAC.

A. CRUDE TAR DISTILLATION.

Approximately 50,000 galls. comprising 90% Saar coke oven tar and 10% Gas Works Tar was worked up in continuous plant erected in 1912 and which has not been improved since.

Scheme of distillation is given in drawing (No.1 facing) the distillation being carried out in three steps :-

(i) Dehydration by steam coils (12 A).
(ii) Distillation to road tar by steam coil and vacuum (the quality of road tar made is such that it does not meet the modern German specification for road tar and the distillation has to be carried to the third stage and the mixture cut back).
(iii) Distillation to Medium Soft Pitch by superheated water coils and vacuum.

Four distillation units of 40/45 tonnes per day capacity were employed.

The total fuel used is high -25% by weight of brown coal brickettes on the tar distilled. (Distillate to 68/70 M.P., K. & S). The fractionation of products obtained as shown below, were obtained on gas works tar, s.g. approximately 1.160 (Horizontal Retorts).

Distillate Stage	1st.	2nd.		3rd.	
Yield by Vol.	5%+	15%		30%	
Oils produced.	Light.	Carbolic.	Naphtha.	Benzole. Wash.	Heavy.
S.G.	0.920	0.970	1.015	1.045	1.11
I.B.P.	90°	89°	203°	209°	266°
10%	102	150	209	218	306
20%	109	161	213	222	324
30%	117	171	216	229.5	335
40%	129.5	177	220	230.5	340
50%	146	181	223	240.5	347
60%	161	186	228	250	355
70%	191	191	235	260.5	360
90%	222	205	290	296	—

+ including Ammonia Liquor.

Products plants were of little interest, Benzol and Light Oil distillation being carried out in small batch units with packed columns and much recycling of the primary products of distillation was necessary. All the naphthalene available was settled out, whizzed, hot pressed and distilled. A part of the pure naphthalene was sublimed. Continuous washing of carbolic oil for tar acids was employed together with continuous de-oiling and springing.

Yields from ~~primary~~ distillation and further working up of products follows.

PRIMARY DISTILLATION OF CRUDE TAR IN CONTINUOUS PLANT, 1942

Throughput and Products in Tonnes

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.	Total
Crude Tar Distlld.	3344	3967	3159	5116	4003	4350	4495	4012	4292	4645	4422	4042	49 847
Yielding Light Oil	39	44	37	59	52	48	46	45	40	47	48	48	553
Carbolic Oil	413	486	386	619	483	530	552	481	555	559	520	501	6 085
Crude Benz.Wash Oil	331	341	337	461	351	314	416	374	412	518	508	371	4 734
Crude Anthracene Oil	376	681	341	746	575	572	565	513	631	706	623	652	6 981
Refined Tar	198	148	302	434	287	731	736	583	363	47	-	178	4 007
Soft Pitch	320	377	232	553	653	645	1033	584	969	1555	1555	1233	9 709
M.S. Pitch	1468	1670	1328	1931	1385	1258	924	1211	1053	986	948	870	15 032
Water	199	220	196	313	217	252	223	221	269	227	220	189	2 746

DECEMBER, 1942 - PRODUCTS MANUFACTURE

Crude Worked		Products	
1 328,2 t	Carbolic Oil		
987,0 t	Caustic Soda Solution	1 113,2 t	Tar Acid Free Oil
		1 202,0 t	Carbolate
2 315,2 t		2 315,2 t	
1 093,2 t	Tar Acid Free Oil (by distillation)	235,5 t	Pyridine Rich Oil
		646,6 t	Diesel Oil & Naphthalene
		170,0 t	Heavy Diesel Oil
		41,1 t	Loss & Water
		1 093,2 t	
1 242,6 t	Carbolate	1 027,6 t	Soda Solution
		215,0 t	Crude Tar Acids
		1 242,6 t	
218,2 t	Pyridine Rich Oil	13,5 t	Crude Pyridine
		204,7 t	Pyridine Free Oil
		218,2 t	
229,6 t	Diesel Oil Naphthalene mixture	50,4 t	Diesel Oil
		179,2 t	Crude Naphthalene
		229,6 t	
170,0 t	Crude Naphthalene	107,1 t	Hot Pressed
		62,9 t	Oil
		170,0 t	
11,0 t	Crude Pyridine	6,1 t	Pyridine bases
		1,0 t	High Boiling Pyridines
		6,3 t	Residues etc.
13,4 t		13,4 t	

aus 234, t Carbolate (Brown Coal)

(over)

155,4 t	Soda Solution (Brown Coal)
79,0 t	Crude Tar Acids
234,4 t	

NAPHTHALENE REFINING

Throughput hot pressed 72.7 t.

Yielding:

Pure Naphthalene	crystals	19,3 t
" "	flakes	34,0 t
Low Quality naphthalene		7,0 t
Recoverable Residues		3,2 t
Dirt		9,2 t

CARBOLIC ACID PLANT

Throughput Crude Tar Acids 150,5 t

Yielding:

Carbolic Acid	22,0 t
O. Cresol	13,9 t
M. Cresol 60%	29,2 t
Cresols (other Grades)	5,7 t
Xylenoles for re-washing	0,8 t
Xylenols	43,4 t
Pitch, loss and water	35,5 t

Throughput Tar Acids from Brown Coal 104,0 t

Yielding:

Mixed Phenols	62,4 t
Phenol	4,5 t
Cresol (45%)	4,0 t
Xylenol	2,1 t
Pitch, Loss and Water	31,0 t

BENZOLE PLANT

Typical yields - December, 1942

Yields from primary distillation of Pyridine Free Light Oil

Throughput		288,2 t
Yields:		
Crude Benzole	10,4 t	
Crude Toluol	35,0 t	
1st Once Run Solvent Naphtha	39,2 t	
2nd ditto	133,1 t	
Heavy Benzole	16,9 t	
Residue	51,3 t	
Distillation Loss	2,3 t	

Refining Yields from Once Run Products.

Crude Benzole throughput		10,5 t
Yielding:		
Pure Benzene	5,9 t	
Crude Toluole thru'put		20,3 t
Yielding:		
"90's Toluol"	6,5 t	
Pure Toluene	11,6 t	
1st O.R.Solv.Naph. throughput		44,1 t
Yielding:		
Pure Xylene	30,6 t	
2nd O.R.S.N.	8,3 t	
Residue	9,1 t	
Loss	2,9 t	

B. CHLORINATED PHENOLIC PRODUCTS.

Raschig operated a number of small scale chlorination processes. All were based on the reaction of Sulphuryl Chloride on the appropriate cresol or xylenol at a temperature of up to 60°C. The processes as operated were old and had no special features. The products were largely used for Raschig's trade in speciality disinfectants.

Plant.

The plant was badly damaged but had consisted of a series of four independent units each comprising a lead lined stirred reaction vessel, capacity 1800 litres (400 gallons), fitted with heating and cooling coils, a feed vessel for SO_2Cl_2 and an air blowing system. The liberated HCl and SO_2 were exhausted by fan and vented via an absorbtion tower, and the residual gas in solution blown out by air.

Processes.

(a) Para chlor meta cresol.

This was worked according to Example 2 of German Patent 232,071.

The process was based on a fractional chlorination of the 60.40 meta-para mixture obtainable from the cresol stills. The meta was preferentially chlorinated and the unaltered para cresol distilled from residue of p chlor meta isomer.

To each 180 kg. 60.40 meta para mixed cresols at 60°C were added slowly 135 kg. Sulphuryl Chloride. The product was distilled at ordinary pressure to separate p cresol at 202°C and p chlor meta cresol at 235°C. The separation was not good and the para cresol contained some chlorinated products. The production amounted to 8,000 kg. per month but the plant was capable of double this output. The product was used in part for chlor thymol.

(b) Chlor Thymol.

This was according to a patent application dated 24.4.1926.

The process was dependent on the availability of p chlor m cresol as a starting material.

The chlor cresol was treated with 5% of the weight of Aluminium Chloride and reacted with Isopropyl Chloride, the adding being controlled by the evolution of the HCl. At the completion of the reaction air was blown in to remove HCl and the mass distilled in a lead lined plant under reduced pressure. After removing unreacted chlor cresol a fraction consisting of Chlor Thymol was obtained and this was recrystallised from Toluol.

100 kg. Chlor Thymol required.
135 kg. p chlor m cresol.
115 kg. Isopropyl Chloride.

The production was only 1 - 2 tons yearly.

(c) Para chlor meta Xylenol.

The chlorination was performed at 60°C with the xylenol melted with a little Xylol. The crude chlorination mixture was air blown to remove HCl and then crystallised. The non-crystallisable fractions containing by-products and some para chlor meta xylenol were sold as mixed disinfectants and for animal repellants.

150 kg. 1.3.5 m xylenol yielded 100 kg. para chlor meta xylenol crystal according to the practice in this works.

This is 52% of the theoretical possible.

C. PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS.

The products falling into this class which are manufactured by Raschig are given below together with the former plant capacity:

Moulding Powders, Resol and Novolak types in approximately equal quantities but the ratio is very variable:	300 t/month
Cast Resins	30 t/month
Hot Setting p.f. Glues for Plywood)made only Glues for paper laminates)during the war.	

A second and more modern factory is situated at Liepzig. In the two plants 3000 t/year of adhesive solution were made, of which only about 80 tons was for paper. The output is at present restricted by shortage of phenol and fuel. No melamine or urea-formaldehyde resins were made. "Dr. Claus Raschig supplied all the information on this subject

Methods of Manufacture.

These products are of two types based on resol or "single stage" resins and novolak resins respectively. The former are the basis of the brightly coloured moulding powders which are not matched by any commercial product made in this country. The colours are as bright and as attractive as those obtained with urea formaldehyde powders and the product has superior mechanical properties and water absorption to these latter materials. It suffers however from a surface darkening in sunlight although this is not a serious disadvantage for temporary uses such as caps for toothpaste tubes. Dr. Raschig thought that they were at a further slight disadvantage because it is essential to use chromium plated moulds for resol powders in order to avoid sticking of the finished moulded article. In this country, where it is standard good practice to use plated moulds the effect would not be troublesome. Only brown and black

powders were made in war time.

1. Manufacture of Resol Resins.

In accordance with normal practice these intermediates are made by an alkaline condensation. A reaction mixture having a phenol/formaldehyde mole ratio of 1:1.5 is reacted with sodium hydroxide as the catalyst (baryta has sometimes been used). The phenol catalyst and formaldehyde in aqueous solution are charged into a mild steel reaction vessel in such quantities as correspond to a 2500 kilo batch of finished resin. The reactor is a cylindrical vessel mounted with its axis at an angle of about 10° from the horizontal and is stirred by a large slow moving axial stirrer. Heating and cooling are effected by a surrounding jacket. A large reactor of 10/M^3 capacity was seen in a damaged area. It had a "dimpled" jacket for 12 atm. steam, was fitted with an horizontal stirrer and was used to make 4000 kilo batches of resin.

The batch is maintained at 100°C for 20 or 30 hrs. during which time water distills off, in the latter stages, under vacuum. The provision of windows in the vessel permits an ingenious method of following the course of the reaction by viscosity measurements. From time to time the stirrer is stopped, a graduated glass tube is inserted in the vessel and the time of fall of a steel ball is observed; in this way a close control of the product can be maintained.

When all volatile matter is distilled off and the viscosity has reached the desired value the product is run off into trays to cool.

2. Novolak Resins.

It is commonly and erroneously believed that novolak resins can only be prepared by acid catalysis and that an alkaline catalysed product is always a resol. This is not true if during the whole course of the reaction a large excess of phenol is maintained. Utilising this fact Raschig have developed a commercial method of novolak manufacture unlike any other known to the authors, although the procedure has previously been described by Huebner.

The recipe used is:

Phenol	1 mole
Aqueous formaldehyde	0.45 mole
Sodium Hydroxide	1% w/w on phenol

and the resin is made in batches of 4,000 kilos in the 10/M^3 vessel. The reaction vessel is similar to that used for resol manufacture but that heating and cooling are effected by coils and stirring is by means of a small vertically mounted "Lightning" type stirrer.

At one time it was thought to be unnecessary to agitate the reaction mixture but better results are now obtained by so doing.

In the course of manufacture the temperature was raised slowly to 160°C whilst the bulk of the water was distilled off. With a large excess of phenol still present the temperature is held at 160°C for an hour, during which time the reaction proceeds to give a 1:09 phenol formaldehyde resin. At the end of this period the excess phenol is distilled off under vacuum to leave the novolak resin which is run into trays to cool. The product is brown and roughly equivalent to an hydrochloric acid catalysed novolak.

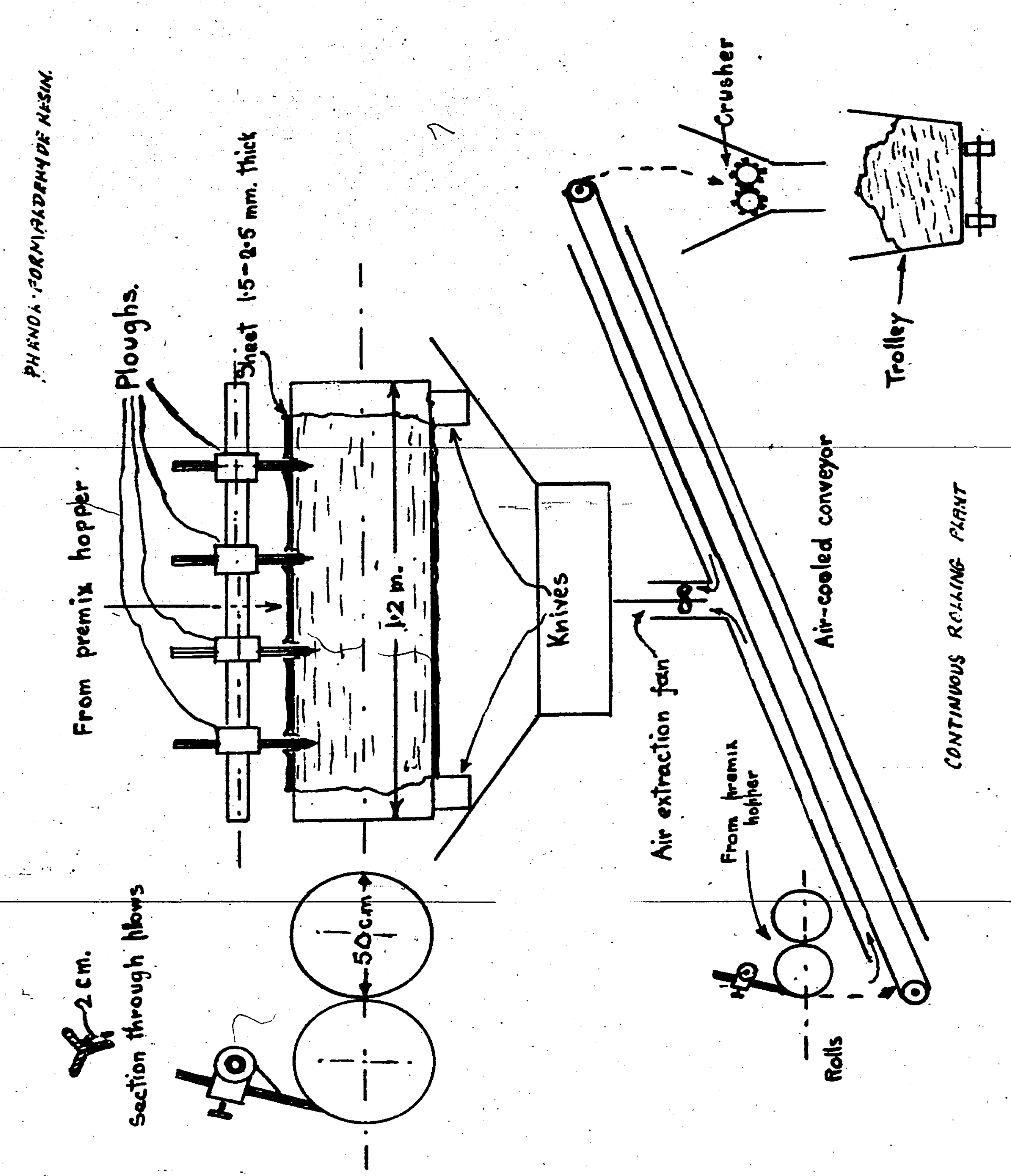
The process involves a long batch time cycle (20 - 30 hrs.) and a very heavy steam consumption because of the great quantity of phenol to be distilled. These factors which might be considered to represent a great disadvantage are said by Dr. Raschig to be offset by the gain obtained by the use of mild steel equipment instead of the glass lined or stainless steel vessels which he says are necessary for the orthodox process. We would challenge both his premises and his conclusions.

Before the war no cresol resins were made but in recent years it has been necessary to do so. For a reason which is not understood lime is used instead of sodium hydroxide when this type of novolak is made. The recovered cresol is different in composition from the starting material and consequently it is essential to exercise care in mixing.

The size of the batch, being very large confers a desirable uniformity on the product and simplifies process control. It was admitted that a continuous process would be more desirable than the present discontinuous method but Dr. Raschig denied that his firm had given serious consideration to this subject. This statement contradicts directly the information obtained by a team which investigated the plant earlier in the year (XXIX/62). Blue prints of a continuous reaction plant were understood by them to be in existence.

<u>Incorporation of Resins into Moulding Powders.</u>

Both types of resin are compounded in one plant. After milling the resin is fed with the other ingredients into a horizontally mounted cylindrical vessel of 10 M^3 capacity which is fitted with a horizontal slow moving stirrer driven by a 50 H.P. motor. A 6,000 kilo batch is mixed here for half an hour before being passed into the hopper above the mixing rolls. During production the mixer is worked semi-batchwise so that the variations in flow can be taken up by the capacity of the hopper.



Rolling is done continuously, the mix being fed onto the middle of the rolls. The material passes naturally to the ends of the rolls without the aid of ploughs exerting a sideways thrust. Ploughs are fitted but their function is merely to break up the sheet and to present new surfaces of the material. The construction of the ploughs is shown in Fig opposite. During operation the following conditions are maintained:

Temperature of front bowl	90°
" " back "	103°C
Back/front speed ratio	1 : 1.15

The rolled material is cut from the sides of machine onto a conveyor belt which is enclosed in a small tunnel. Half way along the tunnel is a duct through which air is sucked by a fan. In this way the crepe is cooled before it drops from the conveyor into a mill from which it is taken in small trolleys for further grinding and then packing.

The recipes for the powders vary according to the resin. Resol based products contain 25% lithopone which is necessary for the development of the full colour of the material. Aniline dyes are used, e.g. Victoria Blue Base from I.G.

Novolak powders are made with 15% hexamethylene tetramine, a proportion greater than is needed for acid catalysed novolak resins.

Only woodfilled powders were described and nowhere was there any sign that other fillers were used. Minor ingredients were magnesium oxide and a lubricant for which aluminium stearate and stearic acid were preferred.

(b) Cast Resins.

Raschig claim to be the originators of this product which was manufactured in quite large quantities. The process is conventional and involves the initial condensation of a 1:2.5 phenol/formaldehyde reaction mixture with sodium or potassium bicarbonate as catalyst, in unstirred jacketted nickel vessels of 2.5 M^3 capacity mostly without stirrers. The viscous product is then neutralised with acid (lactic acid for opaque types and phthalic acid for transparent ones) before being run into moulds for hardening. The moulds are prepared by a dipping technique using molten lead and steel formers from which the lead is stripped after cooling.

Hardening proceeds in simple ovens without an air circulation system maintained at about 70°C. As well as tubes, rods and bars, large blocks are cast and these are subsequently sliced into sheets with a bandsaw, further hardened in ovens and finally buffed.

(c) Hot setting Glues.

These products are one stage resins manufactured in a similar way to those used for moulding powders.

CONCLUSIONS:

This firm is one of the pioneers in the field of phenol-formaldehyde resins and their plant and processes show several unusual features. Among the products, the coloured resol based moulding powders are of particular interest and deserve further consideration as replacements for urea-formaldehyde resins.

The target requires a more detailed study than this team was able to make and in particular the question of the possible existence of blueprints of a continuous resin plant should be thoroughly investigated. It is always possible that the Liepsig plant is worked continuously or that a continuous plant has been developed there.

HCR/MDH
20.11.45

H. C. RAINE.

SYNTHETIC PHENOL PLANT.

The production of phenol is in two stages as follows :-

(1) $C_6H_6 + HCl + \frac{1}{2}O_2 = C_6H_5Cl + H_2O$

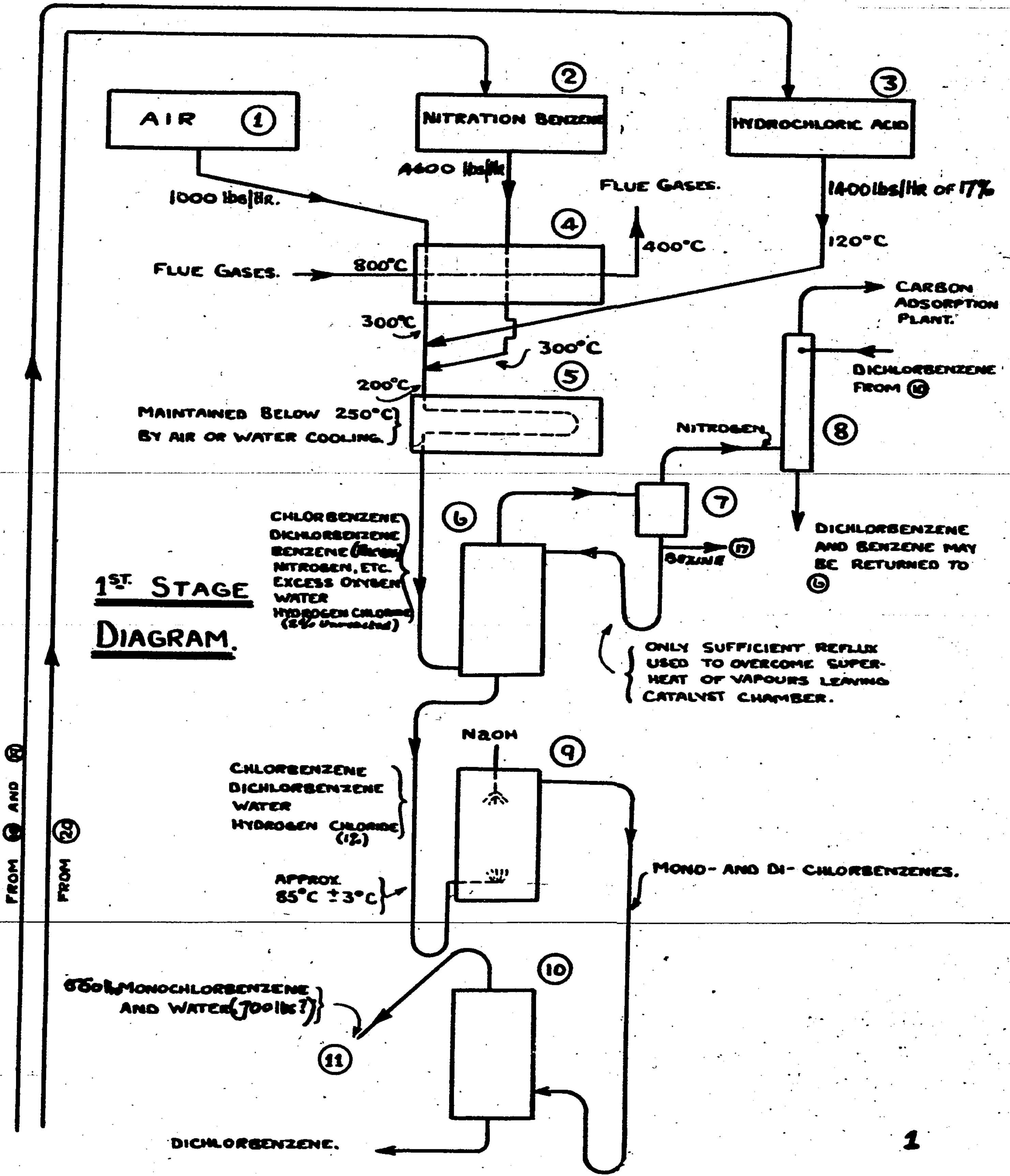
(2) $C_6H_5Cl + H_2O = C_6H_5OH + HCl$

and the process is generally described in a paper by Dr. W. Mathes, (see appendix "G").

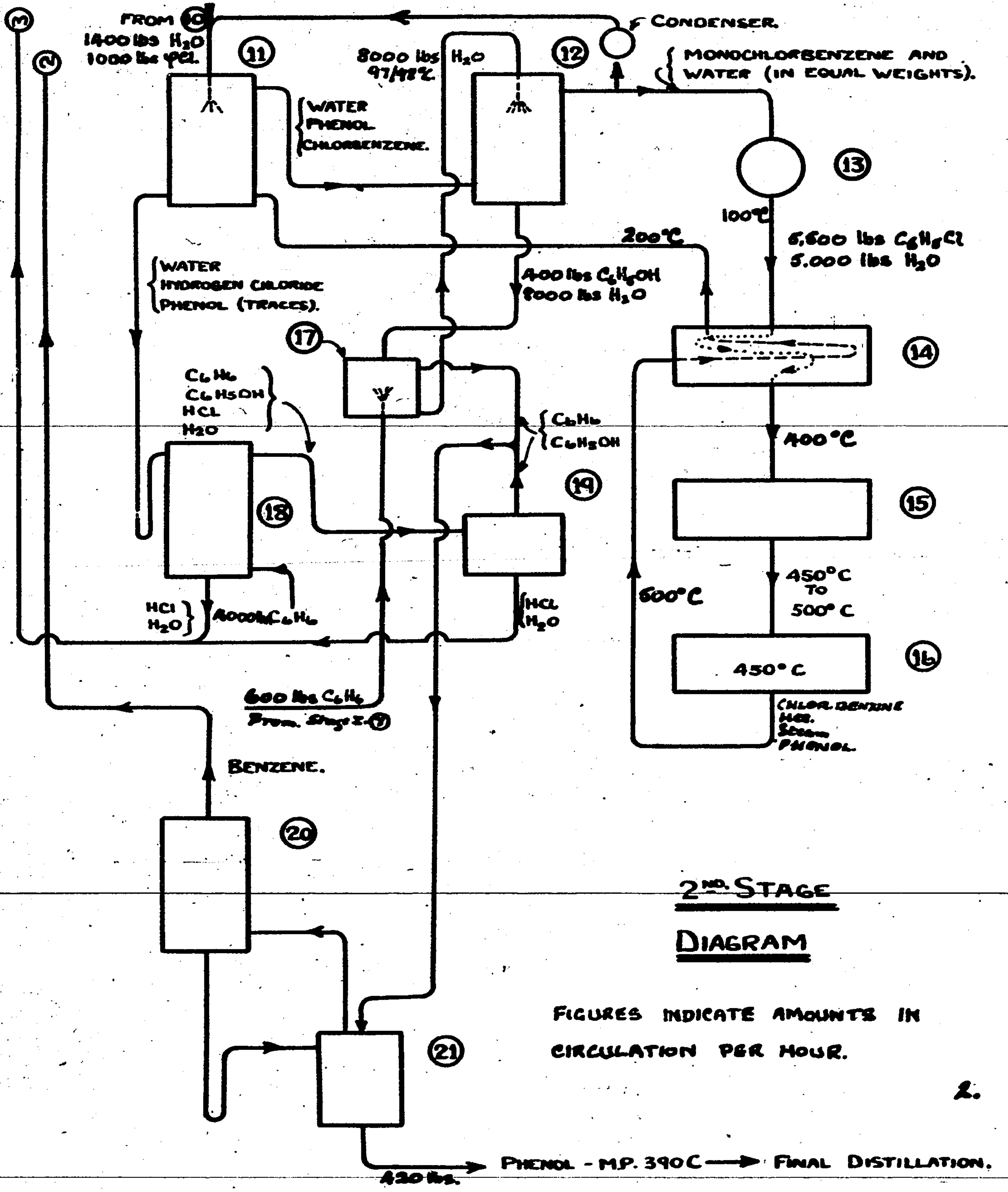
The plant erected at Ludwigshafen was for a production of 4½-tons of phenol per day and was, in effect, a small scale manufacturing unit to act as a pilot plant for a larger capacity one erected in 1940 for the Durez Plastics and Chemical Inc., North Tonawanda, New York State, U.S.A.

