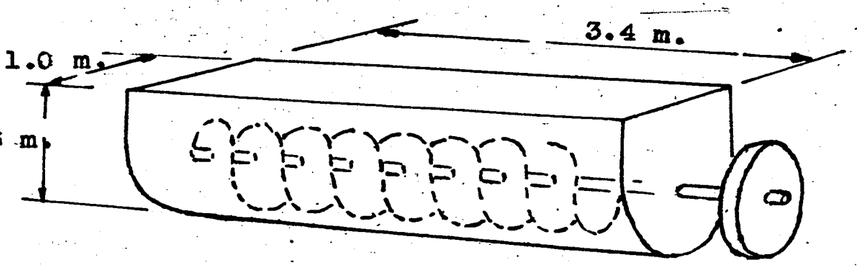


To face p. 9R

and tossed down shutes running between the pans to the ground floor. Here the salts land on sloping wooden grids on a metal framework over rectangular metal tanks where further draining occurs. The final salts with a c.p. of approx. 65°C are shovelled on to a long screw conveyor, which either takes them via a cross conveyor-cum-elevator to railway wagons or, by rotating the other way, to a 'Maische' (see sketch opposite) via a double toothed roller crusher. The resulting mash is whizzed to produce 75-76° c.p. material, which then goes to the Naphthalene press house. Here the material is once more mashed up, and also warmed up, in vertical open cylindrical tanks over the presses, of which there were (whole plant now totally destroyed) two large ones with cages 1.8 m. high and one smaller one with cages 1.2 m. high, all made by the Harburger Eisen-u-Bronzewerke. The operating pressure was about 2½ tons p.s.i. (350 atm.) A hydraulic accumulator was used, fed by two pumps (a) a low pressure direct coupled six stage turbo-pump up to 50-60 atm. pressure and (b) a high pressure ram pump up to the full pressure.

Using only the two large presses the highest production obtained was 66-70 tons/24 hours, but the normal production was approx. 60 tons/24 hours. The weight of pressed material obtained was 175 Kg./press. This is equivalent to

$$\frac{60 \text{ tons}}{3 \times 2} = 10{,}000 \text{ Kg/press/shift} = \frac{10{,}000}{8 \times 175}$$

= 7 presses/hour, or 1 every 8½ minutes.

By means of a pressure recorder charts showing the exact pressing times and when the men took meals and so on were normally kept. The pressed naphthalene was 79° c.p. minimum and was sold as such.

It was said that Dr. Moehrle had intended to press for a complete revision of the naphthalene specifications, contending that a drained, whizzed, washed and distilled product, 76° c.p. minimum, would serve the purpose of industry in most cases equally well with the pure naphthalene and would be much cheaper

because of the elimination of the costly pressing equipment. Most of the pressed naphthalene went to I. G. Ludwigshafen.

Naphthalene and Anthracene Plants in full operation required 60 men each. The naphthalene press plant with two presses working needed one press man and one cake handler per press, one top hand and one cellar man, i.e., six men/shift.

Steam. The Works' boiler plant consists of four Lancashire type and two 3-flue type boilers, of a capacity of approx. 3 tons/hour each. The pressure at the boilers is 15 atm. max. - 12 atm. min. The evaporation figure with gas is approx. 4.9 Kg./N.cb.m., and with oil (usual mixture of approx. 80% pitch and 20% heavy oil) is approx. 11 Kg./Kg.

The maximum steam production in winter is of the order of 14,000-15,000 tons/month with 45,000 tons tar/month - 1/3 ton steam/ ton tar, of which a good quarter is for warming and discharging the tar from rail tanks. Experiments which they have carried out indicate that the lagging of the rail tanks for crude tar is well worth while and results in a considerable saving of steam, since the tar if loaded at the ovens at, say, 60°C arrives at the works at, say, 30°C. They had proposed to complete the lagging of all their rail tanks in due course.

Tar and Oil Stills. A special runway is built out over all the vertical tar and oil stills except one, so that when a renewal of the still is necessary it may be lifted by a travelling block, half the brickwork removed, the still placed on a bogey running on rails along the battery and removed, and a new still put in in the same way. The repair, working days only, lasts a week to 10 days. This system is followed even when a still bottom requires renewal. The columns are supported independently and alongside the stills. In the case of the horizontal stills, these are jacked up and moved out on wooden rollers. One of the vertical batteries has no room for this overhead conveyor system and the difference in time and money to complete the repair is considerable.

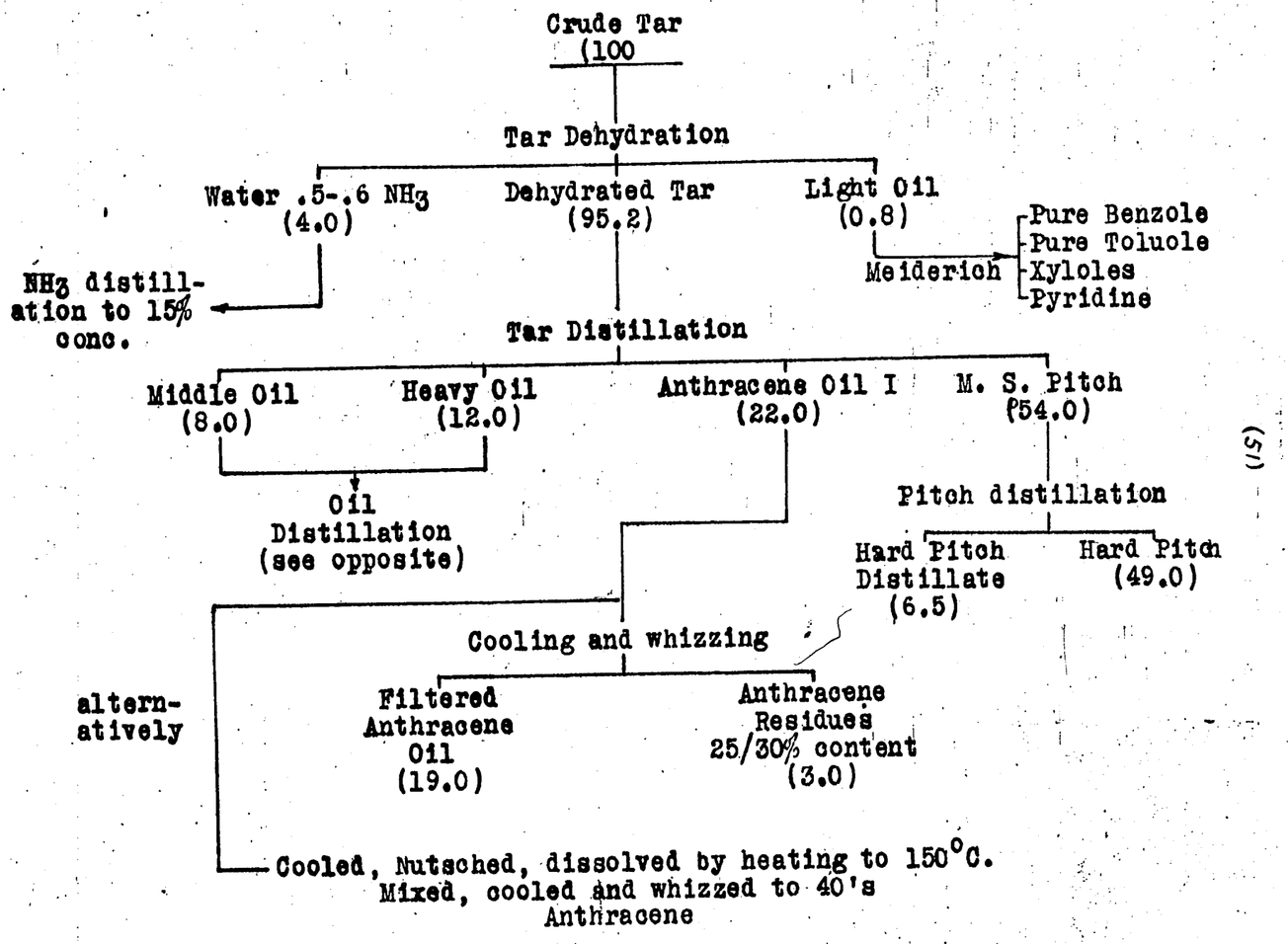
Miscellaneous notes :-

(1) Normal process worker's pay is Rpf.80/hour.

(2) Cost of current is Rpf.4.5/Kwh.

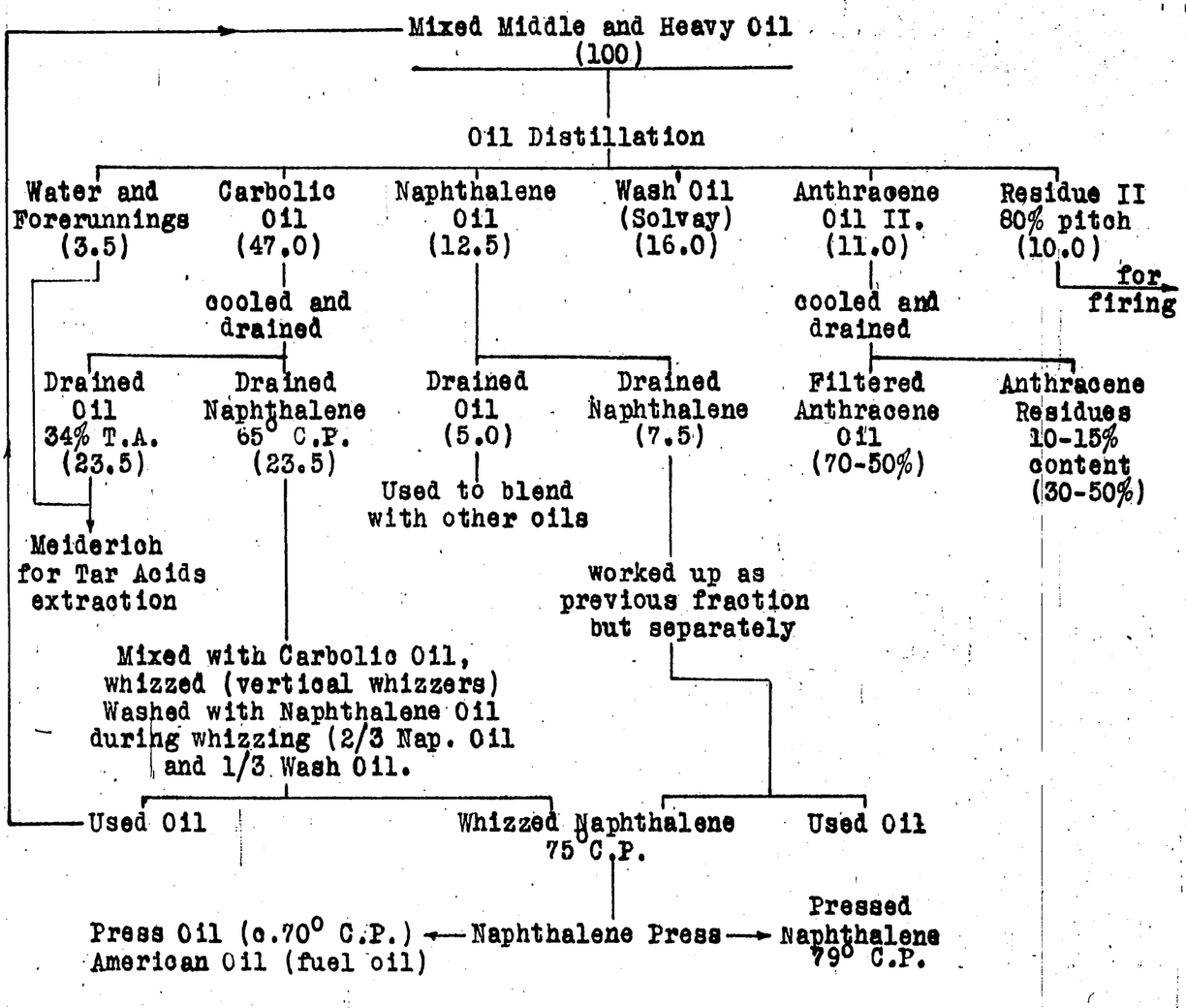
(3) Cost of 1st distillation of tar RM.4.60/ton.

Appendix C



(51)

Appendix C



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APPENDIX D

AVERAGE ANALYSIS OF CRUDE TAR WORKED UP AT R A U X E L

Specific Gravity	1.180
Water Content	4.3%
Chlorine Content	0.063%

Distillation:

		%
up to 180°C	-	5.0 (4.2% water)
180° - 230°C	-	6.0 (0.8% Light Oil)
230° - 270°C	-	7.3
270° - 360°C	-	21.7
Pitch	-	59.6 (Sp. 67°C)
		99.6

	%
Coke	14.3
Ash	0.11
Free Carbon	6.7
Phenol	0.284
Cresol	0.671

Distillation of the above tar under high vacuum yields the following :-

	%
Water	4.0
Light Oil	0.8
Middle Oil	8.0
Heavy Oil	12.0
Anthracene Oil I	22.0
Briquette Pitch	54-56%

Distillation of 100 Kg. briquette pitch to hard pitch yields :-

10-12 Kg. Hard Pitch Distillate
88-90 Kg. Hard Pitch

ANALYSES OF THE FRACTIONS

Hard Pitch Distillate - Sp.Gr. 1.190 - 77% distils between 325-435°C.

Hard Pitch - 50-52% coke: 0.28% ash: 150-160°C. S.P.

Light Oil - Sp. Gr. 0.930. 90% distils below 225°C. The light oil goes to G.f.T. Meiderich for working up.

Ammoniacal Liquor - Contains 0.55% ammonia and is concentrated to 15%.

Middle Oil	-	Sp.Gr. 1.020	90% distils between 190-270°C.
Heavy Oil	-	Sp.Gr. 1.033	90% distils between 212-307°C.
Crude Anthracene Oil	-	Sp.Gr. 1.094	86% distils between 240-360°C.
Filtered Anthracene Oil	-	Sp.Gr. 1.096	82% distils between 245-360°C.

Pitch - Sp.Gr. 1.250. Softening point 60-75°C.

Carbon content		25-30°C.
Coke residue	max.	45%
Ash	max.	0.5%

The Middle Oil - Heavy Oil together, distilled through the oil stills yields :-

Aqueous forerunnings - 3.5%

Carbolic Oil	- 47.0%	Sp.Gr. 1.002. 90% distils between 180-224°C. Approx. 50% naphthalene content of 65° C.P. Tar Acid content of drained oil 34%. The drained oil goes to Meiderich.
Naphthalene Oil	- 12.5%	Sp.Gr. 1.023. 90% distils between 208-247°C. Approx. 60% naphthalene content of 65° C.P.
Solvay Wash Oil	- 16.0%	Sp.Gr. 1.053. 90% distils between 228-290°C. No solids at 0°C.
Anthracene Oil II	- 11.0%	Sp.Gr. 1.094. 86% distils between 270-350°C. 11% anthracene solids of 25% content.

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Residue II - 10.0% 80% pitch content, used as fuel.

150 Kg. hard pitch, softening point 150-160°C. yields on coking :-

70 Kg.	Pitch Coke
20 Kg.	Pitch Coke Oil

The remainder is loss and gas, having a hydrogen content of 78-80%.

Analyses:

Pitch Coke	Water	1.0-1.2%
	Ash	0.4%
	Volatile	0.6%
Pitch Coke Oil	Softening point	40-45°C.
	Water	2.0%

Copy 1

B.I.O.S. FINAL REPORT No. 465

ITEM Nos. 21, 22

HIGH TEMPERATURE REFRACTORIES AND CERAMICS

by Watts, W. ...

BRITISH INTELLIGENCE OBJECTIVES

SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

HIGH TEMPERATURE REFRACTORIES

AND CERAMICS.

Report by:

F/Lt. W. Watt.
Mr. F.H. Clews.
Mr. R.B. Miller.
Mr. J. Walker.
Mr. C.H. Wheatley.

BIOS Target Numbers

C21/838, C21/618, C21/687, C21/612,
C21/912, C21/915, C21/913, C21/914,
C21/916.
C21/921, C22/922, C21/920, C21/916a,

C22/2842, C22/1437, C22/3238, C22/1502,
C22/598, C22/3239, C22/3157, C22/1866,
C22/3240, C22/3241, C22/3242, C22/3243,
C22/3240(a)

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

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE.

HIGH TEMPERATURE REFRACTORIES AND SPECIAL CERAMIC MATERIALS.

Reported by: F/L. W. Watt, R.A.F. (M.A.P)
Mr. F.H. Clews, M. of S.
Mr. R.B. Miller, M. of S.
Mr. J. Walker, M. of S.
Mr. C.H. Wheatley, M.A.P.

OBJECT.

The object of B.I.O.S. trip number 1252 was to study the manufacture of high temperature refractories and ceramic materials and obtain information on the fabrication of ceramic turbine blades.

1. HERMANN GOERING LUFTFAHRTFORSCHUNGSANSTALT VOLKENRODE, NEAR BRUNSWICK.

(a) DATE OF VISIT.

The works was visited on the 2nd and 3rd October, 1945. The personnel interviewed were: Professor Dirksen, Herr Trapp and Herr Bamment.

(b) INTERVIEW WITH PROFESSOR DIRKSEN AND HERR TRAPP.

Dr. Dirksen had been in charge of experiments on the mechanical properties and thermal shock resistance of various refractory ceramic products. He briefly outlined the substance of five reports which appear as Appendix I.

The most important discovery was that although the compressive strength of the ceramic materials tested was considerably greater than the tensile strength at room temperature, the two became approximately the same at about 700° to 800°C.

The apparatus used for this experimental work was exhibited by Herr Trapp. Tensile tests had been

largely abandoned due to the difficulty of obtaining true axial loading of the specimens. Instead measurements of transverse strength were carried out in a horizontal electric furnace heated by sillit rods. Provision was made for measuring the extension of the portion of the test rod in tension and the contraction of that part in compression by means of two mirror systems and thus testing the similarity of the stress-strain curves for tension and compression. Creep tests were carried out in this apparatus in addition to measurements of strength. In vertical compression tests the deformation on opposite sides of the specimen was measured in order to ensure correct alignment of stress. The apparatus was orthodox in other respects.

Tests had also been done on a comparative thermal shock characteristics of ceramic venturis, presumably to ascertain their suitability for combustion nozzles in gas turbines and for rocket propelled projectiles. Combustion Gases at an estimated temperature of 1700°C and approx. 30 atms. pressure issued through the venturi for 5 mins. The cycle was repeated until fracture. The results were poor, most of the ceramic venturis failing by cracking after one or a few cycles. Cutting the venturi into three equal segments and mounting them in a metal case, with or without the backing of another ceramic venturi was found to prolong the life.

(c) INTERVIEW WITH HERR BAMMERT.

Herr Bammert of the engine division was interviewed on the application of ceramics to gas turbines. Blades in various ceramic materials such as sillimanite, alumina, porcelains, etc. which had been made by the following firms were inspected.

Stemag	-	Berlin.
Hesche	-	Hermsdorf.
Degussa	-	Frankfurt.
Koppers	-	Dusseldorf.

State Porcelain Factory - Berlin.
Siemens Halske - Berlin.

No actual turbine had been built with ceramic blades; the work had been only on methods of mounting and on heat resisting properties. A turbine with metal rotor blades and ceramic stator blades had been designed. The mounting of the blades had presented considerable difficulty. The most suitable method was found to be sintering the blade in a slot in a heat resisting steel base with powdered iron. The sintering temperature was 1300°C., the various operations being normal powder metallurgy technique.

The heat resisting properties of the blades were tested in a combustion rig in which they were subjected to a stream of hot combustion gases, the mass flow being of the same order as in a gas turbine, and to various degrees of temperature change, until the blade failed by cracking. The outstanding blade in this test was one consisting of a mixture of silicon carbide and clay with a glazed surface.

One blade, made of sintered alumina, was hollow to permit of hot air being passed through it to mitigate the thermal shock of combustion gases impinging on the exterior. This was considered a promising development.

It was stated that the intention was, had the war proceeded, and conditions allowed, to build a turbine with a water cooled metal rotor and a glazed silicon carbide stator and to arrange for an unequal reaction between stator and rotor so that the metal was more stressed than the ceramic material.

(d) CONCLUSIONS.

It is difficult to assess the value of the work done at Volkenrode. The different divisions of the experimental work seemed to have proceeded independently. For example, Professor Dirksen was not informed of the

composition of the bodies he tested, and the engine section proceeded on the assumption that ceramic materials are weaker in tension than compression when hot, despite Professor Dirksen's experiments. The German workers conveyed the impression that they considered that there was a fair prospect of ultimately providing a method of using ceramic materials in gas turbines.

2. SCHEIDHAUR UND GIESSING, DUISBERG (DIDIER-WERKE, A.G.)

(a) DATE OF VISIT.

A visit was paid to this factory on the 8th October, and Herr Katheriner, the works manager, interviewed.

(b) CONDITION OF TARGET.

The works were badly damaged in parts, other parts were intact. Some of the kilns, pressing shops, and carbon brick kiln were badly damaged. All the grinding and mixing plant was intact. Roughly 25 per cent of the plant was damaged but a considerable output was thought to be possible with the factory as it stood.

(c) PRODUCTS.

The works used to make firebricks (chamotte bricks), silicon carbide products, glass tank refractories, sillimanite products, corundum refractories, graphite stoppers and nozzles, carbon blocks and acid resisting bricks. Total month output 4,000 tons. Sillimanite bricks had not been made during the war owing to the cessation of imports of kyanite. Highly grogged fireclay bricks were made as substitute. The methods of manufacture for most of the products were very similar. We directed our attention chiefly to the sillimanite, silicon carbide, corundum and carbon products.

(d) MANUFACTURING PROCESSES.

The works is equipped with a number of overhead conveyors to deliver raw materials from each main dump to the jaw crushers, from which it passes to the crushing rolls; it is then magnetted, elevated, screened in rotating octagonal sieves or double banks of vibrating sieves operated mechanically. Dust collection by the Beth system (Lubeck) is provided. The fine middle and coarse fractions are conveyed on the same vibrating conveyor belt side by side and can be diverted as required to bunkers collecting the required grade of material. Several openings to different bunkers are provided. Each bunker is equipped with a weighing machine so that each item of the dry batch can be discharged on to a moving belt which in turn discharges it into a receiver on an overhead rail. Two types of mixer were seen, the Werner and Pfleiderer and the Eirich, the latter gradually displacing the former in this works. After 15 minutes dry mixing the slip required to effect the bonding is introduced. This consists of Witterschlik clay, dried and ground in a ball mill with iron or flint pebbles (according to type of mix) and mixed with water and 0.5 per cent Kasseller Braun, 1.5 per cent dextrin, 1.2 per cent soda ash in a blunger. After 15 minutes vigorous mixing the slip is stored in an arc for 2 or 3 days with slow stirring. After further mixing of slip with this dry batch in the Baker Perkins or Eirich mixer, it is delivered into a waggon on the floor below to be taken to the dry pressing or tamping appliances.

The composition of typical mixes was given as:-
Sillimanite Mix. 2½ - 6 mm. calcined kyanite 33 per cent; 1 - 2½ mm. calcined kyanite, 17 per cent; 0 - 1 mm. calcined kyanite, 50 per cent; fine clay added 8 per cent. water content, 5 - 6 per cent.
Corundum Mix. Similar to the sillimanite, replacing the calcined kyanite by fused alumina similarly graded, obtained from Feldmühle.

Silicon Carbide Mix. 1 - 2 mm., 50 per cent; 0 - 0.4 mm., 10 per cent; 0 - 0.1 mm., 40 per cent; 8 per cent of added clay.

For moulding stock silica brick sizes a rotating table type press in which the damp mix is swept in turn into each mould and pressed from below by eccentric pressure action is used. The output was given as 6,000 bricks in 8 hours. A hydraulic press employing 400 atmospheres on the ram and 277 kilo per sq. cm. on the top and bottom of normal sized bricks was seen. The ram presses 3 normal sized bricks per stroke, 1,000 bricks per stroke per hour can be shaped. To obtain the pressure water is pumped to an accumulator at 50 atmospheres pressure; this can be intensified to 400 on the ram of the machine.

The tamping apparatus and method for which this firm is noted was explained by reference to both small and large shapes. The mixture is tamped into the mould using a pneumatic ram with a curved end measuring about 3 in. x 1½ in. having several teeth. For the larger pieces one man continuously feeds the mixture and another continuously tamps. Pieces measuring about 4 ft. x 6 ft. x 6 in. take about 1 hour to make using two men. The moulds are carefully designed of metal so as to be readily disconnected. The process is illustrated in Trans. Ceram. Soc., Wedgwood Bicentenary Volume, 280, 1930 and in "Refractories" by F.H. Norton, McGraw Hill, 2nd. Edition, 1942, pp.245 T 246. Drying of the shapes takes place in a building of several storeys, hot air being passed up through the whole building from a heater at the base.

The firing of the products (other than carbon or graphite) takes place in a small Hoffmann type of continuous kiln with permanent division walls. The dimensions of a chamber are about 8 ft. x 8 ft. x 7 ft. (to the crown). Three chambers out of the 16 are under fire at one time. Firing is to Seger Cone 13, 14, or

15 according to the ware being fired. The crown above the firing zone is of silica bricks.

For making carbon blocks (for blast-furnace hearths) foundry coke of low ash content is used. It is crushed in an edge runner, screened, and mixed in a very strong Baker and Perkins machine at 60° - 70°C. with tar. The mix consists of 84 per cent coke 0 - 4 mm. in size, and 16 per cent tar containing 75 per cent anthracene oil and 25 per cent pitch. After mixing it is discharged on to a warm floor and allowed to cool slightly and tamped or pressed while still warm. The press is a large hydraulic one, the dies are not heated. The operation is similar to the one already described. The blocks are fired, buried in coke dust in four parallel trenches about 4 ft. deep and 4 ft. wide and 150 ft. in length which are heated from the sides by 6 rows of step grate combustion checker work flues, which form the walls of the trenches. Fine coal is fed on to the grates and burnt by hot air drawn along the flues. The coal is thus burnt much in the same manner as a Hoffmann kiln. The fire is made to progress round the circuit, the flue gases eventually passing to a main central flue and to the stack. The temperature attained is a red heat. Three weeks are required to reach top temperature and 3 weeks are allowed for cooling. The coke in the trenches is not covered. Heavy blocks are removed by means of blocks and tackle. Smaller sizes are removed by hand. The blocks are then ground to size, assembled, made to fit, and numbered for reassembly on the site.

The mix for graphite stoppers and nozzles consists of 50 per cent chamotte 0 - 4 mm.; 25 per cent clay 0 - 0.5 mm.; and 25 per cent of Bavarian graphite 0 - 4 mm. This is made into a plastic mass and shaped in hand moulds.

(e) CONCLUSIONS.

The works produced some very attractive examples of tank blocks of sillimanite and chamotte and of silicon carbide for zinc retorts. The accuracy of shape obtained by the S. u B. process originated by this firm was well-known before the war. The works was not particularly well laid out but good use had been made of conveyor systems. Owing to the obvious heat losses the firing process cannot be regarded as efficient.

3. HEINRICH KOPPERS, DUSSELDORF. HEERDT.

(a) DATE OF VISIT.

This works was visited on the 9th, 10th and 11th October, 1945. The personnel interviewed were:-

Herr Schuffler	(Technical Director).
Dr. Frank	(Works Manager).
Herr Kuhn	(Chemist).

(b) CONDITION OF WORKS.

The works was largely undamaged. There was only sporadic damage by artillery and some internal damage and looting by displaced persons.

(c) PRODUCTS.

These may be classified as follows:-

(1) Firebricks.
(2) Silica Bricks.
(3) Magnesite and chrome-magnesite products
(4) Special refractories: sillimanite, silicon carbide, and corundum products.
(5) Sillimanite and sintered alumina laboratory ware.

Groups (1), (2) and (3) had been investigated by a previous team. Attention was paid to group (4) and particularly group (5).

(d) INSPECTION OF PLANT.

Koppers specialize in high quality sillimanite products. All the kyanite is prefired in a large tunnel kiln of cross section approximately 6 ft x 6 ft. This kiln is fired with producer gas made on the site and has a regenerative system for preheating the air. Silica bricks are used for the lining and the temperature of firing is 1500°C. During the war chamotte or chamotte fortified with alumina had to be used.