The full scheme of operation is shown in figures 1, 2 and 3, and the plant itself is diagramatically shown in figures 4 and 5.

Briefly, pure benzene (Nitration quality Barretts specification) after vapourisation and superheating, is passed through the first catalytic furnace with air and hydrochloric acid gas (produced by the evaporation of the constant boiling mixture obtained from stage two of the process) the exothermic reaction being maintained at 200°C. by air cooling to yield chlor benzene etc. The conversion to chlor



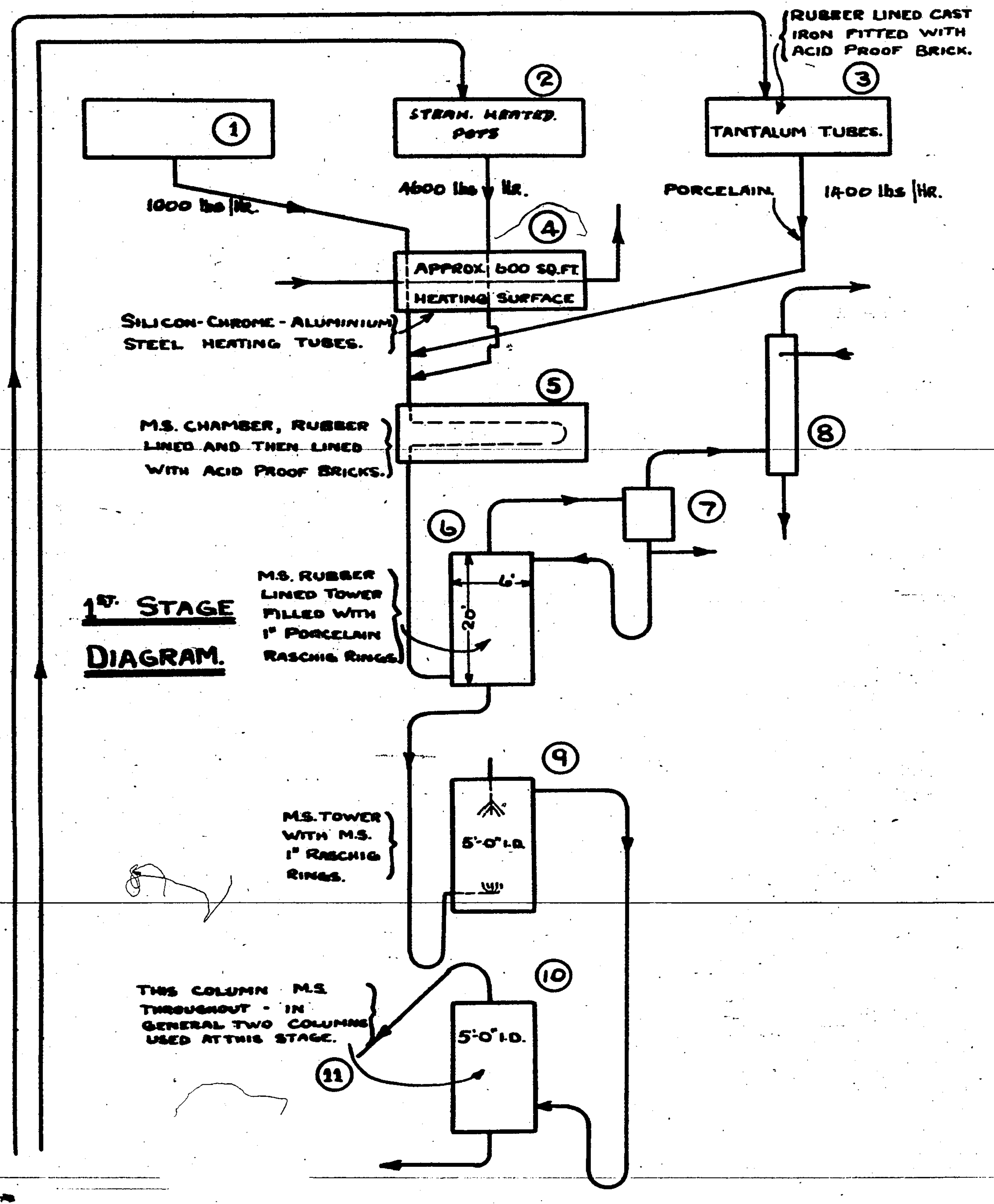
1ST. STAGE DIAGRAM.



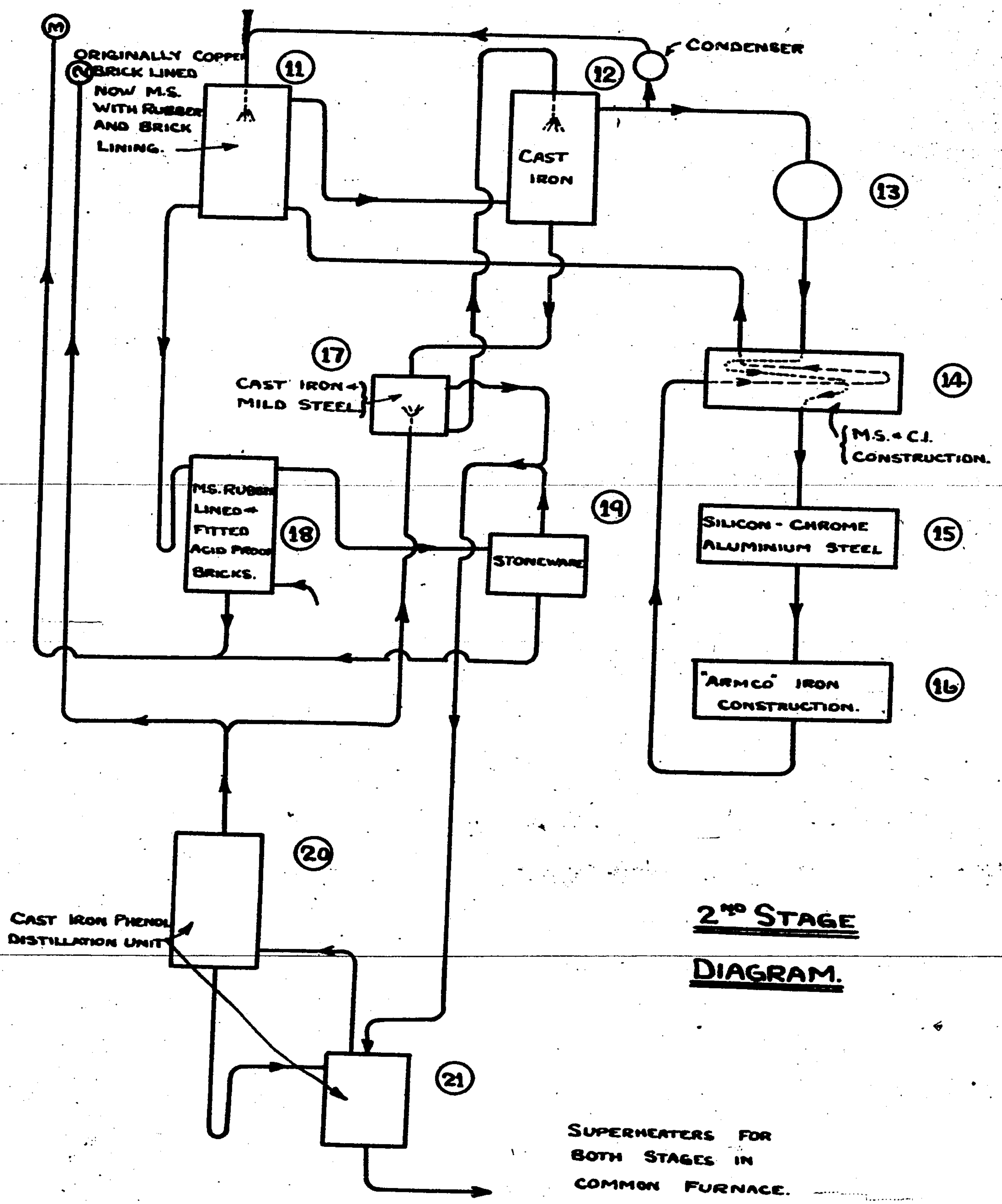
2ND. STAGE DIAGRAM

FIGURES INDICATE AMOUNTS IN CIRCULATION PER HOUR.

① AIR + SUPPLY BLOWER.
② NITRATION BENZENE SUPPLY.
③ HYDROCHLORIC ACID EVAPORATOR.
④ SUPERHEATER.
⑤ CATALYST CHAMBER - 1ST STAGE
⑥ MONOCHLOR-BENZENE STRIPPING COLUMN.
⑦ REFLUX CONDENSER.
⑧ SCRUBBER - DICHLORBENZENE.
⑨ SCRUBBER - CAUSTIC.
⑩ MONO + DICHLORBENZENE FRACTIONATING COLUMN.
⑪ MONOCHLORBENZENE SCRUBBER.
⑫ SCRUBBER. (WATER)
⑬ FAN.
⑭ HEAT EXCHANGER.
⑮ SUPERHEATER.
⑯ CATALYST CHAMBER - 2ND STAGE.
⑰ WATER SEPARATOR.
⑱ HYDROCHLORIC ACID REMOVAL. (BENZINE WASH)
⑲ HYDROCHLORIC ACID REMOVAL.
⑳ BENZENE / PHENOL FRACTIONATING COLUMN.
㉑ PHENOL STILL.



1ST. STAGE DIAGRAM.



2nd STAGE DIAGRAM.

SUPERHEATERS FOR BOTH STAGES IN COMMON FURNACE.

benzene can be raised up to 25% but the proportion of di chlor benzene produced as a by-product increases with increased yield of the mono product, i.e.

Conversion.	Yield.		
	Benzene.	Mono chlor Benzene.	Di chlor Benzene.
5%	94.75%	5%	0.25%
10%	89%	10%	1%
20%	76%	20%	4%

The di chlor benzene contains approximately 70% para and 30% ortho with traces only of the meta compound. The mixed products are fractionated, the recovered benzene being recycled and the mono and di chlor benzene being re-distilled after neutralising to yield the mono product as vapour.

Mono chlor benzene vapour with superheated steam is passed through the second catalytic chamber at 450-500°C. to yield the phenol. A 8-15% conversion is obtained with a 85-95% yield of phenol. Lower phenol yields are obtained with higher conversion.

The mixed vapours are scrubbed first with mono chlor benzene and then with water in two stages, to give :-

(1) hydrochloric acid, and water containing traces of phenol.

(2) a constant boiling mixture of steam and mono chlor benzene

(3) an aqueous solution of phenol.

The hydrochloric acid from 1 is returned to stage one. The constant boiling mixture of water and chlor benzene recycled. The aqueous solution of phenol is washed with benzene and separated by fractionation.

One pound of phenol was obtained from 1.05 pounds of benzene against 0.83 pounds of benzene by theory, but yield figures on the U.S. plant are better- one pound of phenol per 0.97 pounds of benzene, see costing sheet attached.

Preparation of chlorination catalyst.

The material was prepared substantially as in Example 5 German Patent Specification 539,176.

A concentrated Sodium Aluminate solution is prepared by reacting 40% NaOH solution with powdered aluminium hydroxide until saturated.

3 litres of this solution are diluted to 5,000 litres (1100-gallons) with water and precipitated with a solution of 200-gms. Copper Chloride and 30-gms. Ferric Chloride in sufficient concentrated Hydrochloric Acid to neutralise the Caustic Soda used.

The precipitate consisting of a mixture of Aluminium Copper and Iron Hydroxides is washed by decantation substantially free from Chlorides and dried.

The material had a density of about 0.5. and was used on the plant in the form of pellets 4/6 mm size.

In the example the activity was stated to be such that if over 1,000 cc. (500-gms) of such a contact at 200°C there are passed hourly 200-gms. Benzol, 100 cc. of 17% HCl and 50 litres of air, one can separate from the product 40-gms. Chlor Benzol, i.e. in 24 hours a weight of Chlor Benzol equal to weight of catalyst: a figure confirmed by plant operation.

Preparation of hydrolysis catalysts.

The hydrolysis catalyst was stated to be that described in Example 1 of U.S.P. 1,964,768.

The method is as follows.

Three solutions are first prepared -

1. 280 cc. Phosphoric Acid 59.5 Be' are diluted to 70 litres with water.
2. 1.05 litres aqueous Ammonia S.G. 0.91 are diluted to 5 litres with water.
3. 1.3 kg. Calcium Chloride Cryst. ($6H_2O$) are dissolved in 25 litres water.

The Ammonia solution is mixed with the diluted Phosphoric Acid, and to the mixture the Calcium Chloride solution is added slowly (over a period of 1 hour) with continuous and energetic stirring. The precipitate of Tri-Calcium Phosphate is sucked off, freed from impurities by repeated washing, and dried finally in air at 500°C. The mass breaks up to pieces of size of pea or bean and is porcelain-like with a conchoidal fracture.

The activity was stated to be such that if over 1,000 cc. of catalyst at 480°C were passed, 750 gms. Chlor Benzene and 750 gms. water per hour, then 100 gms. Phenol would be obtained with a yield of 90% of the theoretical possible.

Production cost calculation

Cost price of phenol produced according to Raschig's process in the plant at North Tonowanda, NY/USA, (annual production 16,500,000 lbs.) Plant in operation for 330 days a year with a daily production of 50,000 lbs.

	Price per unit.	Daily Consumption during operation	
	$ - Cents	Amounts	Costs %
1. Raw materials			
a) Benzene	2,17 cts./lb.	•48 400 lbs.	1 050.28
b) Muriatic acid 18° Be.	1,26 cts./lb.	•11 990 lbs.	151.07
c) Auxiliary products.			100.--
2. Catalysts.			125.--
3. Energy			
a) Electric energy	1ct./KWh	•7 750 KWh	77.50
b) Steam	50cts./1 000lbs.	825 000 lbs.	412.50
c) Heating Oil	0.31 ct./lb.	15 000 lbs.	46.50
d) Cooling water.	1ct./1 000 gls. 1 gall.=8,345 lbs.	•18 750 000 lbs.	22.50
4. Labor			
a) Working hours.	65 cts./h	280 h	182.--
b) Foremen	100 cts./h	24 h	24.--
c) Superintendent	187,5 cts./h	8 h	15.--
5. Repairs	5% of value of apparatus = $ 1 750 000.-- = $ 87 500.-- div. by 365 days.		239,75
6. Depreciations			
a) Buildings.	5% of value = $ 300 000.-- = $ 15.000.-- div. by 365 days		41.10
b) Apparatus	10% of value = $ 1 750 000.-- = $ 175 000.-- div. by 365 days.		479,50

7. Shut Downs.
35/300 of $ 1 028.22 109.05

8. Cost price of
50 000 lbs. phenol $ 3 075.75
Cost price of 1 lb. 6.15 cents.

WAR DAMAGE SUSTAINED.

As a result of a daylight raid of some 50/100 heavy American bombers very considerable damage was sustained, the whole works being put out of action due to dislocation of all services.

Among the inspected plants totally wrecked were :- the main Tar Storage tanks, the Synthetic Phenol plant, and the Naphthalene settling tanks etc. Plant partially destroyed and heavily damaged included the Raschig Ring manufacturing shops and at least 50% of the general storage sheds and derivative plants. The boiler house received direct hits but two boilers remained in fair condition.

The Tar distillation, Benzole, and Tar Acid plants were only lightly damaged as were the Synthetic Rosin Moulding Shops.

DR. F. RASCHIG GMBH.

CHEMISCHE FABRIK • LUDWIGSHAFEN A. RHEIN

Fernsprecher: Ludwigshafen a. Rh. 61021 • Telegramme: Raschig Ludwigshafenrhein

Steinkohlenteerprodukte

Teeröle: Imprägnieröl, Carbolineum (auch farbig), Heiz- und Treiböl „Diesol", Benzolwaschöl, Naphthalinwaschöl

Naphthalin: Naphthalin-Warmpreßgut, Reinnaphthalin in Brocken, Pulver, Schuppen, Kugeln

Phenole: Krist. Karbolsäure 39/41°, Rohkresol 97/100, D. A. 4, D. A. 6, Orthokresol, Metakresol, Parakresol, Xylenole, symm. Metaxylenol

Phenolderivate u. chemische Produkte: Orthochlorphenol (2-Chlor-phenol), Parachlorphenol (4-Chlor-phenol), Orthochlororthokresol (6-Chlor-o-kresol), Parachlororthokresol (4-Chlor-o-kresol), Dinitroorthokresol (4,6-Dinitro-o-kresol), Orthochlormetakresol (6-Chlor-m-kresol), Parachlormetakresol (4-Chlor-m-kresol), Dinitroparakresol (2,6-Dinitro-p-kresol), Nitroparakresolsulfosaures Natron (Natronsalz der 2-Nitro-p-kresol-6-sulfosäure), Parachlorxylenol (4-Chlor-3,5-dimethylphenol), Trichlorxylenol (2,4,6-Trichlor-3,5-dimethylphenol), Brenzcatechin, Guajakol, Guäthol

Desinfektionsmittel: Kresolseifenlösung D. A. 4, D. A. 6, wasserlösl. „Kresol-Raschig", wasserlösl. Chlorkresolgemisch „Kresol-Raschig Cl", Parachlormetakresol „Raschit", Chlorxylenol, Chlorthymol

Konservierungsmittel: „Raschit", „Raschit W" (wasserlösl.), „Raschit flüssig" gegen Schimmel, Zersetzung u. Fäulnis bei Leim, Kleister, Klebstoffen, Leder, Textilien

Lösungsmittel, Kohlenwasserstoffe: Benzol, Toluol, Xylol, Orthoxylol, Metaxylol, Paraxylol, Solventnaphtha I u. II, Schwerbenzol roh u. gereinigt, Orthodichlorbenzol, 1,2,3-Trichlorbenzol

Andere Steinkohlenteerprodukte: Steinkohlenteerhart- u. -weichpech, destillierter und präparierter Teer, Reinpyridin, Pyridinbasen, Acenaphthen, Kumaronharz

Straßenbaustoffe

Straßenteer (Heißteer) mit und ohne Bitumenzusatz (DIN1995), „Duro"-Wetterteer, Raschig-Kaltteer (DIN1995), „Teeremulsion", Kaltasphalt, „Ralubit" U, H 1, H 2, S, F, V (DIN 1995), „Irga"-Heiß- und Kaltteere, Straßenöl, Bitumen-Pflastervergußmasse (DIN 1996)

Kunstharzprodukte

Edelkunstharz für Drechslerzwecke (in allen Farben in Blöcken, Platten, Stangen, Gießlingen): Künstl. Bernstein „Dekorit", künstl. Elfenbein „Dekorit L", künstl. Glas „Dekorit V", Leucht-Dekorit, im Dunkeln leuchtend für Schmuckstücke und für technische Zwecke

Kunstharzpreßpulver und -preßmischungen: Schnellpreßmassen „Resinol" Typ S (auch ammoniakfrei), S*, 11*, Z2

Kunstharze für technische Zwecke: „Resinol"-Papierleim, „Resinol B 38" für Hartpapier u. Hartgewebe, „Resinol G 2 Sorte C" für Glühlampensockelkitt, „Resinol CW 1" und „CW 2" zur Bindung von Asbestfasern, Faserbindemittel „Vigorol" und „Naviral P" für Herstellung von Lederersatz, Weichmacher „Naviral W", „Resinol L 5" für Lackanstriche auf Holz, Metall, „Resinol K 2" für Herstellung von Schleifscheiben und von Kitten, Kunstharz K 4 Kolophoniumersatz für die Lack- und Gummiindustrie, „Dekorit F" säurefestes Kunstharz in Blöcken, Platten, Stangen für Maschinen- und Apparateteile, „Dekorit-Kitt" zum Verkitten säurefester Plattenbeläge

Künstliche Riechstoffe

Ambrette-Moschus, Xylol-Moschus, Keton-Moschus, Parakresolmethyläther, Metakresolmethyläther, Anisol

Hydrazinpräparate

Hydrazinsulfat, Hydrazinhydrat, Semicarbazidhydrochlorid, Hydroxylaminsulfat, Hydroxylaminhydrochlorid, Natriumazid

Schädlingsbekämpfungsmittel

Schädlingsnaphthalin „Neso", Obstbaumkarbolineum, Baumspritzmittel (Teerölemulsion), Reinnaphthalin gegen Motten

Gießereihilfsmittel

Kernöle: „Wormatol M" für freistehende Kerne, „Wormatol B" für Schalenkerne, „Wormatol L" für selbsterstarrende Kerne, Anspritzöl

Kernbinder: „Porosit 1" für fetten Sand, „Porosit 5" für mageren Sand, „Porosit 6" für Quarzsand, „Quellton" zur Auffrischung von Altsand.

Schmelzpräparate: Zum Abdecken, Reinigen und Entgasen von Schwer- und Leichtmetallguß

Steinmodellmasse: „Stonex"

Formpuder: Formpuder „Cewo"

Dachpappe

Teerfreie „Defra"-Bitumen-Dachpappe, „Triwaldit"-Bitumenklebemasse und -Bitumen-Dachlack heiß und kalt, „Triwaldit"-Faserkitt, Teerdachpappe, „Teerfix"-Teerklebemasse und -Teerdachlack heiß und kalt, „Teerfix"-Teerfaserkitt, Tarnungsanstriche

Produkte für das Baugewerbe

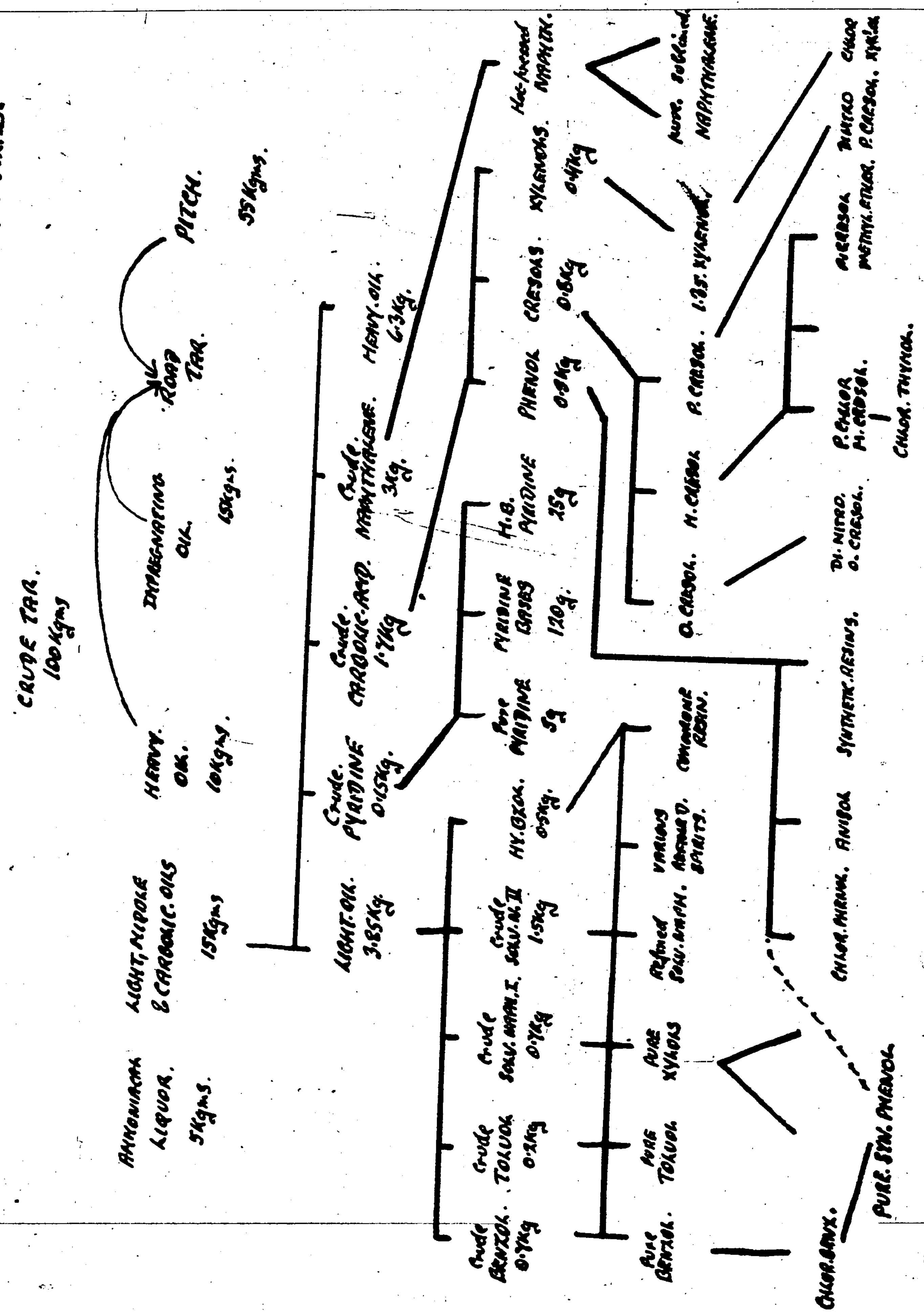
Isolierpappe, „Defra"-Wollfilzpappe, Dichtungsbahn, Schutzbahn, Klebemasse, Bitumenmörtel, säurefester Gußasphalt, „Triwaldol"-Bitumendichtungsaufstriche heiß und kalt, Mauerteer, Streichteer, farbige Isolieranstriche, Schalungsöl, „Impregnin", farbloses Holzimprägnierungsmittel „Trixol", Parkettasphalt heiß u. kalt, Kabelvergußmasse, Muffendichtungsmasse, schwarze Rostschutzanstriche

Füllkörper

„Raschig-Ringe" aus Blech, Gußeisen, Metall, Porzellan, Steinzeug für Destillierkolonnen sowie für Kühlung u. Entstaubung von Gasen

APPENDIX. B.

TAR DISTILLATION SCHEME & PRODUCTION OF DERIVATIVES.



Appendix C.

SONDERABDRUCK
AUS „ANGEWANDTE CHEMIE“ 52, 591 [1939]
Zeitschrift des Vereins Deutscher Chemiker: A. Verlag Chemie, GmbH., Berlin

Das Raschig-Verfahren zur Herstellung von Phenol

Von Dr. W. MATHES, Dr. F. Raschig GmbH., Ludwigshafen

Eingeg. 16. August 1939

Zu den bekannten Verfahren der synthetischen Herstellung von Phenol, nämlich dem Sulfosäureverfahren und der Chlorbenzoldruckverseifung mit Alkali, ist in den letzten Jahren ein weiteres hinzugekommen, das in dem Laboratorium der Dr. F. Raschig G. m. b. H. von *Prahl* und *Mathes* entwickelt wurde.

Dieses Verfahren arbeitet kontinuierlich, drucklos und katalytisch. Sein hervorstechendes Merkmal ist, im Gegensatz zu den bisherigen Verfahren, die Vermeidung jeglichen Chemikalienverbrauchs. Es besteht aus zwei Stufen. Die erste Stufe umfaßt die Herstellung von Chlorbenzol aus Benzol, Salzsäure und Luft, die zweite die Verseifung des Chlorbenzols mit Wasserdampf zu Phenol und Salzsäure.

$$\begin{array}{llr} C_6H_6 + HCl + {}^1/_2O_2 & = C_6H_5Cl + H_2O & (1) \\ \underline{C_6H_5Cl + H_2O} & \underline{= C_6H_5OH + HCl} & (2) \\ C_6H_6 + {}^1/_2O_2 & = C_6H_5OH & \end{array}$$

Die nach Gleichung (2) anfallende Salzsäure wird in der 1. Stufe im Kreislauf wieder verarbeitet, so daß sich als Endgleichung eine Oxydation von Benzol zu Phenol durch den Sauerstoff der Luft ergibt.