The manufacturing process consists in crushing the calcined sillimanite, magnetting, elevating to a 3 tier shaker sieve and collecting the required grain size fractions. A tube mill is provided for fine grinding. Mixing is carried out in an Eirich mixer following practice similar to the S. u G. method. Various proportions of clay may be added. For best quality ware selected sillimanite and only 5 per cent of clay dispersed with Kasseler Braun is used. Wooden moulds, steel-faced, are used for the tamping process. A pneumatic hammer is used for tamping one man working alone for small pieces, roughening the surface before making each fresh addition. Burner blocks for Wistra burners are made by this method using a mould which separates at the junction of the cones. For high temperature furnaces these blocks are made with a mixture of sillimanite and corundum to give an alumina content of 85 per cent. The water content of the tamping masses is 3 - 4 per cent. A vibrating mould hydraulic press is also available based on a design used for making moulds for foundry work. The mould is vibrated while a pressure of 70 atmospheres is applied.

Ware is dried on steel pallets in a Proctor dryer.

The kiln usually employed for firing the sillimanite and special goods was about 230 ft. long. The kiln was about 4 ft. wide and stacked 4 ft. high, fired by Wistra (Wirbelstrahl brenner) burners using coke oven gas and air preheated by recuperation in heat resisting steel and silicon carbide pipes. The temperature of firing is up to 1600°C. Silica bricks are used to line the high temperature zone.

There are several intermittent gas fired kilns for firing sillimanite ware to 1600°C. The goods are introduced into the kiln on a truck measuring about 8 ft. x 12 ft. and stacked about 8 ft. high. Heating is from either side using Wistra burners. Hot air from a cooling kiln adjacent had sometimes been employed for combustion but preheating within the furnace had been discontinued during the war owing to difficulties in obtaining heat resistant steel. The furnaces are lined with 60 per cent porosity sillimanite bricks of their own manufacture. The condition of these bricks was good despite the temperature at which they had been used. The bricks are made of hand-picked calcined kyanite, the grading being 70 per cent 0 - 0.5 mm. and 30 per cent 0 - 0.1 mm. Nine parts of the graded kyanite and one part of Pfelzer clay are mixed. To promote porosity a semi-bituminous coal of only 4 - 6 per cent ash and low swelling properties is added being graded so as to correspond to the grain size of the kyanite and added in an amount which may reach up to 14 per cent of the total weight of the mix. The mass is hand moulded or pressed in a hydraulic press with a limited travel. Firing is normally to 1450°C., but the super quality bricks to withstand 1600°C. on the hot face are fired to 1600°C.

A number of gas fired furnaces for firing alumina and sillimanite to 1800°C. were inspected. They are of circular cross section, diameter 2 ft., internal height 10 ft. Heating is by two diametrically opposed vertical rows of Wistra burners. Alumina and sillimanite tubing up to 2 metres long is fired in these furnaces suspended from a "pipe-rack" slot arrangement in the roof.

This furnace is lined with special quality sillimanite bricks made from hand-picked kyanite bonded with 5 per cent clay. The maximum grain size is 5 mm. and the grading is selected to give close packing. Between 20 and 25 per cent of sillimanite ground to less than 6 μ is included in the mix. Shaping is by pneumatic hammer and the firing is to 1600°C. in a 72 hour cycle. A detailed drawing of the furnace is available on application to the authors.

(e) PROCESSES FOR SILLIMANITE AND ALUMINA WARE.

Sillimanite Ware.

The raw kyanite is fired to 1500°C. for 24 hours then ground by normal methods to a maximum grain size of 3 mm. Further grinding is done in a ball mill with flint pebbles, a typical charge being 1,500 kgm. fired kyanite to 900 litres of water with the mill half filled with flints. The mill is run at cascade speed for 2 days giving a total of 15,000 revolutions. This reduces all the particles to less than 6 μ. The ground slip is then strained through a 10,000 mesh/cm^2 sieve into a mixer in which 1,000 kgm. Pfelzer clay and 500 kgm. kaolin are added. After thorough mixing, passing over a wet magnet and straining through a 2,500 mesh/cm^2. vibrating sieve the slip is filter pressed and the mass aged for 6 months in a cellar. Before moulding the mass is kneaded by machine for three hours to remove air and then is ready for extrusion. Extrusion is vertically downwards, the

tubes being caught on a V-shaped board held at an angle, and pinched off when the desired length has been attained and the extruded tube rolled out on to a flat board. For sizes 1 - 7 mm. in diameter a hand operated press with a simple die plate affixed to an untapered cylinder is used. For larger diameters a motor driven press of similar design with a variable gear coupling is used. The tubes are dried in air for 1 - 3 weeks according to size. If closed ends are required they are affixed while the tubes are in the leather hard state. The rounded end is either slip cast or jolleyed to shape if over 60 mm. diam. The flange for supporting the tubes for firing in the kiln was also affixed at this stage. This was done by cutting off a length from a tube of slightly larger size and making a union with slip. The small sizes were merely deformed at the top and a ring of the body bent round so that the piece could be slung in the "pipe-rack" suspension brick in the roof of the kiln.

In addition to shaping by extrusion, suitably shaped articles are pressed, slip cast or jolleyed. For slip casting 0.5 per cent of water glass ($1Na_2O:1SiO_2$ 34° Baume) is added to the slip. As the required water content is 23.0 per cent (on the dry weight) it is necessary to add dry material to the usual slip from the blunger. Small crucibles below 60 mm. in diameter are slip cast and larger sizes jolleyed in plaster moulds.

Ordinary sillimanite ware, called 10i is fired up to 1600°C then held at 1600°C. The firm consider this grade equal to pythagoras porcelain. Special quality sillimanite ware, 91, made from hand picked kyanite but other-wise processed as above is fired for 2 hours at 1780°C. This ware is gas-tight up to 1500°C. as compared with 1400°C. for 10A. The shrinkage of the 91 sillimanite on firing is 15 per cent.

Alumina Ware.

The raw material is a hydrated alumina of approximate composition $Al_2O_3.3H_2O$. This is wet ground for 3 - 4 hours, filter pressed, briquetted and calcined at 1500°C. for 12 hours. The Na_2O content after calcining is about 1 per cent. After calcining the material is crushed and ground in a rubber lined ball mill. Mill charge is 300 kgm. alumina and 150 litres water.

The grinding is done by hard-fired sintered alumina plates roughly 10 cm. x 10 cm. x 2 cm. with which the mill is half filled. The grinding period is 2 days at 40 revolutions per minute after which all the particles are less than 5 . The slip is then filter pressed and the material air dried for 8 days.

For extrusion a bond made as follows is used:- 600 gm. of a hydrated alumina, approximately Al_2O_3 $1.5H_2O$ obtained from Lautawerke Saxony is treated with 800 cc. of hydrochloric acid (4 parts of concentrated acid diluted with 1 part of water). Then cold water is slowly run in with continuous stirring until the total volume is 3 litres. Heat is developed and on cooling the mass sets to a stiff gel. 25kgm. of this gel is mixed with 100 kgm. of dry ground alumina in a rubber lined Werner and Pfleiderer mixer and the mass adjusted to the desired extrusion consistency by the addition of water.

A suitable amount is then cut off and placed in a simple evacuation chamber which it fits fairly closely. It is compressed while under vacuum and then transferred to the extrusion cylinder. Handling methods follow those for sillimanite ware. Ordinary hardened steel dies are used. Except for the smaller sizes the ends of closed tubes are slip-cast and jointed to the open tubes by slip when both are quite dry. Jolleying methods are used for suitable shapes.

For slip-cast alumina ware a slip is made from 100 kgm. ground calcined alumina, 45 litres of water and 5 litres of hydrochloric acid (4 parts of concentrated acid to 1 part of water). Normal slip-casting procedure is followed. 800 mm. is the greatest depth used in casting. Tubes above 48 mm. diam. are slip cast.

The alumina ware is fired for 2 hours at 1820°C., the temperature being reached in 6 hours. The furnace is allowed to cool overnight. A technique for suspending the alumina tubes similar to that used for sillimanite is employed. Small ware is fired in saggars made of alumina. The shrinkage is 23 per cent from the mould size. No additions are made to restrain the grain-growth during recrystallization. The largest grain size in their ware is stated to be about 0.1 mm.

(f) CERAMIC TURBINE BLADES.

Koppers made a few ceramic blades of sillimanite for the Hermann Goering Luftfahrtforschungsanstalt. The blades were made by extrusion through a die having an obstruction plate on the inside which could be adjusted by trial and error to give equal rates of flow over the different blade thicknesses.

They had no knowledge of the suitability of sillimanite as a material for gas turbine blades.

(g) CONCLUSIONS.

Koppers enjoy a high reputation for their special refractories. The good performance of their special quality sillimanite bricks may be attributed to the careful selection of the sillimanite and its grading and the use of minimum amounts of clay. The kiln for calcination of raw kyanite is inferior in design to one used for this purpose in this country.

In the manufacture of their laboratory alumina

ware the method of obtaining a plastic gel appears to be a special development of this firm. Degussa (Frankfurt) for example, introduce organic combustible material such as gum tragacanth or rubber. The care taken to avoid contamination of the alumina with iron during preparation of the mixes is noteworthy as it avoids the need for subsequent acid washing treatment. A high standard of craftsmanship is attained.

4. FELDMUHLE, LULSDORF/RHEIN - MANUFACTURERS OF FUSED ABRASIVES AND REFRACTORY MATERIALS.

(a) DATE OF VISIT AND PERSONNEL INTERVIEWED.

The works was visited on the 12th October, 1945, and the following members of the staff were interviewed:-

Dr. Holsch, General Manager,
Herr Hack, Chemist,
Herr Schmidt, Engineer,

(b) CONDITION OF TARGET.

The works was very little damaged; a small amount of structural damage due to shelling had been suffered. The management were waiting for material to repair buildings and for permission to restart manufacture.

(c) PRODUCTS.

The firm manufactures a considerable range of chemicals, including the following fused refractory materials in which we were interested.

(1) White fused alumina (Trade name BIKORIT).
(2) Pink fused alumina (Trade name DIRUBIN).
(3) Brown fused alumina (Trade name REDURIT).
(4) Black fused alumina (Trade name REWAGIT).
(5) Fused magnesia.
(6) Fused spinel.
(7) Fused ferro-silicon (by-product).

The above products are fused on a large scale and afterwards crushed and graded for sale to the abrasive, and refractory industries.

(d) MANUFACTURING PROCESSES.

A special feature of the plant is the degree of mechanisation and the continuity of operations.

(1) White fused Alumina (BIKORIT).

Handling and Furnace Feeding Arrangements.

The raw material used is Bayer processed calcined alumina from Martinswerke, Birkheim. A very complete assembly of cyclones and backing pump of the Nash type is used to transfer the raw materials to the various hoppers. The material is sucked from the trucks into the storage hoppers and as required material therefrom is hand-fed to a suction point or sump at ground level, and elevated to the main hopper above the furnace. The return air flow passes through two cyclones and a water filter before returning to the pump, and escape material from the first cyclone returning to the furnace, this amounting to about 0.3 per cent of the charge weight. The material from the main hopper passes from a worm conveyor to a tipping scale pan, delivering batches of about 40 lb. at a time, direct to the furnace through twin delivery shutes. (See diagrammatic sketch No.1.)

Furnace.

The furnace consists of a slightly conical steel cylinder 180 cm. (6 ft.) in diameter by 180 cm. (6 ft.) in depth cooled with a water spray mounted on a base with rail wheels fitted. During fusion the assembly is rotated on a rail turntable, actuated by a reduction gear and pawl rod which engages a rack on the periphery of the base plate. The furnace rotates once every 8 hours thereby producing a symmetrical fusion (see sketch No.2).

The arc rods are vertical and held in water cooled plate electrode holders, suspended from steel beams by a pulley system from an overhead crane. The running conditions are as follows:-

Power .	Single phase supply from a 550 K.V.A. Transformer.
Carbon Rods.	Rectangular 40 xm. x 20 cm. at 90 cm. centres.
Average current.	About 2,000 amps.
Voltage between electrodes.	Approx. 170 - 220.
Arc Starting.	Coke bed, about 60 lb. in weight arranged between electrodes.
Total running time.	50 hours.
Total charge weight.	About 15 to 16 tons.
Fusion weight.	About 14 tons.

Processing.

After cooling by water spray, the conical furnace body is withdrawn and the fusions lifted by crane and dropped onto a steel breaking spike and thence to two stages of jaw crushing, (the jaws are of 12 per cent manganese steel). The product is then passed through manganese steel rollers over a drum - type magnetic separator, and thence to a multi cascade horizontal screen bank of the oscillating type, giving grades from ¼ in. mesh downwards. Finer grades for polishing powders are dealt with in a separate 10 stage vertical sieving bank of the oscillating type and final products fall to bagging hoppers. The grain sizes are those normally required by the abrasive industry.

Fine milling of the fused alumina is carried out in three cylindrical ball mills about 2 ft. 6 in. in diameter and 6 ft. in length with liners and balls of 2 per cent chrome steel. They are connected to a cyclone air separator of the Hardinge type. The direct product from the mill is approximately 30 microns and finer, with a small percentage up to 50

micron size. The air separated material is predominantly up to 10 microns. The iron content is 3 to 4 per cent and is not normally removed. Acid treatment is carried out on a small scale if specially required.

(2) Pink Fused Alumina (DIRUBIN).

The material is produced in a similar manner to the white fused alumina. An addition of 0.5 per cent of chromic oxide is made to the melt.

(3) Brown and Black Fused Alumina (REDURIT and REWAGIT).

Raw Materials.

Bauxite is obtained from Marseilles, France and Hungary. Anthracite is mixed with the charge to reduce the iron oxide. The ferro-silicon formed as a by-product contains 16-18 per cent silicon.

Furnace.

The furnace body is of similar design to the furnace for making white alumina but is larger, being about 240 cm. (8 ft.) in diameter by 190 cm. (6 ft. 3 in.) in depth. It is rotated at a speed of about 1 revolution per 6 hours. The running conditions are as follows:-

Power: Three phase supply from a 2,000 KVA transformer.

Carbon Rods: Three rods 55 cm. (22 in.) in diameter are set vertically at 120 cm. (4 ft.) centres; sections are joined together by means of a heavy male and female cone thread. The total length of the rods is about 8 ft.

Electrode Holders: The electrodes are held by 6 sectional water-cooled clamps secured by bolts passing through an external

peripheral ring which is attached to the lower end of the main metal sleeve supporting each of the suspended electrodes. The ring is also water cooled by by-pass water. These heavy rods are supported by a wire rope pulley system passing to heavy counterbalance weights, and elevation is carried out by a crane above.

Voltage at Electrodes: About 150 volts between phases.

Arc Starting: Coke bed used to bridge the 3 rods.

Total Charge: Bauxite, About 30 tons.
Anthracite Coal. " 2½ tons.

The charge is mixed and fed in by hand from a large steel platform arranged at the level of the furnace top. An operator breaks down the shell formed progressively during the fusing, by means of a steel bar. A head of about 3 in. of material is maintained above arc level, and periodic charging occurs every 15 - 20 minutes.

Total Running Time : 60 hours.

Total Weight of Fusion: About 22 tons.

Useful Weight of Black Fused Alumina: About 13 tons.

The balance consists of outer coating eventually refused, and the by-product ferro-silicon.

Processing.

The fusions are impact broken and jaw crushed, passed through rollers and over drum magnetic separator and thence to multi cascade horizontal bank of screens of the oscillating type, the resulting products passing to bagging hoppers.

In the case of the brown bauxite (REDURIT) the sequence follows direct to a rotary calcining oven,

coal fired to 1200°C. The feed is continuous, and the final stage of the series of operation consists of screening of finer meshes on a special type of sieve designed by the firm, the material being lifted by elevator to the upper hoppers. The special feature about this screening bank is that it introduces a "side" oscillating motion to the screens which are angled in the normal way to the horizontal, resulting in a zig-zag path of movement of the particles giving a high efficiency factory

Each of the Four cascade banks used, consists of two vertical tiers of three sieves linked together, and each bank is suspended by pine leaves to allow transverse motion. This motion is imparted by a floating rotary steel shaft having eccentric sheaves and horizontal rods linking the sieve frame at each end. The shaft is suspended from above at the two bearings by pine leaves, and a motor drive above transmits motion by belt to a pulley in the centre of the shaft, the whole assembly producing a highly efficient oscillating motion. This is a definite improvement on the normal and oscillating type, and will be of interest to screening plant manufacturers.

The products pass to 24 bagging points, giving grain sizes of the normal standard grades required by the abrasives industry.

(4) Fused Magnesia.

Calcined magnesite obtained from Jugo-Slavia or Greece is fused in a similar vertical conical furnace, the size of the body being similar to the furnace for fusing the white alumina (6 ft. diameter x 6 ft. deep) but fed from the platform in a similar manner to the black bauxite furnace.

The supply is single phase taken from a 1,500 KVA transformer, and very large carbon electrodes are used, namely 60 cm. (24 in.) x 35 cm. (14 in.) rectangular section, set to hang at about 25 cm.

(10 in.) apart, and suspended by steel plate electrode holders, (water-cooled), which in turn are suspended from horizontal steel beams which also support the heavy leads. These beams are supported at two points by a rope and pulley system actuated by a crane, so that a horizontal pull on one rope elevates the beam as required.

Very little fused magnesia has been made, and this furnace had been used for making smaller fusions of bauxite. No further running data were available, but it was estimated that fusions of about 12 tons were produced in 45 hours total running time. These large fusions of magnesia cool slowly, and thereby produce large crystals of periclase in the centre; specimens which were seen measured 1½ in. to 2 in. by ¾ in.

(5) Fused Spinel.

The materials used for the manufacture of fused spinel ($MgO.Al_2O_3$) are the white calcined alumina and the calcined Jugo-Slavian magnesite. The magnesia furnace is used. Relatively small amounts of fused spinel had been produced.

(6) Final Grading of Finished Products.

As a safeguard against any faulty screening in the normal processing, three small plants, each consisting of two bank oscillating sieves combined with drum or roller type magnetic separators are provided. Each bag of material is elevated on a bag hoist to one of these units and any oversize or magnetic ingredients removed. The bags are then stencilled with a material and grain-size marking.

(e) CONCLUSION.

This works has been carefully laid out for the large scale production of fused alumina and magnesia. Great pains have been taken to ensure maximum efficiency in manufacture and a uniform series of products.

5. HERAEUS QUARZGLAS GESELLSCHAFT, HANAU and QUARZGLAS FABRIK

(a) Date of Visit 17th and 18th October, 1945.

Investigator: Mr. R.B. Miller

Interviewed Dr. H. Mohn, Works Manager and Engineer

(b) General Report

The Works have been badly damaged. In the sections producing Rotosil (opaque Silica) tubes and pipes, the furnaces, of which they had two, have been badly damaged, but they are repairing parts with the intention of getting one into operation. They still have a number of steel furnace tubes ranging from about 5" to 16" diameter.

The section producing transparent quartz has suffered most, all the forming furnaces having been destroyed, including the furnaces for building up tube billets (ordinary and sub-normal qualities) and also their optical quartz furnaces. Their quartz powder preparing plant, although dislocated, could be put into commission fairly readily. They have a billet redrawing furnace, operated by one man, and are at present drawing tubing, both translucent and transparent from rather poor quality stock billets which had been normally rejected before the Works were put out of commission.

In the blowpipe section, they have about 8 men working, chiefly producing small electric heaters, for boiling tea and coffee, from translucent silica tube with internal element of nickel chrome. Other articles include transparent quartz crucibles for coking tests. They are, however, erecting suction plant (SEE SKETCH NO.1) in another room which will house about 50 blowpipe hands for the production of quartz lamps, etc. The department normally producing these lamps has been totally destroyed.

They have also in operation a small silica moulding furnace for forming opaque crucibles and basins on a limited scale.

They normally employed - pre war 170
during the war 250
at present 40

Estimated damage - furnace sections 90% damage.
fabrication " 75%

The following is a list of their various products:-

TRANSPARENT FUSED SILICA

(1) Electrosil Quality

This vaporising process was not mentioned or known at the time of the visit, but is referred to in C.I.O.S. Report No. XXVIII-67 (Item No.21).

(2) "HOMOSIL" Optical Quality.

This is their best Optical Quality and is used for special blocks, lens, prisms, being relatively free from internal striations, bubbles and strains. End reflecting mirrors for range finders are made from this material.

(3) Normal Quality (SORTE I).

Chiefly tubing and apparatus made therefrom; also plates and other solid shapes for use where Optical Quality is not necessary.

(4) Sub-normal Quality (SORTE 2).

Being chiefly poorer quality rejects from normal quality manufacture, and is sold at reduced prices.

(5) Quartz Wool.

For high temperature insulation.

NON TRANSPARENT FUSED SILICA.

(1) "ROTOSIL" Tubes and Pipes, and apparatus made therefrom.

(2) Moulded Articles such as basins, crucibles, etc.

The following deals individually with the various products normally produced.

(d) TRANSPARENT FUSED SILICA.

(1) Electrosil Quality.

No data obtained.

(2) "HOMOSIL" Optical Quality.

Selected Brazilian Quartz Crystal is acid treated with cold hydrofluoric acid, and water washed with tap water and twice with distilled water, and dried. It is then passed through a rotary silica tube furnace running at about 900°C., the furnace being about 6 feet long by 5" bore, and the emerging crystal is quenched in cold distilled water to disintegrate it into readily friable pieces.

After drying, it is passed to a cone grinder consisting of a stationary quartz crystal about 12" diameter x 8" - 9" high, having a vertical hole 3" diameter, terminating in a 60° cone boredat the lower end. In this cone rotates an agate cone with provision on the driving mechanism to adjust the gap as required.

The setting preferred gives a final product 1 mm. size and below, and the powder is transferred to a simple silica pipe air separator which has the suction adjusted to remove the fines below 0.2 mm. The powder is then stored in glass bottles and is ready for fusing in the optical furnace.

Optical Furnace.

This consists of a special oxy hydrogen blowpipe with a quartz funnel attachment permitting the powder to be entrained in the flame. The powder feed is adjusted by means of the variable speed of a rotary angled silica tube above the funnel, driven by a small motor drive with variable disc traverse, and the preferred feed is about 280 gms. per hour. The burner impinges on a horizontally rotating and opposed quartz rod, this taking place inside a silica pipe economiser. The fused powder builds up within the zone of the oxy hydrogen flame, air being relatively excluded. The billet progressively formed is receded by a traverse mechanism, thereby permitting billets up to

about 20" long to be made, the popular diameter being 40 to 50 mm. diameter. With 2 blowpipes side by side, a billet about 80 mm. diameter can be produced, but the quality is not so reliable.

The billet so formed can be cut direct for discs, or alternatively forged up to larger diameters in a multi blowpipe furnace, and finally moulded in graphite moulds to the required shape.

End reflector mirror plates are formed in this manner, and finally machined with carborundum cutting and grinding wheels to the desired cross section. These blocks are sent to Zeiss, who select and cut where required to produce the best quality active mirror plates, and the bases from any material considered inferior quality. After return, these plates are mounted in a special two part annealing furnace (SEE SKETCH NO. 2) having three side plungers externally spring loaded which hold the plates and base assembly in position against a jig prism mounted in the centre. The whole essembly stands on a smooth silica plate mounted on fused quartz granules in the lower half of the furnace, leaving the lug portions of the side plates exposed for fusing to the base, which is done using optical quartz rod filling and an oxy hydrogen blowpipe. Protection plates of quartz about 10 mm. thick are placed outside the active plates and on top of the jig prism to prevent flame impingement during fusing. The lower portion of the annealing furnace is kept at 860°C., and after fusing, the top portion of the annealing furnace is put on, and raised from an initial temperature of about 860°C to 1060°C and the assembly is then cooled slowly, the whole process taking about 4 hours.

(3) Normal Quality (Sorte 1)

This quality is produced in billet form either solid or hollow, in a special multi-blowpipe furnace, consisting of 4 jets of oxyhydrogen passing through the side of an opaque silica pipe horizontally disposed, which forms an economiser, This is mounted inside a water cooled

steel sheet furnace housing having suction exhausting arrangements fitted at the top. (SEE SKETCH NO. 3). A special sliding platform is arranged through the side, allowing feeding on to a graphite slab, of quartz powder of from 1 to 3 mm. size, this bed being placed in front of the open end of the silica pipe. The fusion is built up initially, on a part quartz billet mounted on the end of a silica working tube, and the operation consists of progressively heating the billet and rolling the softened surface in the quartz powder. For hollow billets the bore is kept open by pushing the hot billet on to a tapered graphite pin outside the furnace.

Billets are produced up to about 24" long and 3½" external diameter, and may be further forged as required, or re-drawn down for tubing of varying sizes from 3 mm. to 30 mm. external diameter in a special furnace.

Redrawing Furnace

This furnace consists of a headstock holding and rotating a billet mounted on a ground silica tube,, which is advanced progressively into the heating unit, which consists of a heat resisting steel burner giving an internal ring or slit frame, arranged for burning either oxy-hydrogen or oxy acetylene, the former being preferred. The tubing is drawn along the 50 ft. bed of the furnace on a rotating carriage mechanism, with a motor drive synchronous with the headstock drive, thereby allowing the drawn down tube to be rotated at the same speed as the billet. The speed of withdrawal of this carriage controls the size of the tubing, and this is arranged by a motor drive at the end of the bed, linked to a variable speed gear actuating a chain drive along the bed, to which the carriage is engaged when required, all controls being operated at a panel adjacent tothe burner.

(4) Sub-normal Quality (Sorte 2).

This material is chiefly supplied from the poorer specimens selected from normal quality production, and therefore follows the same technique of manufacture. Rejected crystal not normally used for either (2) or (3) is acid treated and can be processed in the normal manner thereby economising in raw materials costs.

(5) Quartz Wool.

This is produced on a special machine, (SEE SKETCH NO4) and has been supplied in large quantities for high temperature insulation mats. It consists of a carriage driven along a steel structure bed by a motor drive. On this carriage are clipped in a fairly close spaced row, 20 horizontal quartz rods or tubes, the latter preferred, about 6 to 7 mm. diameter. Each rod passes through a graphite guide and over a vertically disposed oxy hydrogen burner which reduces the fibres to about 0.2 mm. diameter. These fibres pass through a further graphite guide block with 20 holes in it, disposed immediately in front of a bank of 20 axial jet oxy-hydrogen blowpipes, which entrain the fibres and blow them forward in the form of wool.

The wool is finally collected on a rotating drum about 3 ft. diameter, with wire meshing on the periphery. The collecting drum has its speeds adjusted so that no tension is created on the forming wool. This machine is mainly destroyed, and therefore could not be seen in operation, but the method has been previously mentioned in C.I.O.S. Report No. XXVIII - 67. Item No. 21, and B.P. 507951.

NON-TRANSPARENT FUSED SILICA.

(1) "Rotosil".

Tubes or pipes are formed in a steel rotating furnace tube, using Dörentrupe Silica Sand (approx. 99.7% SiO_2) obtained from Lippe, the heating being supplied by an opposed electric arc using current at 220 volts.

The sand is preformed to the required annular depth in the furnace tube by sweeping the bore with a forming tube, controlled externally from brackets mounted on the electrode holders.

The speed of rotation of the furnace tube is varied according to the size used and is arranged to give a common peripheral speed of about 400 ft/min.

The electrodes consist of graphite ends coned into copper electrode tubes which are arranged for water cooling; these in turn held in adjustable clamps carried from

overhead carriages designed to run along steel structure runways disposed axially at each end of the furnace. The arc is struck from one end and progressively fed throughout the length of the furnace at a controlled speed to give the necessary conditions of heating to form the desired wall thickness. A minimum of 20 mm. of sand is left unfused, acting as a heat barrier.

Heavy walls up to about 2" can be formed on relatively small tubes, whilst with the maximum diameter made, namely: 350 mm. (about 14") external, the maximum permissible wall to avoid cracking has been found to be 15 mm. Small sized tubes can be ground on the surface and re-drawn in the furnace previously described, into satin surface tubing.

Building up of tube assemblies and special apparatus is carried out with blowpipes, whilst a limited grinding department deals with the grinding of Rotosil tubes etc.

(2) Moulded Articles

Crucibles up to 15" diameter have been made, but their present small plant can only produce articles about 5" external diameter x 3½" deep, and they are manufacturing such basins with a wall thickness of about 3/16". Experimental tea cups had been made, but the costs were too high to be commercial.

The furnace consists of a turntable carrying 3 rotating tables, each driven direct from a motor. The tables are filled with sand, pre-shaped by hand formers and scoops, and at the fusing position, an arc using 3 electrodes is slowly lowered, and progressively sinters and fuses the shape formed.

A considerable time will elapse before they can attain their pre-war production levels, as apart from their plant dislocation, their buildings are badly damaged.

6. SCHONWALD PORZELLAN FABRIK.

This factory is located at Schönwald, 2 km. from Selb, North-Eastern Bavaria. It belongs to the Kalla group as does the Hescho concern, the latter being located in the Russian zone of occupation. A visit was paid on the 19th October, 1945, in an endeavour to contact some of the Hescho technicians and obtain details of various ceramic turbine blades and stator assemblies which the Hescho firm had made.

The former technical director of the Schönwald Porzellan Fabrik, Dr. Sauer, was interviewed but he had no knowledge of the whereabouts of any of the technical staff of Hescho nor of any of their processes and compositions.

In the Schönwald factory only household porcelain is made. During the war they did, however, apply silver films to electrical porcelain for Hescho who sent the parts to the Schönwald factory for this process. The silvered parts were then shipped back to the plant in Thuringia. This part of the plant was inspected.

The silver solution, which appeared to be a silver colloid in an essential oil medium, and supplied by Degussa, Frankfurt/Main (Reference Nos. 103 and 110), is sprayed onto the ceramic through a mask to give the desired outline, dried in a small oven, then fired at 850°C. for two hours in a small resistance heated tunnel kiln approximately 8 ft. long. This kiln has an ednless ceramic belt 6 in. wide, on which the articles passed through the hot zone. A second sprayed coat is applied over the first after firing, and the article refired. The process gives a very adherent bright silver film on the porcelain.

7. BERLIN STATE PORCELAIN WORKS, SELB.

(a) DATE OF VISIT.

This works was visited on the 19th October, 1945 and Dr. Frank, (Technical Director) and Dr. Koenig (Chief Research Chemist) were interviewed.

The Berlin State Porcelain factory was evacuated to the Paul Müller porcelain works, Selb, Bavaria,

after very heavy damage to their factory in Berlin in a raid on 22nd to 23rd November, 1943.

(b) CERAMIC TURBINE BLADES

The evacuated factory had made turbine blades for the Hermann Goering L.F.A. which were promising from the aspect of resistance to thermal shock. Enquiry revealed that the work on these had been done by a Dr. Müller whose whereabouts were unknown but believed to be in custody as an S.S. suspect.

Personnel questioned said they had no knowledge of the processes or compositions in making the blades, but later admitted they were restarting experimental work on the same kind of material having the previous day received an order from the Hermann Goering L.F.A. (now controlled by the R.A.F.) for a new supply of silicon carbide blades. They were proposing to use a mix containing 70 per cent silicon carbide passing a sieve having 80 apertures per sq.cm. and resting on a sieve having 250 apertures per sq. cm. and 30 per cent of Zettlitz kaolin. Shaping was to be done in the plastic condition in plaster of paris moulds. After firing at 1400° to 1500°C. a porcelain glaze to which a proportion of alumina was added was to be applied and the products refired at the same temperature. A simple porcelain glaze does not wet silicon carbide.

(c) BERLIN PORCELAIN COMPOSITIONS.

Some details of the Berlin porcelains were obtained. The first four are claimed to be impermeable to gases. The remainder require to be glazed with a felspathic glaze.

K Mass

The melting point is given as 1800°C. and the highest temperature of use as 1700°C.

A grog or sinter composed of 60 per cent calcined alumina and 40 per cent felspar is first prepared by grinding these together and firing for three hours at 1500°C. This grog is then ground, mixed with Zettlitz or Halle clay in equal proportions by weight, shaped and fired at 1500°C. for three hours.

Prokorund I

The melting point is given as 1900°C. and the highest temperature of use as 1800°C.

A grog is made from 50 parts calcined alumina and 2½ parts Zettlitz clay, by firing at 1400°C.

The following composition is then prepared:-

40 parts Zettlitz kaolin (raw)

50 parts Zettlitz kaolin (fired at 1400°C.)

10 parts grog.

This is ground and articles made from the mass fired to 1600° to 1700°C.

Prokorund 2.

This mixture comprises 50 per cent Zettlitz kaolin (Raw) and 50 per cent calcined alumina. The articles are fired to 1700°C.

Prokorund 3.

This mixture consists of 30 per cent Zettlitz kaolin (raw) and 70 per cent calcined alumina. The articles are fired at 1700° to 1800°C.

Marquart.

The melting point is given as 1820°C. and the highest temperature of use as 1700°C.

The mixture comprises 46½ per cent calcined alumina, 52 per cent mixed clays and 1½ per cent feldspar, and is fired at 1500°C.

D2 Mass.

The melting point is given as 1850°C. and the highest temperature of use as 1700°C.

The mixture comprises 50 per cent fused alumina

(passing a mesh of 150 openings per sq. cm.) and 50 per cent Zettlitz kaolin and is fired at 1500°C.

D3a Mass.

The melting point is given as 1850°C. and the highest temperature of use as 1700°C.

The mixture comprises 60 per cent. fused alumina and 40 per cent. Zettlitz kaolin and is fired at 1500°C.

D4 Mass.

The melting point is given as 1920°C. and the highest temperature of use as 1800°C.

The mixture comprises 50 per cent calcined alumina (specially low in iron), 50 per cent Zettlitz kaolin and is fired at 1500°C.

(d) INSPECTION OF PLANT.

The plant was that of an ordinary porcelain factory. No special equipment apart from a horizontal extrusion apparatus for extruding porcelain pipes in large diameters (up to 25 cm.) was seen.

The kilns were intermittent and fired with coal and typical of those used for the manufacture of porcelain on the Continent. The goods for glost firing were set in the lower portion of the Kaolin at ground level and those for biscuit firing at higher levels reached from the first and second floors of the factory. No equipment for firing at temperatures higher than the 1500°C. reached in these kilns was available at the Selb factory.

(e) CONCLUSIONS.

The details of manufacture of turbine blade materials which we hoped to obtain were not available owing to the absence of Dr. Müller. Although some plant had been evacuated from Berlin there was very little specialised equipment pertaining to refractory ceramic materials available at Selb.

We gained the impression that the good quality of the

products of this firm were due primarily to the care exercised during manufacture and the craftmanship of the operatives.

8. ROSENTHALL INSULATOR WORKS, SELB.

(a) DATE OF VISIT.

The works were visited on the 19th October, 1945 and the personnel interviewed were Dr. Seigler (Research Engineer), Dr. Kohl (Chief Chemist) and Dr. Ullman (in charge of resistance plant).

(b) SOME SPECIAL CERAMICS.

The above firm make technical porcelain such as high frequency low lose ceramics, electrical porcelain for close tolerance work, special fixed carbon resistors, heater ceramics, etc.

A.E.G. Berlin had asked them to make ceramic turbine blades in small quantities for experimental purposes, but none had been made before the end of the war. A few experimental mixes which it was considered might give high strength material were made and samples in rod shape had been sent to A.E.G. for test but no results were known. A composition considered the most promising had the following composition:-

25 per cent hydrated alumina.
25 per cent calcined alumina.
30 per cent kaolin (two plastic clays).
15 per cent grog (from fired mix of above 3 constituents).
5 per cent titanium dioxide.

It was fired at 1450°C.

This material was claimed to have a high compressive strength (about 12,000 kgm./cm.^{2}). Venturies had been made from it for the Hermann Goering L.F.A., Volkenrode.

They had also experimented with silicon carbide - clay mixes and found the following compositions good for resistance to thermal shock.

(a)	(b)
40 per cent silicon carbide 60 per cent high plastic clay	20 per cent silicon carbide. 20 per cent fused alumina. 60 per cent high plastic clay.

The composition of the electric porcelain for making shapes to close tolerances was given as:-

Talc,	42 per cent
Sericite,	48 " "
Plastic kaolin	6 " "
Calcium bentonite,	4 " "

The sericite mineral is of the horneblende type and approximates to the composition quartz 30 per cent, mica 70 per cent. This mix has a shrinkage of 6 per cent in the direction of pressing and 8 per cent in the direction at right angles on firing to cone 9.

(c) SPECIAL CARBON RESISTANCES

A visit was also paid to a subsidiary factory of the Rosenthal concern making small fixed carbon resistors, consisting of a film of fused glass and graphite on a ceramic former. The details of the manufacture of these were obtained.

Composition of glass used.

Pb_3O_4,	40 parts	
B_2O_3,	10 "	
Na_2CO_3,	5 "	
Silica,	15 "	(fine water ground)
Jena glass	10 "	
ZnO,	10 "	
CaO,	5 "	
Feldspar,	5 "	

This is melted in an electric furnace, granulated in water and finely ground in a pebble mill for one week. The ground glass after drying is mixed with aqueous colloidal graphite in varying proportions, according to resistance required.

Example 1: for 50 - 100 ohms,
1 part glass
1 part colloidal graphite
1 part water

Example 2: for 1,000 ohms,
5 kgm. glass
1.2 kgm. graphite
3.2 kgm. water

Example 3: for 3,000 - 5,000 ohms,
5 kgm. glass
1 kgm. graphite
3.2 kgm. water

The glass graphite mixture is sprayed onto the ceramic formers, hollow cylinders, a film thickness of 0.1 mm. being aimed at in all cases. Spraying is carried out on a rotary table, a hot air dryer forming part of the cycle. The parts are now fired to 800° to 900°C. in a tunnel kiln, nichrome heated, the firing being carried out as quickly as possible, the average time being 1 to 2 minutes. The glass graphite film is fused at this stage. End caps of brass are now pressed on, the whole is lacquered, then the fused film cut on a spiral cutting machine to the desired resistance. The cutting is done with small carborundum wheels cutting right through the film. They have a fully automatic machine which is set so as to stop cutting when a pre-arranged resistance is reached.

The tolerance is about ± 1 per cent of the stated value.

9. GOEBEL-WERKE GROSSALMERODE.

(a) DATE OF VISIT AND PERSONNEL INTERVIEWED.

This firm, before the war, made firebricks and sillimanite, corundum and silicon carbide bricks. It was inspected on the 25th October and Herr A. Schoddel the commercial manager and Herr G. Riemann, the technical manager replied to the questions put.

(b) PROCESSES.

Corundum Bricks.

Corundum is bought from Elektroschmeltz Werke, Kempten

or from Lonza in the required grain size. The usual mix consists of 40 per cent corundum, 0 - 3 mm. in grain size; 40 per cent corundum, 0 - 1 mm. in grain size and 20 per cent finely ground clay. The clay was supplied by Schifferer and Kiercher, Allendorf, Kreis Wetzlar. Its analysis was given as: SiO_2, 44.3 per cent; Al_2O_3 and TiO_2, 38.14 per cent; Fe_2O_3, 1.3 per cent; loss-on-ignition, 12.8 per cent; refractoriness, cone 34. Shaping is carried out by hand tamping of the mix at a water content of 4 to 5 per cent. Firing is to cone 10 (1300°C.). It was claimed that the ta value (temperature of subsidence 6 per cent from maximum height) under a load of 2 kgm. per sq.cm. is 1730°C. and the te value (temperature of 40 per cent subsidence) is 1780°C.

Other products of lower alumina content are made and in pre-war days sillimanite products were also supplied.

Silicon Carbide Bricks.

Similar procedures are adopted for the manufacture of silicon carbide shapes. The material is purchased in the desired grades and bonded with some Allendorf clay. For a finely graded mix the proportions are given as: 42.5 per cent silicon carbide, 0 - 0.1 mm.; 42.5 per cent silicon carbide, 0 - 2 mm.; 15 per cent fine clay; 0.5 per cent addition of sodium silicate. For a coarser mix the proportions are identical except that 42.5 per cent silicon carbide, 0 - 3 mm., is used in place of the 0 - 2 mm. grade. firing is to Seger cones 10 to 11 (1310°C.).

(c) EQUIPMENT.

The main output from the works is chamotte firebricks and the equipment is therefore arranged mainly to this end. For chamotte preparation there are provided a jaw crusher, screen, and a set of rolls. The material passing the screen is conveyed to the storage hopper, the oversize passed to the rolls for further crushing. The storage silos are of metal discharging at the bottom. The clay is treated similarly. The grogged clay mix is prepared by mixing first dry in an Eirich mixer (60 parts of grog to 40 parts of clay), followed by a plastic mixer arranged as a vertical pug from which the mass is shredded as it is discharged through a vertical grid opening in the side of the barrel. The bricks are made either in hand presses or in simple plastic machine presses.

The special corundum or silicon carbide mixes are shaped by hand tamping methods after first mixing the ingredients in an Eirich mixer. Wooden moulds lined with 3/16 in. steel plates are in use. A metal tool is used for tamping and the tamped surface is roughened by scratching before each fresh addition.

The chamotte bricks are dried in chamber dryers heated by waste heat abstracted from the cooling goods in the kiln. Temperature and humidity are under control.

Firing of the ware, both firebrick and silicon carbide, is carried out in a continuous chamber kiln of the Hoffmann type. There are 22 chambers, with permanent walls. Each chamber measures approximately 15 ft. x 10 ft. x 7 ft. Firing is from above on to checkerwork adjacent to the permanent walls. A feature of this kiln is a secondary firing belt across the middle of the chamber. Here coal is fed from the roof of the kiln on to checkerwork of a more open pattern than that adjacent to the division walls. This subsidiary firing zone probably helps to achieve greater uniformity of firing.

(d) CONCLUSIONS.

This works, is probably the most important producer of refractories in the Kasell area. It appeared to be competently directed but nothing really noteworthy was encountered in manufacturing technique or equipment.

APPENDIX I.

LIST OF REPORTS ON THE MECHANICAL TESTING OF CERAMICS AT THE HERMANN GOERING LUFTFAHRTFORSCHUNGANSTALT VOLKENRODE, NEAR BRUNSWICK.

(1) Zusammenstahlung der Bisheringen Versuchenergebnisse und 8 Dusen. May 7th, 1941, NoF 464F/41.

(2) Flickkraft Zugversuch an keramik Schaufelproben by Kalisch, September, 1943, No. 2092.

(3) Versuche zur Bestimmung der Warmefestigkeit von keramik, 18th August, 1944, No. 860701/1.

(4) Festigkeit keramischer Werkstoffe und Warmebelasbarkeit keramischer Bauteile by Dirksen F22/45.

(5) Versuche an Dusen aus Warmfesten Werkstoffe No. 86701/2.

APPENDIX II

VISITS TO WORKS OF SECONDARY INTEREST.

AUG. GUNDLACH, GROSSALMERODE, BEZ KASSEL

C21/921 C22/3241 This firm specialises in the manufacture of Plumbago Crucibles, Covers and Stands.

DATE OF VISIT

October 25th, 1945.

PERSONNEL INTERVIEWED

Mr. Miller - Proprietor. Works seen and questions answered.

GENERAL CONCLUSION

Materials and methods used, and quality of product, all indicated that no progress has been made for many years.

RAW MATERIALS

Main raw materials used were:-

Passau Graphite - 93/95% Carbon. Poor small size crucible flake.

Klingenberg Clay - Well-known crucible clay, refractoriness Cone 32/33.

Grossalmerode Clay - Well-known. Refractoriness Cone 30/31.

Small quantities of electric furnace products were also used. See comments under "Mixings".

MIXINGS

The mixings employed were of old-fashioned

convential type containing 40-50% of plumbage bonded with clay and sand, with up to 15% of electric furnace products where extra resistance to slag or flux was required.

In the case of crucibles used for aluminium, as much as 40% of bond clay was used to give greater protection against perishing or oxidation of the plumbago at the lower furnace temperatures employed in melting this metal. Resistance to cracking must, in consequence, have been sacrificed.

The mixing employed in steel melting crucibles was of the familiar highly grogged type containing only 25% plumbago. The electric furnace products used included the usual silicon carbide (Lonzawerke) ferro-alloys, etc.

PROCESSES

Mixings are dry and wet mixed in Eirich mixers, then pugged and the pug rolls cut up into lengths for maturing. The matured material is repugged and the crucible "balls" built up by the old-fashioned and laborious hand method. The crucibles are shaped from these "balls" by jolleying in plaster moulds and it was claimed that the shaped crucible had a rapid grain.

The shaped products are dried slowly - taking up to five weeks in the case of the larger sizes - in steam heated drying rooms. When dry, the warm crucibles are painted with two or three coats of pottery type glazes

They are then fired in periodic kilns of the type used for firing porcelain ware, built by Paul A.F. Schurlze of Dresden. These kilns have semi-producer type fireholes and are down-draught. The gases, after passing through the floor, are drawn up vertical flues in side walls between the fireholes and, if desired, part of the products of combustion may be short-circuited from the fireholes direct into these vertical flues.

The kiln temperature was given as 1500°C, but considered to be nearer 1350°C. In firing, care is taken to maintain as reducing an atmosphere as possible above 700°C while in both heating and cooling the ware is kept above this temperature for a minimum of time to prevent oxidation of the plumbago.

KERAMISCHE SCHLEIFSCHEIBEN FABRIK (C. KREBS AND RIEDEL) KARLSHAFEN.

(a) Date of Visit and Products Made.

/922
/3242 This firm was visited on the 23rd October and Herr Krebs interviewed. As indicated by its title its chief output is grinding wheels, whetstones and similar articles, prepared by bonding silicon carbide, fused alumina and emery grain. The firm Corund Union A.G., which previously had operated in Karlshafen, had been taken over by Krebs and Riedel.

(b) Processes

The works is small and customary processes are employed. Most of the manufactured articles are bonded with a porcelainic bond, but rubber and sorel cement are used for some clases of ware. A typical ceramic-bonded mix consists of 80 per cent of grain (silicon carbide, emery, etc. of the required grain size) and 6.3 per cent of clay and 13.7 per cent of felspar. The abrasive grain is normally purchased correctly graded and is first mixed dry with the remaining ingredients in one of three Eirich mixers. Water and sulphite lye are then added and further mixing carried out. The wheels were pressed in hydraulic presses operating up to 40 atmospheres on the ram. The pressed wheels are dried on steam heated racks. Firing takes place in small intermittent round or rectangular down-draught kilns to a temperature of 1300°C. The firing cycle extended over 130 to 150 hours. Coal from the Kassel region is normally employed.

A small well equipped shop for dressing and trimming the wheels was provided. A test set for testing the bursting strength of the wheels was inspected.

Although no formally set-out screening plant was used one of the smaller items of interest was a circular sieve about 2 ft. in diameter vibrated by rotating of balance weight and traversed radially by 3 rotating brushes, the whole being suspended by a stirrup. The sieved product passed direct into paper sacks. The machine was used for checking the grading of some of the batches of grain. It was made by Fraisenet of Chemnitz.

BECKER UND PISCANTON
CROSSALMERODE, KASSEL

(a) Date of Visit and Products Made

C21/920
C22/3243 This firm specializes in the manufacture of graphite crucibles, covers and stands. The works manager was away at the time of the visit on the 25th October, 1945 and we were shown round the works by a foreman.

(b) Plant and Processes.

The plant, although larger than Aug.Gundlach, was no more up to date. A ball mill is used for grinding the bond clays, some of which are local and some Bavarian (Klingenberg). Mixing and tempering are carried out in an edge runner pan of old-fashioned type with double rolls and a narrow grinding surface. The mix is then pugged and stored in a cellar for 3 weeks.

The shaping is carried out in plaster moulds, a solid ball being hand shaped first. This is allowed to dry for 4 to 5 days and then the interior is cut out with a steel faced tool. A block and tackle are used to help in the manipulation of heavy shapes. The crucibles are dried on steam heated racks. They are then glazed inside and outside and fired in the same type of Schulze kiln. Temperature of firing was given as 1200° - 1300°C.

It was clear that the quality of the product at this works was attributed more to the care and craftmanship of the workers than any excellence in the plant equipment or its technical control.

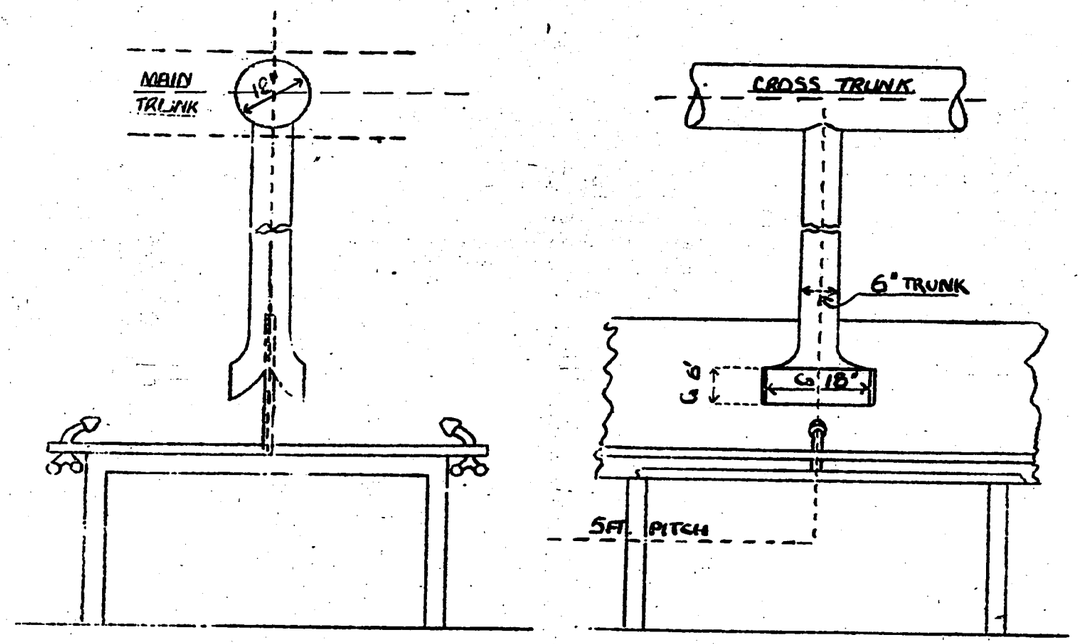
GOEBEL AND SOHN, EPTERODE,
C21/916a NEAR GROSSALMERODE.
C22/3240(a)

This works was visited on the 24th October and the proprietor interviewed. It proved to be a small concern making grogged fireclay crucibles and firebricks. No equipment of real interest was seen, in fact the plant was old-fashioned. The clays of the locality were used. For crucibles, the proportion of chamottes to raw clay was 3:2. A set of vibrating 2-bank screens was available for grading the grog into three sizes. A trommel was used for dealing with the coarser grog used for the larger

articles. The bond clay was ground in a ball mill. The grog-clay mixture was prepared in a vertical pug mixer. Crucibles were shaped by a jolleying process on a wheel. Bricks were made by hand moulding and by wire-cutting to a limited extent. The best clay was reported to contain 38 per cent Al_2O_3 in the fired state. Crucibles were also made from a mix containing 2 parts of fireclay, 1 part of sand and 1 of used graphite crucibles. The graphite is added merely to increase porosity and thermal shock resistance. Firing is to 1100°C.

HERAEUS. HANAU.

SKETCH No.1



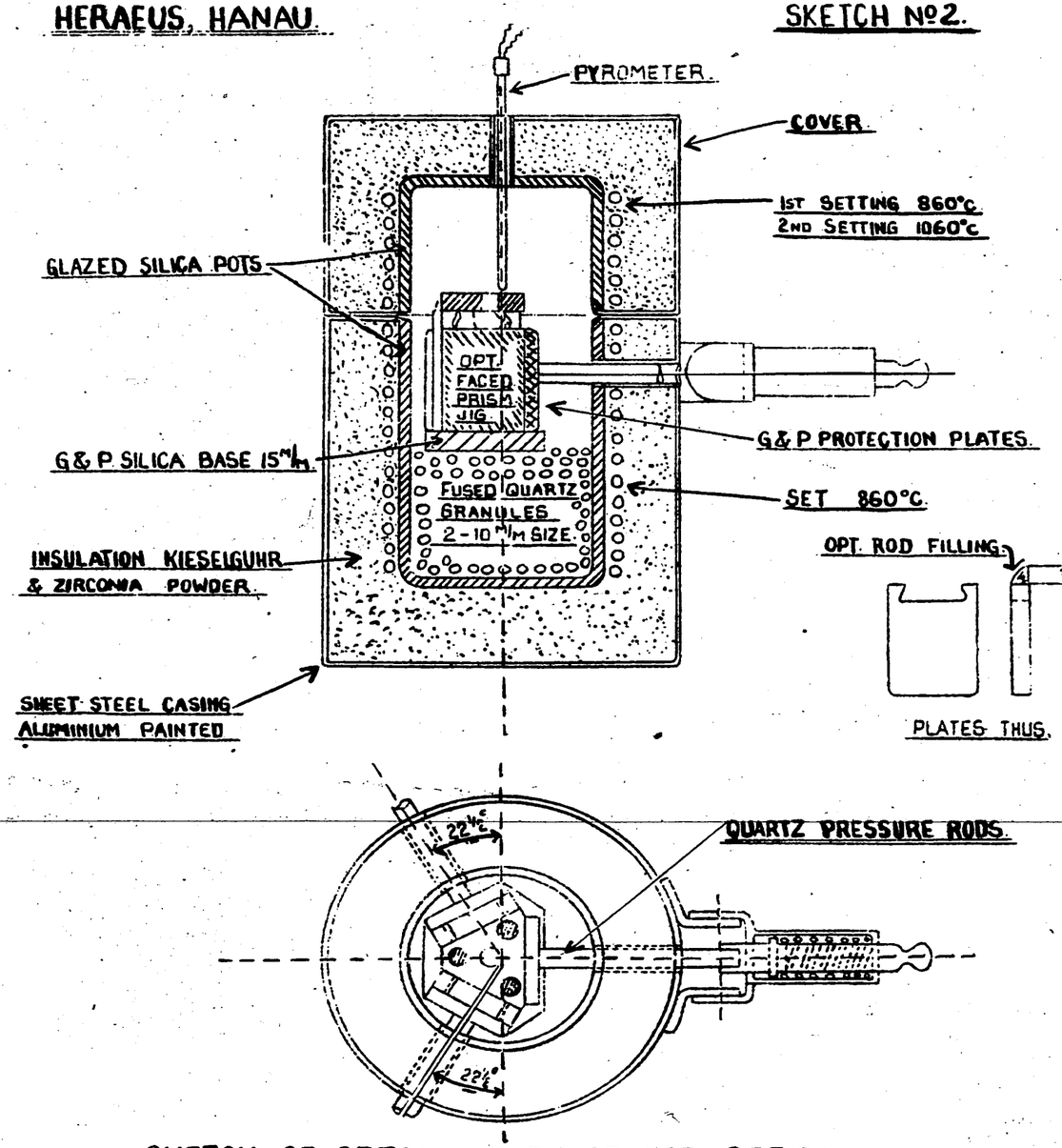
4 THUS PER ROW — 8 B.Ps.

NORMALLY OXY-HYDROGEN USED, BUT AT PRESENT FORCED TO USE OXY-ACETYLENE.

SKETCH OF BLOW-PIPE EXHAUST SYSTEM.

HERAEUS, HANAU.

SKETCH No2.