Die Oxydation der Salzsäure mittels Luft und Kupfersalzen führt im *Deacon*-Verfahren zu Chlor. Eine Chlorierung von Benzol unter den Bedingungen des *Deacon*-Prozesses ~~scheitert jedoch daran, daß das bei über 400°~~ im Gleichgewicht mit Kupferchlorid vorhandene Kupferoxyd zu lebhafter Oxydation des Benzols Anlaß gibt.

Die Aufgabe war also, einen Katalysator zu finden der gestattet, bei so niedriger Temperatur zu arbeiten, daß kein oder möglichst wenig Benzol verbrannt wurde, und der ferner erlaubt, eine wäßrige 15—20%ige Salzsäure zu oxydieren, wie sie bei der Verseifung des Chlorbenzols anfällt.

Ein hierfür entwickelter Katalysator besteht aus aktivem Aluminiumhydroxyd in Vereinigung mit Kupfersalzen. Leitet man über einen solchen Katalysator bei 220—250° Salzsäure und Luft, so erhält man Chlor nur in analytisch gerade nachweisbaren Spuren. Bei gleichzeitiger Anwesenheit von Benzol entsteht jedoch bei gutem Umsatz Chlorbenzol. Diese zunächst überraschende Tatsache wird durch die weitere Beobachtung erklärlich, daß Cuprichlorid mit Benzol bei 250° unter Übergang in Cuprochlorid Chlorbenzol liefert. Cuprochlorid bildet seinerseits bei 250° mit Luft und Salzsäure Cuprichlorid zurück. Es liegt also hier eine klar übersehbare katalytische Reaktion vor. Diese ist stark exotherm. Sie muß unter Wärmeabführung erfolgen, da Temperatursteigerung schnell in ein Gebiet führt, in dem die konkurrierende Reaktion der Benzolverbrennung die bevorzugte ist.

Die Ausnützung der Salzsäure nach dem Verfahren der 1. Stufe kann leicht bis 99,5% getrieben werden. Abb. 1 gibt den Zusammenhang zwischen Ausnützung der Salzsäure, Temperatur und Belastung des Katalysators, letztere ausgedrückt in Gramm Chlorbenzol pro Liter Katalysator und Stunde.

I. 90 g/l/h, III. 75 g/l/h, II. 50 g/l/h.

Praktisch begnügt man sich mit einer Ausnützung der Salzsäure von ~98%, da unter dieser Bedingung die Verbrennung unter 0,2% des durchgesetzten Benzols bleibt.

Außer Chlorbenzol entstehen bei der Reaktion als **Nebenprodukte höher chlorierte Benzole**, deren Menge sich nach dem Umsatz richtet. Mit steigenden Mengen im Reaktionsgemisch vorhandenen Chlorbenzols steigt natürlich die Wahrscheinlichkeit der Chlorierung dieser Substanz. Die umgesetzte Benzolmenge kann in der 1. Stufe Werte bis zu 50% erreichen. Da die untere wirtschaftliche Grenze bei einem Umsatz von ~7% liegt, hat man es in der Hand, sich den Erfordernissen des Marktes anzupassen. Den größten Anteil der mehr als 1 Chlor enthaltenden Produkte liefert das **Dichlorbenzol**, das aus einem Gemisch der Isomeren besteht. Hierin herrscht das p-Dichlorbenzol mit ~70% vor; es wird als Schädlingsbekämpfungsmittel verwendet, während das in ~30% anfallende o-Dichlorbenzol ein Lösungsmittel mit hoher Lösefähigkeit darstellt. Auch Tri-, Tetra-, Penta- und Hexa-Chlorbenzol entstehen in einer dem Massenwirkungsgesetz entsprechenden geringen Menge.

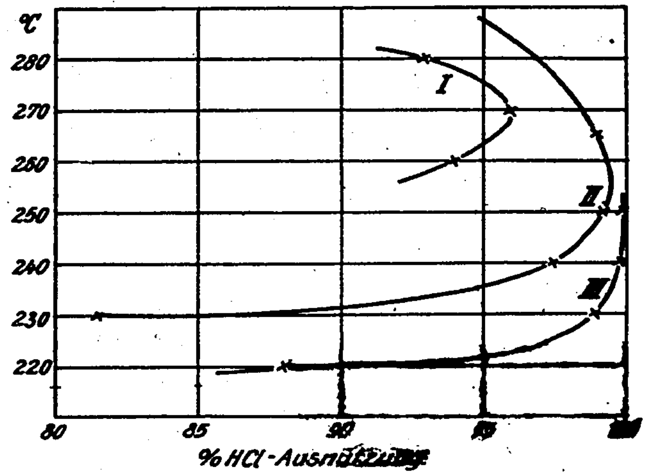


Abb. 1.

Arbeitsweise.

Benzol, Salzsäure und Luft werden auf die Reaktionstemperatur gebracht (s. a. in Abb. 2) und über den Katalysator b geleitet. Aus dem Gemisch mit überschüssigem Benzol, Stickstoff und überschüssigem Sauerstoff werden die Chlor enthaltenden Produkte zusammen mit den nicht umgesetzten ~2% Salzsäure in einer salzsäurefesten, mit *Raschig*-Ringen gefüllten Kolonne c abgetrennt. Überschüssiges Benzol wird kondensiert und nach G geleitet. Das in den Gasen noch enthaltene Benzol wird in einer kontinuierlichen Waschvorrichtung wiedergewonnen.

Die **Verseifung des Chlorbenzols** zu Phenol und Salzsäure findet bei 450—500° statt. Chlorbenzol und ein Überschuß an Wasserdampf werden auf diese Temperatur erhitzt (A) und durch einen Kontaktofen B geschickt. Gute Katalysatoren geben bei 8—15% Umsatz 85—95% Ausbeute an Phenol. Bei einem Umsatz über 15% sinkt i. allg. die Phenolausbeute schnell ab. Die den Kontaktofen verlassenden

Dämpfe enthalten Phenol, Chlorwasserstoff und den Überschuß an Chlorbenzol und an Wasser. Es ist leicht zu überschlagen, daß die Wirtschaftlichkeit des Verfahrens entscheidend davon abhängt, ob es gelingt, die 85—92% nicht umgesetztes Chlorbenzol zusammen mit dem Überschuß an Wasser in Dampfform zu belassen oder ob eine Gewinnung der Reaktionsprodukte nur aus dem Kondensat der Gesamtdämpfe möglich ist. Um eine gegebene Menge Chlorbenzol restlos in Phenol umzuwandeln, ist im letzten Falle ein 7—12maliges Kondensieren und Wiederverdampfen nötig. Es ist gelungen, die Reaktionsprodukte Salzsäure und Phenol auf physikalischem Weg zu gewinnen ohne Kondensation der überschüssigen Chlorbenzol- und Wasserdämpfe.

Die aus dem Kontaktofen der 2. Stufe (B) kommenden Dämpfe gelangen über einen Wärmeaustauscher C in eine säurefeste, mit *Raschig*-Ringen gefüllte Kolonne D, die mit so viel Wasser berieselt wird, als zur Bildung des Gleichgewichts zwischen flüssiger, wäßriger Salzsäure und den in die Kolonne eintretenden Dämpfen ausreicht. Näheres über konstant siedende Gemische im System H_2O, HCl, Chlorbenzol, Phenol kann einer früheren Veröffentlichung entnommen werden[1]). Gleichzeitig wird hier der in Reaktion getretene Anteil an Chlorbenzol und Wasser ersetzt. Die am Kopf dieser Kolonne austretenden salzsäurefreien Dämpfe enthalten noch nahezu das gesamte Phenol. Dieses wird den Dämpfen in einer weiteren mit *Raschig*-Ringen gefüllten Kolonne E durch Berieseln mit viel Wasser entzogen. Chlorbenzol- und Wasserdampf gehen über das den Kreislauf bewirkende Gebläse F, den Wärmeaustauscher C, das Überhitzersystem A in den Kontaktofen B zurück. Die in der Kolonne D anfallende Salzsäure wird von Phenol befreit und fließt dem Verdampfer der 1. Stufe g zu, um erneut den Kreislauf über Chorbenzol anzutreten. Hier wird auch die Salzsäure ergänzt, die mit den mehr als 1 Chlor enthaltenden Produkten aus dem Kreislauf genommen wird. Am Fuß der Kolonne E fließt eine wäßrige Phenollösung ab. Dieser wird das Phenol in einer mit *Raschig*-Ringen gefüllten Gegenstromkolonne G mit Benzol entzogen. Das phenolfreie Wasser kehrt im Kreislauf zum Kopf der Kolonne E zurück. Aus dem phenolhaltigen Benzol wird das Benzol in der Kolonne h abdestilliert und tritt dampfförmig über die Leitung f in die 1. Stufe ein.

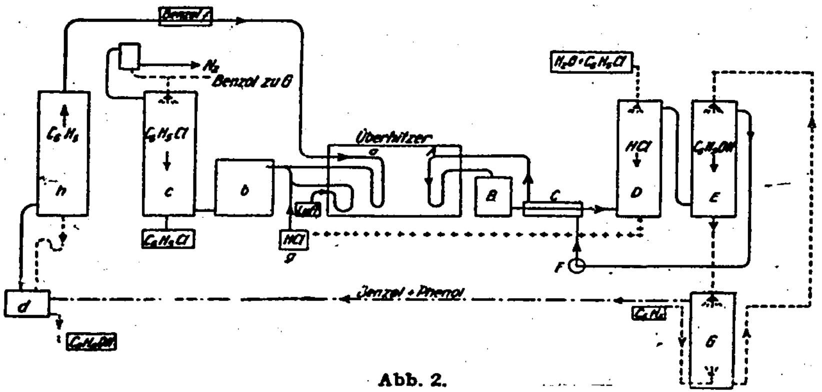


Abb. 2.

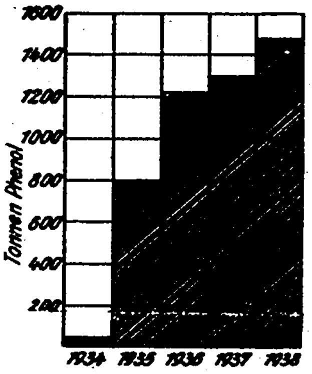


Abb. 3.

Das aus dem Verdampfer d ablaufende Rohphenol hat einen Erstarrungspunkt von ~39°. Eine Destillation trennt die in Mengen bis 1% enthaltenen Nebenprodukte (Diphenyläther, Oxydiphenyl, Chlordiphenyl usw.) ab. Das Endprodukt hat einen Erstarrungspunkt von 40,80°.

Die mit einer Laboratoriumsapparatur von 1 kg/Tag erhaltenen Ergebnisse wurden in den Jahren 1933 und 1934 auf eine Versuchsanlage von 4,5—5 t Tagesleistung übertragen. Die Verarbeitung von wäßriger Salzsäure gehört sowohl in der flüssigen, als auch in der Dampfphase zu den von Chemikern und Ingenieuren gern gemiedenen Operationen. Es gelang aber trotzdem in verhältnismäßig kurzer Zeit, die bei Übertragung vom Laboratoriums- in den technischen Maßstab — zumal bei einem Verhältnis von 1:5000 — immer und überall auftretenden Schwierigkeiten zu beheben. An letzteren hat es, von der Verdampfung wäßriger Salzsäure ganz abgesehen, insbes. deshalb nicht gefehlt, weil in manchen Apparaten neben der flüssigen, wäßrigen Salzsäure bei einer Temperatur von 90—100° gleichzeitig flüssiges Chlorbenzol und Phenol vorhanden sind und hierdurch die korrodierenden Eigenschaften der Salzsäure vervielfacht werden. Es war trotzdem nicht nötig, vom Eisen als dem billigsten Werkstoff abzugehen. Der Überhitzer erfordert eine Sonderlegierung, während nahezu alle anderen Apparate aus Eisen — teilweise mit geschützter Oberfläche — hergestellt werden konnten.

An Hand der **Produktionsziffern** läßt sich die Entwicklung und Vervollkommnung der Anlage erkennen (s. Abb. 3).

Im Zuge der Verbesserung war es auch möglich, von der Unterteilung der Chlorbenzol-Erzeugung in 4 Kontaktöfen abzugehen und die Tagesleistung von ~8 t Chlorbenzol in einem vergrößerten Ofen zu gewinnen.

Wenn bei dem Bau der Versuchsanlage mit einer Stillstands- und Überholungszeit von 3 Monaten im Jahr gerechnet wurde, so konnte diese Frist mit fortschreitender Entwicklung auf weniger als 2 Monate eingeschränkt werden. Eine weitere Verminderung auf 1 Monat wird in der Versuchsanlage sehr wahrscheinlich, in einer unter Verwertung der bisherigen Erfahrungen erstellten Großanlage sicher erreicht werden. Die Sollzahlen der Produktion in der Versuchsanlage wurden 1937 erreicht und im Jahre 1938 überschritten. Sie werden nach den bis jetzt vorhandenen Ergebnissen 1939 eine noch weitere Überschreitung erfahren.

Im Laboratorium wurde zur Herstellung von 1 kg Phenol 1 kg Benzol verbraucht. Dieses Ergebnis konnte in der Versuchsanlage bis jetzt noch nicht erreicht werden, da aus apparativen Gründen die Benzoldampfverluste bis jetzt nicht auf das bei Tankanlagen mit Spezialvorrichtungen gegen Verdunstungsverluste (Ausgleichtank, Absorption an aktive Kohle usw.) übliche Maß eingeengt werden konnten. Nach Ausschaltung dieser nicht im Verfahren selbst begründeten und daher vermeidlichen Benzolverluste kann mit einem Verhältnis von hergestelltem Phenol zu angewandtem Benzol wie 1 zu 1,15 gerechnet werden, wobei von der letzten Zahl der Benzolwert, der den anfallenden Nebenprodukten entspricht, abgezogen werden muß. Die Reparatur- und Unterhaltungskosten liegen seit Erreichen der Sollzahlen der Produktion in der bei chemischen Anlagen ähnlicher Größe üblichen Höhe.

In den Vereinigten Staaten wird zurzeit eine Anlage zur Herstellung von Phenol nach dem *Raschig*-Verfahren mit einer Tagesleistung von 20 t erbaut. [A. 65.]

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[1]) Diese Ztschr. 47, 11 [1934].

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B.I.O.S.—FINAL REPORT No. 450

ITEM No. 30

GESELLSCHAFT FÜR TEERVERWERTUNG m.b.H., DUISBERG–MEIDERICH AND CASTROP–RAUXEL

Waller, C.J. and Murray, C.A.

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BRITISH INTELLIGENCE OBJECTIVES

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LONDON—H.M. STATIONERY OFFICE

GESELLSCHAFT FUR TEERVERWERTUNG m.b.H.
DUISBERG - MEIDERICH
&
CASTROP - RAUXEL

Reported by
C.J. WALLER
&
C. A. MURRAY, JNR.
of
Ministry of Fuel and Power.

B.I.O.S. Target No. 30/7.04.
Fuels and Lubricants

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

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Personnel of Team.

C.A. Murray, Jnr. Ministry of Fuel and Power.
C.J. Waller, " " " " "

PERSONNEL

The general management of the Company is in the hands of

Director Dr. Moehrle (Technical)
Director Dr. Van den Hövel (Commercial)

At Duisburg Works

Dr. Siedler	Technical Director
H. Fischer	Chief Engineer and Works Manager
Dr. Wille	Manager of Pure Products Plant
Dr. Kaffer	Coumarone and Pyridine
Dr. Krüber	Semi-technical production of special products

At Rauxel Works

Dr. Klemm	Works Manager and Director
Dr. Lauenstein	Chief Chemist
Ing. Dunker	Engineer

PRODUCTS MADE

The Works at Duisburg distils 250/300,000 tonnes per annum of crude tar from coke ovens in the Ruhr District, and in addition works up the products of the primary distillation of crude tar from the Company's subsidiary Works at Castrop-Rauxel etc., representing in all a crude tar distillation of 800,000 tonnes per annum. The yearly tonnages of tar distilled and chief products made for the pre-war period 1937-1940 are given below. During 1943, when, despite bombing, production was at a maximum, 800,000 tonnes of crude tar were distilled by the Company.

	1937	1938	1939	1940
Crude Tar distilled	656,000	689,000	735,000	766,000
Products Made				
M.S. Pitch	311,000	320,000	348,000	372,000
Refined Tar	76,000	84,000	78,000	71,000
Pitch-Creosote Mix:	11,000	46,000	96,000	164,000
Fuel & Diesel Oil	56,000	54,000	45,000	26,000
Benzole Wash Oil	18,000	21,000	25,000	28,000
Oil for Hydrogenation	21,000	28,000	29,000	24,000
"Flame Oil" (Army)	50	65	795	2,000
Raw Naphthalene and Anthracene	43,000	46,000	50,000	53,000
Pure Naphthalene	4,700	3,600	4,600	3,400
Benzole & Homologues	7,900	8,700	10,100	10,300
Refined Tar Acid	7,600	7,600	11,100	10,000
Pyridine	315	325	465	405
Other Chemicals	120	50	23	23

DUISBURG-MEIDERICH WORKS

General, Personnel, Bomb Damage, Present Operation.

During full production, i.e. 1943, the total personnel employed numbered approximately 1,100. At the time of the visit 767 persons were employed, of whom over 200 were engaged on bomb repair work. The plants operate normally on a two or three shift system, six days a week.

The works had received damage by air raids on 19 occasions prior to ~~November~~, 1944 but repairs had, up to that time, enabled production to be maintained except for short stoppages. On 30th November, 1944, as a result of a daylight attack by 50 Mosquitoes, 60-70 direct hits were obtained on plant and the works virtually put out of action for the rest of the war, the casualties on this occasion being 10 dead and 60 injured.

The plant totally destroyed included:-

(1) Products tank farm
(2) The crude tar dehydration unit
(3) Three tar distillation units
(4) Naphthalene settling plant
(5) Plant heavily damaged included almost the entire naphthalene plant, pitch filling plant, tar acid washing and once run benzole distillation unit.

At the time of the visit crude tar was being distilled in the remaining batch units for the production of road tar.

The continuous tar distillation plant with small repair and fresh instrumentation could be again operated as could two of the oil distillation units and the major part of the benzole plant. The anthracene settling plant could operate almost immediately but although distillation of tar acids is immediately possible in the new plant, the production of tar acids is impossible due to the need for the repair and complete rebuilding of the washing plant. The steam generating plant is in fair condition but considerable repairs to all services would be required if products plants are again to be put into operation.

(1) Crude Tar Storage and Dehydration.

Crude tar is received from the coke ovens by barge and rail tank car, and is pumped to three crude storage holders of 5,000 tonnes each capacity, two of which were lagged with 9" Bimsstein (pumice) bricks, advantage thus being taken of the temperature at which tar is received during the summer, viz. 50-60°C. From the holders the crude tar is pumped to an overhead feed tank with gravity feed to the dehydration stills.

After settling, the crude tar contains from 3-5% of water and is continuously dehydrated in five pot still units each of a maximum throughput of 200 tonnes per day. Each unit consists of 10 tonnes capacity tar stills of conventional design, gas fired and fitted with a short distillation column built up of two sections each with four trays of normal bubble cap design but without caps. The plates are of 1¼m. diameter with 26" x 2" diameter uptakes; each plate is spaced 6" from the next. The crude tar, after passage through an economiser built by the Deutsch Economic Werk, Dusseldorf and placed in the main chimney flue from the four distillation units attains a temperature of 75/80°C. and is fed continuously at the rate of 175/200 tonnes per day to the centre of the distillation column, the still temperature being maintained at 140-150°C. Water and light oil are distilled off, the light oil representing approximately 0.7% by weight of the crude tar distilled and yielding on redistillation 50% of creosote residues. The dehydrated tar is stored in lagged process tanks for immediate working up in the batch tar stills or continuous plant. It is of interest to note here that due to damage to the dehydrating plant a normal tar distillation unit had been converted for dehydration and that in this case a column of four sections, i.e. 16 plates, had been used with better results.

Repairs to the dehydration plant were stated to have been low, still replacements only being required after 10-15 years life.

Scheme of Dehydration

Crude Tar, after passage through Economiser
at 75/80°C.
Dehydrated continuously at 140/150°C.

Ammoniacal Liquor
(worked up to
ammonia sulphate)

Dehydrated
tar

Light Oil
Worked free of tar
acids and pyridine and distilled
to yield Once Run
white products.

2. Crude Tar Distillation.

Crude tar is distilled in five units:-

(a) A continuous vacuum distillation plant of 8,000 tonnes per month throughput; this plant is of sufficient interest to be the subject of a full subsidiary report (Page 19.)

(b) (c) (d) Three sets of 6 x 16 tonne batch stills, total capacity 17,000 tonnes per month

(e) One set of 2 x 50 tonne batch stills, capacity 6,000 tonnes per month.

The batch units are of conventional design without fractionating columns, gas fired, and working under a vacuum giving an absolute pressure of 160 mm. Hg., which is applied through the receivers. The vapours are condensed in vertical cast-iron coiled water condensers, the coil diameter diminishing from 6" to 3". Corrosion, considered due to the presence of hydrochloric acid gas, was found particularly in the vapour pipes, but no special precautions against it were taken. The stills built up of $\frac{7}{8}$" mild steel welded plates were stated to last approximately 2,000 charges before a new bottom had to be fitted. The still shell normally lasted 6-8,000 charges.

Dehydrated tar at 120/140°C. from the lagged intermediate storage is charged to the stills and distilled to 65/70°C. melting point (K. & S.) pitch which is run into coolers and blown either to pitch bays or to the mould filling plant. The following fractions are taken:-

(a) and (b) "Middle" and "Heavy" Oil fractions which are blended together and redistilled. For the purpose of this report the blend of these two fractions has been designated as Light Oil No. 2.

(c) Crude Anthracene oil fraction.

These fractions are further worked up as per scheme detailed below.

Scheme of Distillation

Dehydrated Tar
(Distilled in batch stills)
95 pts.

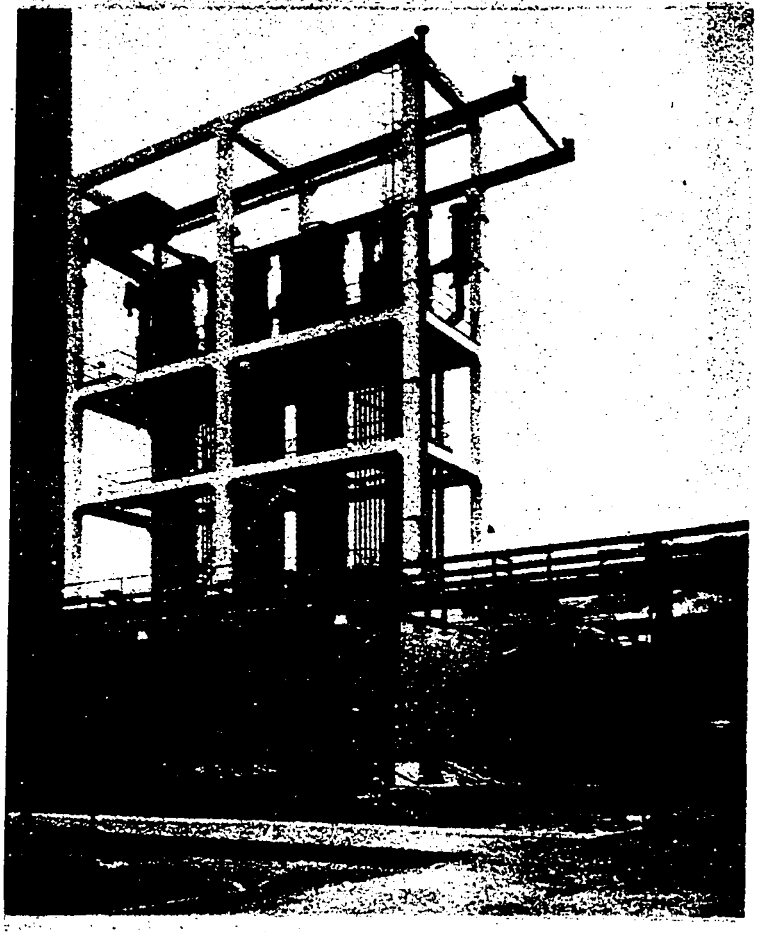
Pitch M.S.
To pitch bays or
moulding plant or
to Blending Plant
for production of
Road Tar or Tar
Fuels

Light Oil
for
redistillation

Crude Anthracene
Oil
Cooled and settled
to give crude
anthracene residue

[redacted]

OIL DISTILLATION PLANT



Shewing gas-fired stills and packed columns.

(3) Working up of Light Oil (No. 1)

(a) Redistillation. The Light Oil produced in the dehydration of the crude tar is washed free of tar acids with caustic soda and then redistilled to give the following four fractions:-

Once-run benzole No. 1	(boiling range 95%-87/134°C.)
Once-run benzole No. 2	(" " " 136/165°C.)
Crude Solvent Naphtha	(" " 90%-165/180°C.)
High Boiling Benzole	(" " " 180/200°C.)

The neutral oil fraction obtained by the redistillation of Light Oil No. 2 (from the distillation of the dehydrated tar), after washing in the tar acid plant, is treated together with Light Oil No. 1.

The older oil distillation plant consists of two batteries each of six stills, one set normally handling Light Oil No. 1 and the other set Light Oil No.2. The stills, of similar design to the tar stills are of 15 tonnes capacity, gas heated and fitted with a packed ring column 1 M. diameter and 6 M. high, complete with dephlegmator and working under a vacuum of 160 mm. absolute pressure. Iron rings of 35 mm. are used and owing to gradual blockage by deposition of resins etc., the rings have to be changed every 80 charges; the rings being cleared for further use by burning out in a furnace with a travelling grate stoker and then rinsed with water in a rotating drum screen.

A new distillation unit had just been completed consisting of 4 x 50 tonne stills fitted with 1.5 M. diameter columns 10 M. high.

Yields of the once-run fractions for the year 1943 are shown below:

Crude tar distilled, 1943 yielding	806,731	tonnes
t Oil No. 1	5,558	"
" " by redistillation of Light Oil No. 2	5,470	"

which oils on redistillation give:-

Once-run benzole No. 1	19.2%	by weight
" " No. 2	9%	"
Crude Solvent Naphtha	9%	"
High Boiling Benzole	10.3%	"
Residue	50%	"

(b) Rectification of Pure Products

The once-run fractions are each washed separately for pyridine bases and with concentrated sulphuric acid for rectification, and are then distilled to yield the appropriate white products required.

The actual yields of white products for the year 1943 are given below, the yields being quoted relative to the Light Oil handled:-

Benzene, pure	3.7%	by wgt.
" 90's	0.2%	"
Toluene, pure	11.1%	"
Xylene 5°	4.2%	"
Solvent Naphtha	3.4%	"
High Boiling Benzole (R.H.N.)	10.7%	"
Cumarone Resin	3.8%	"
Acid Tar Pitch	2.2%	"
Still Bottoms	9.1%	"
Loss	1.6%	"

A full consideration of the treatment and yields obtained by the rectification of the first benzole fraction is given below to give an indication of the efficiency of fractionation obtained in the benzole plant with the packed columns in use.

The once-run benzole of boiling range 87/134°C. is first washed with sulphuric acid of s.g. 1.3 to remove pyridine and is then further washed with concentrated sulphuric acid at the average rate of 2/300 litres for every 15-tonne charge.

The yields per 100-tonnes of once-run benzole are:-

83	tonnes	washed benzole
8.5	"	pyridine
4.5	"	acid sludge
4.0	"	loss

The washed benzole on first distillation yields:-

4% motor benzole (less than 0.5% toluene)
1.5% first benzole intermediates
26% pure benzene (95% distilling 0.8°C. range)
1.5% second benzole intermediates
12.5% first toluene intermediates
12% pure toluene (95% distilling 0.8°C. range)
12.5% second toluene intermediates
9% Crude Xylene
21% Still Bottoms

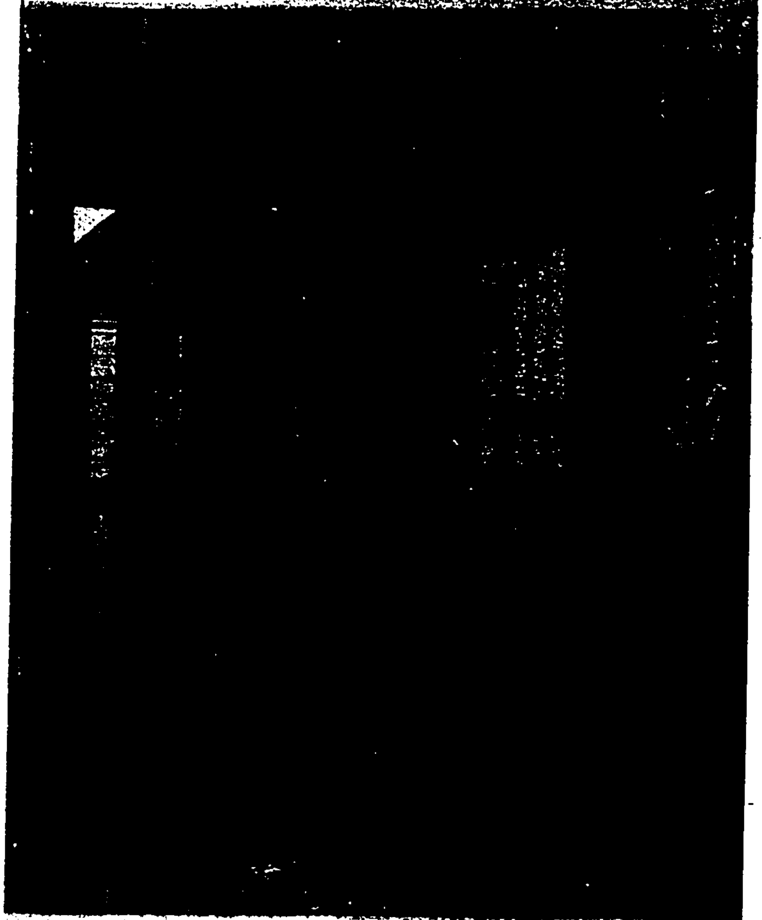
The first and second benzole intermediates are mixed together and on redistillation yield 90% pure benzene. The first and second toluene intermediates are similarly mixed and on redistillation yield 55/60% pure toluene.

Under peacetime conditions as an alternative to the above scheme the once-run benzole No. 1 can be washed with 90% sulphuric acid to yield on distillation motor spirit instead of benzene, toluene and xylene.

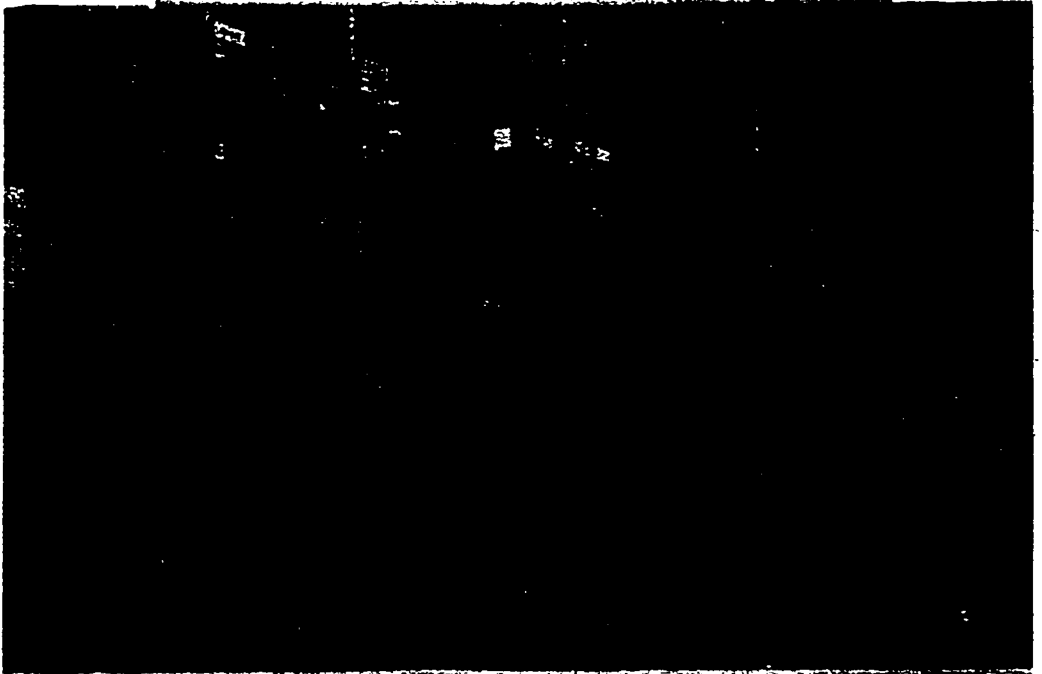
The once-run benzole No. 2, crude solvent naphtha and high boiling benzole are similarly treated except that the high boiling benzole fraction is first polymerised in the washpots with concentrated sulphuric acid for the production of coumarone resin, the process being as follows:-

The heavy boiling benzene fraction distilling 165/180°C. is polymerised by concentrated sulphuric acid in tiled 8- or 15-tonne washers fitted with stainless steel cooling coils and mixers. On average 50/60 litres of 100% acid is added per each 8-tonne batch, agitated to 2-3 hours at a temperature of below 35°C. and the wash allowed to settle for 24 hours.

BENZOL [illegible]



View of polymerising mixers



View of washers

The quantity of acid used may vary as much as from 1% to 5% and it is run very slowly into the mixer and the progress of the polymerisation determined in the laboratory by rapid distillation with open steam. Although the raw fraction is described as Tar Acid and tar base free, it was stated by Dr. Wille that the removal of the last traces of pyridine was not necessary and even inadvisable, the colour and melting point of the final product being improved when polymerisation took place in the presence of pyridine. This statement is contrary to usual practice but no confirmation or otherwise could be obtained from the plant records.

The heavy benzole fraction containing the polymerised resin is distilled without a column from a nickel still under vacuum with super-heated steam, temperature 250-270°C. (Aluminium stills had proved less satisfactory than copper). The melting point of the final resin is variable, with an average melting point of 50-70°C. and the resin is of good colour, varying from pale straw to light brown.

The washing plant consists of ten 15-tonne mixers, six of which are generally employed for normal acid treatment, two for acid sludge treatment and two for polymerisation, and in addition there are two 8-tonne washers specially built for carrying out polymerisations. All the mixers are lined with acid-resisting tiles by Keramchemie, Berggarten and are being constantly repaired and re-pointed, the work being done under contract, one tiler being usually employed for 3-6 months per year. The mixers are of a paddle type.

The distillation plant consists of six 50-80 tonne stills fitted with columns varying between 1,000 and 1,200 mm. diameter and from 8-12 M. high, packed with 1" iron Raschig rings, the columns being fitted with normal dephlegmators. Steam pressure is available at 9 atmospheres and vacuum can be applied for obtaining the high boiling fractions. The normal distillation rate is 1,000 litres per hour, dropping to 2/300 litres per hour when taking intermediate fractions at high reflux ratios of 1:10/12. The total boil-up in the column was 3/4,000 litres per hour.

The acid sludge obtained from the acid washing of the various fractions was treated by washing with tar acid-free creosote to recover the contained light hydrocarbons, neutralising with caustic soda and steam-distilling. The stills used for this redistillation were stated to last many years and the residue was dumped back into the crude tar, thus eventually being sold in the medium soft pitch.

(4) Redistillation of Light Oil No. 2.

The oil is redistilled in plant of identical construction to that distilling light oil No. 1, i.e. from 15-tonne stills under vacuum with packed column 1 M. diameter, 10 M. high. The first fraction taken is the carbolic oil which contains 30% tar acids and the fraction is so taken that the following naphthalene oil cut contains no phenol. The second fraction is a crude naphthalene oil; the third fraction is a so-called "Solvoy" or wash oil, which is free from naphthalene, and the fourth fraction is an anthracene oil which is added back to the anthracene oil fraction obtained by the distillation of crude tar and the residue is put back to the dehydrated tar. It is estimated that this residue on redistillation with the dehydrated tar yields approximately creosote oil, anthracene oil and pitch in equal proportions.

Scheme and Yields

19 Pts. of Light Oil (No. 2)

Carbolic Oil (30% T.As)
7 Pts. (settled for
naphthalene and washed
for tar acids).

Naphthalene Oil 4.2 Pts
free from phenol
(settled for naphthalene)

Returned to dehydrated tar
Residue 3.3 Pts.

Anthracene Oil
1.3 Pts.

Wash Oil
3.2 Pts

(5) Settling and Production of Naphthalene.

Both the crude carbolic and naphthalene oils are settled in a series of 10-tonne settling tanks to give a crude naphthalene of 55/65°C. M.P. which, on whizzing, gives a product of M.P. 75°C. Hot pressing at 350 atmospheres pressure, increases the M.P. to 79°C. The hot presses were built by Harburger Bronzewerk, Hamburg Harburg and it was stated that these manufacturers produced all the hot presses for napthalene production in Germany. A considerable proportion of the total naphthalene production had been sold during the past years for the production of deca and tetra hydro-naphthalene for which purpose a washed, whizzed or hot pressed salt had proved suitable.

The maximum production of pure naphthalene was 3/400 tonnes per month through a conventional plant which yielded a product of 79.6°C. M.P. although some quantities of material with a M.P. of 79.75°C. had been produced for the I.G. Farben by extra washing and closer fractionation. For the production of pure naphthalene the hot pressed salt was washed with sulphuric acid in a normal lead-lined washer (no satisfactory type of acid resisting outlet valve or cock had been found) and then was distilled under vacuum from 50-tonne vertical gas-fired stills fitted with 1,250 mm. diameter packed columns, 10 and 15 M. high complete with dephlegmator. The columns were packed with 1" Raschig rings and experience had shown the 10 M. high column to be fully satisfactory. The average distillation rate used was 500 litres per hour at a reflux ratio of 3/4:1. The distillate after initial cooling to the liquid state was collected in lagged intermediate storage tanks from whence it was run over water-cooled rollers where it solidified and was taken off with a knife set to give a thickness of approximately 2 mm.

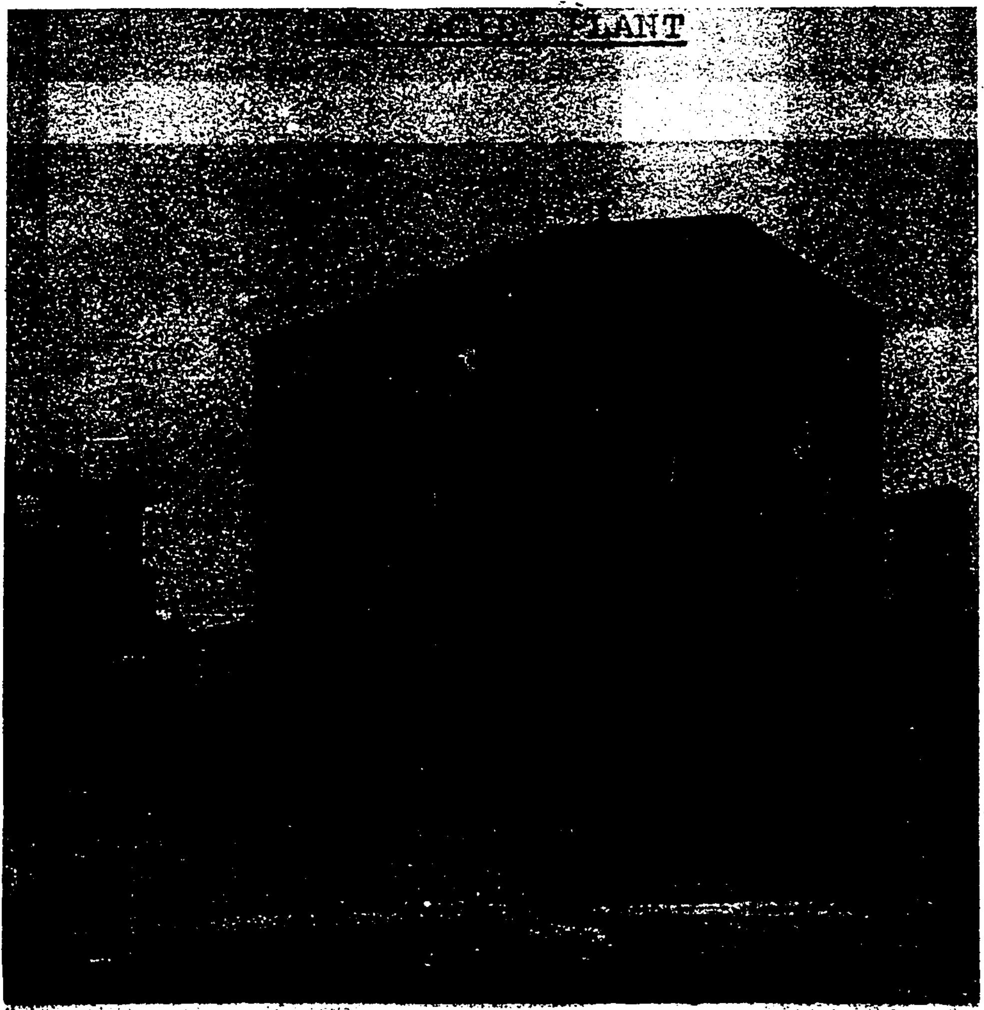
(6) Extraction and Working up of Tar Acids.

(a) Causticising, Washing, De-oiling and Springing Plant.

Note: In addition to the production of tar acids from the distillates obtained from crude tar,

[redacted]

[illegible] PLANT



De-oiling and springing plant

considerable quantities of sodium phenolate from the coke-oven washeries are handled, as it is necessary to reduce the phenol content of all wash waters to below 0.5% before it may be discharged into the river Ruhr.

Four causticising units are in use, two fitted for reaction under pressure, but it has been proved that the use of pressure is not beneficial. The recovered sodium carbonate is heated under vacuum in two continuous boiler plants to increase the concentration of soda from 10% to 20%. Milk of lime of 20% concentration is then added in the causticising units and the mix settled, approximately the top two-thirds is decanted off as clear soda solution and the bottom third filtered in rotary vacuum driers fitted with a Monel metal screen. Before the War linen cloth filters were used. After drying in the open over an extended period, the filter cake tested 52% calcium carbonate and 2/3% sodium carbonate. The soda solution recovered varied from 7/10%. The carbolic oil containing 30% tar acids is washed with sodium hydroxide at 50°C. down to a tar acid content of below 0.5%, the phenolate produced containing 15/20% tar acids.

The sodium phenolate is de-oiled by running it continuously down a packed column at the rate of 5,000 litres per hour, the column being fitted with a heater with closed steam coils and open steam. The temperature of the whole column is raised to 98/100°C. and the continuous discharge of phenolate is practically free from oil and contains 0.025% of pyridine bases (the unpurified phenolate contains a total 1% impurities as oil and pyridine). The distillate from the top of the purifying column on condensation contains 93% water, 3% pyridine bases and 4% oil. The pyridine and oil is recovered by washing the distillate with creosote wash oil.

The oil free phenolate is next continuously saturated at a similar rate by passing down in series two packed columns into which carbon dioxide is blown at the bottom. The carbon dioxide first passes up the secondary column in which the crude phenol from the first column to which carbonate always adheres, is finally treated to throw down the last traces of carbonate as bi-carbonate. The carbon dioxide is then passed up the first saturater where the crude phenol is sprung from the sodium phenolate feed. By this continuous process saturation is complete and the waste gases contain only 2-4% of carbon dioxide. The original gas from the lime kiln contains approximately 35% carbon dioxide.

The plant is of mild steel construction, the purifying towers being 1.5 M. diameter and approximately 12 M. high and the gassing towers 1.2 M. diameter and 9.0 M. high.

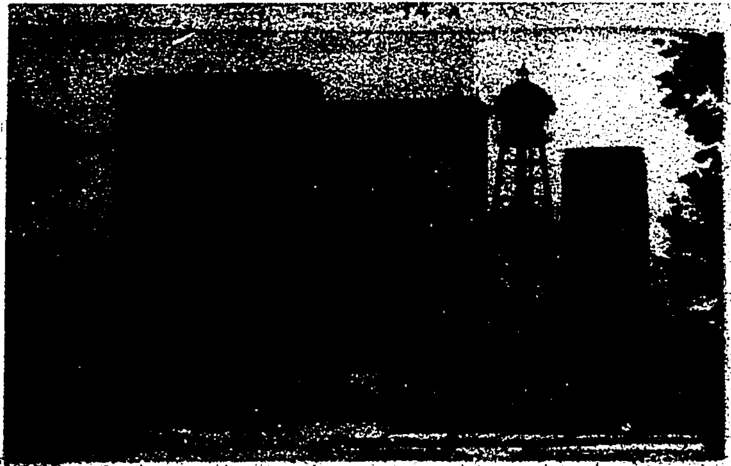
(b) <u>Dehydration Plant</u>.

Dehydration was carried out in two units each consisting of a 10-tonne capacity gas-heated still fitted with a 800 mm. diameter 5 M. high column packed with 1" Raschig rings. The crude tar acids were pumped at the rate of 1,000-1,500 litres per hour by a centrifugal cast iron pump to the top of the column and the still temperature maintained at 160°C. Control of this temperature was considered of the utmost importance and a recording thermometer (one of the very few seen on the Works) was installed to register the temperature of the liquid content of the dehydrating still. No vacuum was employed during dehydration. A cast iron plate condenser (as used on the continuous tar distillation unit, and fully described in the report thereon) was utilised as a final condenser and partial heat exchanger, the top half having water circulating and the bottom the crude tar acid feed, the temperature of which was raised to 40°C. by the condensing vapours: vapour temperature at the top of the column was 80°C.

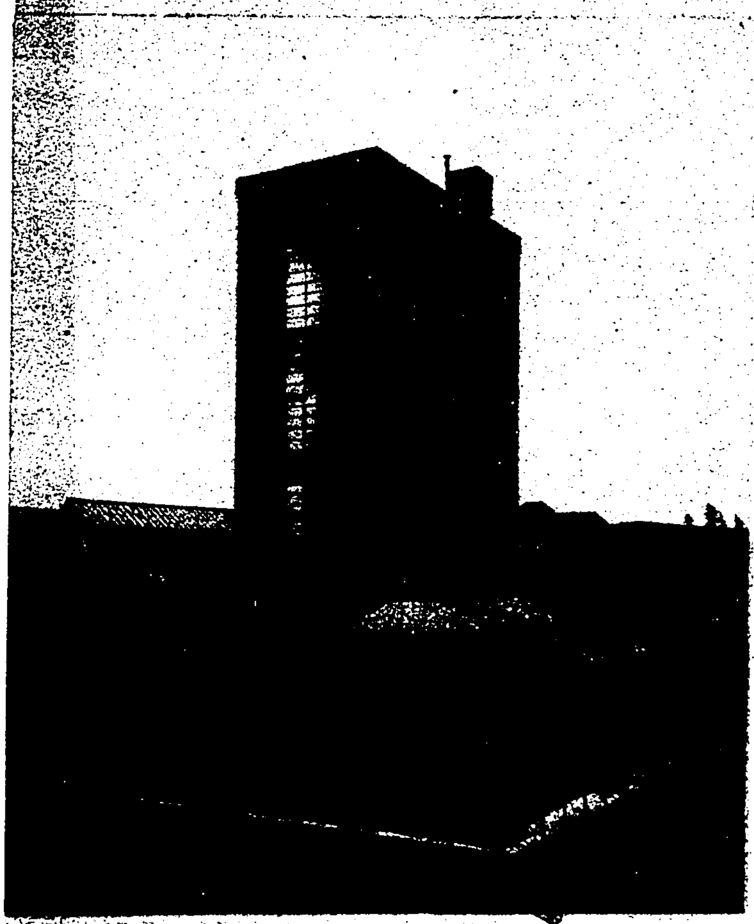
The water content of the crude tar acids was reduced from 15 to 20%, to below 0.3% and the condensed distillate contained approximately 4% dissolved phenols and 1.3% of phenolic oil. This phenolic-water/phenolic-oil mixture was first settled and the separated phenolic oil returned to the benzole plant for washing. The phenolic water was washed with neutral oil at 50°C., the phenol

TAR ACID PLANT

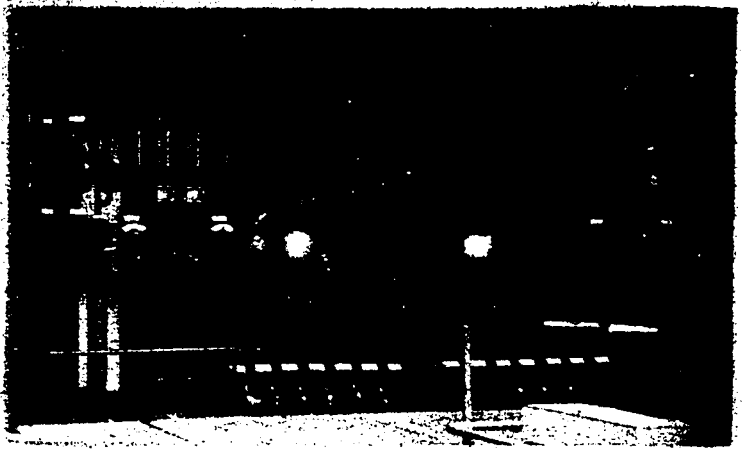
Distillation Units



(1) View shewing dehydration and 1st distillation plant.



(2) View shewing stills and column house of dehydration and 1st distillation plant.



(3) Detail showing receivers and control sight glasses, valves and run-off manifold.

content of the water being reduced to 0.2%.

(c) Primary Distillation Plant.

The first distillation of the dehydrated phenol was carried out in two 50-tonne stills fitted with columns 10 M. high, 1,500 mm. diameter and packed with 1" Raschig clay rings with plate dephlegmators working under a vacuum to give 50-60 mm. of absolute pressure; the vacuum was applied in the normal manner to the coolers via an oil-washer of the same type as described fully on the report of the continuous crude tar distillation plant.

The mild steel stills that had been supplied durigg the war had to be replaced after approximately 300 charges due to corrosion which occurred in the form, at first, of pinhole pitting, extending in time over the whole plate. Before the war it had been found that the stills lasted normally 400 charges, although the steel was not of a special grade. It was thought that the corrosion was due to compounds present in the high boiling xylenols (oxy. hydrindine?) which decomposed on heating to give off nascent hydrogen. Two phenol cuts together with an ortho and meta rich cresol fraction were taken off during the primary distillation, the xylenols being left in the residue which was run to storage until sufficient quantities were accumulated for further distilling.

(d) Redistillation Plant.

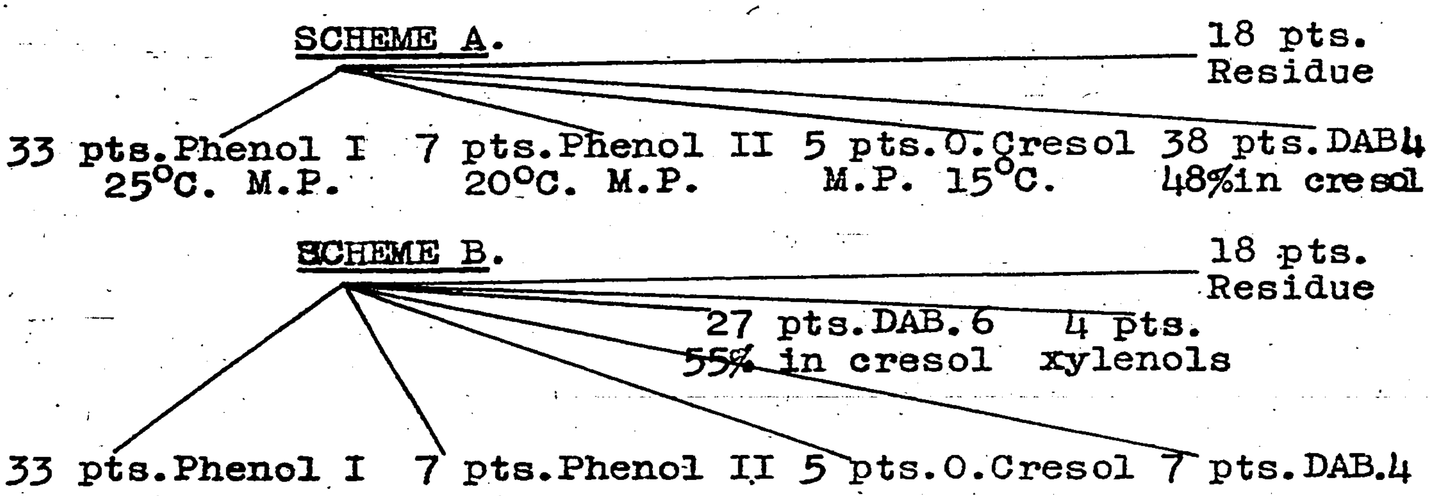
Re-running of the various fractions was carried out in the old distillation plant which, before the erection of the new dehydrating and primary distilling plant, handled both the primary and secondary distillations. The plant consisted of seven 20-tonne stills, steam heated, with columns 10 M. high and 1 M. diameter and packed with 1" steel Raschig rings, fitted with tubular dephlegmators and working under a vacuum of 50-60 mm. absolute pressure. In addition to these stills there were two 10-tonne stills fitted with columns 3 M. high, 800 mm. diameter, packed with 1" steel

Raschig rings, steam heated and working under vacuum, which plant was used for stripping the xylenols from the residue of the primary distillation. The steam pressure available was at 8-10 atmospheres. The plant was capable of handling an absolute maximum of 1,500 tonnes per month.

No excessive corrosion was found in either the primary or secondary distillation units, despite the use of steel rings in the latter. The colour of the products was good and no attempt made to add stabilising chemicals to the crude tar acids before distillation.

Specimen Scheme of Distillation

100 Pts. Dehydrated Crude Tar Acids.



SCHEME A.

18 pts. Residue

33 pts. Phenol I 25°C. M.P.

7 pts. Phenol II 20°C. M.P.

5 pts. O. Cresol M.P. 15°C.

38 pts. DAB4 48% in cresol

SCHEME B.

18 pts. Residue

27 pts. DAB. 6 55% in cresol

4 pts. xylenols

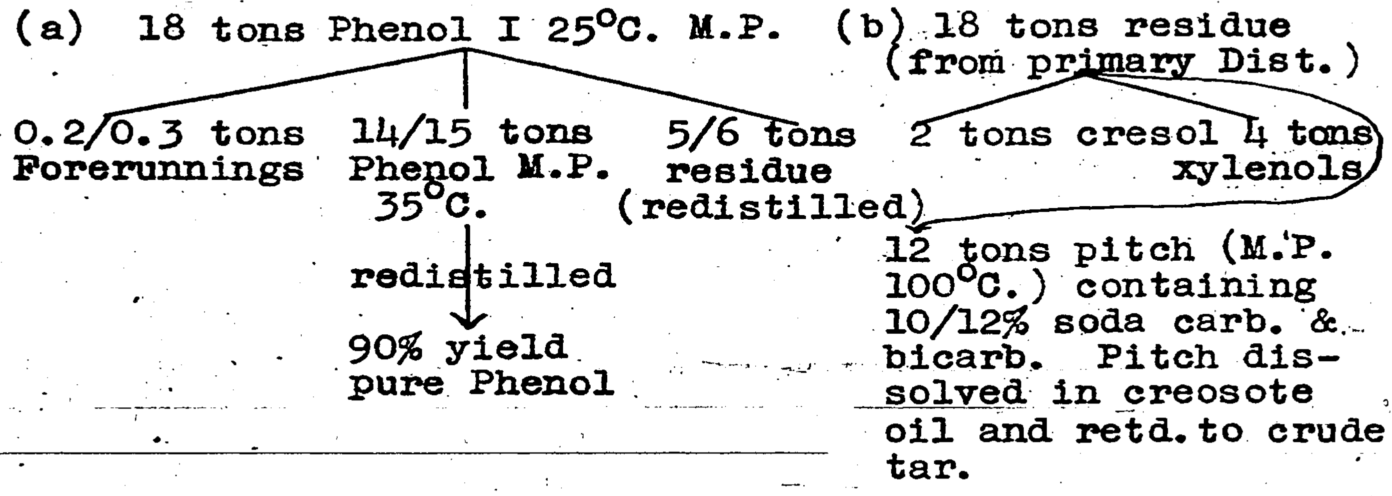
33 pts. Phenol I

7 pts. Phenol II

5 pts. O. Cresol

7 pts. DAB. 4

REDISTILLATION



(a) 18 tons Phenol I 25°C. M.P.