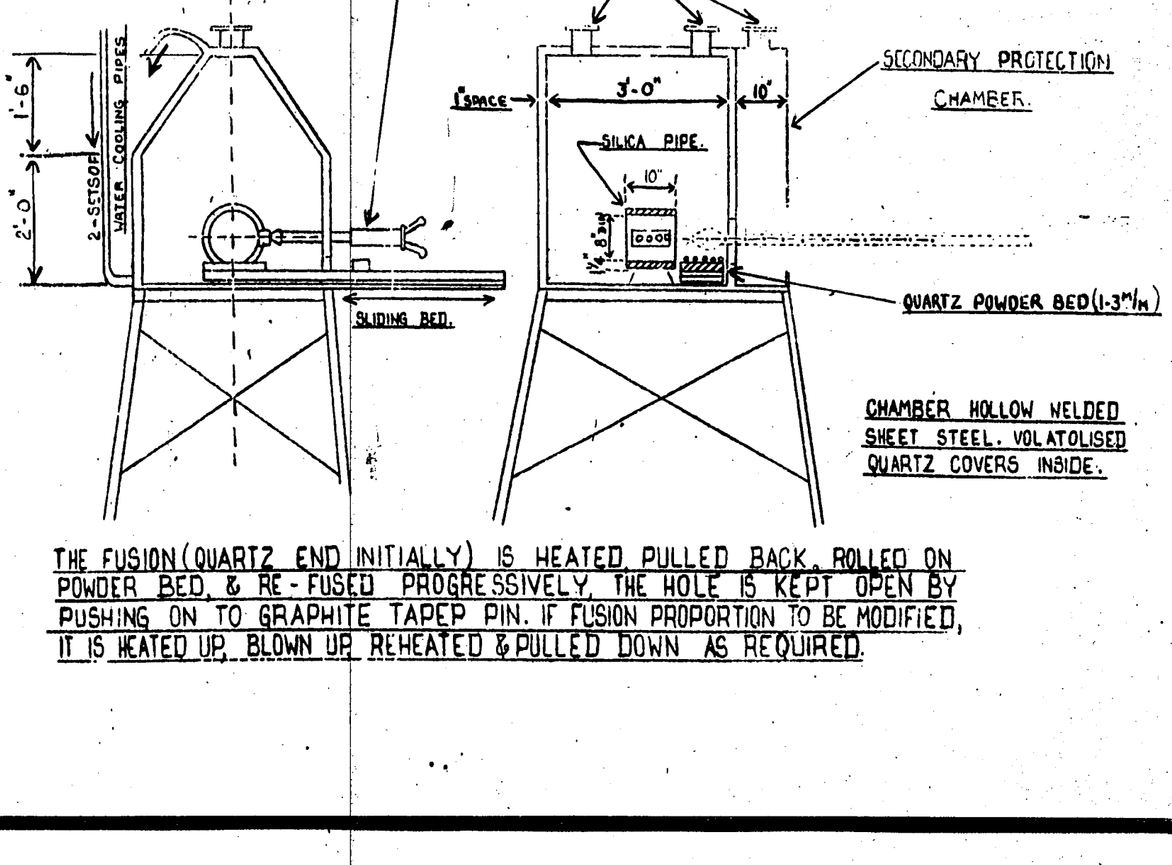


SKETCH OF SPECIAL FURNACE FOR OPTICAL QUARTZ PLATE ASSEMBLY (SCALE Ca: 3" = 1 FT.)

HERAEUS HANAU

SKETCH Nº 3.

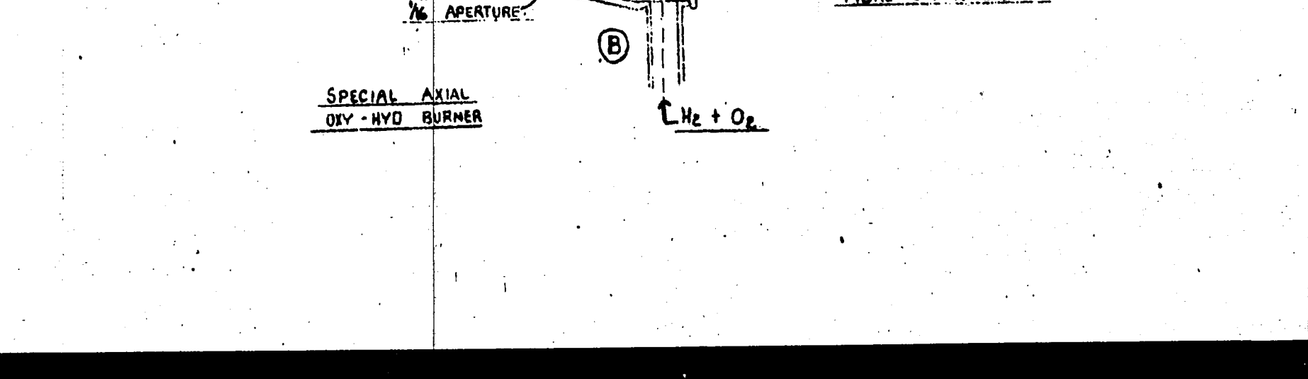
FURNACE FOR MAKING NORMAL QUALITY BILLETS



THE FUSION (QUARTZ END INITIALLY) IS HEATED, PULLED BACK, ROLLED ON POWDER BED, & RE-FUSED PROGRESSIVELY. THE HOLE IS KEPT OPEN BY PUSHING ON TO GRAPHITE TAPER PIN. IF FUSION PROPORTION TO BE MODIFIED, IT IS HEATED UP, BLOWN UP, REHEATED & PULLED DOWN AS REQUIRED.

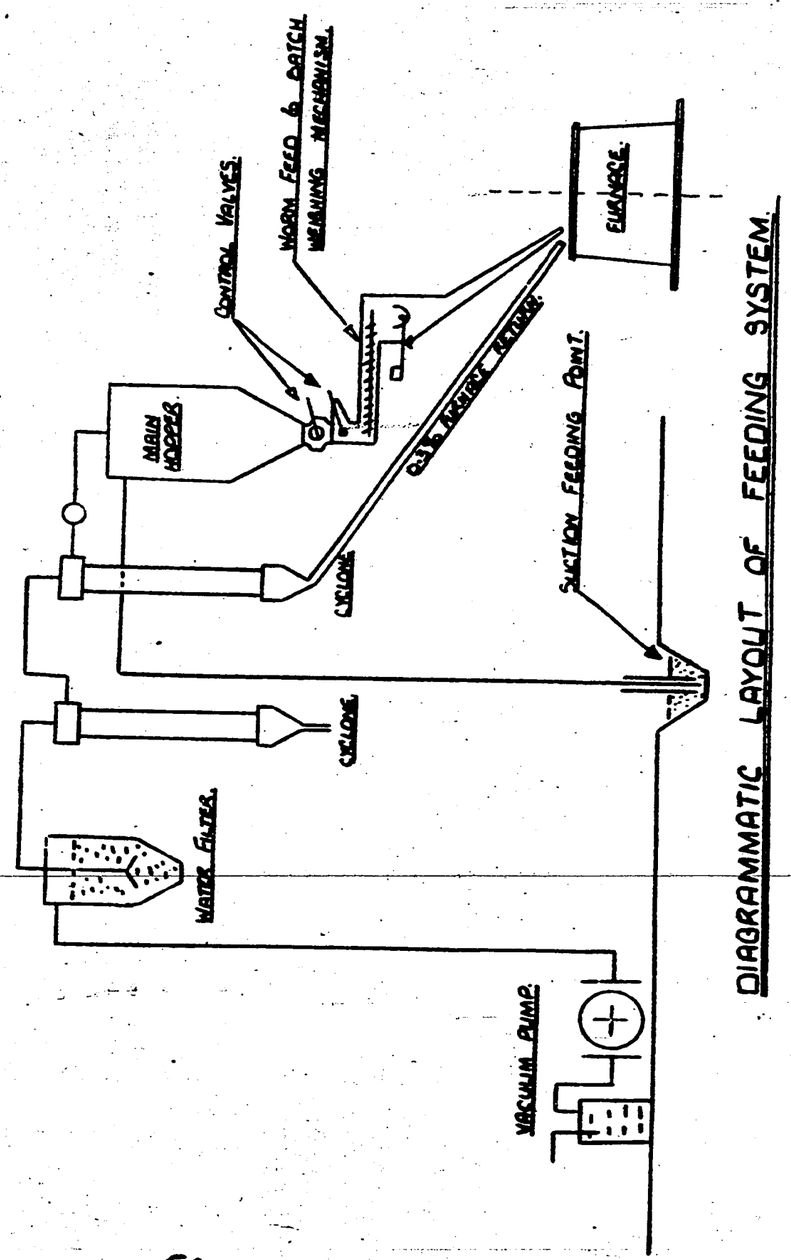
HERAEUS, HANAU

SK: Nº 4.



SKETCH No. 1

FUSED ALUMINA (WHITE) FURNACE.

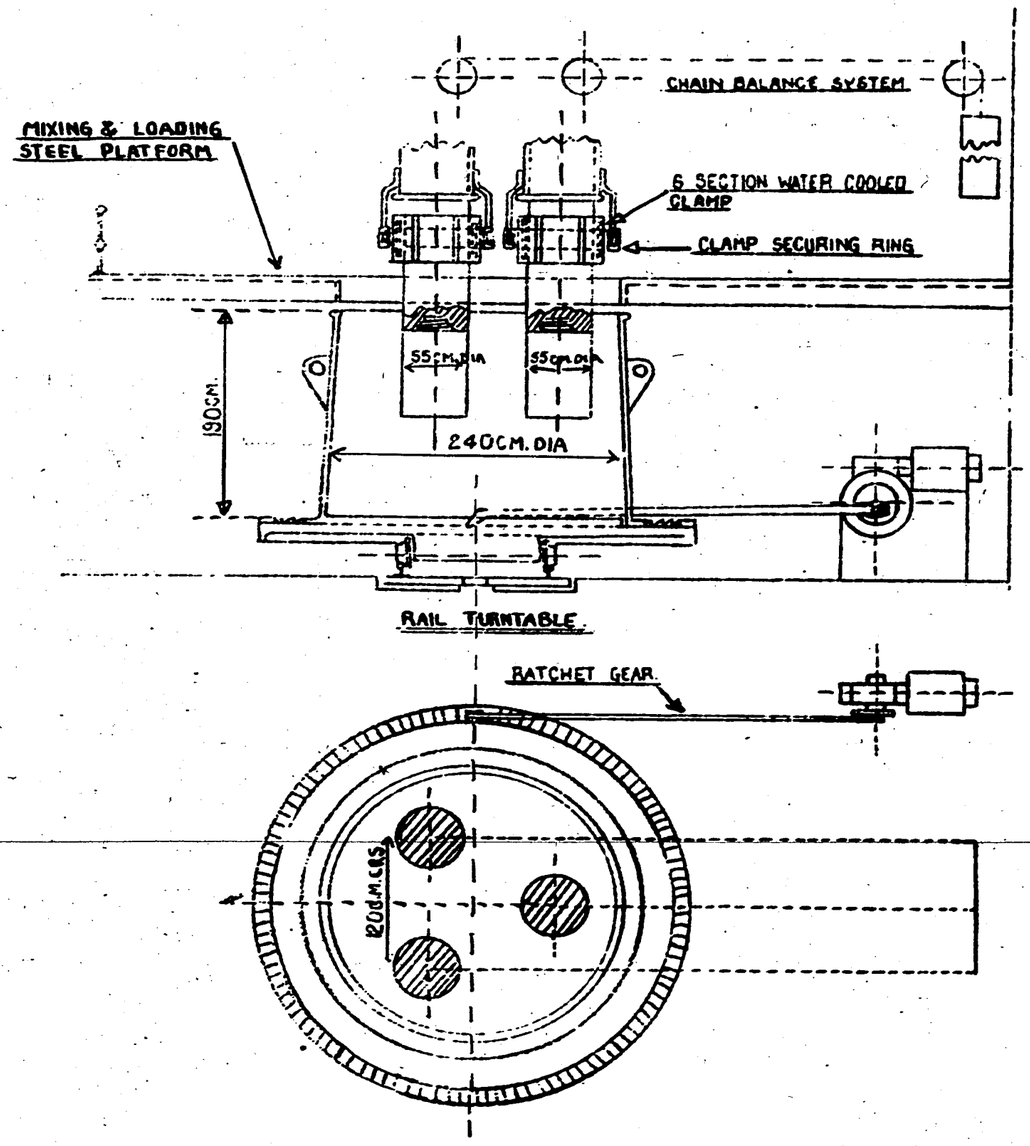


DIAGRAMMATIC LAYOUT OF FEEDING SYSTEM.

FELDMÜHLE

FELDMUHLE

SKETCH Nº 2

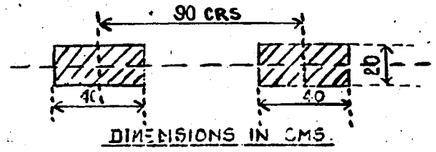


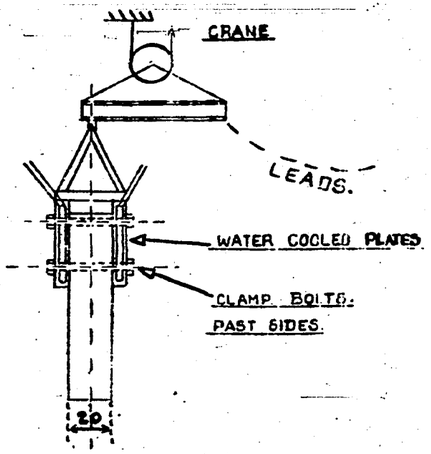
LAYOUT OF FUSED ALUMINA (BLACK) FURNACE.

FELDMÜHLE

SKETCH Nº3.

FUSED ALUMINA (WHITE) FURNACE
ELECTRODE ARRANGEMENT

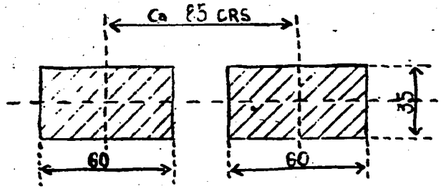


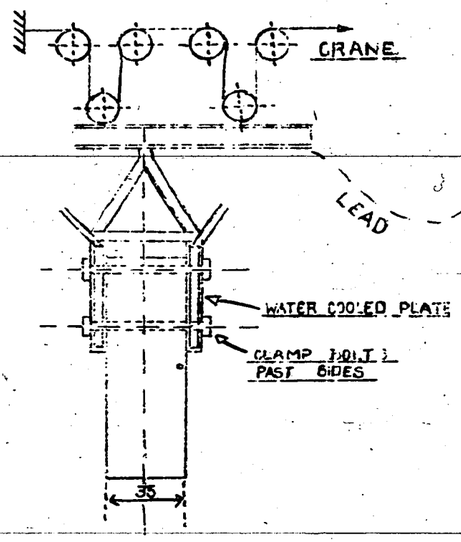


FELDMÜHLE.

SKETCH Nº 4

FUSED MAGNESIA FURNACE
ELECTRODE ARRANGEMENTS

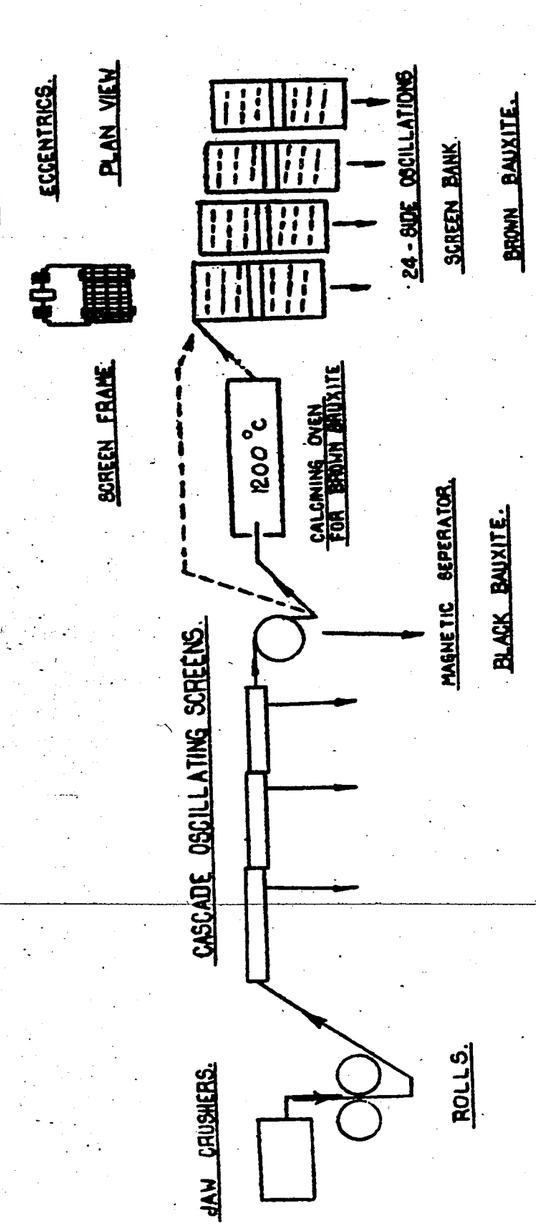




52.

SK: Nº 5.

DIAGRAMMATIC LAYOUT OF FUSED ALUMINA (BROWN & BLACK) PROCESSING.



FELDMÜHLE.

53.

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FINAL REPORT NO. 122

ITEM NO. 30

WIRTSCHAFTLICHE FORSCHUNGSGESELLSCHAFT m.b.H.

INTERROGATION OF HERR HELMUT PLOTE OF THE CONSTRUCTION DEPARTMENT

West, H. L.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

WIRTSCHAFTLICHE FORSCHUNGSGESELLSCHAFT

m. b. H.

Interrogation of Herr Helmut Plote of the Construction Department (Evacuated to Hitzacker),

July 8th - 11th, 1945

Reported by:-

Mr. H. L. West
British Ministry of
Fuel & Power

BIOS Target No. C 30/1.19(c)

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

CONTENTS

Personnel of Team

Lt. Col. H. F. Jones	British, War Office
Major L. Rosenfeld	British, Ministry of Fuel & Power
Mr. H. L. West	British, Ministry of Fuel & Power

SUMMARY

1. Due to the bombing of Berlin the various departments of the WIFO Headquarters had evacuated to separate locations, that chosen by the Construction Department being the WIFO, Hitzacker. Herr Plote was located during an investigation of this target and interrogated on the organisation of WIFO.

2. Herr Plote appeared an intelligent man and appeared to have a good, if somewhat limited, knowledge of the organisation and supplied quite a wealth of information on the whole concern.

3. Information was obtained on some of the WIFO activities outside Germany proper, their work taking them to locations in most, if not all, of the occupied countries.

4. Amongst the other activities of importance are included the various pipe lines, including five across the Rhine, the Tanksholzanlager and the relationship of the Construction Department with the Geilenberg programme.

5. Seven bags of documents and drawings were evacuated dealing with the topics given above and also giving drawings of some of the installations in which WIFO were interested.

INTRODUCTION

It was already known from the CAFT Assessment Report that the Construction Dept. of the WIFO Headquarters, Berlin, had been evacuated to Hitzacker and that Herr Plote, in charge of this department, was also resident in the town. The opportunity was therefore taken, as part of the investigation of the WIFO, Hitzacker, of interrogating this man on the subject of the organisation of WIFO.

The following information was obtained during this interrogation and by a cursory examination of the considerable collection of files and records of this department.

INTERROGATION OF HERR PLOTE

Aged 37 and trained as a mechanical engineer, Plote had been employed on rail, loco and rolling stock construction for the Reichsbahn until WIFO was founded in 1934, when he was transferred by direction of Berlin to the latter organisation. Allegedly forced to join the S.S. in 1933, Plote admitted that he was a member of the Nazi party, but stated that he had only been a

member of the S.S. for a short while. (This was subsequently found to be untrue, as some correspondence was found addressed to him as S.S.Unterleiter and dated 1945). Plote spoke very good English but appeared to be a nasty but knowledgeable character, and although seemingly co-operative, it was felt that he did not disclose any more information than he thought was necessary to keep him out of trouble. Replying to the question as to why he had not destroyed his records (see later section on documents), he stated that "he had seen what happened to the French and people in other occupied countries who had destroyed their documents". Certain documents bearing on the party relationship of both Herrn Plote and Levsen were found and handed in at G(T) C.W. branch, 21 Army Grp. BAD OEYNERHAUSEN for forwarding to the proper authority.

ORGANISATION OF WIFO

The Wirtschaftliche Forschungsgesellschaft m.b.H. was founded in 1934 with a capital of Rm. 100,000, the capital being jointly subscribed by the I.G.Farben one part and the Government four parts. The original object was to store petroleum products and to manufacture nitric acid. Later in 1934 the capital was increased to Rm.100,000,000, all held by the Government, the object then being to store all military and economic reserves, particularly petroleum products, both for the Wehrmacht and industry, and to manufacture certain chemicals (apparently these were the main chemicals required for explosives).

ADMINISTRATION

The management of the concern was directed by a board of directors and five main departments. The General Director was Franz Wehling, deputy General Director Friedrich Frey with Hans Attig, Albert Henne and Prankel to complete the board. The main departments were Administration, Mineral Oil, Transport, Construction and Factories. The information obtained concerning these departments was limited by two factors, namely, the main interest of the investigating team was in the Mineral Oil Department, and the fact that Plote was himself in charge of the Construction Department and this was naturally his chief interest. Below is given the constitution of the board of directors and the Mineral Oil and Construction Departments showing the inter-relation between the board and the Departments.

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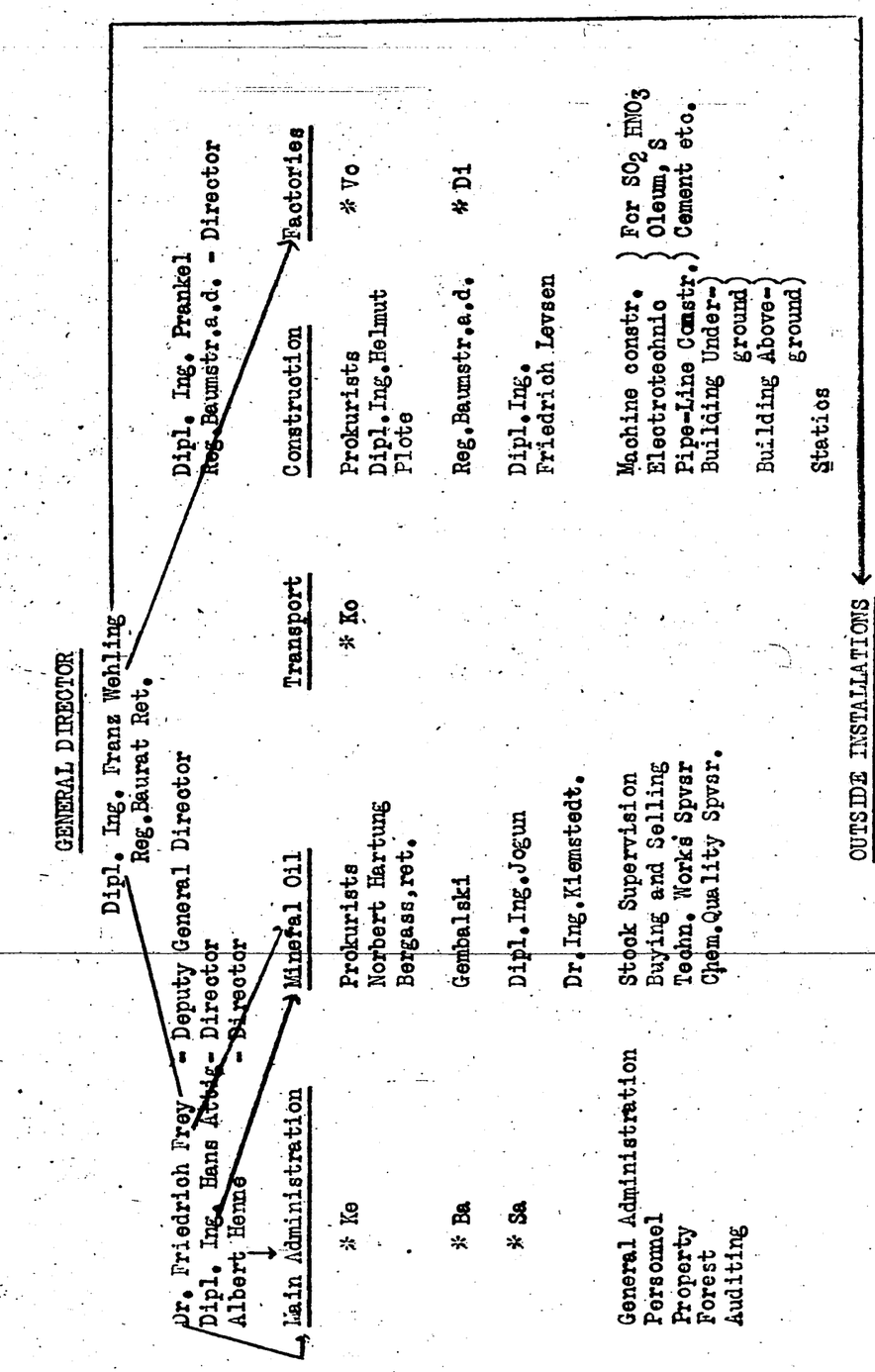

* The names of these individuals were not sought but are probably well-known.

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The functions of WIFO and the sub-division of the Departments are given in Appendix A. This shows the wide field of interest of the WIFO organisation.

Because of the bombing of Berlin the various departments evacuated as follows:

Mineral Oil Dept.	to Derben(or if that was in danger to Stassfurt)
Transport Dept., Construction Dept., Chemical Manufacturing Dept.	to Neuberg on the Danube to Hitzacker to Melbeck-Embsen (I.G.Farben plant) (Prankel, with others of this department, was apprehended at Bienenbüttel which is close by. See CAFT report).

ACTIVITIES OF THE MINERAL OIL DEPARTMENT

As stated above the main interest of the investigating team was in the Mineral Oil Department. Information in regard to the Construction, Transport and Chemical Factories Departments was not sought and such as was obtained was more by accident than design.

The working of the department was in the hands of four prokurists (executive chief clerks) the duties being sub-divided as follows:

Norbert Hartung	-	Stock Supervision
Gembalski	-	Buying and Selling
Dip.Ing.Jogun	-	Techn. Works Supervisor
Dr.Ing.Kiemstedt	-	Chemical Quality Supervisor.

The Mineral Oil Department operated largely as a commercial undertaking, buying raw materials and products from the refineries and synthetic manufacturers and also from foreign countries, re-selling finished, blended products to the Air Force, Army, Navy and to industry.

The connection between the sub-divisions of this department and the respective Ministries and the personnel involved is given in the following table.

LIST OF THE CHIEF EMPLOYEES OF WIFO AND THE MINISTRIES WHICH CO-OPERATED ON MINERAL OIL PROBLEMS

	WIFO	MINISTRY
a. AIR FORCE Fuels & Lubricants		
1. Quantities and disposition	HARTUNG	AHRENS
2. Frontline supply and recalls	HARTUNG	BAUM
3. Quality control	Dr.Kiemstedt	Dr.Beyer
4. New Construction and Extensions of plants	Plote and Levsen	Dr.Nocker, Griebel, Frigate Capt.(OKW)
b. ARMY Fuels and Lubricants		
1. Quantities and disposition	HARTUNG)	HEYNOLD until beginning '44
2. Frontline supply and recalls	HARTUNG)	NORKUS from beginning 1944.
3. Quality control	Dr.Kiemstedt	Dr.Hagemann Dr.K.O.Müller
4. New Construction and Extensions of Plants.	Plote and Levsen	HEYNOLD until beginning'44 NORKUS from beginning 1944

Before the war WIFO was concerned mainly in buying aviation, army and industrial products for reserve storage. For example, in 1935 to 1936 WIFO bought aviation products direct from U.S.A. (from the Standard Oil Co. of New Jersey, in which transactions the Deutsch-Amerikanische Petroleum Gesellschaft were intimately connected) and from Mexico. These products were transferred from tankers to barges on the Weser and Elbe and shipped to the WIFO depots. Later they bought direct from Roumania via Astra, Romano Americana and Creditul Minier. Subsequently, as other countries were over-run WIFO (in Paris 1940) purchased stocks and products from French Companies, undertook constructional repairs to refineries and arranged manufacture: the French WIFO organisation was practically independent of the WIFO H.Q. Berlin. Much the same type of organisation existed in other occupied countries. Evidence was found of Plote himself having lost personal effects due to bombing at Bucharest and of purchasing articles at the German Army shop in Paris. Also in the Eastern countries trusts were formed to purchase Roumanian and Russian products.

Inside Germany WIFO purchased from the Z.B.(Zentral Büro für Mineralöl, comprising all German oil firms - Shell, Standard, Olex etc.) which handled all motor fuels and lubricants for German industry. As the war progressed WIFO tended to by-pass the Z.B. and purchase direct from the refineries, producers of synthetic products and coal tar manufacturers.

It has been noted that large stocks of odd chemicals have been found at WIFO installations and it appears that these were dispersal or transit stocks held at least partly for the chemical branch of the undertaking.

Plote alleged that all Ethyl Fluid plants were constructed and owned by WIFO.

AUSSENSTELLE

The oil storage and blending installations were divided into four classes, namely, "Grosslager" or "Hauptlager" - large installations dealing mainly with products for the Luftwaffe and to a smaller extent with Army supplies; "Heereslager" or "Heerestanklager" - being, as the name suggests, depots concerned solely with Army products; "Luft-tanklager" - depots concerned only with Air Force products (they had facilities for T.E.L. blending); and "Marinelager" - depots concerned only with stocks for the Navy.