0.2/0.3 tons Forerunnings

14/15 tons Phenol M.P. 35°C.

redistilled

90% yield pure Phenol

5/6 tons residue (redistilled)

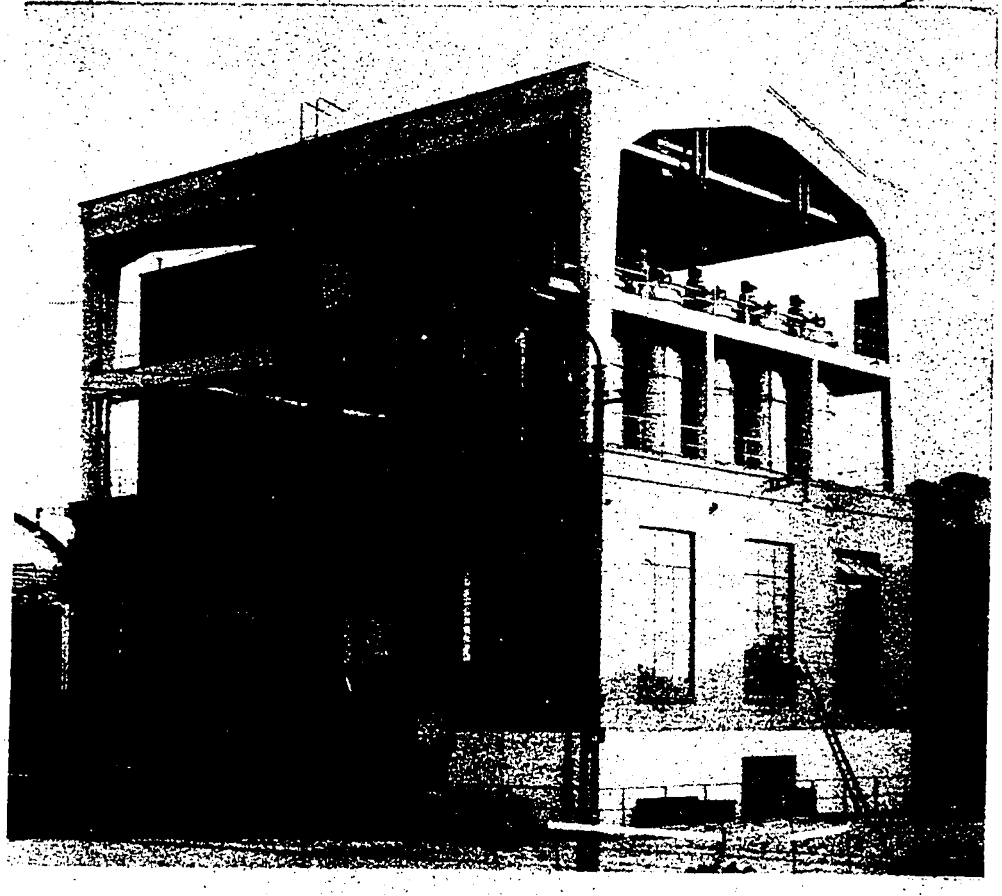
(b) 18 tons residue (from primary Dist.)

2 tons cresol

4 tons xylenols

12 tons pitch (M.P. 100°C.) containing 10/12% soda carb. & bicarb. Pitch dissolved in creosote oil and retd. to crude tar.

ANTHRACENE PLANT



View showing house and settling mixers

Detail [illegible]

Normally no special xylenol fractions are taken, the fractions stripped from the residue being sold as high boiling tar acids, but some 1.3.5 xylenol has been made by collecting the mixed xylenol fractions in sufficient quantity to put them through one of the primary distillation units, when a product with a boiling range of 218/228°C. was taken, which product had a M.P. of 25/28°C. Due to the method of extracting the tar acids from the distilled carbolic oil fractions only, the quantities of xylenols produced are small and no efforts had been made to wash heavier creosote oils to produce xylenols despite having separated the 1.2.4, 1.3.4, 1.4.5, 1.3.5, and 1.2.3, xylenols on a large laboratory scale; the reason given was due to lack of demand.

(e) Pure Phenol Production.

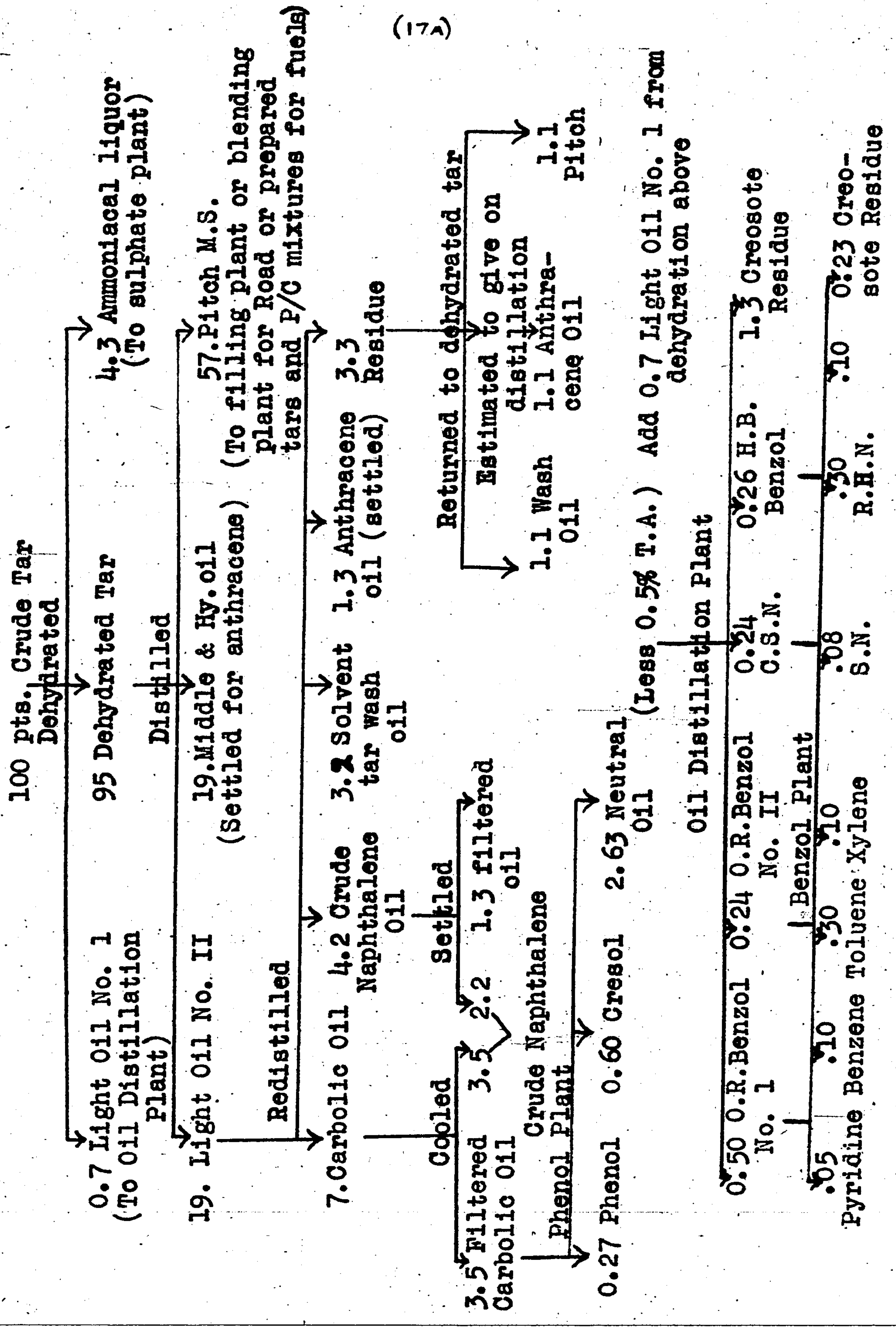
Distillation was carried out in two 20-tonne and one 50-tonne stills fitted with a M.S. column 15 M. high, 1 M. diameter and packed with 1" rings with a steel tubular condenser but with silver distillation pipes and cooler. Vacuum, to give 40 mm. absolute pressure was applied at the condenser. No trouble was found as regards colour of product, which was excellent even after one year, and this was considered due to good separation of phenol during the primary distillation of the crude tar acids; it was even considered unnecessary to use silver lined pipes.

(7) Settling and Production of Crude Anthracene

The mixed middle and heavy oils are pumped to feed tanks set in the top of the anthracene building and charged by gravity into twenty 10-tonne anthracene water-jacketted cooling mixers. After cooling the slurry leaves the mixers through a worm outlet and flows to a set of six 1-tonne horizontal centrifuges, built by C. G. Haubold A.G. of Chemitz, built with cast iron casings, mild steel buckets and with a speed of 720 r.p.m. A yield of 10% crude anthracene residues on the mixed oil is obtained and the residue tests as follows:-

Oil	2.5/3.0%
Water	Less than 2%
Anthracene	25/30%

SCHEME FOR WORKING UP OF CRUDE TAR (BATCH PROCESS)



Carbazole	20/22%
Acenaphthene	1/1.5%
Phenanthrene	The remainder

The grade of anthracene produced was used mainly by manufacturers of carbon black.

CONTINUOUS VACUUM TAR DISTILLATION PLANT

A description of the plant including distillation ranges of the oils produced and services required is given in Appendix B in the form of a contribution made by the chief engineer W. Fischer to "Verfahrenstechnik" Nr. 1,1944,S.13 bis 29.

In considering the fuel economy of the plant, the following points should be observed, viz:

(1) that tar already dehydrated is used as the feed to the plant

(2) that when adding the fuel required for dehydrating to the fuel for distillation, an allowance should be made for the heat picked up in the heat exchanger through which the crude tar passes to the dehydrater and which recovers the heat from the three main batch distillation units, which units distil roughly twice the amount put through the continuous plant,

(3) that the light oil recovered as distillate from the dehydration plants requires redistillation to recover the light fractions in a form comparable with that obtained on most continuous plants in England. The calculation given below for total fuel consumption ignores the last two points mentioned above.

Total fuel requirement per ton tar distilled

Coke oven gas: continuous plant	29.4 M^3
" " " for dehydration	18.5 M^3
	47.9 M^3
Average calorific value of gas	4,100 Cals/M^3
equivalent to	196390 Cals.
Steam: continuous plant	30 Kgms. per tonne
" : dehydration "	10 " " "
	40 " " "
equivalent to	32,800 Cals.
Electricity: continuous plant	4 kWh/tonne
equivalent to	3,440 Cals.

giving a total fuel consumption of 232,630 Cals.per ton.

The general scheme of the plant is shown in Appendix C.

The plant was fully instrumented with instruments of both indicating and recording type but no attempt had been made towards automatic control. No special metals had been employed in the construction of the plant and during the $2\frac{1}{2}$ years it had been in use no particular corrosion troubles had occurred, and no replacements for this reason had been required. The plate condenser on the anthracene column was built by Zimmerman & Jensen, Duren, and had been used because of the large quantity of vapour it had to pass compared with the quantity of condensate. The stated throughput of the plant was 12 tonnes per day, although in this connection it is worth noting that 86,000 tonnes had been put through during 1943.

It is interesting to note that the pipestill is operated under a pressure of 3 atmospheres, regulation being obtained by a valve on the outlet placed immediately before the discharging point to the flashing column. The reason given by the engineer for this method of operation was that it prevented vaporisation in the pipe-still thereby reducing corrosion and coking to a minimum.

When designing the plant very special considerations had been given to reducing back pressures across the distillation columns to a minimum so that the vacuum could be applied at one point, viz. at the vapour outlet to the last column and there still be maintained at the bottom of the first column a vacuum equivalent to at least 100 mms. HG. absolute pressure. By the employment of packed ring columns using $1\frac{1}{2}$" diameter iron Raschig rings the total drop in vacuum across all the columns had been reduced to 45 mm. HG. The distillation ranges of the oil as shown in Appendix B gives an indication of the efficiency of the column and the distillation ranges shown therein were stated to have been obtained without the use of the reboilers on the wash oil and naphthalene oil column, which reboilers had been installed in the plant to increase reflux ratio on these two columns and thus improve fractionating if required. It is to be noted that special precautions had been taken to distribute the reflux as evenly as possible across the top surface of the column packing and furthermore, particular care had been taken when filling the columns with the Raschig rings, the column being filled evenly 2-3" at a time.

Gas and Steam Consumption - 1943 Figures

(The consumptions quoted are relative to the crude material handled in the process)

A. Distilling and once running of oils. Crude Tar throughput 292.885 tonnes

Crude Material	Process	Thru'put Tonnes	M^3Gas/ Tonnes	Tonnes Steam @ 8 A.
Crude Tar	Dehydrating	292,885	18.5	.057 (a) Pumping
				.025 (b) Distilling
				.028 (c) Handling
Dehydrated Tar	Distilling:			
	(a) Continuous Plant	85,899	30.3	
	(b) 18 Ton Stills	136,930	64.8	
	(c) 50 ton Stills	49,049	38.8	
Light Oil No. II	Distilling	79,440	76.7	0.10

B. Processing of products from Crude Tar. Throughput 806,731 tonnes

Crude Material	Process	Thru'put Tonnes	M^3Gas/ Tonnes	To Steam @ 8 AP.
Light Oil No. I	Redistillation	11,026	82.0	0.20
Crude Tar Acids	(a) Dehydrating	14,398	77.1	2.13 (a) Working and purifying
	(b) Distilling		257.7	3.96 (b) Distilling
	(NOTE First distillation per tonne charged		188.7	
	Second distillation per tonne charged		297.1)	
Once run Benzols	Working and distilling	5,500	Nil	10.4

Calorific value of Coke Oven Gas 4,000/4,250 Cals./M^3

Boiler Plant requires 198.5 M^3 Gas per tonne of steam (12.A)

Total Gas used during year, 30,553,208 M^3

Steam raised ... ... 246,631 tonnes

Appendix A

CIOS CONSOLIDATED ADVANCE FIELD TEAM

ASSESSMENT REPORT

To: G(T) and CW B1/15/21

1. TARGET NO: 126

2. FULL TITLE OF TARGET: Gesellschaft fur Teerverwertung

3. LOCATION: DUISBURG (in town known as MEIDERICH) Varziner Strasse

4. CONDITION OF TARGET: Damaged

5. DESCRIPTION OF CONTENTS: This plant distills and remanufactures crude coal-tar which it receives from coking plants in the Ruhr, such as August Thyssen-Hutte AG (Target 24/14b). Of special interest to wood preservers is a new plant built in 1943; a new continuous process for distilling coal-tar at low temperatures (320°) by means of vacuum to produce Karbol, Naphthalene, Creosotes and pitch was developed after 8 years of research. Process should be further investigated by those who are interested in field.

   Plant slightly damaged, but can not operate due to shortages in power, gas, etc. Producing distillation products (30% of normal production) in regular stills - about 300 tons crude coal-tar per day.

   See other firms:- Verkaufsvereinfgung fur Teererzeungnisse, BOCHUM and Rutgerswerke, CASTROP-RAUXEL. Teerverwertung operates several other smaller distilleries.

6. ITEMS GUARDED: -

7. PRIORITY ASSESSMENT: -

8. OTHER REMARKS: Interrogation made through Dr. Edward Moehrle, General Director, Mr. W.E. Brown, British Officer in charge of Industry at DUISBERG, assisted with the investigation. Removed papers, as follows: "Schema des Betriebsganges, No. 1-6077A2" and "Copies of Patents relating to continuous process". Other copies of these still remain at plant.

(25)

9. DATE OF ASSESSMENT: 29 JUN. 45

10. ASSESSOR'S NAME(S): F. W. GOTTSCHALK, US Civilian
CIOS - T11C

Army Group: 21
Item GrouP: 22G

Sonderabdruck aus dem Z. VDI-Beiheft „Verfahrenstechnik“ Nr. 1, 1944; S. 13 bis 29

Stetige Destillation des Vielstoffgemisches Steinkohlenteer*)

Von Obering. Dipl.-Ing. **W. Fischer** VDI, Duisburg-Meiderich

In der Verfahrenstechnik bereitet die Trennung von Vielstoffgemischen besondere Schwierigkeiten. Erhöhte Wirtschaftlichkeit der Trennverfahren läßt sich nur bei stetigem Betrieb erreichen. Um eine gleichzeitige Verschlechterung der Qualität der Fraktionen gegenüber einer mehrstufigen Blasendestillation zu vermeiden, ist es erforderlich, die Apparaturen sorgfältig durchzurechnen, wozu theoretische Grundlagen gegeben werden. Versuche mit einem neuen stetigen Verfahren zur Teerdestillation stehen mit den Vorausberechnungen in guter Übereinstimmung

Einleitung

Die älteste industrielle Anwendung der Destillationstechnik, die Gewinnung von hochprozentigem Alkohol, hat schon Mitte des vorigen Jahrhunderts zum ersten stetigen Destillationsverfahren geführt, doch hat sich der stetige Betrieb nur langsam durchgesetzt.

Auch die Destillation von Mineralölen erfolgte durch Jahrzehnte absatzweise aus Retorten, selbst dann noch, als große Durchsatzmengen Batterien bis zu 100 Einheiten erforderten. Erst um die Jahrhundertwende setzte eine stürmische Entwicklung der stetigen Destillation des Erdöls und seiner Derivate ein, nachdem der Franzose *Lennard*1) den Röhrenofen erfunden hatte.

Die Entwicklung der stetigen Teerdestillation ging weit langsamer vor sich. Nicht etwa — wie es häufig nach dem Schrifttum den Anschein hat — weil die deutschen Teerdestillateure gegenüber der amerikanischen Erdölindustrie rückständig blieben und erst in jüngster Zeit ihr die sogenannten „pipe-still-Destillationen“ abgesehen haben, sondern weil die theoretische und praktische Entwicklung nicht genügend fortgeschritten war, um die weit schwierigere Teerdestillation mit Erfolg stetig durchzuführen. Übrigens wird in USA, wenn überhaupt, Steinkohlenteer heute noch vorwiegend in Blasen absatzweise destilliert.

Die Blasendestillation scheint verfahrenstechnisch einfacher zu sein, ist es aber in Wirklichkeit nicht. Zwar kann man durch öfters wiederholte Destillation und geschickte Mischung der Fraktionen viel erreichen und aus komplexen Gemischen, wie dem Teer, Stoffe von hoher technischer Reinheit abtrennen, aber man darf dabei nicht nach dem Aufwand an Zeit, Energie und Apparatur fragen. Da die Vorberechnung von Blasenapparaturen infolge der nicht stationären Vorgänge zum Schwierigsten gehört, was es in der Destillationstechnik gibt, hat man sich bis in die jüngste Zeit mit krasser Empirie begnügt und Mängel der Apparatur durch mehrfache Destillation und entsprechenden Aufwand ersetzt.

Die Forderung erhöhter Wirtschaftlichkeit in Verbindung mit einfachen und leistungsfähigen Apparaturen läßt sich nur in stetigem Betrieb erfüllen. Eine gleichzeitige Verschlechterung der Qualität der Fraktionen gegenüber einer mehrstufigen Blasendestillation kann dabei nur durch weitgehende theoretische Durchrechnung der Apparatur vermieden werden, weshalb sich die Verfahrenstechniker im letzten Jahrzehnt besonders eingehend mit der Schaffung von Grundlagen für solche Rechnungen befaßt haben; dabei haben ihnen verständlicherweise die Vielstoffgemische besondere Schwierigkeiten bereitet. Unter Vielstoffgemischen werden hier Gemische verstanden mit sehr vielen teils bekannten, teils unbekannten Komponenten, während die Mehrstoffgemische nur wenige bekannte Bestandteile enthalten.

Abtrieb und Spontanverdampfung

Vorweg sind die Begriffe Abtrieb und Spontanverdampfung zu klären. Wir verstehen unter Abtrieb die Verdampfung der leichtsiedenden Bestandteile aus dem vorgelegten Rohgemisch in mehreren oder vielen Stufen, wobei das schon Verdampfte der Berührung mit dem Restgemisch fortlaufend entzogen wird. Dies hat eine dauernde Veränderung (Verarmung) des Gemisches an Leichtsiedendem und damit eine während des Abtriebs zunehmende Temperatur zur Folge.

Unter Spontanverdampfung wollen wir die spontane (plötzliche) Verdampfung aller flüchtigen Bestandteile auf einmal bis zum Rückstand verstehen. Der Gesamtdampf befindet sich dabei in Berührung mit dem Restgemisch. Der Abtrieb kann sowohl unstetig aus Blasen als auch stetig mit Hilfe von Abtriebsäulen technisch durchgeführt werden. Er hat den Vorteil einer sauberen Abtrennung des Rückstandes.

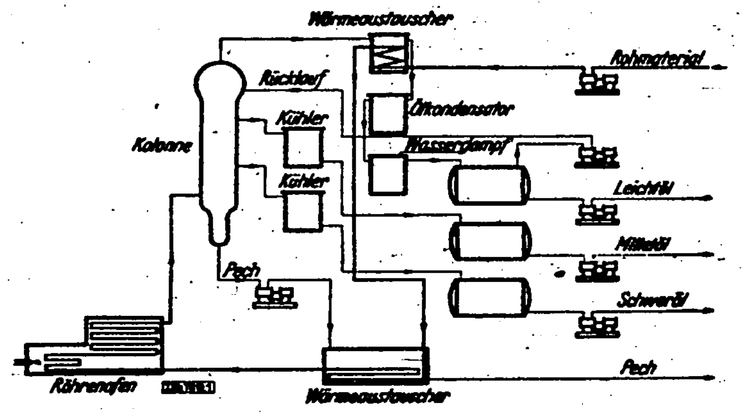


Bild 1. Stetige Teerdestillation nach *Foster Wheeler*

Die Spontanverdampfung (single flash) findet man nur bei stetigen Verfahren. Sie wird bisher ausschließlich mit Hilfe eines Röhrenofens und nachgeschalteter Verdampfungskammer praktisch verwirklicht. Die spontane Trennung von Gesamtdampf und Rückstand geschieht meist unrektifiziert, kann aber durch Kunstgriffe, wenn nötig, schärfer eingestellt werden. Der abziehende Dampf wird nach Bedarf in einer oder mehreren hintereinandergeschalteten Kolonnen rektifiziert. Eine typische Röhrenofenanlage zeigt Bild 1, deren Anordnung aus der Erdöldestillation fast unverändert für Teer übernommen wurde. Das Prinzip der Spontanverdampfung ist nur dann eindeutig verwirklicht, wenn unten in der Rektifizierkolonne keine Wärmezufuhr, also in dieser keinerlei Abtrieb stattfindet.

Das ausschlaggebende Kennzeichen der Spontanverdampfung ist die Möglichkeit der Verarbeitung großer Mengen bei beträchtlich gesenkter Destillationstemperatur und kürzester Erhitzungsdauer. Hieraus ergibt sich eine Reihe von noch zu besprechenden Vorteilen, insbesondere bei der Verarbeitung von wärmeempfindlichen Stoffen.

Die grundlegende Bestimmung der Spontanverdampfungstemperatur kann bei Vielstoffgemischen exakt nur durch Versuche geschehen, z. B. durch Nachahmung des Verfahrens im Laboratorium.

Bild 2 zeigt eine Anordnung2), welche sich insbesondere für hochsiedende Gemische, wie z. B. Teer, eignet. Die

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*) Aus einem Vortrag im Haus der Technik, Essen.

1) DRP. 50 152.

2) *K. Moehrle*: Glückauf Bd. 73 (1937) S. 302/06.

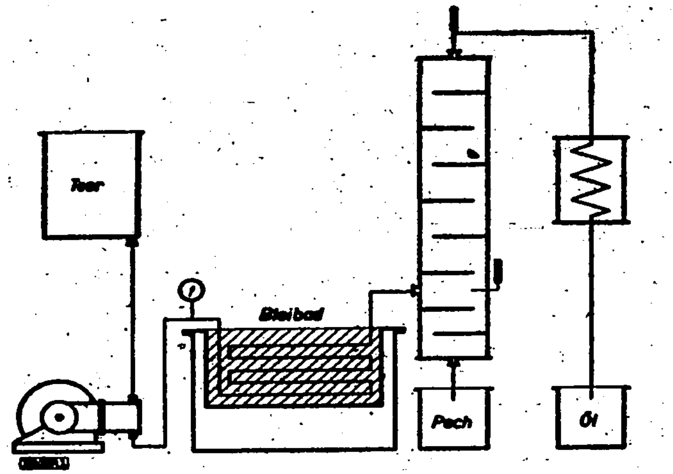

Bild 2. Stetige Teerdestillation im Laboratorium nach *Moehrle*

Spontanverdampfungstemperatur kann unmittelbar gemessen werden, die Kolonne rektifiziert nicht, sondern enthält nur Ausdampfböden.

Es gibt noch eine Reihe[3]) von anderen elektrisch beheizten Apparaturen, mit deren Hilfe man die Spontanverdampfungstemperatur durch Verarbeitung kleinster Mengen messen kann.

Piromoov und *Beiswenger*[4]) haben ein graphisches Verfahren angegeben zur angenäherten Ermittlung der Spontanverdampfungstemperatur aus der Siedeanalyse; sie haben empirische Beziehungen ermittelt zwischen der mittleren Siedekennzahl (wobei nach der Engleranalyse die Ausdampfung $a = 0{,}5$ beträgt) und der spontanen Ausdampfung von $a = 0{,}5$, ferner Beziehungen zwischen der Neigung der Siedekennlinie und der Spontanverdampfungslinie.

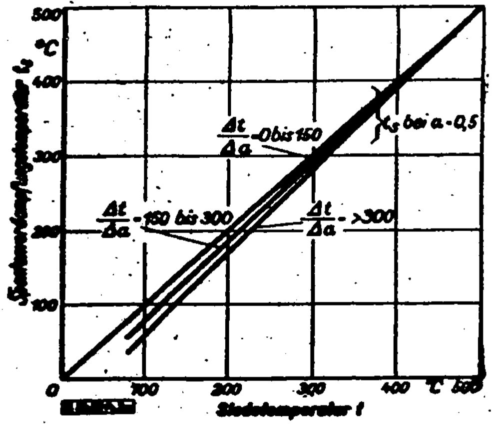

Bild 3a. Spontanverdampfungstemperatur t_s, abhängig von der Siedetemperatur t bei einer spontanen Ausdampfung $a = 0{,}5$ für verschiedene Neigungen $\Delta t/\Delta a$ der Siedekennlinie nach *Piromoov* und *Beiswenger*

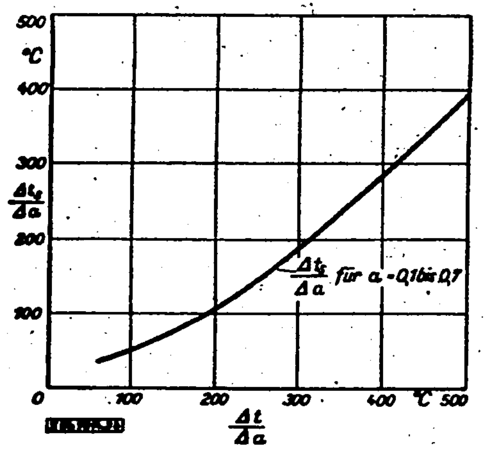

Bild 3b. Neigung $\Delta t_s/\Delta a$ der Spontanverdampfungslinie, abhängig von der Neigung $\Delta t/\Delta a$ der Siedekennlinie für $a = 0{,}1$ bis 0,7

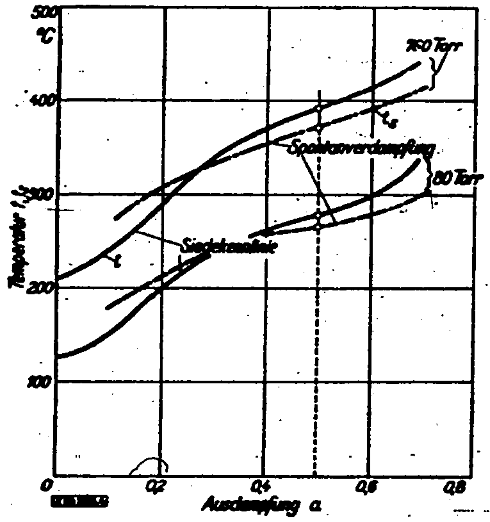

Bild 4. Spontanverdampfungstemperatur t_s und Siedetemperatur t eines entwässerten Steinkohlenteers, abhängig von der Ausdampfung a für 760 und 80 Torr

Bild 3a und b geben diese Beziehungen wieder, dabei bedeutet für die Siedeanalyse (Siedekennlinie)

t die Siedetemperatur in ° C,
a die Ausdampfung in Bruchteilen der anfänglichen Blasenfüllung,
$\frac{\Delta t}{\Delta a}$ die Neigung der Siedekennlinie,

für die Spontanverdampfung
t_s die Spontanverdampfungstemperatur in ° C,
$\frac{\Delta t_s}{\Delta a}$ die Neigung der Spontanverdampfungslinie.

Schwach geneigte Siedekennlinien ergeben bei $a = 0{,}5$ Ausdampfung $t \approx t_s$, bei stärkerer Neigung (also bei weitsiedenden Gemischen $t_s < t$. Die Neigung der Spontanverdampfungslinie ist stets schwächer als die der Siedekennlinie.

Nach dem beschriebenen Verfahren erhält man z. B. die in Bild 4 für einen entwässerten Steinkohlenteer dargestellten Kurven. Infolge der schwächeren Neigung der Spontanverdampfungslinie schneidet diese die Siedekennlinie bei $a = 0{,}25$. Die Spontanverdampfungstemperatur ist unterhalb dieses Wertes also höher, oberhalb niedriger als die nach der Siedeanalyse gefundene Temperatur. Werden aus dem Teer z. B. 50 % abdestilliert, so ist die Spontanverdampfungstemperatur etwa 25° niedriger als die Endtemperatur des Blasenabtriebs. Unter dieser ist hier stets die Temperatur der aus der Blase abziehenden Dämpfe zu verstehen, während die Restflüssigkeit in der Blase nicht unbeträchtlich überhitzt ist. Im Falle der Spontanverdampfung ist die Temperatur t_s stets für Flüssigkeit und Dampf gleich.

Da die Spontanverdampfungstemperatur nichts anderes darstellt als eine Gleichgewichtstemperatur bei gegebener Ausdampfung und gegebenem Druck, kann sie für verschiedene Drücke bestimmt werden. Liegt sie nur für zwei Drücke, z. B. 760 und 80 Torr, gemessen vor (Bild 4), so kann man durch geradlinige logarithmisch-hyperbolische Interpolation die Temperatur t_s bei beliebigen Drücken auch für Vielstoffgemische ohne Kenntnis ihrer Zusammensetzung ermitteln.

Kennt man die Dampfdrücke p_1 und p_2 sowie die absoluten Temperaturen T_{s1} und T_{s2}, so lassen sich aus den Gleichungen

$$\ln p_1 = A - \frac{B}{T_{s1}} \text{ und } \ln p_2 = A - \frac{B}{T_{s2}} \quad . \ (1)$$

die Konstanten A und B berechnen und damit auch weitere Wertepaare p und T_s zu jeder Ausdampfung a [5]).

Destillation bei Unterdruck

Im allgemeinen ist man bisher mit dem Destillationsdruck nur dann vom Atmosphärendruck nach unten oder oben abgewichen, wenn entweder sehr niedrig siedende Stoffe oder sehr hoch siedende Gemische vorlagen, um die Anwendung der üblichen Heiz- und Kühlmittel (Wasserdampf und Wasser) zu ermöglichen und um Zersetzungen zu vermeiden. Bei sehr hoch siedenden Gemischen (Schmieröl, Asphalt, Teer usw.) ist die Vakuumdestillation üblich, wodurch man mit den Temperaturen in dem apparativ bequem zu beherrschenden Bereich unter 350° bleibt.

Es erscheint nun wichtig, die Frage zu klären, ob bei vom Atmosphärendruck abweichenden Drücken die Trennung der verschiedenen Bestandteile des Gemisches erleichtert oder erschwert wird, insbesondere im Hinblick auf die Vakuumdestillation.

Der Abstand der Siedepunkte zweier Stoffe bei 760 Torr im Vergleich zu dem Abstand der Siedepunkte bei einem anderen Druck gibt über diese Frage keinen Aufschluß. Es ist vielmehr notwendig, die Dampfteildrücke der verschiedenen Bestandteile des Gemisches bei der Destillationstemperatur in Beziehung zu setzen.

Bezeichnet man mit

x_d, y_d	die Molanteile des Leichtsiedenden x und Schwersiedenden y im Dampf,
x_f, y_f	die Molanteile des Leichtsiedenden x und Schwersiedenden y in der Flüssigkeit,
P_x, P_y	die Dampfdrücke bei der Destillationstemperatur,
P	den Gesamt-(Destillations-)Druck,
K_x, K_y	die Henrysche Konstanten (Verdampfungsbestreben),
K_x/K_y	das relative Verdampfungsbestreben (volatility),

so lassen sich die Gesetze von *Raoult* bzw. *Henry* in bekannter Weise durch nachstehende Gleichungen darstellen:

$$\left.\begin{array}{c} x_d = x_f \dfrac{P_x}{P} = x_f \cdot K_x; \quad y_d = y_f \dfrac{P_y}{P} = y_f \cdot K_y \\ \dfrac{x_d}{y_d} = \dfrac{x_f}{y_f} \cdot \dfrac{P_x}{P_y} = \dfrac{x_f}{y_f} \cdot \dfrac{K_x}{K_y} \end{array}\right\} \quad (2).$$

Das relative Verdampfungsbestreben (volatility) P_x/P_y bzw. K_x/K_y ist ein Maß für den Unterschied im Verdampfungsbestreben des Stoffes X gegen den Stoff Y. Wächst dieses Verhältnis mit sinkender Temperatur bzw. sinkendem Druck, so wird die Trennung durch Drucksenkung erleichtert. Dies ist z. B. bei den paraffinischen Kohlenwasserstoffen, von denen in Bild 5 eine kleine Auswahl dargestellt ist, der Fall.

Es ist zur Verdampfungstemperatur als Abszisse das relative Verdampfungsbestreben, bezogen auf das relative Verdampfungsbestreben P_{x0}/P_{y0} bei 760 Torr, aufgetragen.

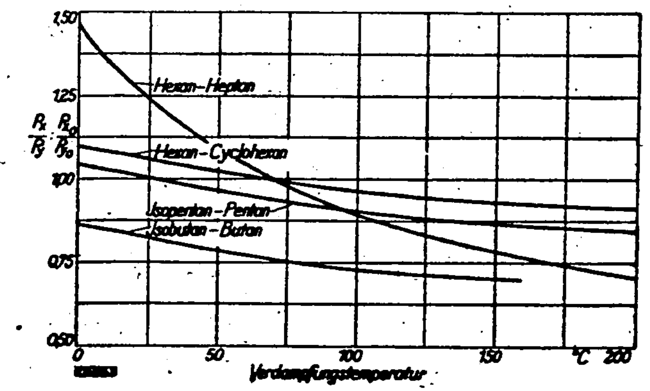

Bild 5. Relatives Verdampfungsbestreben $\frac{P_x}{P_y} : \frac{P_{x0}}{P_{y0}}$, abhängig von der Verdampfungstemperatur für einige paraffinische Kohlenwasserstoffe

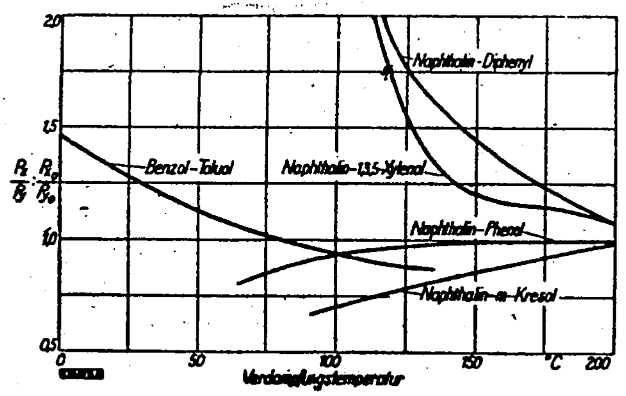

Bild 6. Relatives Verdampfungsbestreben $\frac{P_x}{P_y} : \frac{P_{x0}}{P_{y0}}$ von Teerkohlenwasserstoffen, abhängig von der Verdampfungstemperatur

Da die Linien mit fallender Verdampfungstemperatur steigen, wird also die Trennung günstiger.

Nicht ganz so einfach liegen die Verhältnisse bei den im Steinkohlenteer enthaltenen Kohlenwasserstoffen. Man findet hier, daß bei einer Reihe von Stoffpaaren das relative Verdampfungsbestreben mit sinkender Verdampfungstemperatur zunimmt, bei anderen wieder abfällt.

Bild 6 zeigt als typisches Beispiel das Verhalten der sauren Öle gegenüber dem Naphthalin. Es ergibt sich die auffallende Tatsache, daß das relative Verdampfungsbestreben von Naphthalin mit dem Phenol und den Kresolen abnimmt, während es mit 1,3,5-Xylenol zunimmt. Benzol-Toluol und Naphthalin-Diphenyl zeigen normal steigenden Verlauf.

Aus dieser Sachlage ist für die Praxis der Destillation zu folgern, daß je nach dem Destillationsdruck das Naphthalin sich entweder mehr dem niedrig siedenden oder höher siedenden Phenol zuneigt. Eine vollständige Trennung des Naphthalins von den homologen Phenolen ist bekanntlich durch Destillation überhaupt nicht möglich. Da aber die meisten übrigen im Teer enthaltenen aromatischen Kohlenwasserstoffe mit sinkender Verdampfungstemperatur steigendes relatives Verdampfungsbestreben zeigen, wird ihre Trennung in Ölfraktionen durch die Vakuumdestillation im allgemeinen verbessert.

Im Steinkohlenteer finden sich allerdings auch eine Reihe von Gemischen, deren Ausdampfung nicht dem Raoultschen oder Henryschen Gesetz folgt, da sie Maximum-Siedepunkte aufweisen. Solche Gemische bilden hauptsächlich Säuren und Basen, z. B. Anilin mit Phenol und Pyridin mit Phenol. Das letztere Gemisch wurde erst kürzlich von *Wille*[6]) beschrieben und chemisch als Additionsverbindung gedeutet. Destillationstechnisch sind dann die Einflüsse des Druckes nicht mehr so einfach wie vor zu übersehen, und die leichtsiedenden Komponenten ziehen sich in höhere Fraktionen hinein als nach ihrer Siedelage zu erwarten wäre.

Der Röhrenofen

Als Mittel zur Übertragung der Destillationswärme bedient man sich heute bei stetigen feuerbeheizten Anlagen fast ausschließlich des Röhrenofens. Er wird mit Kohle, Öl oder Gas beheizt. Verschiedene neuere Veröffentlichungen befassen sich mit seinen verfahrenstechnischen Grundlagen, seinen Bauarten und der Wärmeübertragung[7]) [8]) [9]).

Für die stetige Teerdestillation kommen nur Bauarten in Frage, die eine besonders schonende Beheizung gewährleisten, da die Teere meist sehr wärmeempfindlich sind und in den heißen Strahlungszonen der Öfen Zersetzungen und Verkokungen vermieden werden müssen.

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[3]) *W. L. Nelson*: Petroleum Refinery Engineering, New York und London, 1936, S. 66.

[4]) *X. Piromoov* und G. A. *Beiswenger*: Amer. Petr. Inst. Bull. Bd. 10 (1929) S. 52.

[5]) Weitere Verfahren vgl. a. *W. Hoffmann* und *F. Floris*: Z. VDI, Beiheft Verfahrenstechnik 1943 Nr. 2 S. 47/51.

[6]) *H. Wille*: Brennstoff-Chemie Bd. 23 (1942) S. 271/73.

[7]) *W. L. Nelson*: a. a. O. S. 406 ff.

[8]) *K. Thormann*: Chem. Apparatur Bd. 27 (1940) S. 97/99.

[9]) *N. Mayer*: Öl und Kohle Bd. 38 (1942) S. 985/95.

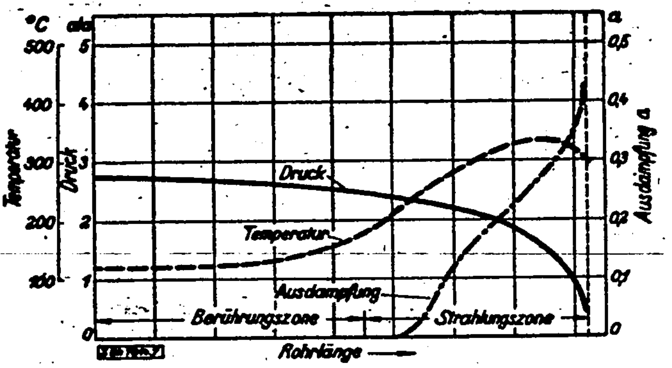

Bild 7. Druck- und Temperaturverlauf in einem Röhrenofen für Steinkohlenteer

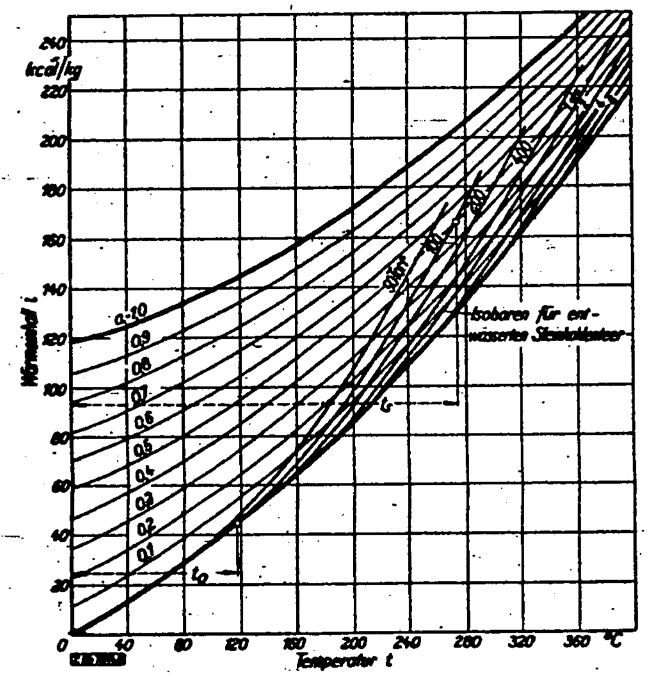

Bild 8. *i,t*-Diagramm für Teer und Teeröle

Thormann[8]) hat die thermodynamischen Vorgänge im Ofen grundsätzlich geklärt. Längs des Rohrweges nimmt der Wärmeinhalt des Destillationsgutes und seine Temperatur zu, der Druck nimmt ab, außerdem tritt je nach dem Druckverlauf bereits im Rohrsystem eine mehr oder weniger bedeutende Ausdampfung auf, so daß ein Gemisch von Dampf und Flüssigkeit den Ofen verläßt.

Bild 7 zeigt den gemessenen Druck- und Temperaturverlauf eines Röhrenofens für Teer, an den sich eine Vakuumanlage anschließt, wobei der Druck am Ofenaustritt bereits unter 1 ata gesunken ist und infolgedessen eine lebhafte Ausdampfung a stattfindet.

Für den Verfahrenstechniker ist es wichtig, den Druck- und Temperaturverlauf vorauszubestimmen. Der Verfasser hat schon früher[10]) ein *i,t*-Diagramm für Teer- und Teeröle angegeben, das ergänzt durch Isobaren in Bild 8 nochmals wiedergegeben ist.

Oben wurde gezeigt, wie zusammengehörige Werte für Druck und Temperatur bei verschiedener spontaner Ausdampfung erhalten werden. Da in dem *i,t*-Diagramm die Ausdampfung mit aufgenommen ist, lassen sich die Drücke zu den Temperaturen auf den Linien gleicher Ausdampfung abtragen. Werden dann noch Punkte für gleiche Drücke verbunden, so erhält man die Isobaren. Das *i,t*-Diagramm wird so zu einem geeigneten Mittel, die Zustände längs der Ofenrohre zu verfolgen. Streng genommen müßte für jeden Rohteer, entsprechend *seiner* verschiedenen Zusammensetzung und seinem Siedeverhalten, ein besonderes *i,t*-Diagramm gezeichnet werden, jedoch läßt sich das dargestellte für Kokereiteer mit genügender Genauigkeit allgemein verwenden, ja sogar für die aus dem Teer abdestillierten Öle, mit Ausnahme der Isobaren, die nur für den entwässerten rohen Teer gelten. Für leichtersiedende Öle ergeben sich andere Isobaren entsprechend ihrer Ableitung aus den Spontanverdampfungslinien.

Der Gesamtwärmeaufwand für die einfache Destillation ohne zusätzliche Rektifikationswärme, der im Ofen zu übertragen ist, ergibt sich zu der geforderten Ausdampfung und der Spontanverdampfungstemperatur unmittelbar aus dem *i,t*-Diagramm. Will man z. B. aus einem rohen entwässerten Steinkohlenteer das Öl bis auf einen Rückstand von 50 % Pech abdestillieren, so findet sich der Wärmeaufwand auf der Linie $a = 0{,}50$ zu derjenigen Temperatur, die an der Stelle der Spontanverdampfung herrscht. Kennt man den Druck an dieser Stelle, so ist damit auch die Temperatur t_s gegeben und aus dem *i,t*-Diagramm abzulesen.

Die Berechnung der Heizfläche der Berührungszone von Röhrenöfen, in der lediglich eine Vorwärmung des Destillationsgutes stattfindet, ist eine aus dem Dampfkesselbau geläufige Aufgabe, während für die Auslegung der Strahlungsheizfläche im ersten Entwurf meist die Formel von *Wilson, Lobbo* und *Hottel*[8]) [9]) [11]) [12]) benutzt wird. *Mayer*[9]) hat auch feinere Berechnungsverfahren angegeben. Dabei erscheint es durchaus angängig, die Wärmeaufnahme der Heizfläche in der Strahlungszone als Ganzes anzusetzen, da die Temperaturänderung des Gutes in ihr gering ist gegenüber der ganz wesentlich höheren Temperatur des Strahlungsraumes. Die Zunahme des Wärmeinhaltes im Rohr längs der Strahlungszone ist also linear, und man kann im *i,t*-Diagramm durch Ziehen von Abzissenparallelen diese in Abschnitte unterteilen. Die Schnittpunkte der Abzissenparallelen mit den Isobaren ergeben dann jeweils die Temperatur und die Ausdampfung in jedem Punkt des Rohrweges, sofern nur der Druckabfall bzw. Druckverlust bekannt ist. Dieser kann ungefähr vorausberechnet werden, wozu eine Druckverlustformel benutzt werden muß, die sowohl für dampfförmige als auch flüssige Medien anwendbar ist.

Bezeichnet man mit

G das Durchströmgewicht in kg/s,
ΔP den Druckverlust in kg/m²,
l die Rohrlänge in m,
d den Rohrdurchmesser in m,
w die Strömungsgeschwindigkeit in m/s,
ϱ $\frac{\gamma}{g}$ = die Dichte in kg s²/m⁴,
ζ die Widerstandszahl,
η die absolute Zähigkeit in kg s/m²,

so ergibt sich aus der Energiegleichung

$$\Delta P = \zeta \frac{l}{d} \frac{w^2 \varrho}{2} \quad \ldots \ldots (3)$$

mit dem Wert von *Blasius*

$$\zeta = 0{,}3164\,\mathrm{Re}^{-0{,}25} \quad \ldots \ldots (4),$$

der Reynoldsschen Zahl

$$\mathrm{Re} = \frac{w\,d\,\varrho}{\eta} \quad \ldots \ldots (5)$$

und

$$w = \frac{4\,G}{g\,\varrho\,\pi\,d^2} \quad \ldots \ldots (6)$$

durch Einsetzen von Gl. 4 bis 6 in Gl. 3 eine einfache Form der Druckverlustgleichung

$$\Delta P = \frac{4{,}44 \cdot G^{1{,}75} \cdot l}{10^3 \cdot d^{4{,}75}} \cdot \frac{\eta^{0{,}25}}{\varrho} \quad \ldots \ldots (7),$$

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[10]) *W. Fischer*: Z. VDI Beiheft Verfahrenstechnik 1938 Nr. 6 S. 178/84.

[11]) *D. W. Wilson, W. E. Lobbo* und *H. C. Hottel*: Industr. Engng. Chem. Bd. 24 (1932) S. 486.

[12]) *W. L. Nelson*: a. a. O. S. 413.

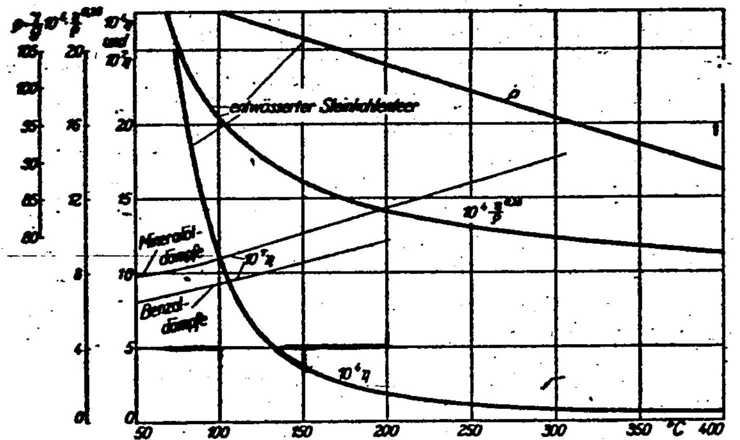

Bild 9. Zähigkeit und Dichte von Teer- und Mineralöldämpfen, abhängig von der Temperatur

die den Vorteil hat, daß man den Einfluß der einzelnen Größen leicht übersehen kann. Lediglich der Faktor $\eta^{0,25}/\varrho$ ist von der Temperatur, der Zähigkeit und der Ausdampfung a abhängig.

Man kann die Gl. (7) mit ausreichender Genauigkeit sowohl für Flüssigkeiten als auch für Dampf anwenden, ja sogar für ein Gemisch aus beiden. Man berechnet in diesem Falle ϱ für das Gemisch aus den anteiligen Volumina

$$\varrho = \frac{1}{g\,[a \cdot v_d + (1 - a)\,v_f]} \quad \ldots \ldots (8),$$

worin v_d das spezifische Volumen des Dampfes in m³/kg, v_f das der Flüssigkeit in m³/kg sind, und berücksichtigt dadurch eine zutreffende Strömungsgeschwindigkeit in den Rohren. Die Zähigkeit wird stets für die Flüssigkeit eingesetzt, da diese bei teilweiser Ausdampfung $a < 0{,}5$ zwar nicht volumetrisch, wohl aber energetisch überwiegt und größere Ausdampfungen praktisch in den Rohren der Öfen kaum vorkommen. Bei den letzteren würde sich nämlich der Druckverlust zu groß ergeben.

In Bild 9 ist die Zähigkeit η und der Wert $\eta^{0,25}/\varrho$ für einen Steinkohlenteer dargestellt. Es ist ersichtlich, daß man für jenen über 150° C auch innerhalb größerer Temperaturbereiche mit Mittelwerten rechnen darf. Die Zähigkeit von Benzol- und Mineralöldämpfen ist zur Orientierung ebenfalls eingetragen.

Da der Druckverlust ΔP von der Temperatur und der Ausdampfung abhängig ist, läßt sich Gl. (7) nicht explicit auswerten, es ist vielmehr der Druckverlust, ausgehend vom Ofenaustritt, wo der Druck meist bekannt ist, für die Rohrstrecke abschnittsweise anzunehmen, aus dem *i,t*-Diagramm mit Hilfe der aus dem Wärmeübergang bestimmten *i*-Werte Temperatur und Ausdampfung zu entnehmen und der angenommene Druckverlust nach Gl. (7) rechnerisch nachzuprüfen. Gegebenenfalls ist das Verfahren mehrfach zu wiederholen, was durch die einfache, leicht logarithmisch auszuwertende Form der Gleichung nicht sehr mühsam ist.

Die zahlreichen Krümmer oder Umkehrstücke in den Öfen werden zweckmäßig als zusätzliche Länge gleich einem Vielfachen des Rohrdurchmessers berücksichtigt. Für die üblichen Umkehrstücke gibt *Nelson*[13]) $l = 40\,d$ an.

Die stetige Rektifikation

Eine stetige Destillation ist nur dann vollkommen, wenn unmittelbar anschließend an die Spontan-Verdampfung der flüchtigen Bestandteile des Ausgangsgemisches diese in zweckentsprechender Weise in einem Arbeitsgang rektifiziert werden. Diese Trennung in Fraktionen soll so weitgehend sein, daß eine wiederholte Destillation der Erzeugnisse nicht erforderlich wird.

Die Rektifikation von Zweistoffgemischen ist in den letzten Jahren insbesondere durch die zahlreichen Arbeiten von *Kirschbaum*[14]) sowohl für Bodenkolonnen als auch für Füllkörpersäulen in weitgehendem Maße geklärt worden, und es ist möglich, die theoretische Bodenzahl für einen bestimmten Trenneffekt mit guter Sicherheit zu berechnen. Auch für Vielstoffgemische sind Verfahren zur Berechnung der theoretischen Bodenzahl entwickelt worden[15]) [16]), wenngleich diese einen ganz beträchtlichen Rechenaufwand erfordern.

Es kann nicht Aufgabe dieser Arbeit sein, diese Rechnungsverfahren im einzelnen zu behandeln, wohl aber scheint es notwendig, allgemeine Folgerungen aus solchen Rechnungen an Hand eines Prinzip-Schaubildes zu besprechen, Bild 10.

Als Abszisse ist eingetragen die eingebaute Bodenzahl oder, was dasselbe ist, die Bauhöhe einer Füllkörperschicht. Diese ergibt sich aus der theoretischen Bodenzahl geteilt durch das Austauschverhältnis, das angibt, wie sich ein praktischer Boden zu einem theoretischen Boden verhält. Die Bauhöhe der Füllkörperschicht ergibt sich ebenfalls aus der theoretischen Bodenzahl, geteilt durch den Bodenwert, der angibt, wieviel theoretische Böden einem Meter Füllkörper entsprechen.