Some confusion appears to have existed as to the meaning of the terms "Umschlaglager" and "Nachschublager" applied to both the Grosslager and Heereslager. It would seem that these terms, if taken in their strict literal translation, viz. "transfer or turn round depot" and "reserve storage depot" might be applied to either or both with equal aptitude. It is known also that the Army and Air Force had smaller storage depots, the Army for packed products and the Air Force at aerodromes.

Below is given a list of the WIFO oil storage and blending depots. Before the war most of these depots had camouflage names which were used in an endeavour to retain some secrecy as to their exact location. As far as they are known these names are included in the list below. During the war the use of these names has been almost discontinued. It will be noted that all the camouflage names for the Grosslager end in "berg", those for the Heereslager end in "au" whilst those of the Lufttanklager end in "al".

(a) Grosstanklager

DEPOT	CAMOUFLAGE NAME	TOTAL FUEL TANK CAPACITY IN 1000 cu.metres.	DATE OF CONSTRUCTION.
Derben	Löwenberg	160	1934
Drugehnen	Hegeberg	?	End of 1934
Farge	Wasserberg	220	1936
Hitzacker	Hellberg	100	End of 1935
München	Münchberg	100	1934-1935
Neuburg	Buchenberg	100	1935-1936
Nienburg	Kuhberg	100	End of 1934
Raudnitz	-	60	1940
Stassfurt	Bela	220	1934
Vienna	-	140	1940
(b) Heerestanklager			
Amstetten	Ammenau	7.2	-
Ebrach	Eberau	7.2	-
Eickeloh	Rodenau	7.2	-
Heiligenstadt	Heiligau	7.2	1937-1938
Mährisch-Schönberg	-	5.2	-
Münchenbernsdorf	Sonnenau	7.2	-
Neuenheerse	Bekenau	7.2	-
Rüthen	Steinau	7.2	-
Vorderheide	Heidenau	?	-
Zarrentin	Ludwigsau	7.2	-
(c) Lufttanklager			
Annaburg	Elbtal	-	-
Bad Berka	Erftal	-	-
Dülmen	Westtal	-	-
Ebenhausen	Kirchtal	-	-
Ehmen	Elendstal	-	-
Lahgenselbold	Burgtal	-	-
Löwenhagen	Osttal	-	-
Niederullersdorf	Ullertal	-	-
Weissenhorn	Horntal	-	-
Later the Luftwaffe built the following:			
Kloster Loccum	-	-	-
Oldendorf	-	-	-
Buchholz	-	-	-
(d) Marinelager			
Achim	-	-	-
Bleckede	-	-	-

(d) Marinelager (continued)

Einswarden	-	-	-
Farge	-	-	-
Flemhude	-	-	-
Monkeberg	-	-	-
Nordholz	-	-	-
Sande	-	-	-
Schafstedt	-	-	-
Wilhelmshafen	-	-	-

From examination of the Grosslager and Heereslager and a study of the layout of the remaining depots it would appear that the construction of both of these types of depot follow a standard layout with minor variations due to topography and in the ultimate storage space used. In general it can be said that if a depot of each of these types has been visited, little fresh will be learned by visiting other depots of the same type. This is not so, however, with the Stassfurt depot - now in Russian hands - which was from its very inception regarded as a special depot.

The management of these outlying depots was in the hands of three senior officials known as the Mechanical Engineer Manager, the Commercial Manager and the Chemical and Technical Manager. These men were directly responsible to the General Director and not to any subordinate official. The director would appoint any one of these three to be "Deputy Works Leader", this post would usually fall to the one who was the most reliable party member. The duties of the individual managers are given in Appendix "B" which is an abbreviated translation of a Headquarters circular.

DISTRIBUTION

Herr Plote was not very well informed on distribution but it is known that the WIFO installations had to inform Berlin of their stock position daily and it can be assumed that stocks were kept at a reasonable level. Orders would be sent from H.Q. Berlin for supplies for the Luftwaffe or the Army and the depot would prepare the necessary quantity, notifying Berlin when ready for despatch. According to the district in which the depot was situated the central distribution office (Hamburg for Hitzacker) - which was usually associated with the Reichsbahn - would call forward a train and/or other transport which would be loaded and despatched. The only indication of the destination of the products would be the train reference number: the personnel of the installation never knew where the products were going. It is known, also, that the Army could order supplies direct from the Heereslager.

Although the Luftwaffe drew the bulk of their supplies of fuels and lubricants through WIFO, the army only obtained about 30 to 40% from this source, the remainder being obtained direct from the distributing companies e.g. Rhenania, Ossag, Vacuum, D.A.P.G., Olex etc. The Army did give the WIFO certain special tasks i.e. glycerol (and substitutes ?) and greases. As transport difficulties increased both the Luftwaffe and the Army tended to draw stocks from the most convenient source, a practice which resulted in an increasing use being made of the distributing companies. It is known that the Army used quick coupling piping (the "Perrot" system) for pumping supplies to forward areas.

During the war the Luftwaffe took over the Luftanklager and operated them independently of WIFO and even constructed some additional installations. The Navy was, as might be expected, very independent, managing their own depots without reference to WIFO.

As the war progressed and other countries were over-run WIFO set up installations to serve the advancing Armies, making use of existing storage installations in the occupied countries and where necessary, even building new storage capacity. It is difficult to say exactly where all these installations were located but the Table below gives those in occupied France. These were all called Heereslager and were operated by the French under German supervision.

WIFO IN FRANCE

Places in which in 1940 Heereslager were set up in France

1. Paris .
   Paris - Genevilliers
   - Soc. Maritimes
   Paris - St. Ouen
   Soc. Carburants.
2. Honfleur
3. Rouen
4. Cherbourg
5. Rennes
6. Nantes-Donges
7. La Rochelle
8. Raum Bordeaux (zu Beginn etwa 8 Anlagen)
9. Sens
10. St. Florentin

In the beginning of 1944 new erections were set in the following places for safety from bomb attack.

Sens
Bazancourt bei Reims
Lyon
Le Mans

The names of those places used in other occupied countries were not obtained but it is known that Oslo was used in Norway. In Appendix C a list of names of places is given where it is known that WIFO had an interest; these may not refer to petroleum storage only, but may also be for the chemical department.

Tankholzanlager

As is well known the Germans relied to a considerable extent on the use of producer gas generators for operation of internal road transport. Whereas civilian transport had to make do with coal, coke, anthracite etc., producers, those used for the armed forces operated exclusively on wood. This was due no doubt to the fact that it was found that less trouble was experienced with producers operating on this fuel. It apparently fell to WIFO to arrange for supplies of chipped wood for this purpose. Evidence was found, in searching through the documents, of storage depots for wood which included machinery for sawing up the logs and reducing these to chips. This type of storage went under the name of "Tankholzanlager". It is believed that most of these were situated in the eastern occupied countries.

Pipe Lines

It is probably already known that pipe lines were used by the Germans for transportation of their petroleum supplies. The information given here will, therefore, either confirm or supplement that already known. The pipe lines constructed did not necessarily relate entirely to petroleum as some were laid to feed chemical works with natural gas for such purposes as synthetic rubber manufacture. The following petroleum pipe-lines are known to have been laid or to have been under construction or consideration.

Oil Pipe Lines

Ploesti to Giurgiu
Raudnitz (Roudnici) to Vienna. (300 mm diam.1940)
Neusiedl to Vienna
Stassfurt to Güssen
Farge to Osterholz
Five pipe lines across the Rhine.

Natural Gas Lines

Bentheim to Hüls
Langensalza
Rumanian gas lines

Of the above projects probably the most interesting is the five pipe lines across the Rhine, as it would appear that this is the first intimation that has been obtained of their existence. It is known that three of these were completed, but it is not possible to give more exact information without consulting the documents. These were no doubt intended to maintain supplies to forward areas if road or rail transport should fail due to destruction of bridges.

Other activities

The Construction Department of WIFO had many diverse and wide-spread activities. Considerable evidence exists of constructional work having been carried out at chemical manufacturing plants, particularly those belonging to the I.G.Farbenindustrie. This is perhaps explained, somewhat, by the statement mentioned earlier of the financial interest of the I.G. in the founding of WIFO. Two places of particular interest are the Melbeck/Embsen plant, to which, it will be remembered, the Chemical Department evacuated and the Niedersachswerfen location. Ruhrbenzin and Ruhrchemie at Oberhausen/Holten also had a close relationship with WIFO.

Another activity for which no explanation has yet been given is the erection of "Hoko" plants. Evidence was obtained of such plants being erected at Heidebreck, Oberhausen, Döberitz, Embsen and Neuenkirchen. The extension at Embsen was being carried out with plant removed from France.

It was learned from the documents that orders were issued that the various rocket fuels, components etc., were not to be known by their usual names, e.g. T. Stoff etc., but were all to be called Sonderstoff. Many storage plants for these materials, particularly T.Stoff, were being erected, the locations named being Parey, Ebrach, Krumnussbaum, Mitteldeutschland and Diedringen. In addition it is most likely that the existing Grosslager were also being enlarged to include Sonderstoff storage

One rather unusual undertaking was known as "Operation Philipp". This was the proposed engine test laboratory being built for the RLM and DVL at or near the Neuberg on the Danube, WIFO installation. This has been located and was not completed,

but the leader of the section of the DVL who apparently gave his name to the operation - Dr. A. von Philippovich - has been located in this area.

Bomb Damage to Oil Installations

From documentary evidence it is known that several of the Grosslager and Heereslager were damaged by bombing. For example, the depots at Drugehnen and Vordeheide were out of use on the 1st February, 1945. Similarly it is known that on the 18th December, 1944, repair work was in hand at the Vienna and Nienburg depots, to make good damage due to air attack. From the report on the Heiligenstadt depot it is known that four tanks were damaged on Good Friday 1945, whilst at Hitzacker the extension to the site was damaged, one set of five tanks receiving a direct hit and the railway siding being damaged. Most of the bombs however, fell well outside the target area.

Geilenberg Programme

It would appear that in the later years of the war, and, presumably, after the initiation of the Geilenberg programme, most of the WIFO constructional work was co-ordinated in this programme. Thus the pipe lines under the Rhine and some of the other lines previously mentioned were being carried out as part of this programme; so also were extensions and improvements at the following depots - Drugehnen, Hitzacker, Vienna, Raudnitz, Munich, Neuberg, Farge, Derben, Nienburg and Stassfurt. Naturally bomb damage repair came under this heading as also did much of the Sonderstoff storage and the "Operation Philipp".

On or about 18th December, 1944 some endeavour was being made to increase storage of residual oils suitable for fuel oil. This may have been due to the accumulation of stock not being used due to the curtailed activity of the Navy. In addition to work at Marinelager mentioned earlier, a special measure in the Geilenberg programme in contract to the Reichminister for Armaments and War Production, Raw Materials Dept., was being undertaken for the storage of petroleum residues and coal tars. This consisted in the use of clay pits at OTTENSEN, LAA I and LAA II and NEU WEIDENBACH.

Documents

The large mass of files and drawings belonging to the H.Q. Construction Department were sorted and seven bags of material

of possible use were evacuated. The contents are as below:

BAG NO. 4489A	Rohrleitungen über den Rhein (Pipe lines across the Rhine) Aussenstelle, WIFO, Germany Official Instructions and Circulars Assorted Micro Films.
BAG NO. 4489B	Technical Drawings and Calculations of WIFO plant installations
BAG NO. 4489C	Technical Drawings and Calculations of WIFO plant installations. Organisation and Scope of WIFO A.R.P. and Bomb Damage at WIFO installations Technical Papers (including information on Petroleum Industry USSR).
BAG NO.4489D	Oil and Gas Pipe Lines Sundry Papers Geilenberg Program.
BAG NO.4489E	WIFO activities outside Germany WIFO building programme Evacuation Measures DVL Test Laboratory (Operation "Philip") TEL Blending Tankholz Anlagen
BAG NO. 4489F	Sonderstoff Sundry Films Maps and Drawings
BAG NO. 4489G	Miscellaneous Drawings, Plans and Maps.

The documents relating to the pipe lines across the Rhine include detailed drawings showing the location of these projects, explaining their use and constructional difficulties.

From the Technical papers relating to the USSR Petroleum Industry it would appear that this subject was being carefully studied so as to make the best use of the facilities when, and if, they should be available.

Conclusions and Recommendations

The WIFO organisation appears to have been one of the most important of the State organisations connected with the prosecution of the war. Not only were its connections with the petroleum producing and distribution concerns of importance but its obvious connections with the chemical producers would appear to merit further investigation. The fact that it would appear that only trusted Nazi party members were allowed to hold executive office indicates that its activities may not be above suspicion.

The relation between WIFO and the armed forces as regards supplies of petroleum products is not yet clear and its exact functions, difficulties encountered, success or failure would appear to warrant further attention; particularly is this so with supplies to forward areas. There is no doubt that the outlying depots were well, almost elaborately, equipped and it would be surprising if such an elaborate organisation should not return dividends in efficiency or ease of operation. It is noteworthy too that few of these depots have been materially damaged by air attack.

To further clarify the picture of quality control and demands for petroleum products by the various sub-divisions of the armed forces, it would appear to be worth while interrogating the members of the various ministries mentioned in this report and also some of the service chiefs concerned with the supply of petroleum products.

The relationship between the I.G. Farbenindustrie and WIFO appears to have been very intimate and might merit further investigation.

Further information concerning many of the subjects mentioned in the body of the report can be obtained by a study of the documents mentioned above.

HLW/BMO.

APPENDIX "A"

FUNCTIONS OF WIFO

LIST OF CODES FOR THE DIFFERENT BRANCHES USED FROM THE 1st APRIL, 1943 ONWARDS

G. MANAGEMENT

G-GDW	Management	- General Directorate	Wehling
G-DFR	"	- Directorate	Frey
G-DAT	"	- "	Attig
G-DHE	"	- "	Henne
G-DPR	"	- "	Prankel

relating Management Groups.

GDW	General directorate group	Wehling	(General Secretariat)
DFR	"	Frey	
DAT	"	Attig	
DHE	"	Henne	
DPR	"	Prankel	

G. DEPARTMENTS IMMEDIATELY UNDER THE MANAGEMENT

GBU	Work Organisation
GRA	Auditing and Contract Supervising
GCL	Chemistry and Laboratory
GWT	Scientific and Technical Development.

H. MAIN ADMINISTRATION

HZB	Central Accounting
HPV	Main Personnel Office
HEM	Central Buying and Stores Management
HAV	General Administration
HRV	Contract and Legal Department
HGF	Ground, Forest, Agriculture

M. MINERAL OIL CHIEF DEPT

Departments.

MBK	Buying
MVK	Sales
MLV	Stores Administration
MBB	Works Accountancy
MTB	Technical Works Supervision
MWL	Works Guard and A.R.P.

APPENDIX "A" continued

F. CHIEF DEPARTMENT FACTORIES

FBV Works Administration
FRP Accounting and Price Control
FBB Works and Constructions Book-Keeping
FBS Works Supervision and Construction of Nitric Acid Plant
FBT " " " " Toluol and Sulphur Plant
FET Electrotechnics

B. CHIEF DEPARTMENT CONSTRUCTION

Departments

BVP	Survey and Planning	)
BKS	Constructions and Statics	)
BBT	" Underground	)
BBH	" above Ground Level	) Constructional
BBF	" of Factories	) Engineering

BSP Spray Plant
BMR Machinery and Pipe Line Construction
BET Electrotechnics
BRB Accounting and Price Control Constructional Engineering
BRM " " " Machines and Electrotechnics
BBA Book-keeping and Accountancy
BPV Personnel and General Administration

T. CHIEF DEPARTMENT TRANSPORT

Departments

TTB Technical Supervision and Quality
TKV R.T.W. and Vehicle Administration
TTD Transport Disposition
TFT Freights and Tariffs
TBA Book-keeping and Accountancy
TPV Personnel and General Administration.

Seen and Agreed
by Management

Berlin, 22.3.43. (sgd) Wehling, Franz.

APPENDIX "B"

Abbreviated Translation

CIRCULAR NO.596

TO ALL AUSSENSTELLEN

Ref: Scope and Responsibility of principal employees (Mineral Oil Storage).

We send you enclosed the new instructions for our branch (Aussenstelle) Managers which will be valid as from 1.4.43.

This cancels circulars No.7 and 53.

Berlin 23.3.43.

WIFO . (sgd) Wehling(?).

1 encl.

* * * * * * * * * * *

A). Competence and Responsibility

I. Branch Management

As a rule there are threemanagers in a mineral oil store (subsequently called AUSSENSTELLE), i.e.

1. mechanical engineer manager (A)
1 Commercial manager (B)
1 chemical & Technical Manager (C)

They are immediately subordinated to the managing direction to which they are also responsible.

When absent or otherwise prevented the managers are represented as follows - if a special representative has not been delegated by the chief administration.

(A) by the plant engineer nominated by the managing direction.
(B) by the commercial employee designated by the managing direction.
(C) by the chemist designated by the managing direction.

II. Works Manager

The General Director as works leader of WIFO designates

APPENDIX "B" continued

one of the managers to be "Deputy Works Leader" in compliance with the law on the regulation of national labour at the branch. He is called "Works Manager" or by special nomination "Works Director". He is chiefly responsible for the complete management of the branch, for the continuous and complete readiness for operation of the plant and for its safety. He represents the whole plant outwards.

III. Scope of the Mechanical-Technical Branch Managers

Foremost responsible for the operation and readiness of the plant and for the safety within his province. He is responsible for:

1) The care of technical personnel, i.e. engineers and technicians; plant inspectors and foremen; works office-typists; machinists, stokers, drivers; communication, telephone, teleprinter personnel; helpers, auxiliary personnel.

2) Contact and negotiations with authorities, officials and private firms on general technical matters and subsequently named subjects.

3) Disposition for storage, mixing and despatch of fuel, oil etc.

4) Control and supervision of quantities moved and mixed.

5) Cleansing of containers, maintenance and repair

6) Tank car cleaning, maintenance (minor) repair.

7) Maintenance of all works equipment (buildings, machinery, apparatus containers, pipes).

8) Machine Shops etc., etc.

IV. Scope of Commercial Branch Manager

1) Care of commercial personnel, treatment of matters concerning personnel of whole branch, in conjunction with mechanical-technical and chemical-technical manager for their staff.

2) Cash accounts.

3) Wages

4) Orders and Bills

5) Freights etc., etc.

APPENDIX "B" continued

V. Scope of Chemical-Technical Branch Manager

Complete and sole responsibility in all questions relating to fuel and oil quality. In charge of laboratory. Responsible for all operational measures effecting quality. Sole responsibility for supply of fuel and oil to the armed forces true to specification.

1) Care of laboratory personnel i.e. chemists, chemo-technicians, chemist's assistants, auxiliary personnel, office staff.

2) Instruction of new staff for laboratory and test bench.

3) Course of instruction and current co-operative testing within WIFO, ordnance and official institutions, and industry etc., etc.

B. INSTRUCTIONS

General instructions on competence and co-operation between managers. Daily discussion of mail. Signing of letters. Mail of the "defence deputy" (ABWEHRBEAUF-TRACTER) is subject to special treatment.

etc., etc.

WIFO

(sgd) Wehling (?)

Berlin 1.4.43.

APPENDIX "C"

GERMANY	AUSTRIA	POLAND	ROUMANIA	RUSSIA	BULGARIA	HUNGARY
Döberitz	Vienna	Krasnik	Albesti	Pleskov	Varna	Bucharest
Dulmen	Raudnitz	Warsaw		Dombroviza		
Ebenhausen	Iglau	Kattowitz		(Dombrowa)		
Embsen	Krummussbaum	Auschwitz		Rostov		
Erfurt	Pinavarth			Dunaburg		
Hameln						
Herbern						
Heydebreck						
Kelheim						
Kolin						
Köln-Niehl						
Langelsheim						
Lindenbrück						
Linz						
Lotzen						
Lowenberg						
Melbeck						
Neusiedl						
Norkitten						
Oberau						
Recklinghausen						
Rudgershagen						
Sonderhausen						
Sorau						
Waldenburg						
Weissenhorn						
Wolfen						

LATVIA	ESTHONIA	CZECHOSLOVAKIA
Riga	Reval	Prague

FRANCE	BELGIUM	HOLLAND
Paris, etc.	Brussels	Rotterdam

NORWAY	SERBIA	CORSICA
Oslo		

SARDINIA	GREECE	UNABLE TO TRACE
	Salonika	Persenkofka
		Piesteritz

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BIOS Final Report No. 510
Item No. 30

SAMPLES OF PETROLEUM PRODUCTS COLLECTED FROM THE HAMBURG, HANNOVER, BREMEN AND KIEL AREA

Withers, J. G.

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

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON - H.M. STATIONERY OFFICE

SAMPLES OF PETROLEUM PRODUCTS COLLECTED FROM THE HAMBURG, HANNOVER, BREMEN AND KIEL AREAS

September 31st - October 29th 1945

Reported by:

Mr. J.G. Withers, British, Ministry of Fuel and Power.
Maj. W.H. Thomas, British, Ministry of Fuel and Power.
Maj. E.B. Robinson, British, R.A.S.C., B.O.A.R.

BIOS Target Numbers

C30/400, C30/1.19c, C30/402, C30/403, C30/52, C30/307, C30/404, C30/1.18, C30/405, 30/3.01, C30/55, C30/406, C30/36, C30/407, C30/45, C30/58.

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

TABLE OF CONTENTS

SUMMARY.

The collection of samples from the Hamburg, Hannover, Bremen and Kiel areas was part of the object of B.I.O.S. trip No. 1248, and lists of samples required were given in the briefing instructions for that trip.

The personnel responsible for the collection of the samples were :-

Major W.H. Thomas, British, Ministry of Fuel and Power.
Mr. J.G. Withers, " " " "
Major E.B. Robinson, British, R.A.S.C. loaned by the B.O.A.R.

The collection of samples was carried out over the period 31st September to 29th October 1945.

The samples have an initial reference number in the order in which they were obtained and this initial number is followed by the reference number in the briefing instructions where available.

The notes on each sample are headed with the sample number, name of product, quantity available and source. In the case of samples obtained from manufacturers, the products are of their own manufacture unless otherwise stated.

SOURCES OF SAMPLES.

1. Bulk Storage

C30/400	(a)	Barges "Freienwaldia" and "No. 210" on the canal at Fallersleben.
C30/1.19c	(b)	Wifo Grosstanklager, Hitzacker.
C30/402	(c)	Wifo Grosstanklager, Schäferhof.
C30/403	(d)	Navy Storage, Flemhude, Kiel.
C30/52	(e)	Kriegsmarinewerft, Achim, Bremen.

2. Research Institutes.

C30/307	(a)	Chemisch -Physikalische Versuchsanstalt der Marine, Dänisch Nienhof, near Kiel.
C30/404	(b)	Torpedo Versuchsanstalt - Nord, Eckernförde.

3. Manufacturers.

C30/3.18	(a)	Deurag-Nerag, Hannover - Misburg.
30/3.01	(b)	Rhenania-Ossag Mineralölwerke A.G., Hamburg - kl. Grasbrook.
C30/405	(c)	Ernst Schliemann's Oelwerke, Hamburg - kl. Grasbrook.
C30/55	(d)	Oelwerke Julius Schindler G.m.b.H., Hamburg - Neuhof.

C30/406 (e) Deutsche Vacuum Oel A.G., Wedel and Bremen - Oslebshausen.

C30/36 (f) Deutsche Erdölwerke A.G. Hemmingstedt.

C30/407 (g) Lüneburger Wachswerke A.G., Lüneburg.

C30/45 (h) Mineralölwerke F. Harmsen, Kiel - Hassee.

C30/58 (i) Vereinigte Asphalt- und Teerprodukten - Fabriken G.m.b.H. Shell Haus, Hamburg.

DATA ON INDIVIDUAL SAMPLES.

1. Blended Aviation Fuels.

- 1-7

No samples of any of these fuels were obtainable since all stocks had either been used or contaminated. Large samples have already been sent to Dr. Mason at the A.I.D. Laboratory.

- 8 MA 1 Experimental Fuel

This fuel was only blended in small batches. H. Stolte of Wifo, Hitzacker believed the composition was as follows :-

60%	VT 708
18%	Benzole
20%	ET 110
2%	Aniline
+0.16%	T.E.L.

2. Aviation and Motor Gasoline Components.

129/15 Inhibitor ZV1, 4½ gal., Wifo Grosstanklager, Schäferhof.

Sample drawn from a barrel.

118/16 Kybol, 2 litres, Wifo Grosstanklager, Hitzacker

Small laboratory sample only.

130/17 VT 330, 4½ gal., Wifo Grosstanklager, Schäferhof

Sample drawn from underground tank at Weser pump station.

131/17 VT 708, 2 litres, Wifo Grosstanklager, Schäferhof

Small laboratory sample only.

132/18 ET 120, 4½ gal., Wifo Grosstanklager, Schäferhof

Sample drawn from a barrel.

119/21 Ethyl Fluid - Blue, 2 litres, Wifo Grosstanklager, Hitzacker

Two engine tests cans available in laboratory store, seals unbroken and in packing case.

120/22 Ethyl Fluid - Green, 2 litres, Wifo Grosstanklager, Hitzacker

Two engine test cans filled from barrel marked 1-T Green.

3. Blended Lubricating Oils.

135/9 S3 Aero Lubricating Oil, 40 gal., Wifo Grosstanklager, Schäferhof.

Top sample from tank No. 114.

136/10 V2 (Aero Shell Mittel), 40 gal., Wifo Grosstanklager, Schäferhof.

Top sample from tank No. 119.

162, 163/11a Rotring (Duosol), 9 gal., Deutsche Vacuum Oel, Wedel.

This oil was manufactured in the Bremen Duosol plant.

164, 165/11b Rotring (half synthetic), 9 gal., Deutsche Vacuum Oel, Wedel.

Composed of equal parts of synthetic and mineral oil components.

The synthetic component could be either SS 1106 (Pölitz) or SS 906 (Leuna) of 5-6°E./100°C.

The mineral oil component, of viscosity 7°E./50°C., could be either Vacuum Duosol SS 707, Shell Edeleanu SS 607 or Nerag Furfural SS 807.

Since the stock from which the sample was obtained had been blended by Wifo, it is impossible to state which components were used. This oil is obviously the same grade as S3.

196/12 LP 295 III EN Torpedo Oil, 4½ gal., Dänisch Nienhof.

Composition stated to be :-

40% mineral oil 4-5°E. at 20°C.
29% " " 6.5°E. at 50°C.
15% normal Torpedo oil (Mixture of Neat's Foot Oil and Rape Oil)
10% Tricresyl phosphate
3% Paraflow

plus about 3% thickened rape oil.

Specification :

Appearance	clear
Colour	green (dyed)
Smell	mild
Mechanical impurities	none
S.G. at 20°C.	0.92 - 0.94
Viscosity °E. at 50°C.	3.1 - 3.7
" " 20°C.	12.0 - 14.0
Pole height	not more than 2.5
Flash Point (P.M.) °C.	not less than 150
Mineral acids	none
Neutralisation No.	not more than 0.4
Ash	" " " 0.05%
Behaviour at -30°C.	flowing
Behaviour after 1 hour at -40°C.	A sample of 50 cc. in a pour point glass must clarify after 30 min. at +20°C.
Pour Point	Below -40°C.
Ageing (Jentzsch) R 500	not more than 0.5%
R 500A	" " " 5.5%
h	" " " 3 mm. (Flocculent)
Lubricity on the torpedo brake	Drop in load not more than 1.3% in comparison with normal torpedo oil.

207/12 LP 295 III EN Torpedo Oil, 1 litre, Harmsen, Kiel

Composition as delivered to the Navy :-

10.2.43	1.2.45
15% Original torpedo oil	15% Original torpedo oil
3% Blown rape oil	3% Blown rape oil
10% Tricresyl phosphate	10% Tricresyl phosphate
3% Paraflow	72% Z.d.M.9
38% Spindle oil raffinate 5.2/20	
31% Machine oil raffinate 6.5/50	

LP 295E had also an addition of 3% Emulphor X.

Typical analysis :-

Appearance	clear
Colour	green
Smell	mild
S.G. at 20°C.	0.933
Viscosity °E. at 20°C.	12.35
" " 50°C.	3.15
Pole height	1.90
Flash Point °C.	163
Mineral acids	none
Neutralisation No.	0.23
Ash	0.0055%
Pour Point °C.	-43

199/13 ET 42 Torpedo Oil, 4½ gal., T.V.A. Eckernförde

Trackless grade.