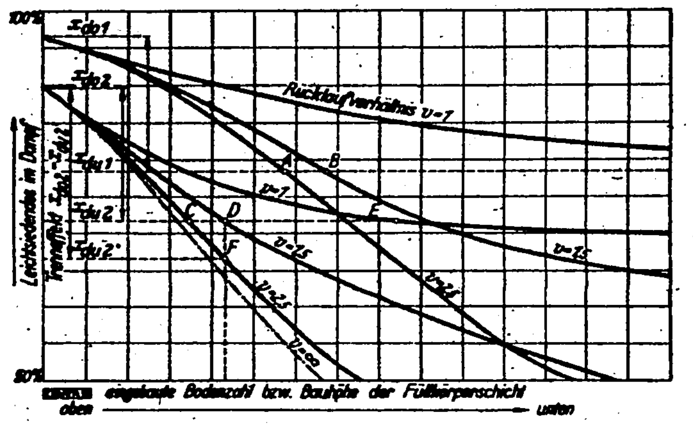

Bild 10. Konzentration x_d an Leichtsiedendem im Dampf abhängig von der eingebauten Bodenzahl bzw. von der Bauhöhe der Füllkörperschicht längs einer Rektifiziersäule

$$\text{Bodenzahl} = \frac{\text{theoretische Bodenzahl}}{\text{Austauschverhältnis}}$$

$$\text{Bauhöhe der Füllkörpersäule} = \frac{\text{theoretische Bodenzahl}}{\text{Bodenwert}}$$

Als Ordinate ist in dem Schaubild eingetragen der Gehalt an Leichtsiedendem im Dampf längs der Rektifiziersäule. Ist also z. B. der Gehalt an Leichtsiedendem oben am Kopf der Säule x_{do1}, so nimmt dieser bei einem Rücklaufverhältnis $v = 1$ längs der gezeichneten Linie ab. Wird nun eine Verbesserung des Leichtsiedenden längs der Säule von x_{du1} auf x_{do1} verlangt, so würden wir bei dem Rücklaufverhältnis $v = 1$ nur mit einer unendlich großen Bodenzahl zum Ziel kommen. Wird hingegen das Rücklaufverhältnis auf $v = 1{,}5$ gesteigert, so erhalten wir in Punkt B die einzubauende Bodenzahl. Das Rücklaufverhältnis v liegt also unter dem für den Trenneffekt erforderlichen Mindest-Rücklaufverhältnis, während das Rücklaufverhältnis $v = 1{,}5$ bereits eine praktisch brauchbare Bodenzahl ergibt. Steigern wir das Rücklaufverhältnis weiter auf $v = 2{,}5$, so vermindert sich die Bodenzahl entsprechend Punkt A.

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[13]) *W. L. Nelson*: a. a. O. S. 160.

[14]) *E. Kirschbaum*: Destillier- und Rektifiziertechnik, Berlin 1940.

[15]) *R. L. Smith*: Trans. Amer. Inst. Chem. Engrs. Bd. 37 (1941) S. 333/55.

[16]) *W. L. Nelson* und *C. H. Roland*: Industr. Engng. Chem. Bd. 30 (1938) S. 730; siehe auch Z. VDI, Beiheft Verfahrenstechnik 1939 Nr. 4 S. 133/34.

Soll das Kopferzeugnis nur einen Gehalt an Leichtsiedendem von x_{do2} erreichen, so gilt nicht mehr das obere Kurvenbündel, sondern das untere. Ist ein Trenneffekt von x_{du2} auf x_{do2} notwendig, so läßt er sich mit der durch den Punkt E gekennzeichneten Bodenzahl erreichen. Wird das Rücklaufverhältnis v auf 1,5 erhöht, so wird die Bodenzahl erheblich bis D verringert, während für $v = 2{,}5$ nur eine weitere Ermäßigung der Bodenzahl auf C eintritt.

Eine wesentliche Verringerung der Bodenzahl läßt sich, wie aus der strich-punktierten Linie ersichtlich ist, auch bei unendlich großem Rücklaufverhältnis nicht mehr erzielen. Wie sich eine Vergrößerung des Rücklaufverhältnisses bei gleicher Bodenzahl und Erhöhung des Rücklaufverhältnisses von 1,5 auf 2,5 im Trenneffekt auswirkt, zeigen die Punkte D und F.

Wir entnehmen aus diesen Betrachtungen, daß man durch Erhöhen des Rücklaufverhältnisses v entweder mit geringerer Bodenzahl auskommen kann oder auch die Trennung bei gleicher Bodenzahl entsprechend verbessern kann. Diesen Auswirkungen sind aber Grenzen gesetzt. Man kann nämlich bei zu geringem Rücklaufverhältnis auch durch noch so viel Böden keine Verbesserung im Trenneffekt mehr erreichen, und man kann ebenso bei gegebener Bodenzahl selbst mit unendlich großem Rücklaufverhältnis den Trenneffekt nicht mehr steigern.

Zahlenmäßig sind diese Grenzen abhängig von der Anreicherung im Kopfprodukt x_{do} und im Bodenablauf x_{du}, von dem zu trennenden Gemisch und der praktischen baulichen Wirksamkeit der Kolonnenkonstruktion, also dem Austauschverhältnis bzw. dem Bodenwert.

Es ist Sache der Erfahrung und des Geschicks des Konstrukteurs, hier den richtigen Mittelweg zu finden zwischen dem Aufwand an Rückfluß, der Wärme kostet, und dem Aufwand an Apparatur, der Baustoff erfordert. Dabei können für Vielstoffgemische die vorerwähnten Berechnungsmethoden nur Anhaltspunkte liefern.

Der Wärmeaufwand

Mindestens ebenso wesentlich wie die Erzielung einer guten Rektifikation ist bei der Destillation von Vielstoffgemischen die Abschätzung des Wärmeaufwandes. Da die Vielstoffgemische in ihren Bestandteilen nicht bekannt sind, ist es nicht möglich, die spezifische Wärme des flüssigen Gemisches und seine Verdampfungswärme aus den Werten für die Einzelstoffe zu ermitteln. Der Verfasser hat früher[10] bereits festgestellt, daß man hier jedoch sehr gut summarisch vorgehen kann, wenn nur die Änderung der spezifischen Wärme und Verdampfungswärme mit der Temperatur ausreichend berücksichtigt wird. Diese sind bei Mineralölen stark veränderlich, und außerdem zieht sich die Destillation im allgemeinen über einen großen Temperaturbereich hinweg.

In dem i,t-Diagramm, Bild 8, ist näherungsweise eine lineare Abhängigkeit der mittleren spezifischen Wärme und der Verdampfungswärme für Teer zugrunde gelegt, nämlich

$$\left.\begin{aligned} c_m &= b_0 + b\,t = 0{,}308 + 0{,}0006\,t \\ r &= e_0 - e\,t = 118 - 0{,}16\,t \end{aligned}\right\} \qquad (9),$$

worin c_m die mittlere spezifische Wärme in kcal/kg° C zwischen 0° und t°C und r die Verdampfungswärme in kcal/kg bei t °C bedeuten. Genauere Messungen liegen nicht vor, schon weil Teer ja kein einheitlicher Stoff ist. Die Bestimmung des Wärmeaufwandes bei Spontanverdampfung ist, wie oben ausgeführt, einfach.

Soll diese aber mit dem theoretischen Wärmeaufwand für die Destillation in Blasen verglichen werden, so ist zu berücksichtigen, daß die Temperatur einer Blasenfüllung sich während des Betriebes dauernd ändert, Bild 11.

Der Verlauf der Temperatur ist bei gleichbleibender Destillationsgeschwindigkeit mit dem Abtrieb weitgehend geradlinig. Wenn auch die Temperaturfunktion nicht während des ganzen Abtriebs durch eine Gerade wiedergegeben werden kann, so doch fast immer durch einige wenige mit verschiedener Neigung. Zur Berechnung des gesamten Wärmeaufwandes einschließlich der Rücklaufwärme bei nachgeschalteter Rektifizierkolonne werden nachfolgende Annahmen gemacht:

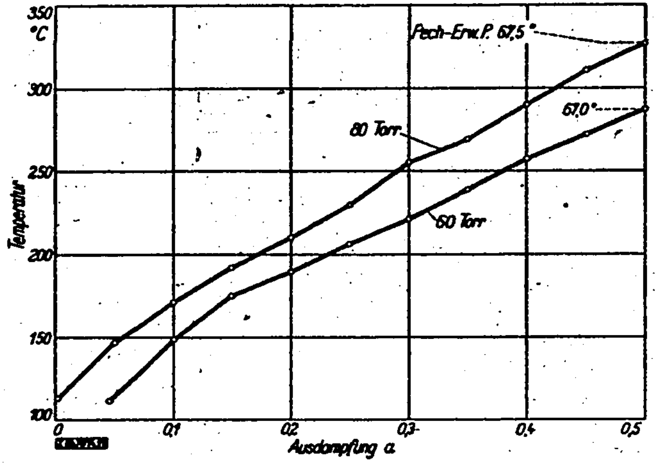

Bild 11. Destillationstemperatur t beim Abtrieb eines Steinkohlenteers aus Blasen, abhängig von der Ausdampfung a

1. Die abziehenden Dämpfe und der in die Blase eintretende Rückfluß haben gleiche Temperatur.
2. Die Überhitzung des flüssigen Blaseninhaltes bleibt unberücksichtigt (Phasengleichgewicht zwischen Dampf und Flüssigkeit in der Blase).
3. Die Destillationsgeschwindigkeit und das Rückflußverhältnis v bleiben während des ganzen Abtriebs konstant.

Es bedeuten:

B die jeweilige Blasenfüllung in kg,
J die gesamte Wärmezufuhr in kcal,
D die abgetriebene Menge in kg,
t die jeweilige Destillationstemperatur in ° C,
t_0 die Temperatur, bei welcher die Ausdampfung beginnt in ° C,
t_1 die Temperatur bei Beendigung des Abtriebes in ° C,
i_f den Wärmeinhalt der Flüssigkeit in kcal/kg,
i_d den Wärmeinhalt des Dampfes in kcal/kg.

Der Wärmeinhalt der Blasenfüllung ist dann

$$B \cdot i_f.$$

Wird die Wärmemenge $\mathrm{d}J$ zugeführt und dabei die Menge $\mathrm{d}D$ unter Temperaturerhöhung abdestilliert, so erhöht sich der Wärmeinhalt der Blase auf

$$(B - \mathrm{d}D)\ (i_f + \mathrm{d}i_f).$$

Aus der Blase entweicht mit dem Dampf die Wärmemenge

$$(1 + v)\,\mathrm{d}D \cdot i_d.$$

Der Rückfluß führt in die Blase die Wärmemenge

$$v\,\mathrm{d}D\,(i_f + \mathrm{d}i_f)$$

zurück, somit muß sein

$$B \cdot i_f + \mathrm{d}J = (B - \mathrm{d}D)\,(i_f + \mathrm{d}i_f) + (1 + v)\,\mathrm{d}D \cdot i_d - v \cdot \mathrm{d}D\,(i_f + \mathrm{d}i_f) \quad \ldots \ldots \quad (10);$$

mit

$$i_d = i_f + \mathrm{d}i_f + r$$

folgt

$$\mathrm{d}J = B \cdot \mathrm{d}i_f + \mathrm{d}D \cdot r \cdot (1 + v) \quad \ldots \quad (11).$$

Hierin sind alle Werte außer dem konstanten v mit der Temperatur t veränderlich. Gl. (11) gilt allgemein für jede Blasendestillation. Für die Teerdestillation kann zur Integration Gl. (9) und eine Abhängigkeit der Temperatur von der Zeit bzw. Destillationsgeschwindigkeit analog Bild 11 benutzt werden, die zweckmäßig wir folgt gefaßt wird:

$$B = B_0 - D = B_0 - \frac{t}{K} + \frac{t_0}{K}; \quad \mathrm{d}D = \frac{\mathrm{d}t}{K}. \quad (12),$$

wobei $K =$ konst. die Neigung der Temperaturkurve berücksichtigt und B_0 die ursprüngliche Blasenfüllung bedeutet. Ferner ist

$$\left.\begin{aligned} i_f &= c_m\,t = (b_0 + b\,t)\,t \\ \mathrm{d}i_f &= b_0\,\mathrm{d}t + 2\,b\,t\,\mathrm{d}t \end{aligned}\right\} \quad \ldots \quad (13).$$

Integriert man nun Gl. (11) mit Hilfe der Gl. (9), (12), (13) zwischen Anfang und Ende des Abtriebes, also zwischen den Temperaturen t_0 und t_1, und setzt $B_0 = 1$ so folgt

$$\int_{J=i_0}^{J=i_1} \mathrm{d}J = \int_{t_0}^{t_1} \left(1 - \frac{t}{K} + \frac{t_0}{K}\right)(b_0\,\mathrm{d}t + 2\,b\,t\,\mathrm{d}t) + \int_{t_0}^{t_1} (1+v) \times (e_0 - e\,t)\,\frac{\mathrm{d}t}{K}$$

$$(i_1 - i_0) = \left[b_0\left(1 + \frac{t_0}{K}\right) + (1+v)\,\frac{e_0}{K}\right](t_1 - t_0) + \left[b\left(1 + \frac{t_0}{K}\right) - \frac{b_0 + e\,(1+v)}{2\,K}\right](t_1^2 - t_0^2) - \frac{2\,b}{3\,K}\,(t_1^3 - t_0^3) \qquad (14).$$

Zur Vereinfachung kann geschrieben werden

$$(i_1 - i_0) = c_1\,(t_1 - t_0) + c_2\,(t_1^2 - t_0^2) - c_3\,(t_1^3 - t_0^3) \quad (14\mathrm{a}).$$

$(i_1 - i_0)$ ist also der Wärmeaufwand für den Abtrieb von $B_0 = 1$ kg Blasenfüllung von t_0 bis t_1. Die Wärmezufuhr zur Aufheizung des Blaseninhaltes von der Temperatur, mit der die Blase gefüllt wird, bis zum Beginn der Verdampfung bei t_0 ist in Gl. (14a) nicht einbegriffen, ihre Berechnung bedarf aber keiner weiteren Erläuterung. Der Wärmeaufwand für einfachen Blasenabtrieb ohne Rektifizierkolonne folgt aus Gl. (14) mit $v = 0$. Zwischen der abgetriebenen Destillatmenge $(D_1 - D_0)$ und K besteht nach Gl. (12) die Beziehung

$$D_1 - D_0 = \frac{t_1 - t_0}{K} \quad \ldots \ldots \quad (12\mathrm{a}).$$

Für $B_0 = 1$ und $D_0 = 0$ entspricht der Wert D_1 der im Falle der Spontanverdampfung auf einmal erfolgenden Ausdampfung a in Bruchteilen des Ausgangsgemisches.

Es ist nunmehr möglich, vergleichende Ermittlungen des theoretischen Wärmeaufwandes für Blasenabtrieb und Spontanverdampfung bei verschiedenen Destillationsdrücken anzustellen, Bild 12.

Häufig wird zur Temperatursenkung auch Einblasung von Wasserdampf vorgesehen, was natürlich einen zusätzlichen Wärmeaufwand verursacht, da der Wasserdampf wieder kondensiert werden muß und seine Wärme nur zum geringsten Teil zurückgewonnen werden kann. Bild 12 enthält auch für 2,5 und 10% Wasserdampfzusatz den theoretischen Wärmeaufwand.

Die Darstellung gilt für einen entwässerten Steinkohlenteer bei Destillation auf Normalpech ohne Rektifizierkolonne, wenn der Teer mit 100° zur Verfügung steht. Zu der Spontan-Verdampfungstemperatur ist der Wärmeaufwand in kcal/kg Teer angegeben. Die Werte, welche gleichen Destillationsdrücken zugeordnet sind, wurden durch Isobaren verbunden.

Die vergleichsweise Eintragung des Wärmeaufwandes bei Blasenabtrieb macht etwas Schwierigkeiten, weil ja während des Blasenabtriebs sich die Temperatur ändert. Es wurden die Endtemperaturen des Blasenabtriebs gewählt und durch Verschiebung des Abszissenmaßstabes die gestrichelte Linie so in das Bild gelegt, daß die Isobaren auch für diese gelten.

Die Werte für praktisch ausgeführte oder vorgeschlagene Anlagen sind durch hervorgehobene Punkte bezeichnet. So findet man z. B. für eine Blasendestillation bei 760 oder 100 Torr auf der Abszisse die Endtemperatur, auf der Ordinate den theoretischen Wärmeaufwand, ferner Temperatur und Wärmeaufwand für eine stetige Wasserdampfdestillation mit 2% Wasserdampfzusatz und für eine Spontanverdampfung ohne Wasserdampfzusatz bei 760 und 90 Torr.

Es ist deutlich erkennbar, daß die Spontanverdampfung bei gutem Vakuum (90 Torr) sowohl hinsichtlich der Temperatur als auch des Wärmeaufwandes alle anderen Möglichkeiten weit unterbietet.

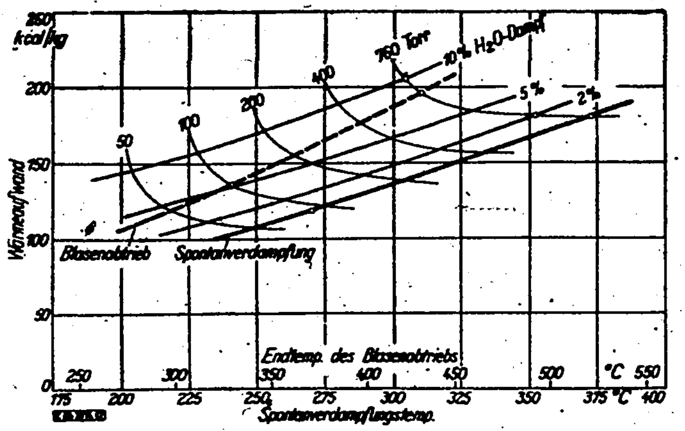

Bild 12. Theoretischer Wärmeaufwand, abhängig von der Spontanverdampfungstemperatur bei der Destillation von entwässertem Teer auf Pech von 67° Erw.-P.

Man könnte daran denken, daß der Kraftaufwand zur Erzeugung eines guten Vakuums die Wärmeersparnis wieder aufhebt. Dies ist aber, sofern das Vakuum mechanisch durch Luftpumpen erzeugt wird, keineswegs der Fall, denn der laufende Energieaufwand für die Aufrechterhaltung des Vakuums dient ja lediglich dazu, etwa durch Undichtigkeiten eingedrungene Luft in der Apparatur zu entfernen und verhältnismäßig sehr geringe Mengen inerter Gase abzuziehen.

Neues Verfahren zur stetigen Teerdestillation

Obgleich zahlreiche Verfahren und Apparaturen zur stetigen Teerdestillation vorgeschlagen und beschrieben wurden, haben bei uns in Deutschland nur einige wenige wesentliche praktische Bedeutung gewonnen, so die Verfahren von Raschig[17] und Koppers[18]. Das erstere arbeitet im Vakuum mit mehrstufigem Abtrieb und mittelbarer Heißwasserheizung, das Koppers-Verfahren mit Röhrenofen, Spontanverdampfung und Wasserdampfeinblasung.

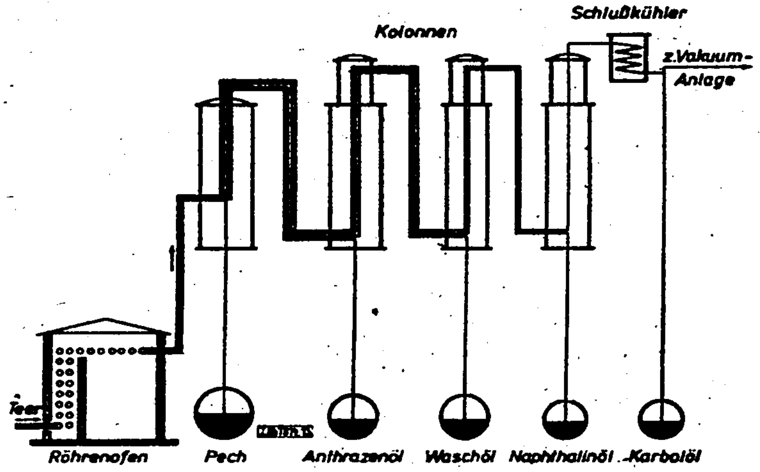

Bild 13. Schema der stetigen Teerdestillation nach dem Teerverwertung-Koppers-Verfahren

Ausgehend von dem geringen theoretischen Wärmeverbrauch der Spontanverdampfung im Vakuum ohne Wasserdampfeinblasung ist ein neues Verfahren entstanden, das sich bereits im Großbetriebe bewährt hat[19]. Es arbeitet nach dem Schema Bild 13.

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[17] *B. Neumann*: Z. angew. Chem. Bd. 34 (1921) S. 193/95.

[18] *O. Eisler, Z. Zamrzla* und *W. Weinkopf*: Glückauf Bd. 72 (1936) S. 184/91.

[19] Das Verfahren wurde von der Gesellschaft für Teerverwertung m. b. H. entwickelt und wird von der Fa. H. Koppers gebaut.

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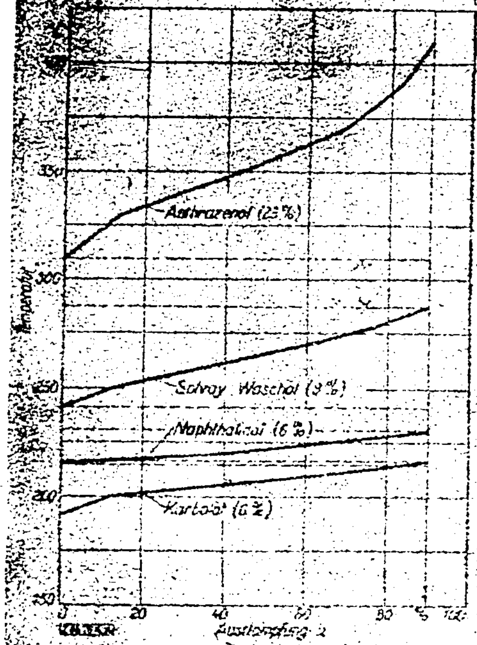


Bild 14 (links). Siedeanalysen der mit dem Teerverwertung-Koppers-Verfahren erhaltenen Teerölfraktionen

Bild 15. Röhrenofen und Betriebsgebäude

Was die Ölausbeuten betrifft, so sind sie in Klammern gesetzt, da sie natürlich von dem zur Verarbeitung kommenden Teer abhängig sind. Wesentlich ist aber, daß infolge der schonenden Destillation die Ausbeute für den gleichen Teer 3 bis 5 % höher ist, und zwar erhält man das Mehr an Öl nicht als hochsiedendes Anthrazenöl, sondern wegen der guten Rektifikation als leichtere Öle.

Nach monatelangem Dauerbetrieb ergaben sich folgende Betriebszahlen:

Leistung an entwässertem Teer	12 t/h
Wärmeverbrauch	
a) Koksofengas	29,4 nm³/t
b) Dampf	30,0 kg/t
Stromverbrauch	
a) für die Vakuumanlage	2,5 kWh/t
b) für Pumpen	1,5 kWh/t
Wasserverbrauch	1,5 m³/t

Der außerordentlich niedrige Wärmeverbrauch des mit Koksofengas geheizten Röhrenofens entspricht rund 112000 kcal/t, also etwa dem theoretischen Wert nach Bild 12. Die unvermeidbaren Wärmeverluste werden durch Ausnutzung eines Teiles der Wärme des heiß anlaufenden Pechs gedeckt.

Der Stromverbrauch von 2,5 kWh/t für die Vakuumpumpen fällt energetisch gar nicht, wertmäßig kaum ins Gewicht.

Der Dampf wird benötigt zum Anwärmen von Pumpen, Armaturen usw., zum Durchblasen von Leitungen sowie für die Beheizung einer hier nicht dargestellten Zusatzeinrichtung zur besonders weitgehenden Ausnutzung des Phenols im Karbolöl. Die beträchtliche Senkung der Destillationstemperatur in Verbindung mit der Rektifikation in einer Hitze hatte zur Folge:

1. eine Senkung des Wärmeverbrauchs wesentlich unter alle bisher bekannten Werte,
2. eine Erhöhung der Ölausbeute,
3. die Beherrschung aller korrodierenden Einflüsse,
4. die Vermeidung jeglicher Koksbildung in den Rohren des Ofens.

Bild 15 bis 17 zeigen die ausgeführte Anlage.

Bild 17. Aufnehmerraum mit Meßwarte

Bild 18 (links). Kolonnen mit Rückflußkondensatoren

Abgesehen von dem einem Röhrenofen nachgeschalteten Ausdampfraum, in welchem die Spontanverdampfung stattfindet, besitzt es drei hintereinander geschaltete Kolonnen mit Rückflußkondensatoren. Die Rektifikation in diesen erfolgt ohne zusätzliche Wärmezufuhr, wobei das Rücklaufverhältnis entsprechend dem Anteil der Fraktionen infolge ihrer wirksamen Bauart und der günstig gewählten Druckverhältnisse ausreicht, um diese genügend scharf zu trennen. Der theoretische Wärmeverbrauch entspricht also demjenigen nach Bild 12 ohne Rektifikation. Die Rückflußwärme wird aus der Kondensationswärme der Fraktionen gedeckt.

Die Qualität der erhaltenen Fraktionen ist aus Bild 14 zu entnehmen.

Das **Anthrazenöl** läuft mit beträchtlicher Siedelücke in einer hochsiedenden Avenarin-Qualität ab und liefert nach Abscheidung der festen Rückstände ein einwandfreies Heizöl.

Das **Waschöl** ist ebenfalls durch eine Siedelücke vom Naphthalinöl getrennt und entspricht der Solvay-Qualität.

Das **Naphthalinöl** enthält die Masse des Naphthalins und ist praktisch frei von Phenol.

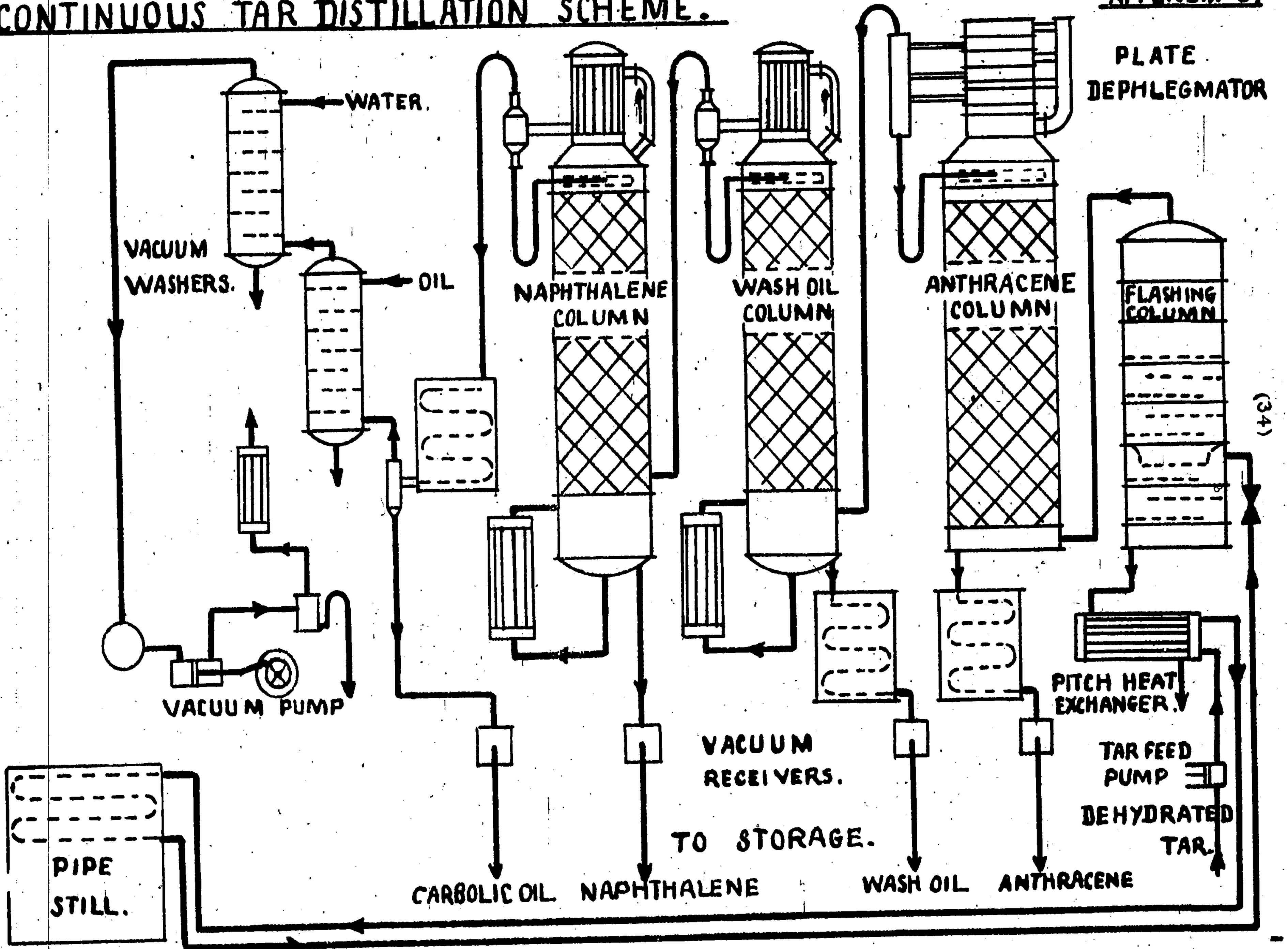
Im **Karbolöl** ist das Phenol angesammelt, es ist ebenso wie das Naphthalinöl kühlhaus[illegible]

Zusammenfassung

Verfahrenstechnische Berechnungen von Anlagen zur Destillation von Vielstoffgemischen scheinen schwierig zu sein, da diese von wechselnder Beschaffenheit und in ihrer Zusammensetzung unbekannt sind. Ausgehend von den Destillationstemperaturen gelingt es aber, die Verhältnisse beim Abtrieb und der Spontanverdampfung für beliebige Destillationsdrucke zu übersehen. Die Vorgänge im Röhrenofen, in den Rektifizierkolonnen und der theoretische Wärmeaufwand werden näherungsweise berechenbar. Die praktischen Ergebnisse eines [illegible] Verfahrens zur Teerdestillation bestätigen die Vorausberechnungen, insbesondere wird der theoretisch [illegible]

APPENDIX C.