The following information was obtained from Dänisch Nienhof :-

Contains 40% Clophen A (chlorinated diphenyl).

Specification :-

Appearance		clear and transparent
Colour		red (dyed)
Smell		mild
Mechanical impurities		none
S.G. at 20°C.		1.090 - 1.120
Viscosity °E. at 80°C.		2.1 - 2.3
" " 50°C.		5.8 - 6.5
" " 20°C.		35 - 45
Pole height		not more than 3
Flash Point (P.M.)		not less than 180°C.
Mineral acids		none
Neutralisation No.		not more than 0.4
Ash		" " " 0.05%
Behaviour after 1 hour at -30°C.		A sample of 50 cc. in a pour point glass must clarify after 30 min. at +20°C.
Pour Point °C.		below -30
Ageing (Jentzsch)	R 500	not more than 0.5%
	R 500A	" " " 5.0%
	h	" " " 3 mm. (flocculent)

225/13 ET 42 Torpedo Oil, 4½ gal., Harmsen, Kiel

Trackless grade.

Composition as delivered to the Navy.

1.11.43	8.2.45
6% Paraflow	2% Paraflow
25% Original Torpedo Oil	25% Original Torpedo Oil
29% Machine Oil Raffinate 6.5/50	33% Machine Oil Raffinate 6.5/50
40% Clophen A 60	40% Clophen A 60

Typical analysis :-

S.G. at 20°C.	1.100
Viscosity °E. at 20°C.	39.4
" " 50°C.	6.06
Pole height	2.65
Flash Point	215°C
Neutralisation No.	0.10
Ash	under 0.01%
Pour Point °C.	-33

197 LP 297 Torpedo Oil, 4½ gal., Dänisch Nienhof

The following data was given by Dänisch Nienhof :-

Composition :-

72% Z.d.M.7
10% Mineral Oil 4-5°E. at 20°C.
10% Cold test improver
5% Thickened rape oil
3% Mixture of 60 parts Emulphor X and 40 parts mineral oil 4-5°E. at 20°C.

Specification :-

Appearance	clear
Colour	yellow-red
Smell	mild
Mechanical impurities	none
S.G. at 20°C.	0.905 - 0.920
Viscosity °E. at 20°C.	38.0 - 45.0
" " 50°C.	7.0 - 7.8
" " 80°C.	2.4 - 2.8
Pole height	not more than 2.8
Flash Point DVM °C.	above 180°C.
Mineral acids	none
Organic acids given as % SO_3	0.05
Neutralisation No.	not more than 0.5
Ash	" " " 0.02%
Behaviour at -30°C.	flowing
-40°C.	A sample of 50 cc. in a pour point glass must be clear and flowing after 30 min. at room temperature.
Pour Point	below -35°C.
Ageing Test (Jentzsch)	
R 500	up to 0.5%
R 500A after 30 min.	" " 5.0%
Sludge height	" " 3 mm.
Sludge nature	flocculent, yellow to dark brown

Lubricity

All batches of over 20 tons must have a brake test made by the T.V.A. Gotenhafen.

110/39 Motorenöl der Wehrmacht-Summer, 4½ gal., Wifo Grosstanklager, Hitzacker.

Sample drawn from pump house of tank No. 129.

111/40 Motorenöl der Wehrmacht-Winter, 4½ gal., Wifo Grosstanklager, Hitzacker.

Sample drawn from pump house of tank No. 131.

115 Ul Lubricating Oil, 4½ gal., Wifo Grosstanklager, Hitzacker.

Sample drawn from pump house of tank No. 159.

194 Z.d.M.6 Lubricating Oil, 4½ gal., Flemhude.

Reclaimed Z.d.M.6-engine oil for diesel-engined high-speed boats.

195 Z.d.M.7 Lubricating Oil, 4½ gal., Flemhude.

Reclaimed Z.d.M.7-engine oil for diesel engines.

4. Lubricating Oil Components.

101/23 Oppanol Mixture, 10 gal., Deurag-Nerag, Hannover-Misburg.

Oppanol Gemisch B.15 supplied by the I.G. The quantity of pure oppanol in the mixture was not known but a method for its determination is given in Appendix 1. This sample was drawn and canned by the above firm.

116/23 Pure Oppanol, 10 lb., Wifo Grosstanklager, Hitzacker.

This sample was found in the laboratory and was stated to have been supplied for experimental purposes.

117/23 Oppanol Mixture B.15, 1 gal., Wifo Grosstanklager, Hitzacker.

Sample found sealed in sample store.

167, 168/23 Oppanol Mixture B.15, 9 gal., Rhenania-Ossag, Hamburg Kl. Grasbrook.

Sample drawn and canned by the above firm. In one report it is stated that it contains 50% Oppanol B.15 and 50% of mineral oil, type unknown, and in another that it contains

20% Oppanol and 80% Shell CY2. Supplied ready mixed by the I.G. Rhenania-Ossag ref. PP01569, 16.1.41,

Viscosity	°E. at	20°C.	approx. 500
"	"	90°C.	" 13

133/24 ZS1 Inhibitor, 4½ gal., Wifo Grosstanklager, Schäferhof.

Sample drawn from a barrel.

-/25 Polyisobutylene, Rhenania-Ossag, Hamburg-Kl. Grasbrook

Oppanol consists largely of polyisobutylenes and Rhenania-Ossag, like other lubricating oil manufacturers, obtained their supplies from the I.G.

169, 170/26 Paraflow, 9 gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Paraflow Extra. Sample drawn and canned by the above firm. Rhenania-Ossag ref. PP01675, 18.4.44.

Specification :-

Density at 20°C.	0.896
Flash Point (open)	185°C.
Pour Point	-22°C.
Neutralisation No.	0.4
Saponification No.	1.0
Viscosity °E. at 50°C.	6

219, 220/31 Wax for Synthetic Oil SS1006, 4 lb., Rhenania-Ossag, Hamburg-Harburg.

Laboratory sample available.

221, 222/32 Cracked Spirit, Polymerisation Feed Stock, ½ gal., Rhenania-Ossag, Hamburg-Harburg.

Laboratory sample available. SS1006 production.

171, 172/37a Endvoltol, 9 gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Samples drawn and canned by the above firm.

Endvoltol 25/100, Rhenania-Ossag ref. 29652, 6.10.37.

Composition :-

2/3 CY2 Diesel engine Oil Ref. 24595
1/3 Rape Oil, Ref. RE0803.

Specification :-

Density at 20°C.	0.922
Neutralisation No.	about 0.4
Saponification No.	" 60
Viscosity °E. at 100°C.	" 25

173, 174/37b Halbvoltol, 9 gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Samples drawn and canned by the above firm. Rhenania-Ossag ref. 29625, 26.9.41.

100% Voltolised rape oil.

Specification :-

Density at 20°C.	0.920
Flash Point (open) °C.	300
Neutralisation No.	1-2
Saponification No.	150-170
Colour (Union)	-4½
Viscosity °E. at 50°C.	40
" " 100°C.	8

134/34 SS 607, 4½ gal., Wifo Grosstanklager, Schäferhof.

Sample drawn from top of underground tank. For information see 175/34 below.

175/34 SS 607, 4½ gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Sample drawn and canned by the above firm. Rhenania-Ossag ref. 64970, 10.8.42.

Mineral oil component for aviation lubricating oil made by Rhenania-Ossag:

18% ref. 24971 Edeleanu Raff. 4/50
82% " 24973 " " 9/50
+0.1% ref. PP01581 Ozocerit

Specification :-

Density at 20°C.	0.902
Flash Point (open) °C.	240
" " (P.M.) °C.	225
Pour Point °C.	-30
Water	nil
Neutralisation No.	0
Asphalt	nil
Ash	nil

Colour (Union)	2½
Conradson	0.14
Viscosity °E. at 50°C.	7.5 - 8.0
Melting Point of Ozocerit	80 - 90°C.

210/35 SS 707, 10 gal., Deutsche Vacuum Oel, Bremen-Oslebshausen.

Sample drawn and canned by the above firm.

Duosol raffinate of viscosity 7°E. at 50°C. Made by Deutsche Vacuum Oel A.G.

-/36 SS 807, Deurag-Nerag, Hannover-Misburg.

No sample was available as none had been made since June 1944 on account of damage to the plant and all stocks had either been used or destroyed.

The following is the delivery specification as given by D. von Eynatten :-

The lubricating oil must be clear, free from water and mineral acids and contain no solid impurities. It is composed entirely of natural oil base stocks.

Density at 20°C.	Max. 0.897	
Viscosity at 50°C.	6.8-7.9°E. = 51-60 c.s.	
" 100°C.	Min. 1.77°E. = 9.35 c.s.	
Pole height	Max. 2.08	
Slope Constant	Max. 3.65	
V.I.	Min. 89	
Pour Point	Max. -16°C.	
Flash Point (open)	Min. 222°C.	
Ignition Point	Min. 258°C.	
Neutralisation No.	Max. 0.05	
Saponification No.	Max. 0.17	
Evaporation Residue (Noack)	Max. 12%	(weight)
Conradson Carbon Residue	Max. 0.3%	(weight)
Ash	Max. 0.01%	(weight)
Hard Asphalt	Nil	
Water	Nil	

Approximate composition: 35% Cylinder Oil from Nienhagen Distillate, propane deasphalted, double furfural solvent-extracted, clay treated and dewaxed: 65% Neutral Oil from Nienhagen crude, furfural solvent-extracted, V.G.C. 0.810, clay treated and dewaxed.

Typical inspection data on the components :-

Cylinder Oil

Density at 20°C.	0.901
Viscosity °E. at 50°C.	27.3
" " 100°C.	3.65
" S. 100°F.	2019
" S. 210°F.	130.8
V.I.	94
V.G.C.	0.822
Conradson Carbon Residue	0.73
Pour Point	-16°C.
Neutralisation No.	0.01
Colour (Union)	8+
Flash Point (open) °C.	296

Neutral Oil

Density at 20°C.	0.880
Viscosity °E. at 50°C.	3.8
" S. 100°F.	220
" S. 210°F.	47.5
V.G.C.	0.820
Pour Point	-18°C.
Neutralisation No.	0.02
Colour	2½+
Flash Point (open) °C.	217

114/37, SS 407, 4½ gal., Wifo Grosstanklager, Hitzacker.

Blending component made by the Oderfurter Mineralolwerke. Sample drawn from pump house of tank No. 163.

106-109/38, SS 1106, 18 gal., Wifo Grosstanklager, Hitzacker.

Synthetic blending component ex Pölitz.

Samples drawn from pump house of tank No. 147.

190, 191/42, SS 1006, 80 gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Synthetic blending component ex Rhenania-Ossag, Harburg.

Samples drawn and barrelled by the above firm and incorrectly marked 190, 191/30. Ref. 22947 or 32947, 30.3.42.

Specification :-

Density at 20°C.		0.877
Flash Point (open)	°C.	310
" " (P.M.)	°C.	295
Water		nil
Neutralisation No.		0
Asphalt		nil
Ash		under 0.01
Colour (Union)		-3½
Viscosity °E. at 20°C.		330
" " 50°C.		45
" " 100°C.		5.4

112, 113/43, SS 3500, 9 gal., Wifo Grosstanklager, Hitzacker.

Synthetic oil ex Ruhrbenzin.

Samples drawn from pump house of tank No. 157. For information see 176/43 below.

176/43, SS 3500, 4½ gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Synthetic oil ex Ruhrbenzin.

Sample drawn and canned by Rhenania-Ossag and incorrectly marked 176/42.

Specification, ref. 72996-41, 28.4.42.

Density at 20°C.		0.848
Flash Point (open)	°C.	215
" " (P.M.)	°C.	200
Pour Point	°C.	-50
Water		nil
Neutralisation No.		0
Asphalt		0
Ash		0
Colour (Union)		1
Conradson Carbon Residue		0.06
Viscosity °E. at 20°C.		29
" " 50°C.		6.3
" " 100°C.		1.8

161/44 Etrol C, 4½ gal., Deutsche Vacuum Oel, Wedel.

It consists of a mixture of highly sulphurised mineral oil and nitrochlorbenzene.

Double Duosol raffinate from Reitbrook crude is treated at elevated temperature with 15-20% sulphur. The sulphur appears to combine chemically and does not separate on cooling. Since this sulphurised oil was similar to "Faktis" products obtained by sulphurising rape oil, castor oil and other fatty oils, and double Duosol raffinate had the reference "EDS", this highly sulphurised mineral oil was given the works reference "EDS-Faktis".

Various mixtures of EDS Faktis and nitrochlorbenzene were prepared and were known as "Etrol". The most used mixture, which was mainly employed in the production of gear oils, was known as Etrol C. Its composition is :-

60% Nitrochlorbenzene
40% EDS - Faktis.

Gear oils had an addition of 1% Etrol C.

The sample obtained was drawn and canned by the above firm.

208/45 Hexathion, 1 lb., Deutsche Vacuum Oel, Wedel.

From its method of production and analysis this substance is believed to be oxyethyl thiocarbonicacid tetra-sulphide. Up to now it has only been made in the laboratory. Sulphur monochloride is reacted with sodium xanthogenate, the sodium chloride formed is removed, and the remaining liquid distilled under vacuum. A complete description of the method of preparation and application is given in the following patent specifications :-

D.92.925 IV/120
D.92.926 IVd/23c

The sample available had been standing in the laboratory for a long time and may have deteriorated.

127 Inhibitor r, 4 oz., Rhenania-Ossag, Shell Haus.

Small laboratory sample available.

137 Inhibitor s, 4 oz., Rhenania-Ossag, Shell Haus.

Small laboratory sample available.

5. Specialised Lubricating and Protecting Oils.

-/46 Rail Road Axle Oils, Deurag-Nerag, Hannover-Misburg.

No samples available on account of damage to plant. The following are the delivery specifications :-

(a) Summer Grade

Density at 20°C.	0.980
Visc. °E. at 50°C.	8-10
Flash Point	above 160°C.
Neutralisation No.	not above 2.5
Hard Asphalt	Max. 0.2% w.
Ash	Max. 0.3% w.
Rise in U tube	at least 10 mm. at -5°C.
Approximate Composition:	55% w. Nienhagen Furfural Cylinder Oil Extract
	45% w. Nienhagen Spindle Oil Distillate, dewaxed, pour point -17°C.

(b) Winter Grade

Density at 20°C.	0.980
Visc. °E. at 50°C.	4.5 - 8
Flash Point	above 140°C.
Neutralisation No.	not above 2.5
Hard Asphalt	Max. 0.2%
Ash	Max. 0.3%
Rise in U tube	at least 10 mm. at -20°C.
Approximate Composition:	36.4% w. Nienhagen Furfural Cylinder Oil Extract
	58.7% w. Nienhagen Spindle Oil Distillate, dewaxed, pour point -26°C.
	4.9% w. Propane asphalt

(c) D-Axle Oil

Density at 20°C.	<0.950
Viscosity °E. at 50°C.	>3.5
Flash Point °C.	>125
Hard Asphalt	<1.0% w.
Water	<0.2% w.
Ash	<0.3% w.
Rise in U tube	at least 10 mm. at -25°C.
Diesel fuel	<10% w.
Approximate Composition:	35.9% w. Nienhagen Furfural Cylinder Oil Extract and Furfural Extract from Nienhagen and Reitbrook Neutral Oils.
	49.5% w. Nienhagen Spindle Oil Distillate, dewaxed, set point -26°C.
	7.7% w. Propane Asphalt
	6.9% w. Straight-run Reitbrook Gas Oil or Cracked Gas Oil.

Components :-

Nienhagen Furfural Cylinder Oil Extract

Density at 20°C.	1.038
Flash Point °C.	281
Visc. °E. at 99°C.	39

Nienhagen Spindle Oil Distillate, dewaxed, set point -17°C.

Density at 20°C.	0.896
Visc. °E. at 20°C.	2.7
" S 100°F.	57.1
V.G.C.	0.850
Pour Point	-18°C.
Neutralisation No.	0.31
Colour	$3\frac{1}{2}$
Flash Point (open)	162

Nienhagen Spindle Oil Distillate, dewaxed, set point -26°C.

Density at 20°C.	0.878
Visc. °E. at 20°C.	2.8
" S. 100°F.	57.8
V.G.C.	0.852
Pour Point °C.	-28
Neutralisation No.	0.30
Colour	$3 - 3\frac{1}{2}$
Flash Point	163

Mixed Furfural Extract

Density at 20°C.	1.018
Flash Point °C.	224
Visc. °E. at 50°C.	29.6

Propane Asphalt

Density at 20°C.	1.027
Flash Point (open) °C.	above 330
Ring and Ball	50 - 58
Penetration	16 - 35

	Reitbrook Distillate Gas Oil	Cracked Gas Oil
S.G.	0.860	0.880
10% to °C.	232	213
50% " "	271	241
90% " "	312	287
Flash Point (P.M.) °C.	86	78
Pour Point °C.	-70	-40

The composition of all the grades of axle oil varied with the variation in the viscosity of the cylinder oil extract.

177/56 Metallschutzöl TL 6013, 4½ gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Shell Oil No. 3230.

Composition : (Rhenania-Ossag ref. 23230, 5.1.43)

59% 23806 Spindle Oil Raffinate
41% 23835 Light Machine Oil Raffinate

Specification :-

Density at 20°C.		0.893
Flash Point (open)	°C.	180
" " (P.M.)	°C.	165
Pour Point	°C.	below 0
Water		nil
Neutralisation No.		below 0.05
Asphalt		nil
Ash		below 0.01
Colour (Union)		3
Viscosity °E. at	20°C.	9.0
" "	50°C.	2.5

103/57 Waffenschmieroel TL 6021, 4½ gal., Fallersleben

Sample drawn from a barrel.

178/58 Stossdampferoel TL 6027, 4½ gal., Rhenania-Ossag, Hamburg-Kl. Grasbrook.

Shell Oil AB11, Hydraulic and Buffer Oil.

Composition : (Rhenania-Ossag ref. 24623, 5.3.45)

85% Spindle Oil Raffinate 6.5°E./20°C.
15% Spindle Oil Distillate 3.5°E./20°C.
16% Oleum
1% Caustic soda
3% Alcohol
3% Fuller's Earth
As buffer oil coloured violet.

Specification :-

Density at 20°C.		0.873
Flash Point (open)	°C.	160
" " (P.M.)	°C.	145
Pour Point	°C.	-40
as hydraulic oil		-50

Neutralisation No.	not above 0.05
Saponification No.	" " 0.15
Colour (Union)	-2
Viscosity °E. at 20°C.	about 5

102/59 Bremsool TL 6026, 4½ gal., Fallersleben.

Hydraulic brake oil. Sample taken from a barrel, marked Shell Oil AB11, 60/40, Rhenania-Ossag.

149/66 Schutzöl 39, 4½ gal., Schliemann.

Corrosion protecting oil, water soluble, TL 147. See 143/84g.

Sample supplied by Schliemann (made up specially as no stocks were available). The following data was obtained from Rhenania-Ossag, which probably does not refer to this particular sample.

Composition : (Rhenania-Ossag ref. 29155, 31.10.44)

39.0%	50/50 Resin/Spindle Oil Distillate blend
1.0%	Oleic acid
4.8%	40° Bé caustic potash solution
12.0%	Boring Oil HD
16.0%	Water
27.2%	Spindle Oil Distillate.

Specification :-

Pour Point °C.	about -10
Water	16%
Neutralisation No.	about 17
Viscosity °E. at 20°C.	25 - 40

183/79 Shell Special Oil 54, 4½ gal., Rhenania-Ossag.

Also briefing reference 55. Anti-corrosion oil for cooling systems.

Composition : (Rhenania-Ossag ref. 29160, 31.10.44)

41.0%	50/50 Resin/Spindle Oil Distillate blend
1.0%	Oleic acid
5.1%	40° Bé caustic potash solution
6.0%	Boring Oil HD
15.0%	Water
31.9%	Spindle Oil Distillate.

Specification :-

Pour Point °C.	about -20
Water	" 20%
Neutralisation No.	15 - 20
Viscosity °E. at 20°C.	30 - 40

125/84n Transformer Oil, 4½ gal., J. Schindler.

See report on B.I.O.S. trip No. 1248. Sample drawn from a rail tank car.

126/84p Turbine Oil, 4½ gal., J. Schindler.

See report on B.I.O.S. trip No. 1248. Sample drawn from a rail tank car.

138/84a Turbine Oil, 4½ gal., E. Schliemann.

See report on B.I.O.S. trip No. 1248.

139/84b Transformer Oil, 4½ gal., E. Schliemann.

See report on B.I.O.S. trip No. 1248.

141/84e Cutting Oil with Sulphur, 4½ gal., E. Schliemann.

Spindle oil distillate with 1-2% sulphur addition.

142/84f Cutting Oil with Sulphur and Fatty Acid, 4½ gal., E. Schliemann.

As 141/84e with up to 5% fatty oil.

143/84g Cutting Oil - Water Soluble, 4½ gal., E. Schliemann.

Sample made up specially as no stocks were available.

Composition :-

15% Sulpho naphthenic acid
76% Spindle Oil
2% Caustic soda solution 40° Bé
4% Alcohol
3% Water.

This had the following uses :-

(1) Water soluble cutting oil
(2) Boring oil
(3) General rust preventative
(4) Rust preventative 39
(5) Hydraulic oil
(6) Radiator protection
(7) Base for winter spray for fruit trees
(8) Wool industry.

144/84h Refrigerator Oil-Light, 4½ gal., E. Schliemann.

See report on B.I.O.S. trip No. 1248.

145/84j Refrigerator Oil-Medium, 4½ gal., E. Schliemann.

See report on B.I.O.S. trip No. 1248.

184/101 Schmiertel Hö. 4½ gal., Rhenania-Ossag.

Originally delivered from the I.G. Pour Point -2°C.

185/102 Hydraulic Oil Fl., 4½ gal., Rhenania-Ossag.

Fl. Druckoel/Shell Nero Hydraulic Oil.

Composition : (Rhenania-Ossag ref. 21490, 4.12.44)

98% gas oil
2% halb Voltol (29625)
+0.006% Fluorol 5.G.

Specification :-

Density at 20°C.		about 0.880
Flash Point (open)	°C.	at least 105
Pour Point	°C.	-60
Saponification No.		about 3.0
Viscosity °E. at	-50°C.	not above 200
" "	+20°C.	at least 1.6

186/103 Shell AB11 Green, 4½ gal., Rhenania-Ossag.

Composition : (Rhenania-Ossag ref. 24624, 10.11.44)

100% Spindle Oil Raffinate 25824
+0.05% Paraflow
+0.8% Green colour solution.

Specification :-

Density at 20°C.		0.890
Flash Point (open)	°C.	160
Pour Point	°C.	-50
Neutralisation No.		below 0.1
Ash		trace
Viscosity °E. at 20°C.		3.5 - 4.7

187/104 Shell AB11, Not Green, 4½ gal., Rhenania-Ossag.

Identical with 178/58 Stossdämpferöl TL 6027.

188/105 Shell Oil 1499, 4½ gal., Rhenania-Ossag.

Lens polishing.

Composition : (Rhenania-Ossag ref. 21102, 10.10.44)

95% Gas Oil
5% Cylinder Oil

Specification :-

Density at 20°C.		0.880
Flash Point (open)	°C.	above 100
Pour Point	°C.	under -70
Neutralisation No.		0.03
Saponification No.		0.14
Colour (Union)		2½
Viscosity °E. at 20°C.		1.5
" " 50°C.		1.2

189/106 Shell Product M2 Cutting Oil, 4½ gal., Rhenania-Ossag.

Boring Oil B. Gr. 1.

Composition : (Rhenania-Ossag ref. 29154, 30.11.44)

25.0%	50/50 Resin/Spindle Oil Distillate 5-6/20
9.0%	Naphthenic Acid
2.2%	Water
5.5%	40° Bé Caustic Potash Solution
13.8%	Spindle Oil Distillate 3/20
43.1%	" " " 5-6/20
1.4%	Alcohol.

Specification :-

1 : 10 emulsion satisfactory	
Neutralisation No.	15 - 20
Viscosity °E. at 20°C.	30 - 40

104 Aero MGT Oil, 4½ gal., Fallersleben.

Property of the Army. Sample taken from a barrel marked in addition "Hamic" and "frostsicher" (low cold test). MGT probably means machine gun turret. This oil may be equivalent to Waffenschmieröl Frostsicher, TL 6025B, briefing reference 60.

105 Oel f. Feinmechanik TL 6010, 4½ gal., Fallersleben.

Instrument Oil, sample taken from a barrel.

128 Shell Hypoid Gear Oil, 4 oz., Rhenania-Ossag.

Small laboratory sample.

160 Intava Waffenoel Blau, 4½ gal., Deutsche Vacuum Oel, Wedel.

Composition :-

67.7% Low pour point spindle oil distillate 1.7°E. at 20°C.

30.0% Low pour point spindle oil distillate 3.2°E. at 20°C.

2.0% EDS Faktis (see 161/44)
0.2% Nitrochlor benzene
0.1% Sudan blue G.

211 HWA TL 6023, 4½ gal., Achim.

No information.

223 Z.d.M.32, HWA TL 6025, 4½ gal., Achim.

No information.

224 Z.d.M.31, HWA TL 6024, 4½ gal., Achim.

No information.

6. Greases.

-/49 Flugzengfett Blau.

No sample but the following information was obtained from Rhenania-Ossag, ref. 26320, 7.1.44.

Composition : (c.f. 154/72)

8%	Dist. vegetable fatty acid
3%	Stearic acid
4%	Split fatty acid
2%	Endvoltol
2.5%	Lime
80.5%	Transformer oil 3.5-4.0/20

plus blue colouring.

Specification :-

Water	about 1%
Ash	2.5
Fat content	about 15%
Drop point (Ubbelohde) °C.	about 95

218/50 Thickened Oil, 2 lb., Rhenania-Ossag.

Containing Silica Gel K3B.

192/51 Silica Gel K3B, 10 lb., Rhenania-Ossag.

See report on B.I.O.S. trip No. 1248.

152, 153/54 Intava New Instrument Grease, 80 lb., Deutsche Vacuum Oel, Wedel.

Composition :-

5.4%	Stearin white 1a
1.1%	Montan wax St
1.0%	Lithium Hydroxide
0.6%	Glycerine (or Clycerogen)
91.9%	Low pour point Spindle Oil Raffinate, 4.2°E./20°C.

The grease is rose coloured by the addition of 0.04% Sudan orange and 0.02% Sudan red.

148/61 Schutzfett 40, 20 lb., Schliemann.

TL 6017. See report on B.I.O.S. trip No. 1248. The sample was made up specially as no stocks were available.

The following data was obtained from Rhenania-Ossag relevant to their own manufacture of Schutzfett 40 Tp/Shell corrosion protecting grease H.

Composition : (Rhenania-Ossag ref. 28405, 27.1.43)

10.0%	Ozocerit
1.4%	Caustic soda solution 36° Be
88.6%	Cylinder oil, 6°E./100°C., set point 0°C.
Drop point (Ubbelohde) °C.	above 75

214/62 Waffenfett, 20 lb., Achim.

Manufactured by the Schlafhorst Chemische Werke. Probably to TL 6006 specification.

The following data was obtained from Rhenania-Ossag relevant to their own manufacture of weapon grease.

Composition : (Rhenania-Ossag ref. 26228, 14.1.41)

8.0%	I.G. wax S
8.0%	I.G. wax TV
4.0%	Wool fatty acid
4.5%	Caustic soda solution 36° Bé
2.5%	Aluminium hydroxide
75.5%	Machine oil raffinate 25°E./50°C.

Specification :-

Neutralisation No.	0
Ash	2.0
Fat content	16.0
Drop point (Ubbelohde) °C.	150

193/63 Instrument Grease, 20 lb., Rhenania-Ossag.

TL 6009.

Composition : (Rhenania-Ossag ref. 26408, 3.11.44)

8.0% Stearic acid
1.35% Lithium hydroxide
90.65% Spindle Oil Distillate 3.9°E./20°C.

Specification :-

Neutralisation No.	about 0.5 alk.
Drop Point (Ubbelohde) °C.	" 180

-/65 Kuhlstoffpumpenfett

TL 147/745. No sample. The following data was obtained from Rhenania-Ossag.

Water pump grease/aircraft cooling-liquid pump grease.

Composition : (Rhenania-Ossag ref. 26384, 30.3.43)

16.0% Fatty acid second runnings
4.0% Ozocerit
0.2% Acetic acid
3.0% Lime
76.8% Machine oil distillate 4.5°E./50°C.

Specification :-

Water	not above 2.0%
Ash	" " 3.8%
Drop Point (Ubbelohde) °C.	90 - 95
Fat content	about 20%

-/67 Schutzfett 401

TL 147/770. No sample. The following data was obtained from Rhenania-Ossag.

Shell corrosion protecting grease L.

Composition : (Rhenania-Ossag ref. 28404, 19.3.42)

30% Wax feed stock, M.P. 52°C.
50% Cylinder Oil 6°E./100°C.
10% Ozocerit
10% Wax, M.P. 58 - 60°C.
Drop Point (Ubbelohde) °C. about 60

-/68 Schutzfett 40H

See 148/61.

217/70 Calypsol Grease, 20 tubes, Achim.

Grade 285.

154/72 Intava Blue Aircraft Grease, 40 lb., Deutsche Vacuum Oel, Wedel.

Composition : (c.f. -/49)

17.8%	Mixed tallow
2.5%	Calcium hydroxide
79.7%	Low pour point Spindle Oil Raffinate 3.2°E./20°C.
+0.05%	Sudan blue G.

204/73 Invarol Grease. 5 lb., Harmsen, Kiel.

Invarol Grease PX, 30.6.43.

60%	Shell Oel AB11
30%	Nova Oil (Schwechat)
10%	Synthetic Oil R.2000

Specification :-

Drop Point	147°C.
Cold Test	-36°C. solid
Consistency	0.9C kg./20

158 Vacuum Grease 1238, 40 lb., Deutsche Vacuum Oel, Wedel

Composition :-

5%	Emulsifying Wax PS
5%	Hard Fatty Acid
1%	Sodium Hydroxide
89%	Machine Oil Distillate 6.5°E./50°C.

159 Vacuum Stiff Grease B3, 40 lb., Deutsche Vacuum Oel, Wedel.

Composition :-

8.1%	Crude Montan Wax
2.9%	Split Fatty Acid
2.9%	Last Run Fatty Acid
1.6%	Calcium Hydroxide
C.7%	Sodium "
83.8%	Spindle Oil Distillate 2.5°E./50°C.

203 Ball Bearing Grease, 4 lb., Harmsen, Kiel.

Probably Grade No. 1011a - 1072 for civilian use.

4.3.45

11%	Technical Tallow
1%	I.G. Wax O
2%	Synth. Fatty Acid
1%	Calcium hydroxide
42%	Extract Oil
43%	Machine Oil Dist. 4.1°E./50°C.

5.5.45

10%	Technical Tallow
5%	Oil Fatty Acid
2%	Calcium hydroxide
83%	Machine oil raffinate 4.5°E./50°C.

This grease may satisfy the Z.d.M.21 Ball Bearing Grease Specification :-

Drop point		above 150°C.
Flow point		140°C.
Ash		not greater than 2%
Water		" " " 0.5%
Consistency at	-15°C.	1.9
	+20°C.	0.7
	+70°C.	0.6
Oil Separation at 75°C.		not more than 0.5%
Neutralisation No.		0.5 mg. KOH/g.

Change in the consistency data for Z.d.M.21 :-

at -15°C.	not more than 3
at +70°C.	not less than 0.5

205 Machine Grease, 4 lb., Harmsen, Kiel.

No. 1010a for civilian use.

8.1.43

6%	Crude Montan Wax
8%	Synthetic Fatty Acid
2%	Marble Calcium hydroxide
84%	Spindle Oil Distillate 2.5/20

10.11.45

15%	Oil Fatty Acid
2%	Calcium hydroxide
83%	Machine Oil Distillate 4.5/50

206 Red Lubricating Grease, 4 lb., Harmsen, Kiel.

1071a for civilian use.

24.5.43

13%	Technical Tallow
2%	Calcium hydroxide
2%	Crude Montan Wax
4%	Last Run Fatty Acid
79%	Spindle Oil Raffinate 2.5/20

30.3.45

15%	Oil Fatty Acid
2%	Lime
83%	Machine Oil Distillate 4.5/50

212 Meteorfett, 10 lb., Achim.

Specification :-

Colour	grey-black
Appearance	opaque
Reaction	weakly alkaline
Ash	1.7%
Lime in ash	present
Saponification No.	25.63
Fatty Oil (calculated)	13.42%
Separation	none
Smell	soapy
Flow Point	82°C.
Drop Point	85°C.
Water content	0.4%
S.G. at 20°C.	0.840

213 Korrosionfett, 10 lb., Achim.

Corrosion protecting grease.

215 Flugzengfett, 15 lb., Achim.

Aircraft grease.

216 Verschlussfett, 20 lb., Achim.

Sealing grease for guns.

Specification :-

Colour	red-brown
Appearance	opaque
Ash	2.29%
Lime in ash	present
Saponification No.	13.5
Fatty Oil (calculated)	7.1%
Separation	none
Reaction	alkaline
Boiling test with HCl :	
After colour with reflected light	yellow
" " " transmitted light	yellow
S.G. at 20°C.	0.898
Viscosity °E. at 20°C.	6.3

7. Bitumen Products.

Laboratory samples were made up specially by the Vereinigte Asphalt- und Teerprodukten-Fabriken, Shell Haus, Hamburg and Harburg as follows :-

246, 247 Euphalt U/Bitumuls U

Unstable bitumen emulsion for road construction.

Recipe (2 ton charge) :

1020 Kg. Bitumen (Ebano 200) are thoroughly mixed with 16-20 Kg. Stearin Pitch at a temperature between 100 and 110°C. The following are mixed in the water measuring vessel: 980 Kg. water, 12 Kg. 50% Caustic Potash and 1 Kg. Soda. They are warmed to 65-70°C. and led into the agitator. Finally the bitumen mixture is passed into the alkaline water with agitation during a period of about 10 minutes.

238, 239 Euphalt H/Bitumuls H

Semi-stable bitumen emulsion for road construction.

This emulsion is produced from the unstable emulsion U by adding 3% of emulsifier MP and thoroughly stirring.

Emulsifier MP is a resin-soap solution of the following composition :-

25% w. Bressin resin
7.5% w. Caustic Potash Solution (33%)
67.5% w. Water.

The above are boiled with stirring until the complete solution of the Bressin resin is obtained.

244, 245 Euphalt S/Bitumuls S

Stable emulsion for road construction.

Produced from unstable emulsion U by adding 5% of emulsifier MP and thoroughly stirring.

228, 229 Eubit Paste

Insulating coating - emulsion basis.

Composition :-

8 parts Kassel Brown (humic acid powder) are dissolved by short boiling in 17 parts water with the addition of 1.3 parts ammonia (S.G. 0.91). The humic acid is converted to the calcium salt by the addition of 2.6 parts of 33% calcium chloride solution. Into this product, at a temperature of 40-45°C., 50 parts of Ebano 3 at 100°C. are slowly run in with vigorous agitation. As soon as half the bitumen has been stirred in 5 parts of water are added. When all the bitumen is stirred in the mixture is made up to 100 parts (weight) by the addition of water at 20°C.

242, 243 Eukabit A

Insulating coating - solution basis.

Composition :-

24% w. H.V.B. 80/90
26% w. Panmex 1
2% w. Stearin Pitch
48% w. Solvent Benzine.

The bitumen is melted together with the stearin pitch at about 140-150°C. and stirred to a uniform consistency. The mixture is then cooled to about 110°C. and the Solvent Benzine added slowly while stirring.

240, 241 Eukabit D

Roof coating - solution basis.

Composition :-

75% Ebano 6 is warmed to about 90-100°C. and 25% Solvent Benzine dissolved in it by stirring.

232, 233 Eukabit K

Insulating coating for green fodder and potato silos.

Composition :-

25% Panmex 13
25% Ebano 1
1% Montan Wax
49% Solvent Benzine

The bitumen is melted together with the montan wax at about 150°C. and stirred to a uniform consistency. After cooling to about 110°C. the solvent benzine is slowly stirred in.

230, 231 Eukabit - Spachtelmasse

Roof repairing compound - solution basis.

Composition :-

10% Panmex 13
50% Panmex 11
4% Stearin Pitch
36% Solvent Benzine

The bitumen and stearin pitch are melted together at about 150°C. and stirred to a uniform consistency. The solvent benzine is then stirred into the mixture, cooled to 100-110°C.

To 75% parts of the above 25% parts of waste asbestos fibre are stirred in.

234, 235 Dachklebemasse

Hot working sealing compound for millboard roofs.

Composition :-

50% Ebano 6
10% Dark Mineral Oil
40% Panmex 11

The above are stirred together at 130-140°C. to a uniform consistency.

226, 227 V.A.T. Schalungsöl A

Cement stripping oil.

Composition :-

16 parts of neutralised sulphite waste liquor 32° Bé are warmed to about 20-25°C. and passed into an agitator. Then 50 parts of slack wax at about 40°C. are slowly fed in, the rate being such that the total time is at least 25-30 minutes. Stirring is continued until a jelly-like paste is produced. Finally a suspension of 2 parts of Bentonit in 32 parts of water (temp. about 20°C.) is stirred in.

236, 237 Calol F

Wood impregnating medium.

Composition : (4 ton charge)

360 kg. of neutralised sulphite waste liquor 32° Bé is heated to about 25°C. and fed into an agitator and 800 kg. slack wax (35-40°C.) is added over a period of at least 25-30 minutes. Agitation is continued until a jelly-like emulsion is produced. A suspension of 60 kg. of Bentonit in 840 kg. of water at 25-30°C. is then fed in, slowly at first and then quickly, with agitation. The following solution is then stirred in: 80 kg. of sodium fluoride, 80 kg. of zinc chloride lye 70° Bé, 200 kg. of ammonia S.G. 0.91, in 1540 kg. of water.

8. Miscellaneous Products

179, 180/76a Lubricating Oil Extract, 9 gal., Rhenania-Ossag.

Bulked extract from Austrian Oils.

Rhenania-Ossag ref. 25390, 1.11.40.

Density at 20°C.	1.120
Neutralisation No.	3.8
Viscosity °E. at 50°C.	37
" " 100°C.	3.8

181, 182/76b Lubricating Oil Extract, 9 gal., Rhenania-Ossag.

Lubricating Oil Extract from 22506.

Rhenania-Ossag ref. 25206, 6.7.44.

Density at 20°C.		0.990
Flash Point (open)	°C.	170
Pour Point	°C.	-30
Neutralisation No.	for 29329	max. 0.5
	for 29325	max. 1.5
Ash		0
Viscosity °E. at 50°C.		2.6

166/77 Reitbrook Crude Oil, 40 gal., Deutsche Vacuum Oel, Wedel.

198/78 Heide Crude Oil, 40 gal., Hemmingstedt.

209 Nienhagen Crude Oil, 40 gal., Deutsche Vacuum Oel, Oslebshausen.

The above title covers mixtures of north-west German paraffinic crude oils, in particular, Hänigen, Oberg and Nienhagen. The properties vary according to the proportions of the different components.

-/80 Optan 35

Tank No. 26 at the Wifo Grosstanklager, Hitzacker, containing Optan 35, had been penetrated by heavy bombs. There were special difficulties in obtaining a sample of the material still in the tank and, on account of the doubtful value of a sample, none was taken.

123/81 Roxyl G, 4½ gal., Wifo Grosstanklager, Hitzacker.

Technical Xylene. An average sample was taken through the manhole cover of tank No. 25.

121/82 Opthyl 70, 4½ gal., Wifo Grosstanklager, Hitzacker.

Sample drawn through manhole cover of tank No. 22. The tank was nearly empty and there was water present. The sample was attacking the internal paint of the jerricans but no other suitable containers were available.

122/83 Opturan 60, 4½ gal., Wifo Grosstanklager, Hitzacker.

Sample drawn through manhole cover of tank No. 23. Other remarks as 121/82.

140/84d White Oil for Ointments, 4½ gal., Schliemann.

Ointment oil was produced from paraffinic spindle oil distillate, refined with sulphuric acid and treated with 30-40% acid and about 3% clay. It is of light yellow colour and cloudy and served in the production of ointments, hair oils and similar preparations. No special specification was laid down.

146/84k Tallow Substitute, 30 lb., Schliemann.

This product was made from refined petrolatum (brought to a dark green colour with 10% Fuller's Earth) and 15% of synthetic fatty acid last runnings. It is very tenacious and shows unusual pressure withstanding properties. It was used in the metal industries where these properties were valuable such as in pressing and cold drawing, and in the light metal industry for cold forming.

147/84l Vaseline, 30 lb., Schliemann.

See report on B.I.O.S. trip No. 1248.

124/84m White Liquid Paraffin, 4½ gal., Schindler.

Sample drawn from a barrel. For further information see report on B.I.O.S. trip No. 1248. Feedstock ex Nerag.

151/109 Naphthenic Acid - Sodium Salt, 4½ gal., Schliemann.

For water soluble cutting oils.

150/111 Winter Spray Oil, 4½ gal., Schliemann.

Specially prepared laboratory sample as no stocks were available. Water soluble oil.

Composition :-

70% Spindle Oil Distillate 2/50
19% Sulpho-Naphthenic Acid
3% Resin
5% Crude Cresol
3% Alcohol
3.5 Caustic Soda Solution 40° Bé.

Used at the beginning of the year in a 5-8% emulsion as a spray on fruit trees.

155 Nachlauffettsäure, 4½ gal., Deutsche Vacuum Oel, Wedel.

Fatty acid last runnings. This material was obtained by vacuum distillation of oxidised wax.

First runnings - Used for washing and wetting agents.
Middle " - Used for soap manufacture.
Last " - Used for grease manufacture.

According to the quality of the feed stocks for the wax oxidation and the plant conditions so the quality of the fatty acid varied. The last runnings contained in general fatty acids with more than 18 carbon atoms. Different deliveries were distinguished by consistency and saponification no.

156, 157 Emulgierwachs PS, 40 lb., Deutsche Vacuum Oel, Wedel.

Produced by the I.G. and believed to be synthetic.

It was used in the production of greases and boring pastes and other emulsifiable metal-working products.

200 Oxidation Hard Synthetic Wax, 5 lb., Lüneburger Wachswerke.

See report on B.I.O.S. trip No. 1248.

Fischer-Tropsch wax oxidised using Kolophonium.

201 Phlegmatisierungswachs, 5 lb., Lüneburger Wachswerke

See report on B.I.O.S. trip No. 1248.

Fischer-Tropsch wax oxidised using special catalyst.

202 Fischer-Tropsch Synthetic Wax, 100 lb., Lüneburger Wachswerke

Originating from either :-

Rheinpreussen, Bad Homberg or

Ruhrchemie A.G., Oberhausen - Holten, or I.G.

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104	Aero MGT oel	"	"	20
105	Oel f. Feinmechanik TL 6010	"	"	20
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108/38	"	"	"	11
109/38	"	"	"	11
110/39	Motorenoel d.W. Summer	"	"	7
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112/43	SS 3500 lubricating oil	"	"	12
113/43	"	"	"	12
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115	U I " "	"	"	7
116/23	Pure Oppanol	Small Box	"	7
117/23	Oppanol B 15	5 litre can	"	7
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148/61	Schutzfett 40	"	"	22
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156	Emulgierwachs PS	"	" "	32
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158	Vacuum Fett 1238	"	" "	24
159	Vacuum Starrfett B 3	"	" "	24
160	Waffenoel blau	20 l. can	" "	20
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216	Verschlussfett	"	" "	26
217	Calypsol grease	20 tubes in box	" "	24
218/50	Thickened oil containing Silica gel K 3 B	Tin	Rhenania-Ossag	21
219/31	Wax for synthetic oil SS1006	"	" "	8
220/31	" " " " "	"	" "	8
221/32	Krackbenzin	Bottle (1 litre)	" "	8
222/32	"	" "	" "	8
223	Z.d.M.32, HWA TL 6025	20 l. can	Kriegsmarine Werft Achim	21
224	Z.d.M.31, HWA TL 6024	"	" "	21
225/13	ET 42 Torpedo Oil	Jerrican	Harmsen, Kiel	5
226) 227)	Schalungsoel	small tin	V.A.T.	29
228) 229)	Eubit Paste	" "	"	27
230) 231)	Eukabit Spachtelmasse	" "	"	28

Serial No.	Sample	Quantity	Source	Page No.
232) 233)	Eukabit K	small tin	V.A.T.	28
234) 235)	Dachklebemasse	" "	"	29
236) 237)	Calol F	" "	"	29
238) 239)	Euphalt H	" "	"	27
240) 241)	Eukabit D	" "	"	28
242) 243)	Eukabit A	" "	"	28
244) 245)	Euphalt S	" "	"	27
246) 247)	Euphalt U	" "	"	27

INDEX TO PRODUCTS OF WHICH SAMPLES WERE NOT OBTAINABLE

While in the case of certain products mentioned in the briefing instructions samples were unobtainable, it was possible to obtain information on them. These are listed below.

APPENDIX

ESTIMATION OF OPPANOL IN OIL MIXTURES

20 g. of the mixture to be examined is placed in a pear-shaped centrifuge vessel of capacity 125 cc. and dissolved in 100 cc. of amyl alcohol by shaking.

The solution is then centrifuged at normal room temperature at about 5000 r.p.m. until it is quite clear. The time taken is dependant on the oil but in general is 30-60 minutes.

The clear solution is then poured off and the residue washed with 10 cc. of amyl alcohol. The Oppanol, separated as a residue on the glass walls, is dissolved in 10 cc. of thiophene-free benzene at the temperature of boiling water and, without removing it from the centrifuge vessel, is concentrated to 3 cc. To the benzene solution is then added 20 cc. of amyl alcohol a little at a time and the whole recentrifuged. The separation should this time be completed in about 10 minutes. The clear solution shall then be poured off and the residue washed twice with 10 cc. of amyl alcohol.

The Oppanol cannot be weighed in the centrifuge vessel on account of the difficulty in removing the remains of the amyl alcohol. The Oppanol is redissolved in benzene and poured into a weighed glass dish. The dish is then placed on an electric hot plate to evaporate off the amyl alcohol and benzene, placed in a drying oven at 105°C. for half an hour, cooled in a desiccator and weighed.

There are oils which have the unusual tendency of partial inclusion with the separated Oppanol. Such can be recognised by the yellow colour of the Oppanol. It is then necessary to repeat the second separation in the centrifuge vessel after solution in benzene.

Misburg 3.3.42.

Translator's Note. Some modification to the quantities will be necessary to estimate Oppanol in Oppanol blending mixtures containing 25% Oppanol and over.

D 63604-1 1,350 D/d R.122 5/46 R.R.P.

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BIOS Final Report No. 511
Item No. 30

RUHR-CHEMIE A. G. STERKRADE HOLTEN

INTERROGATION OF DR. O. ROELEN

Withers, J. G. and West, N. L.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON - H.M. STATIONERY OFFICE

RUHR-CHEMIE A.G. STERKRADE HOLTEN

Interrogation of Dr. O. Roelen at Wimbledon
November 15th and December 20th 1945

Reported by :

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

H.L. West, British, Ministry of Fuel and Power.

B.I.O.S. Target No. 30/ 5.01

Fuels and Lubricants

(1946)

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

Note see p. 1

27 p. diags.

CONTENTS

ACKNOWLEDGEMENT.

Translations of Dr. Roelen's reports, reproduced in this report, were made by K.G.C. Kirkpatrick.

1. INTRODUCTION.

This report gives translations of three documents prepared by Dr. Roelen of Ruhr Chemie A.G. at Wimbledon over the period November 15th - December 20th 1945.

2. THE FISCHER-TROPSCH SYNTHESIS AND ITS PRODUCTS.
BY DR. OTTO ROELEN.

A. Various Catalysts and Their Conditions of Use.

(1) 'Synthol'
(2) Ruthenium as a Catalyst
(3) The 'Iso'-Synthesis
(4) Nickel Catalysts.

B. Iron Catalysts.

(1) Historical Development
(2) Peculiarities of the Iron Synthesis
    (a) Possible variations
    (b) Hydrogenating power
    (c) Boiling range
    (d) Amount of branching
    (e) Formation of oxygen-containing products.

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    (b) Working period
    (c) Reactor regeneration
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    (a) General characteristics
    (b) Gasol
    (c) Benzine
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    (e) Hydrocarbons of high and extremely high molecular weight.

D. Future Possibilities.

A. Various Catalysts and Their Conditions of Use.

(1) Synthol

As early as 1923 it was shown by Fischer and Tropsch that a complicated mixture of alcohols, esters, ketones and other oxygen-containing compounds can be obtained from water-gas using alkalised iron at pressures of 100 atm. and above. This mixture is called Synthol.

(2) Ruthenium as a Catalyst.

Fischer and Pichler found that ruthenium is an excellent catalyst for the synthesis of high and very high molecular paraffin hydrocarbons. At 100 atm. pressure, for example, the use of ruthenium produced the biggest hydrocarbon molecule so far obtained, one having well over 100 carbon atoms in the molecule.

The work was confined to the initial laboratory experiments because of shortage of ruthenium.

(3) The Iso-Synthesis.

More recently, it was found by Fischer and Pichler that, under certain conditions, using thorium dioxide as catalyst, strongly branched chain or cyclic hydrocarbons can be obtained directly from carbon monoxide and hydrogen.

The working conditions that must be maintained are not simple; they are among others, high temperatures, e.g. 400 °C.; high pressure, e.g. 100 atm. and above, as well as complete absence of even traces of metals of the iron group, particularly iron itself.

These severe conditions supply the reason why the iso synthesis has so far been restricted to the laboratory scale, although the products are very interesting, e.g. high-octane benzine, naphthenes and aromatics.

During the war we tried to erect a semi-technical plant at Ruhrchemie for the iso synthesis, but could not obtain the necessary special steel high pressure equipment.

(4) Nickel Catalysts.

In 1931 it was discovered by Fischer and Meyer that like cobalt and iron, Ni can bring about the formation of higher hydrocarbons than methane from carbon monoxide and hydrogen. This action also takes place at normal pressure. Nickel catalysts were perfected to such an extent as to produce more than 100 g. of liquid products per cubic meter of synthesis gas on passing the latter only once through the system.

Successful semi-large scale work has been done with such catalysts, but these have two great drawbacks which cannot be overcome :

a. They produce mainly saturated hydrocarbons and only small amounts of olefines.

b. More methane is formed than with cobalt or iron catalysts so that the same maximum yield cannot be obtained.

For these reasons all trials with nickel catalysts were given up and have not since been re-commenced.

B. Iron Catalysts.

(1) Historical Development.

The Fischer-Tropsch synthesis was first carried out using an iron-zinc oxide catalyst in 1925. From then on, research was continued for four years at the Kaiser Wilhelm Institut für Kohlenforschung at Mühlheim in the Ruhr, using chiefly iron catalysts, until it was discovered in 1929 that cobalt catalysts could be much more easily and rapidly developed to give the highest yields.

Only during the war, when cobalt became increasingly scarce, was iron again tried in the Fischer-Tropsch process. Work was based on the extensive experiments made during the development of the cobalt synthesis, above all when using the increased working pressures which had been introduced in the intervening period (medium pressure synthesis at 10 to 20 atm.). In a comparatively short time, considerable progress was made. Soon iron catalysts were known which gave yields equal or even surpassing those obtained with cobalt. However, owing to various factors, the development of iron catalysts was still in full swing at the end of the war and had to be broken off at a particularly interesting and promising stage.

When research with iron catalysts was renewed, the temperatures employed were at first about 300° to 250°C. Later iron catalysts were found for temperatures of about 230° to 250°C. A large scale plant for Italy (Arezzo) was based on this. The problem arose to replace cobalt by iron in the German plants already extant. The maximum temperature which could be reached in these installations was only 225°C. This necessitated the development of new and considerably more active iron catalysts effective below this maximum temperature. This, too, was substantially achieved, but at first only for the medium pressure synthesis.

Even this, however, came very recently to be regarded as insufficient and the aim was to fill the normal pressure synthesis reactors with iron catalyst. Usable iron catalysts fulfilling all the requirements of normal pressure synthesis are not yet known, although good progress has also been made in this direction. Although it is possible to obtain good yields with iron catalysts at normal pressure and below 225°C. there is one main difficulty (apart from the present unavoidable production of more low boiling products and methane). This is that CO_2 is formed and not water as with cobalt. This leads to a considerably larger volume of residual gas and consequently to quite different conditions in all the pipe lines, reactors, separators etc. after the first stage reactor.

At medium pressures (10 atm. and above) water formation can be successfully brought about at the present time with iron catalysts, at least to the degree necessary in the conversion of water gas with a CO : H_2 ratio of 1 : 1.25. Thus the position is now, that the known iron catalysts at working temperatures below 225°C. are quite suitable for medium pressure syntheses but not for those at normal pressure. Consequently all the following data on iron catalysts relates to working pressures of 10 to 20 atm.

(2) Peculiarities of the Iron Synthesis.

(a) Possible variations.

The chemistry of iron catalysis is considerably more complex than that with cobalt. On the one hand, this involves greater developmental difficulties but on the other hand, there are more varied possibilities. Even today, so many products can be obtained using iron catalysis, that it is only possible to cite merely a few as typical. Only examples for the limiting possibilities can be given, between which there can be produced all manner of intermediate stages. The details are as follows :

(b) Hydrogenating power.

The hydrogenating power of the 3 metals of the iron group diminishes strongly in the order Ni, Co, Fe. Thus nickel, when used as a Fischer-Tropsch catalyst, gives only saturated hydrocarbons together with quantities of methane, while iron yields most easily more olefines and less methane. Cobalt occupies an intermediate position.

In the case of iron, the hydrogenating power can be altered by the composition and mode of production of the catalyst, either to fall to a minimum or to increase, e.g. by small additions of copper or nickel. Since the degree of saturation of the products can be influenced by the CO : H_2 ratio as well as by the mode of working (once-through or circulating), it is possible when using iron catalysts to produce either predominantly saturated or highly olefinic hydrocarbons, e.g. in a range of 10 to 90% olefines.

Only mono-olefines are produced, mainly those with a terminal double bond.

(c) Boiling range.

The use of iron catalysts gives the greatest latitude in adjusting the boiling range of the products. Predominantly low boiling or predominantly high molecular or the highest molecular hydrocarbons can be produced with all kinds of intermediate stages. This is exemplified in the following compositions:

	Benzine (200 °C.)	Heavy Oil 200-230 °C.	Soft Wax 320-460 °C.	Hard Wax over 460 °C.
(i)	81%	13%	6%	
(ii)	59%	24%	14%	3%
(iii)	17%	16%	17%	50%

All the above figures are from semi-large scale trials.

(d) Amount of branching.

As yet, no exhaustive knowledge of the degree of branching with the higher hydrocarbons from the iron synthesis is available. For one thing, there are no sufficiently simple and reliable analytical methods for carrying out large numbers of serial estimations with these high molecular hydrocarbons.

Further, the so-called "branching numbers" obtained up to now, e.g. using antimony pentachloride, are not regarded as sufficiently trustworthy. None the less, there are several unobjectionable observations which show that more strongly branched products are obtained in the iron synthesis. Among other compounds, we produced a primary benzine (up to 200°C.) with the octane number 72, the careful fractionation of which revealed the unmistakable presence of the corresponding iso-hydrocarbons.

(e) The formation of oxygen-containing products.

Whereas with nickel or cobalt catalysts, oxygen-containing by-products are produced either not at all or only in quite small amounts, very variable quantities are formed with iron catalysts, according to conditions; indeed so much may occur that it may be regarded as a means for a direct synthesis of higher primary alcohols from water-gas. (What is under consideration here is a synthesis of mixtures of higher alcohols of the most varied molecular weights at medium pressures. This should not be confused with the synthesis of e.g. isobutanol with oxide catalysts at high pressures, circa 200 atm., developed from the methanol synthesis). Besides the alcohols, large amounts of esters are formed, but less aldehydes and acids. The ratio of these products to one another as well as their total quantity is strongly dependant on the composition and mode of preparation of the catalyst as well as on experimental conditions. For example, the proportion of oxygen compounds in the total product can vary from 5% through all proportions to about 70% and more.

All these oxygen compounds are saturated. So far, there is no reliable confirmation of the occurrence of compounds containing both oxygen groups and olefinic double bonds.

C. Cobalt Catalysts.

(1) State of Development.