CONTINUOUS TAR DISTILLATION SCHEME.



RAUXEL WORKS

General: The Rauxel Works suffered severely from air attack. There were eleven attacks in all, of which those on 2nd and 3rd January and 15th March 1945 did nearly all the serious damage. A total of 465 bombs (and 148 unexploded) fell on the works, killing 9, employees and injuring 12.

The damage and destruction included: 2 of the 3,000 ton tanks and one third of one of the 5,000 ton tanks for the storage of crude tar destroyed. Entire Naphthalene plant destroyed, including pan house, whizzer house and press house. A great part of the Anthracene plant destroyed, including the pan house. One battery of oil stills destroyed. Much miscellaneous damage to ancillary plant - pipe lines, railway tanks, weighbridges, storage boilers, etc.

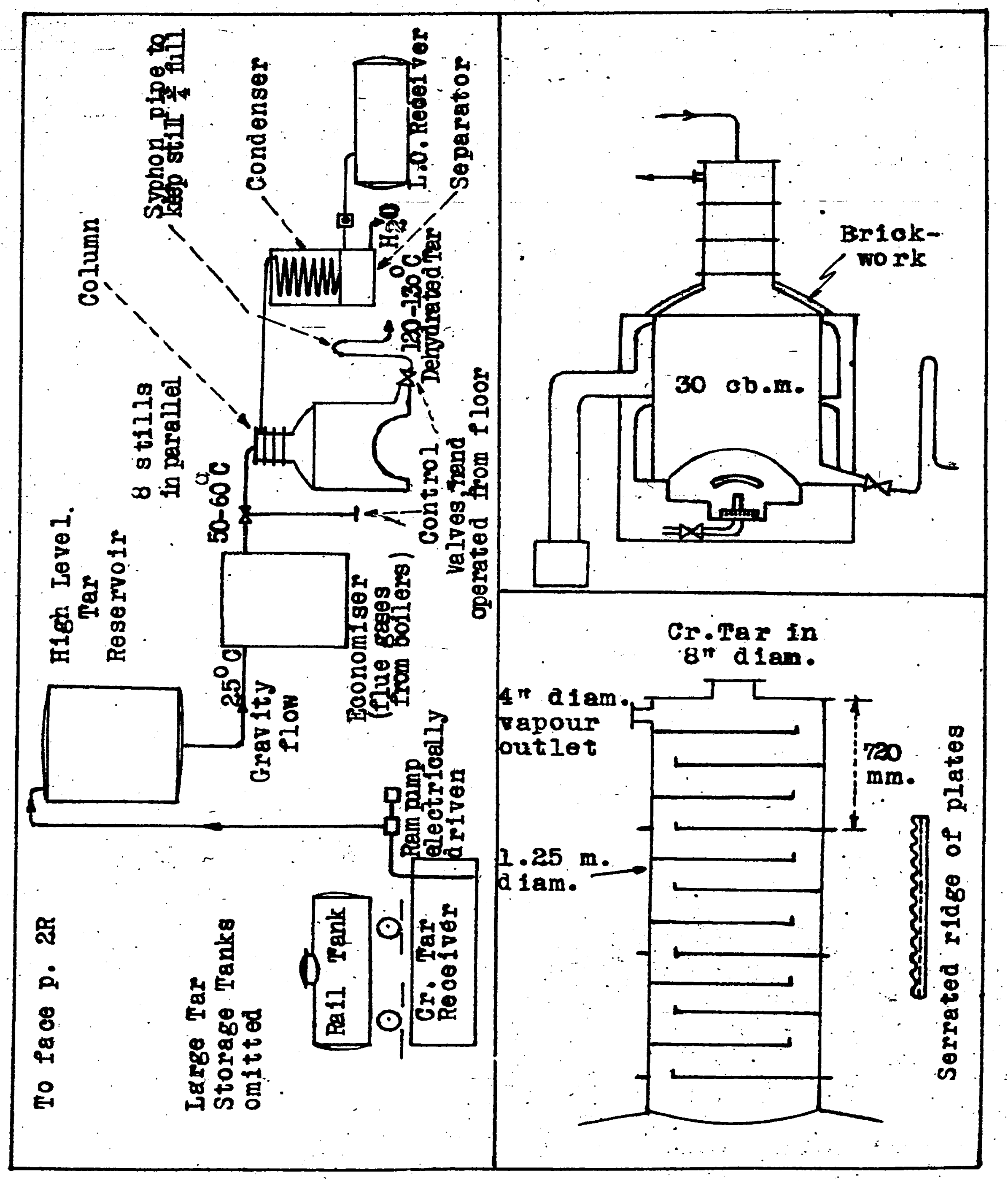
The maximum capacity at Rauxel is 45,000 tons/month, and the average throughput 1939-1944 was 37,000 tons/month.

The present personnel of the works, including office staff, is approximately 565. The complement in full production was 675, including 100 women (February 1945). The works normally operates on three shifts on a six day week, but when the adjoining hard pitch coking plant was in operation, on a seven day week, since the ovens were working continuously.

The works distils the coke-oven tar produced at various ovens in the vicinity, 26-28 plants in all. No gas-works tar is distilled and no intermediates taken in except 200 tons/month of middle oil from Lothringen Colliery, who take Benzole Absorbing Oil in exchange.

The available storage for Crude Tar was 20,000 tons, the tanks being 3 x 3,000 tons, 2 x 5,000 tons and 2 x 1,000 tons.

Tar Distillation Plant: The crude tar is dehydrated continuously in a battery of eight vertical gas-fired stills, in parallel, under atmospheric pressure.



A rough sketch of the discharging and dehydrating process is shown opposite. The economiser, using the boiler flue gases, is of the usual vertical type with scrapers, and raises the temperature to 50°-60°C from say 25°C, to which it was raised by closed and open steam in discharging, etc.

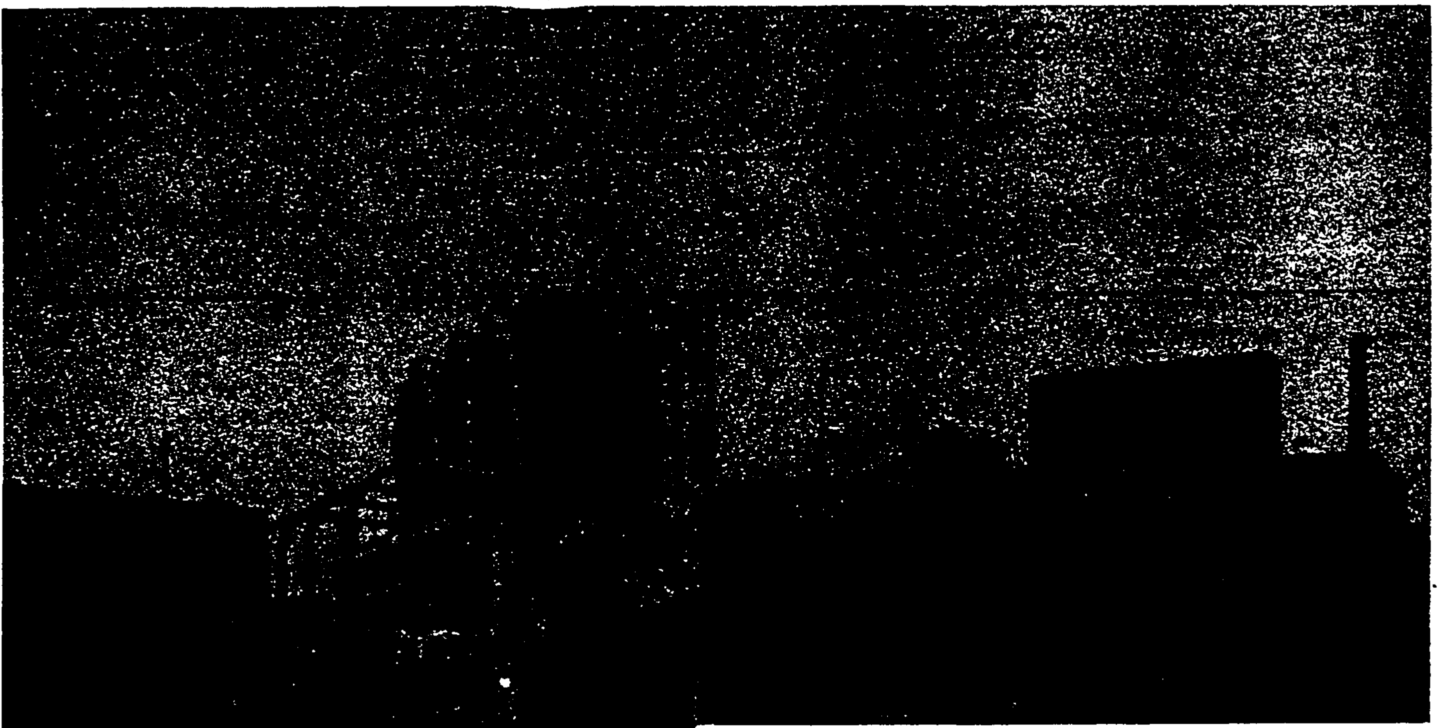
A rough section of a dehydrating still ~~and~~ details of a column are given opposite. The column is of cast iron in three sections, each with four flat plates cut away for six inches at alternative sides. The diameter is 1.25 m. and the plate thickness $\frac{3}{8}$"; the outer edge of each plate is a serrated ridge equivalent to approximately $\frac{1}{2}$" semicircles at 1" centres about $\frac{1}{2}$" above the plate level.

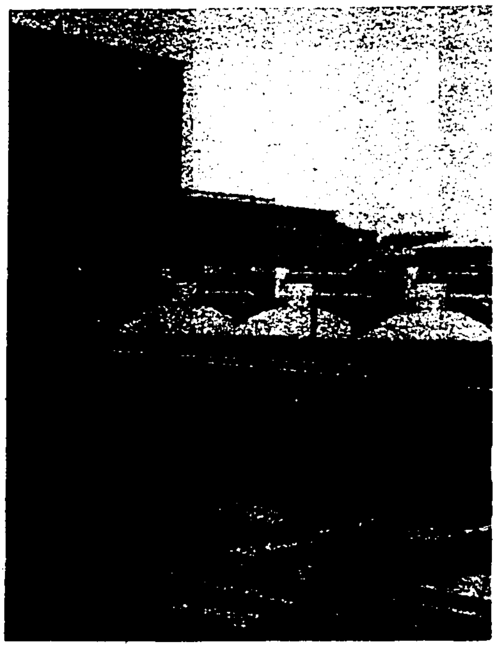
The still is of 30 cb.m. content, 5080 mm. high by 3000 mm. diameter, with bottom dome 970 mm. high. The flue system is simply as shown, the brickwork being 400 mm. thick and the flue width 200 mm. The flue brickwork continues to within 400 mm. of the top dome. There are square manholes in the side and the flue gases leave through a circular refractory-lined metal flue 400 mm. in diameter. A so-called 'mushroom' is fitted over the vertical gas burner below to prevent injury to the still bottom by the hot-gases. This is made of a heat resisting cement, poured on to a wooden mould or form., After the cement has set and dried it is placed in position and the woodwork burnt away. The mushrooms have a long life. The capacity of the plant is approximately 10 tons/still per hour with crude tar containing 3-4% water. With 5-6% water the throughput falls to 8 tons/hour.

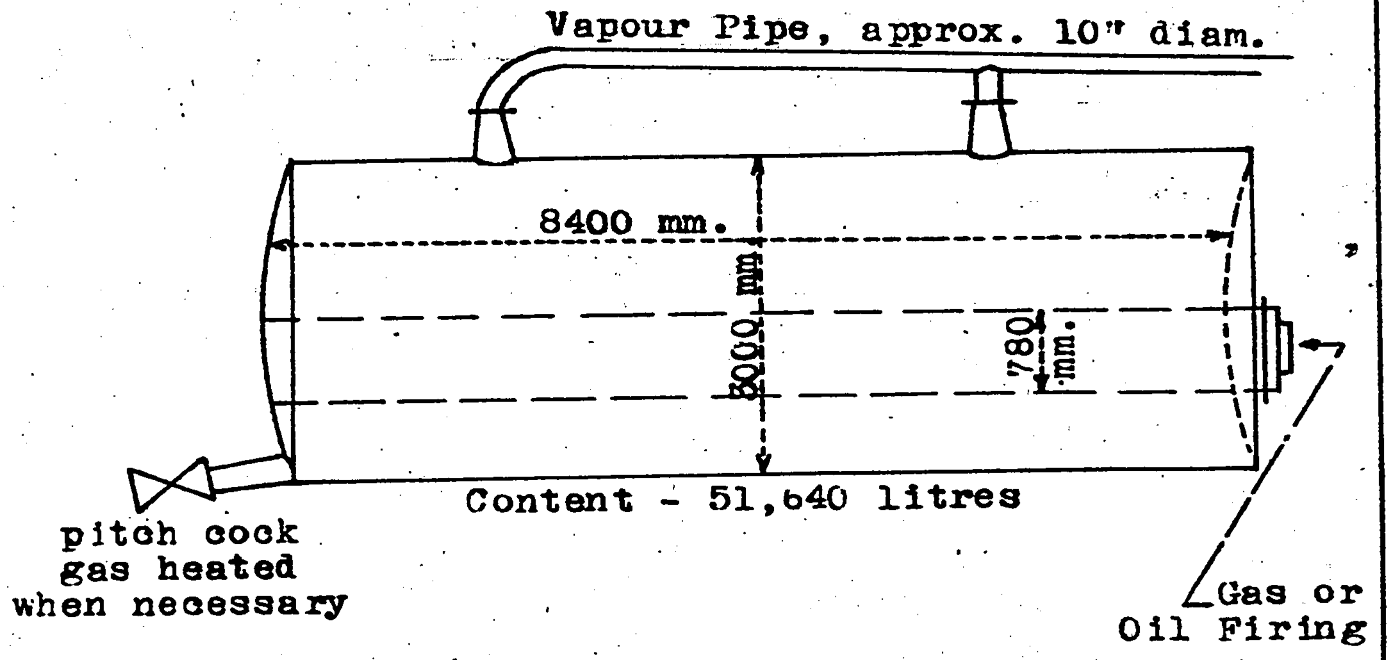
The stills last about two years. They are shut down and cleaned every 18 days, after 4-5,000 tons throughput. The labour with gas firing is one man/shift, who handles the firing, transfer of material, etc. Gas heating was started in 1929. On the first day an explosion occurred, due to ignition of explosive mixture in the flues, but since then operation has been a complete success.

The dehydrated tar (the firm's analyses of tar and of products attached hereto) is distilled in three

[redacted]







To face p. 3R.

batteries of tar stills without columns. Two batteries are each of seven horizontal twin fire tube stills (Lancashire boiler type, approx. 50 tons content, 8.39 m. long, 3.01 m. diam.) The firing is either gas or a heavy pitch-creosote mixture (80% pitch, 20% anthracene oil) and the layout of the stills is approximately as shown opposite. There are two off-takes in the top of each still, and a ten inch common vapour pipe leads to the usual helical coil condenser (of diminishing pipe diameter) and receiver tank, to which the vacuum lead is connected. The pitch cock is gas heated by a ¾" pipe with holes along the upper surface; the cock key is 6-8 feet long. Steam jacketted cocks are not used. The pitch runs down into a vertical egg from which it can be blown to the pitch pans or bays. The working pressure of the stills is said to be normally 20-40 mm. Hg. The distilling time is 8-10 hours. The stills are shut down for cleaning every 24-30 charges. This is said to take only 24 hours cooling and about 3-4 hours cleaning with three men. The reason for the two vapour off-takes is the delay caused by the constriction in the system if only one is used, and even so, owing to the fact that the battery was originally of four stills and has been enlarged the condensers and vapour pipe system are not all alike - some vapour pipes being longer than others - and these stills as a whole are not regarded as so satisfactory in operation as the vertical type. The gas passages are different from those of a Lancashire boiler; the final gas passages (the 'side flues') are insulated from the still, since the gas temperature is lower than that of the still contents.

The third battery of stills contains seven vertical tar stills, also of approx. 50 tons content, fitted and fired with gas in the same manner as the dehydrating stills, but in batch process. The distilling time, etc. is said to be about the same as the horizontal type, but operation is more uniform and controllable and more economical.

The gas is normal coke oven gas, approx. 4,300 Cal/Ncbm., obtained from the 'Ruhrgas' (ring main in Ruhr) or directly from the Erin Coke Ovens at Castrop (5 Km. away), and is received at a pressure of 2-3 atm. and reduced to 20-40 cm. W.G. for operation. Sensitive pressure controllers are fitted at the still batteries to ensure uniformity. The consumption for dehydration is said to be 16 cb.m. gas/ton, and for distillation - horizontal stills: 45 cb.m./ton, vertical stills: 36 cb.m./ton or 1600 kg. coal. A recent result for dehydration of tar with coal is - 850 tons tar for 12,703 Kg. coal. The life of a still with gas firing is at least 50-60% longer than with coal and of course the fractionation is much better. Cost of gas at works 2.2 Rpf./N.cb.m.

The labour on the tar stills is two men/shift/plant. Pitch of up to 150°C softening point is made on the same stills, both types, as will be described later.

The system of tar distillation is outlined in Appendix C and the analyses of crude tar and fractions as given by the firm are in Appendix D.

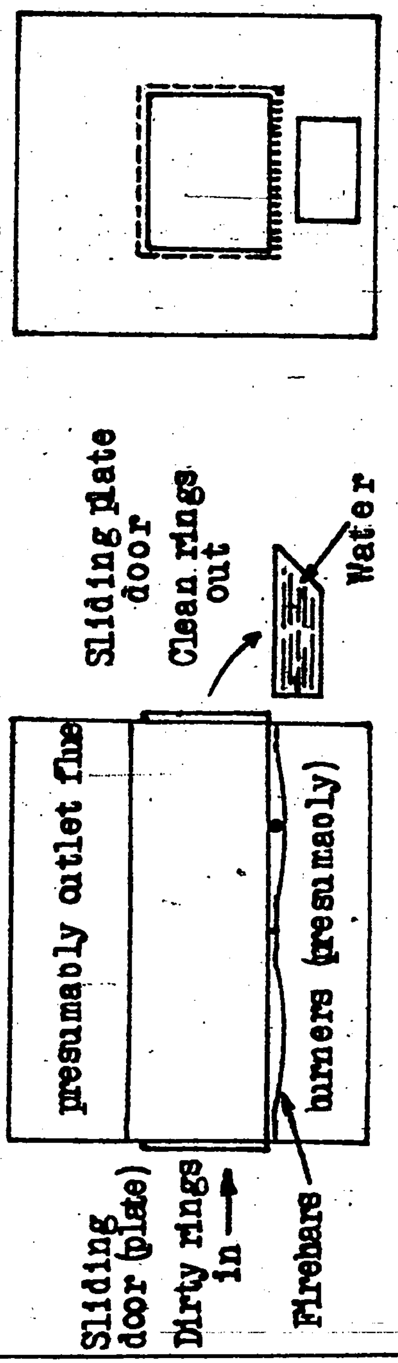
Fractions from Crude Tar - Treatment:

(1) Water - approx. 4.0%. Contains 0.5-0.6% NH_3 which is worked up in a small ammonia plant to 15% concentration.

(2) Light Oil - approx. 0.8%. Goes to G.f.T. Works at Duisburg-Meiderich for distillation to Pure and Motor Benzole, Pure Toluole, Xylenes, and the extraction of Pyridine Bases.

(3) Dehydrated Tar - approx. 95.2%. Distilled as shown in Appendix C. Treatment of the fractions thus obtained is as follows :-

(1) Middle Oil - Heavy Oil. These fractions were originally separated, but on occasion had to be lumped together when distilling to hard pitch, since there are only three receivers to each still and another receiver was needed for the heavy distillate beyond anthracene oil. In practice they are always collected as one fraction and re-distilled in the oil stills. There are two batteries of these, each with five vertical stills of 50 tons content. The stills are fitted



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with dephlegmators over columns 10 m. high and 1.5 m. diameter, lagged and packed with 35 mm. iron Raschig rings; charges are distilled off in 18-20 hours. The iron rings collect resinous material and much sulphur, and have to be removed and burnt out every 6-8 weeks (after about 50 charges). They are run out of the bottom of the columns and a fresh quantity of previously cleaned rings put in at the top. The cleaning out lasts about two days (done piece work). The dirty rings are put into a double sided furnace with firebar bottom gas fired and burnt out, with much smell of sulphur and black smoke. The cleaned rings are raked out into a water pan on the far side (approx. sketch opposite) for cooling and collected in old 45 gallon drums after a rough sorting out of the old corroded rings. When a replacement is necessary the drums are easily hoisted to the column top and poured in. The vacuum in the column is approx. 20 mm. Hg. top and 40 mm. bottom. The vacuum pumps on the works are all either Klein, Schanzlin and Becker or Pokorny and Wittekind, both of Frankenthal, each still having its own pump. The normal size is about 750 mm. diameter and its capacity 1,000 cb.m. free air per hour at 150 r.p.m. driven by 'V' belts by 22 Kw. flameproof motor. In order to prevent wear and tear on the pumps and also loss of material with the permanent gases a vacuum washing outfit is connected between the receiver and the vacuum pump on each of the various oil and tar stills. This consists of a pair of small scrubbers of the same design as the dehydrating still column, diam. 60 cm. and height approx. 9 feet, of which the first is fed with water from the works' water supply and the second with a circulating system of anthracene oil (with centrifugal pump) which gradually thickens and in due course is replaced by new.

The gas consumption for oil distillation is 72-75 cb.m./ton. The reflux in the column is approx. 6-8:1.

Middle and heavy oil mixture is normally distilled down to Residue I, which includes also the Anthracene Oil. Further distillation is not practicable because of the necessity of leaving a certain proportion of the charge in the still. Normally four or so Residues I are collected and re-distilled, either in an old still without a column, or by by-passing the column and taking a pipe from the still top mount to the condenser (which is not desirable because of the difficulty of keeping the plant tight under the conditions of extremely hot still and cold column), or, best of all, by distilling through a column without ring packing and without dephlegmator.

No steam at all is used in the oil or tar distillations.

(ii) The Anthracene Oil I is treated in one or two ways.

(a) For manufacture of 40's Anthracene the oil is cooled in vertical cylindrical tanks equipped with slow stirrers (at most 30 r.p.m.) (old Anthracene plant has shaft and belt drives to agitators, new plant has individual motor and reducing gear drives), the solids separated by use of a Nutsch filter (about 3 feet wide and deep, with rounded bottom, rather like a section of a screw conveyor, and about 6 feet long, fitted with bronzed steel filter cloth supported by perforated plate) then made mushy by heating to 150°C or more, well mixed mechanically, cooled in a similar cooler to above and finally whizzed in vertical suspended electrically driven whizzers to 40's.

(b) For ordinary anthracene residues the oil is cooled usually in two stages, one by air cooling and a further stage by water cooling - similar coolers but water jacketted - and then whizzed. The product in this case is 25-30% Anthracene and is used in very large quantities for the preparation by controlled combustion of carbon black for Buna rubber. The new plant is fitted with two Haubold horizontal totally enclosed continuously-running centrifugal machines, whose capacity is (each) approx. 75 tons Anthracene Oil/24 hours. Each charge should take one hour but normally takes 1½ hours, so that there is about five charges/shift. With a solids content of about 12-14% the production of Anthracene residues is about nine tons/24 hours.

(iii) Pitch.

(a) Medium soft: The still is stopped when the softening point of the pitch is 60-75°C and the pitch run out by gravity into a vertical cylindrical pressure vessel, from which it is normally blown by compressed air into an elevated tank in the covered pitch hall. If the quality of the pitch is not quite right (too hard) or if road tar is required, it is adjusted by mixing back with the necessary quantity of anthracene oil. The pitch is then run into flat-bottomed pivoted shallow pans, which are in an elevated position over railway tracks. When the pitch has set the pans are tripped and the pitch broken loose by hand, when it drops into railway wagons placed below. The tipping pans, of which there are about 50, hold 4½-5 tons each, the layer being 6"-8" thick. The average rate of discharge to wagons was 60/70 tons/shift, and the piece rate was Rpf. 23/ton. Pipes also lead from the overhead tank by which the pitch may be filled into 'blocks'. These are moulds in the form of cylinders, of about 20 gallons capacity, made of steel plate in two halves - i.e., two semi-cylinders which are clipped together. They are open top and bottom and whitewashed. When stood on end the pitch is run in, sets, the clips are loosened and the plates knocked back, and the pitch is available as a solid block.

As a safety measure a large pitch bay is also available on to which pitch is run when there is no demand for loose pitch (from the tipping pans) or for blocks. This is served by a pipe, approx. 4" diameter, from the overhead tank.

(b) Hard Pitch: If this is required for the neighbouring battery of pitch coke ovens, distillation proceeds in the normal way as far as medium soft pitch. The fire is then extinguished and

air is slowly sucked by the vacuum pump through the still through two 'agitator pipes'. One of these is the normal crude tar charging pipe, fitted with a 'T' piece and valve opening to the atmosphere, and the other is a separate but similar pipe at the opposite side of the still top. (Hard pitch distillation is carried forward in both vertical and horizontal stills, but preferably in the former) The resulting distillate is collected in the final receiver and is a very heavy, almost buttery material, known as 'hard pitch distillate'. During the air-sucking the temperature continues to rise for a time, indicating that internal oxidation is taking place, up to almost 375°C from say 320°C. After about 3 hours, suction is stopped momentarily and a sample of the pitch from the still is coked in the laboratory as a test. When the residue is 50% the still is considered finished and the contents are at once pumped to the adjoining pitch coke ovens. Here there is a continuous circulation of pitch in a ring main system, approx. 20% being taken off to charge the ovens. This system is necessary as otherwise, the pitch being so hard, the whole system would set solid almost at once

The pitch coking plant (for electrode coke) was not further investigated, but it is understood to consist of 40 Koppers ovens (2 x 20) of normal type. The pitch has to be run in very slowly because of the extremely rapid evolution of vapours and gas - three hours charging time and about 12-14 hours coking time.

The fractions from the Middle Oil-Heavy Oil distillation are shown also on (C) and their systematic treatment indicated. A few further remarks follow.

Naphthalene. The Naphthalene pan house contains 32 rectangular pans of 11 m. x 2.5 m. x 1 m. dimensions and 25 tons capacity, in four storeys. After settling for about 24 hours, the oil is drained off and the drained salts dug out by hand