In contrast to the iron catalysts, the development or cobalt catalysts reached a definite conclusion a long time ago. A certain cobalt catalyst was recognised as the best chemically and technically at that time and has been manufactured since then in large quantities, its composition and mode of preparation remaining unchanged.

The products obtained with this so-called "cobalt mixed catalyst" (100 Co : 5 ThO_2 : 10 MgO 200 Kieselguhr) can therefore be more precisely described as regards yield and properties.

It must be added that a series of variations are also possible here, depending on the conditions of synthesis. Further variations in the liquid products are also made possible by reason of advances made recently in laboratory trials with catalysts, namely the development of types of cobalt catalyst which contain as an activator, either manganese (among other metals), or exclusively magnesium. The pure magnesium catalysts yield more low boiling hydrocarbons, while the cobalt catalysts containing manganese yield considerably more high molecular hydrocarbons.

We have also succeeded in preparing and testing successfully on the semi-technical scale, cobalt catalysts which not only convert the oxygen of the carbon monoxide exclusively into water, but also, to a considerable extent, into carbon dioxide. This represents a further possibility of processing carbon monoxide-rich gases with cobalt catalysts and obtaining correspondingly varied products.

All the following treatment refers solely to the normal Co - Th - Mg - Kgr mixed catalyst.

(2) <u>The Relation of the Products to the Conditions of Synthesis</u>.

(a) <u>Working pressure</u>.

The pressure at which the synthesis is carried out can have a considerable effect on the course of the reaction. An increase from atmospheric pressure to about 10 to 20 atm. (medium pressure) brings about a substantially increased formation of high and very high molecular hydrocarbons. In contrast to normal pressure synthesis, this does not involve clogging the catalyst with wax and so bringing conversion to a standstill. Thus medium pressure synthesis makes possible the continuous formation of high molecular solid hydrocarbons.

If the distribution of the molecular sizes of the hydrocarbons formed is altered, either by means of the catalyst or the conditions of synthesis, then the change does not generally occur regularly throughout all the molecular groupings. It is much more usual for the low boiling and highest molecular fractions to disappear or increase, while the quantity of the mean molecular weight compounds (heavy oil 200-320°) remains more or less unchanged (about 15 to 30%). For this reason no real diesel oil synthesis has been achieved so far, either with the normal pressure or the medium pressure process, although more benzine or hard wax may be preferentially produced.

(b) Working period.

Catalytic activity, as measured by gas conversion or from the yield, gradually decreases in the course of running. This can be counteracted to some extent by gradual temperature increase. After 4-6 months, however, this measure no longer succeeds and the catalyst must be renewed.

In order to keep down costs, or for other reasons, the catalyst may be used as long as possible. Or, in order to maintain unvarying conditions and maximum yield the catalyst may be changed after a certain life period, without using up its residual activity. Both methods, and variations of them, were used, according to the needs of the moment.

The working period influences not only the yield, but also the quality of the products. With increasing length of working, the hydrogenating power decreases (because of wax clogging, partial poisoning by unremoved sulphur in the gas etc.). This leads to an increase in olefine content. Similarly, the proportion of low boiling hydrocarbons rises (because of the higher working temperature, among other reasons).

(c) Reactor regeneration.

In the course of normal pressure synthesis, the high molecular wax which collects in the catalyst must be removed from time to time, e.g. by solvent extraction, by hydrogenation using hydrogen, by combining these two methods or by some other procedure. This regeneration varies greatly from works to works, depending on local conditions.

The frequency and thoroughness of the regeneration process in removing the reactor wax is reflected in the state of the catalyst filling and consequently, depending on circumstances, also in the quantity and quality of the product. In general, however, this influence is not very great.

(d) Mode of running.

Alteration of the running conditions can cause considerable changes in the relative proportions and constitution of the hydrocarbons formed. The process may be run either in one or two or more stages one following on the other. Between the separate steps, only condensible higher hydrocarbons and water may be separated, or the lighter hydrocarbons (benzine, gas-oil) now remaining in the vapour can also be removed. The gas can be passed once through the system or parts of it can be re-cycled to a greater or lesser extent. Re-cycling can be carried out with or without removal of the benzine or gas-oil.

All these steps influence the course of the synthesis more or less strongly and not only as concerns the total amount of yield. It is above all, a matter of olefine behaviour. These can react further during a lengthy stay in the reaction zone and become either hydrogenated or take part in the formation of higher hydrocarbons. Thus all conditions tending to decrease the length of time spent by the reaction products in the reaction zone increase the proportion of low boiling and olefinic hydrocarbons.

(e) Gas composition.

With the Co.Th.Mg.Kgr. catalyst, higher hydrocarbons are formed fairly closely to the equation :

$$CO + 2H_2 \longrightarrow (CH_2)_x + H_2O.$$

Correspondingly, normal synthesis gas contains carbon monoxide and hydrogen in the ratio of 1 : 2. This is maintained as closely as possible in the synthesis plants, mainly in view of the yield, but also on chemical grounds. If, for example, excess hydrogen is present it accumulates in the final gas and causes increased formation of methane and light hydrocarbons as well as hydrogenation of the olefines. Conversely, the production of olefines and higher hydrocarbons is favoured by increasing the carbon monoxide content. This is hardly practicable with a simple through passage of the gas, since carbon separates from undiluted carbon monoxide rich gas and soon renders the catalyst inactive.

This trouble can be avoided in the medium pressure synthesis by re-cycling gases rich in carbon monoxide, i.e. using them diluted. For example, the process may be carried out in several stages, starting with ordinary water-gas having a CO : H_2 ratio of 1 : 1.25, circulating it and attaining the CO : H_2 ratio of 1 : 2 before the last stage of addition of hydrogen or hydrogen rich converter gas and then working up the residual gas. In this way conditions favourable to olefine formation are combined, namely, a larger CO content than corresponds to 100 : $2H_2$ and decreased time in the reaction zone. This method of working makes possible the manufacture of products containing a considerably higher proportion of olefines with even the normal Co.Th.Mg.Kgr. catalyst. Such olefines are extremely valuable for further chemical processing.

A medium pressure, water gas, circulating plant of this type was being built by Ruhrchemie at Oberhausen-Holten and was nearly complete, but never came into operation.

(3) The Products of the Cobalt Synthesis.

(a) General characteristics.

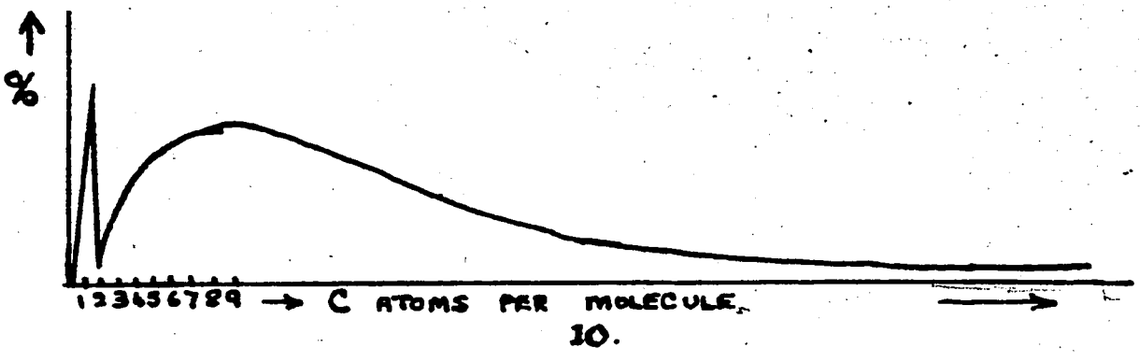
The products of the cobalt synthesis contain no carbon ring compounds, i.e. no naphthenes or aromatics. Only very small amounts of oxygen containing compounds are formed as by-products and simple, effective, methods are available for their removal.

A continuous, uninterrupted series of aliphatic hydrocarbons is produced, from methane up to high molecular hydrocarbons with 100 and more carbon atoms in the molecule. The only exception is the two C_2 hydrocarbons, the quantity of which is vanishingly small (ethane and ethylene).

The hydrocarbons formed are partly olefinic, but mainly saturated. The olefines are always mono-olefines, those with a terminal double bond predominating. The content of olefines with the double bond elsewhere is greater, the longer they are submitted to the action of the catalyst.

As was shown in section 2, although the same catalyst may be used throughout, the boiling range and degree of saturation may undergo more or less big changes for the most varied reasons, depending on the working conditions. Naturally, this is very evident on comparing the products of different plants, but can also be observed at a single plant. This fact should be kept in mind when any numerical data are being weighed up.

The following curve represents the approximate distribution of molecular size that can occur with normal pressure synthesis :



63604-2

The greater part of the hydrocarbons are straight chain molecules. The amount of iso-compounds increases with the size of the molecule. Of course, there is no marked branching but probably, at the most, only methyl groups or short branch chains. The individual isomers have been isolated and identified up to about C_6.

(b) Gasol.

Under the name Gasol are grouped together those hydrocarbons which do not condense at normal pressure and temperature, i.e. mainly C_3 and C_4. They can be removed from the residual gas simultaneously with the light benzine, by using, for example, activated charcoal, and then separated by fractionation. Compressed in steel cylinders, they can be sold as auto-fuel. If desired, the olefinic portion may be removed beforehand for use in various chemical processes, e.g. polymerisation, etc.

(c) Benzine.

The benzine fraction boiling up to 200°C., e.g. 62% with about 30% of olefines, has only a low O.N., because of the chemical structure of these hydrocarbons, and cannot be used unprocessed as a fuel. There are many ways of overcoming this. Blending with higher knock-rating fuels from other sources may be resorted to, e.g. with benzol, polymerisation benzines etc. Certain fractions may be leaded with good results as can be seen from the following examples :

	O.N. of the fraction :		
	E.B.P. 125°	E.B.P. 150°	E.B.P. 180°
unleaded	62	57	47
+ 0.5 ml./lt. T.E.L.	76	73	67

The O.N. may also be increased by catalytic treatment of the benzine so as to displace the olefinic double bond. In the originally formed hydrocarbons the double bonds are almost completely terminal. This does not correspond, however, to the equilibrium of the various isomers. It is therefore possible catalytically to displace the double bond to the middle of the molecule, which brings about a marked improvement in O.N. (This is the so-called "hot refining" process (Heissraffination)).

(d) Diesel oil.

The chemical structure of synthetic heavy oils is such as to give outstanding combustion behaviour in diesel engines, e.g. maximum ease of ignition, clear exhaust even at overload, somewhat smaller consumption (because of the high hydrogen content), very smooth combustion etc. Synthetic diesel oils can therefore be very successfully blended with heavy oils from other sources which are unsuitable or unsatisfactory when used alone as diesel fuels. The greatest use was made of this possibility in Germany. It was found that the properties of the blending components were markedly improved as regards ease of ignition, pour point, viscosity, sulphur content etc. A well fractionated synthetic diesel fuel (200-320 °C.) has usually a sufficiently low pour point so that no special de-waxing, e.g. by solvent extraction is necessary. The viscosity is usually too low (about 1.18 °E.) so that it is convenient to add a small amount of lubricating oil if the unblended product is to be used. Sulphur is absent, as it is not contained in the source. The acid by-products are removed by washing with caustic solution.

The cetane number of the 200° - 320 °C. fraction is above 70, that is considerably higher than with any commercial diesel fuel. It can therefore be used for testing the ease of ignition of other such fuels, and for this purpose Ruhrchemie prepared a standardised hydrocarbon fraction designated "RCH - Reference - Diesel Oil" which was delivered to the various centres carrying out engine tests for ignition quality.

"RCH Reference Diesel Oil" was also used in the analytical estimation of the asphaltic compounds separating from blends of oils from different sources. Its use here was based on the fact that this pure paraffinic oil gives the maximum precipitation of such compounds.

The cetane used for comparison purposes in the estimation of ease of ignition, was prepared from naturally occurring materials not obtainable in Germany. Ruhrchemie prepared a substitute called "RCH Cetane" which consisted of a closely cut hydrogenated fraction of synthetic hydrocarbons boiling near 300 °C. and whose cetane number was continually tested so as to remain at 100. This "RCH Cetane" was eventually in general use throughout Germany.

The length of the C-atom chain in the 180 °-320 °C. fraction lies in the region of those fatty acids and fatty alcohols necessary for the manufacture of soaps and sulphonated washing media. By means of the Oxo synthesis, the heavy oil olefines mentioned can be converted to such fatty acids or

alcohols with very good yields. Intensive tests showed that the synthetic soaps and washing media prepared in this way behaved excellently. Consequently, a large scale Oxo plant was under construction at Holten for the manufacture of fatty alcohols from the heavy oil olefines produced in the medium pressure, water gas re-cycling synthesis. This plant did not reach the operating stage, however.

(e) Hydrocarbons of high and extremely high molecular weight.

Hydrocarbons exceeding Diesel oil in molecular weight are also formed. They are obtained either as distillation residues from the products continually leaving the reaction chambers or, by extraction, from the catalyst filling. The lower members of these hydrocarbons are barely liquid or are even solid at ordinary temperatures. The highest members have more than 100 carbon atoms in the molecule with melting points above 100 °C. They are processed according to the particular use in mind.

They can be changed to lower molecular olefines by cracking, more recently with only small gasification and considerable control of the molecule size required. The olefines so obtained have proved to be particularly valuable raw materials for further chemical treatment, e.g. in the manufacture of anti-knock benzine, synthetic lubricating oil, higher alcohols of the most diverse nature, plasticisers, solvents, washing media etc.

Large quantities of the 320°-460 °C fraction were delivered as crude paraffin wax to the "Märkische Seifenindustrie" Witten - Ruhr, which produced fatty acids therefrom, by means of atmospheric oxidation, for soaps and cooking fats.

The higher molecular primary hydrocarbons can also be separated by physical means, e.g. by fractional distillation or melting etc., according to size of molecule and the products so obtained may be used as such. Fractions with a narrow melting point range, e.g. 50-52 °C., are designated block wax and are at least equal in quality to commercial products from different sources known by the same name.

Still higher fractions form the various kinds of so-called hard wax. The different varieties vary according to mode of preparation and degree of refining, in melting point, colour, hardness etc. Special qualities may be developed by blending different fractions, e.g. plastic waxes from high and low melting point components.

The applications of these products were very numerous, especially since during the war substitutes had to be found for similar products from natural sources (the manufacture of candles; floor and shoe polishes; water proofed materials, such as paper; oxidation to high molecular acids for emulsifying agents, etc.). It was discovered, however, that the market for hard waxes is not without limit and that the quantities produced in the Fischer-Tropsch plants exceeded the amount wanted for processing in Germany.

There is no difference between products of this type from normal pressure and medium pressure synthesis, except in the relative quantities of molecules of different sizes.

D. Future Possibilities.

The development of the catalytic hydrogenation of carbon monoxide, especially that occurring in the Fischer-Tropsch process, has so far taken place almost exclusively in Germany. It has therefore been very greatly influenced by special conditions, e.g. by the requirements and scarcities of war. The technical level attained can not therefore be taken without comment as a measure even of the present potentialities of catalytic carbon monoxide hydrogenation in other and possibly more favourable circumstances.

It may be assumed that new plants will differ from those already extant, apart from general technical improvements; that in addition to fuel they will furnish increasing amounts of raw material for further chemical treatment. A pointer to this is the increased production of olefines and definite oxygen containing compounds of the most varied nature. Probably the catalytic hydrogenation of carbon monoxide will become the raw material basis for completely new branches of the chemical industry.

Wimbledon - London 10.12.45.

3. SYNTHETIC LUBRICANTS MADE BY RUHRCHEMIE A.G.

A. Olefine Polymerisation.

Experiments on the preparation of lubricating oils by olefine polymerisation were carried out by Dr. Clar. He has compiled an extensive report giving his results which is already in the hands of the Military Government, so that it is not necessary to say any more here.

The large scale plant in Holten was directed by Dr. Goethel.

B. Lubricants from Fatty Acids.

Small quantities of fatty acids are formed directly as by-products of the Fischer-Tropsch synthesis. They are removed as a crude solution in the course of the alkaline washing of the hydrocarbons. Besides the soaps in question, these crude solutions contain iron, hydrocarbons, very malodorous compounds etc.

The extraction and use of such fatty acids was dealt with in various ways at the synthesis plants. The main deciding factor was whether the crude solution was from the crude condensate or from the hydrocarbon fraction after distillation. In the first case a mixture of lower and higher fatty acids results, which it is necessary to separate. The second case is simpler. For example, the diesel oil fraction even gives fatty acids in the crude alkaline solution whose molecular size lies substantially in the saponaceous fatty acid range.

The fatty acids removed from the diesel oil fraction in this way were sent originally, in the crude solution, to the firm of Th. Goldschmidt, Essen. Goldschmidt made a drawing grease from them, using a DRP method, which grease was then sent to wire works etc. Later, Ruhrchemie itself undertook the processing of the diesel oil crude lye. We made tablet soap from it, which was given to the works personnel, who were very pleased with its quality.

At other plants, greases for industrial purposes were prepared from these fatty acids.

C. Lubricants from 'OXO' Products.

(1) Lubricating Oil Carboxylic Acids.

By means of the "OXO" synthesis it is quite easy to prepare aldehydes from the olefinic lubricating oils derived from the $AlCl_3$ olefine polymerisation. These aldehydes are always one carbon atom higher than the original hydrocarbon and can be converted into the corresponding carboxylic acids by atmospheric oxidation. Such compounds are completely new, containing on the one hand a carboxylic group, and on the other hand, a hydrocarbon stem which has itself the properties of a high quality lubricant. Experimental trials with these substances were just commencing, so that only laboratory results are so far available.

(a) Esterification.

The lubricating oil carboxylic acids can be esterified with lower alcohols, as with ordinary fatty acids. In this way, lubricants can be obtained combining the advantages of both synthetic lubricant and ester oil structure. This is especially so when branched chain "OXO" alcohols are used for esterification. The lubricating oil carboxylic acids can be esterified with lubricating oil alcohols, produced by the hydrogenation of the corresponding aldehydes. This yields very high molecular ester oils.

(b) Lubricating oil carboxylic acid soaps.

Analogous to the fatty acids, the lubricating oil carboxylic acids form salts, with characteristic properties, soluble in mineral oil. These can be used both as additives in the usual way, and in grease manufacture. The soaps of sodium, calcium, lead etc., are among those so utilised. Special mention may be made of the jelly-like aluminium soap which can be drawn out into extraordinarily fine threads.

A blend of synthetic oil with lubricating oil carboxylic acid soaps when tested in the test gear at Rheinmetall, Düsseldorf, proved to be an excellent gear oil.

(2) Lubricating Greases and Boring Oils from 'OXO' Fatty Acids.

(a) The "OXO" synthesis renders it easy to prepare from olefinic hydrocarbons, fatty acids with one more carbon atom. This is a simple way of making the various soaps, e.g. of sodium, calcium etc., which are used in the normal way for grease manufacture.

(b) The production of synthetic boring oils via the "OXO" synthesis is particularly simple. The starting material is the olefine containing heavy oil fractions which can be obtained both directly from the Fischer-Tropsch synthesis and also by cracking the high molecular hydrocarbons. Probably olefinic mineral oil fractions can also be used.

Water-gas is condensed with these olefines by means of the "OXO" synthesis. The crude aldehydic product plus the calculated quantity of lime is stirred, while air is blown in. On warming, the calcium soap is formed and immediately dissolves in the unchanged saturated hydrocarbons. After completion of the reaction, the mixture of calcium soap and mineral oil can either be used as such, or water may be added, whereby stable emulsions are readily formed. Practical results with cutting and boring oils of this type were excellent.

(3) Ester Oils.

By means of the "OXO" synthesis, the corresponding carboxylic acids and alcohols are prepared from olefinic hydrocarbons of the appropriate molecular dimensions. The two are utilised to form esters with one another in the normal way and then freed from unchanged hydrocarbons by distillation. Excellent ester lubricating oils are obtained in this manner.

For example, cracking olefines yielded ester oils which besides having a good pole-height etc., possessed pour points of -70^{c} and below. Such low pour points are a consequence of the nature of the ester oils prepared as described, since they consist of blends of countless different isomers.

(4) Hydraulic Liquids and Similar Compounds.

(a) Ester oils.

If correspondingly low molecular olefines are used, then ester oils may be obtained (as described under 3) which are suitable for use as hydraulic fluids etc.

(b) "Isols"

An additional method for the production of hydraulic and similar fluids is provided by the possibility of preparing a large number of mixes of isomeric, branched primary alcohols and their derivatives (e.g. esters). This can be done by condensing the aldehydes obtained in the "OXO" synthesis, by the action of alkali or some other means, to give aldols. On hydrogenation, the latter form branched chain alcohols. Such

mixtures of branched primary alcohols are termed "Isols" and have already been prepared in considerable numbers and in quantities up to semi-large scale production. Their low vapour pressure and pour point are among their distinguishing features.

(c) The large number of possible combinations permits of the preparation of the greatest variety of hydraulic fluids, brake oils, buffer oils, recoil oils etc., all based on the "OXO" process. The physical properties of such oils can, within very wide limits, be adjusted as required so that, to a large extent, an oil can be made to suit any particular requirements.

London - Wimbledon, 11.12.45.

(signed) Roelen.

4. TOWN GAS AND METHANISED GAS FOR AUTOMOTIVE PROPULSION BY DR. OTTO ROELEN.

A. Untreated Town Gas and Coking Gas.

(1) Organisation
(2) Technical Installations.
(3) Uses.
(4) Operational Results.

B. Methanisation.

(1) Historical Development.
(2) Technical Details.
  (a) Gas purification.
  (b) Methane synthesis.
  (c) The methanisation of gases rich in carbon monoxide.
  (d) Catalyst equipment.

(3) Operational Results.
  (a) Methanisation plant.
  (b) Gas constitution.
  (c) Compressors and automotive vehicles.
  (d) Summary.

A. Untreated Town Gas and Coking Gas.

In 1935 the first long distance journey with a gas driven omnibus supplied from steel cylinders was undertaken by Director Dr. Traenker of Ruhrgas A.G., Essen. The gas supply for the whole journey from Essen to Koenigsberg (East Prussia) was contained in steel cylinders stored in a trailer. There were no difficulties. This run proved that the use of town gas for automotive propulsion was a practical proposition.

Further development was concerned primarily with the building up of a filling station network. This was done in conjunction with the already existing filling station organisations for liquid fuels, such as that of the Benzol Verband, Bochum. These installed the gas filling stations for public supply, which were fed among other methods, by long distance gas pipe lines, e.g. from the Ruhrgas A.G.

In addition, the larger cities and industrial plants had their own gas filling stations for car parks.

(2) Technical Installations.

Only a comparatively small number of vehicles depended on gas supply at normal pressure, e.g. in "balloons". The great majority carried the gas at high pressure in steel cylinders or, more recently, in spherical steel containers of various designs.

The high pressure gas filling stations had compressors (Demag, Duisburg) working to a maximum of 300 atm. Large supply reservoirs were filled at this pressure. The output was 180 c.m./hr. per unit or a multiple of the same.

Besides the gas cylinders, reduction valves and mixing apparatus were built into vehicles running on gas fuel. Latterly such equipment became very simple in design.

(3) Uses.

The chief use of compressed town gas was in lorries and, secondly, in private cars. It was not used in military vehicles. The gas was also used for running-in engines. It was planned in 1944 to use compressed and methanised town gas on a large scale for running in tank engines.

(4) Operational Results.

Town gas and coking gas contain a series of impurities which proved capable of causing considerable trouble.

Part of these impurities have a more or less strong corrosive action, e.g. on the walls of the steel cylinders. Hydrocyanic acid (HCN) was particularly dangerous in this respect. There were two ways of combating these difficulties. Firstly, by storage in large reservoirs for at least several hours after compression. During this time the water drops containing the corrosive agents in solution had a chance to settle. Because of the big demands made on the gas filling stations, this precaution could not always be properly carried out. Secondly, the gas was subjected to intensive cooling after leaving the compressor and before entering the storage vessels so as to separate water and all condensable constituents as far as possible.

Another part of the impurities caused deposits, gum formation, incrustations etc. This lead to valve trouble in automotive engines and piston ring sticking in the compressors. This latter was particularly unpleasant and was a definite disadvantage. The compressor repairs which became necessary continually put the gas filling stations out of action after more or less short running periods.

B. Methanisation.

(1) Historical Development.

There are a series of drawbacks to the use of compressed but otherwise unaltered town gas for automotive fuel. They are partly technical and partly fundamental in origin and led to the consideration of the possibility of catalytically converting the carbon monoxide and hydrogen content to methane. The grounds for such a methanisation were as follows :

(a) The calorific value of the gas per unit volume is much increased. Consequently the same volume of gas gives a greater radius of action and refueling is less frequent or for the same distance the dead weight of the containers is less.

(b) The same filling station can supply more fuel with unchanged compressor performance.

(c) The careful gas purification prevents corrosion and compressor disturbances.

These advantages were the reason for a questionnaire directed to German industry in 1941 as to whether filling station methanisation appeared possible with the technical resources then available. The unanimous reply from the industries in question was negative, for the following reasons:

(a) No practical method of sufficient simplicity was known for the purification of town gas in small filling stations, with intermittent running, to the extent necessary for catalytic hydrogenation of carbon monoxide.

(b) No sufficiently active catalyst was known which could produce methane at sufficient speed at a low enough temperature in small simple reaction vessels using water as coolant.

(c) It was thought impossible to interrupt the synthesis at will, without upsetting the gas composition and without tiresome supervision.

When Ruhrchemie A.G., (Oberhausen) was asked, I said that the problem could probably be solved. Work was immediately commenced, in autumn 1941. By June 1942 the first plant in Altenessen was put into operation and worked satisfactorily until destroyed by air attack in autumn 1944.

Based on this experience, Ruhrgas-Essen and Ruhrchemie Oberhausen undertook jointly, the practical application of the process, whereby Ruhrchemie supplied the catalysts and Ruhrgas looked after the building and operation of the plants. The first mass-produced type of plant was installed at Opel-Ruesselsheim and gave trouble free operation until it too was destroyed by air attack.

Further plants did not pass the constructional stage.

(2) Technical Details.

(a) Gas purification.

The chief difficulty in developing the process lay in purification of the gas. None of the large number of methods already proposed and described could simply be taken over. The method used for water gas, that of attaining a high degree of purity by using ferric oxide alkaline carbonate (Roelen and Feisst) is not suitable for distillation gases such as town gas. Catalytic decomposition of the organic sulphur compounds has been known for a long time and has already been used technically. But the catalytic action, flow rate and life period were insufficient for filling station methanisation.

At first we achieved satisfactory results with a catalyst containing finely divided copper. Later we discovered a simple solution by using the spent nickel catalyst from the methane synthesis. The spent catalyst was submitted to a comparatively simple after treatment for this purpose, but complete regeneration was not necessary.

The gas stream after passing through 1.5 liter of this catalyst at 425° with a velocity of 1 c.m./hr., is then cooled and freed from hydrogen sulphide with an ordinary gas purifying filling.

The degree of purity attained was sufficient with a catalyst life period of about 1500 working hours. A vessel containing activated charcoal was coupled on and could be regenerated with steam in the usual way.

(b) Methane synthesis.

We were soon able, with our experience of the Fischer-Tropsch synthesis, to evolve a new nickel catalyst with maximum activity for methane synthesis. This catalyst, which has given very satisfactory results, contains magnesium as activator and is precipitated on kieselguhr by means of soda. The flow velocity is 1 c.m./hr. through 1.2 to 1.5 litres of catalyst, whose life period may safely be reckoned at 500 uninterrupted working hours.

The very low reaction temperature is also noteworthy. Earlier methane syntheses required temperatures or 300° and above, with a minimum of 250 . According to Fischer and Tropsch, higher hydrocarbons are formed below temperatures suitable for methane synthesis. Thus Fischer and Meyer prepared higher hydrocarbons with nickel catalysts at 185° . It follows, that to produce methane the lowest possible temperatures are 200° and above. Our new synthesis worked, however, at 170°-190°, and without forming even a trace of the objectionable higher hydrocarbons, a proof of the extraordinary activity of the new RCH nickel catalyst.

The synthesis can also be carried out at the increased pressure present in the long distance gas pipe lines, e.g. the Altenessen plant worked at 6 atm.

(c) <u>The methanisation of gases rich in carbon monoxide.</u>

Gases of town gas quality contain a proportion of hydrogen varying inversely with the carbon monoxide content. Thus as the latter increases, the proportion of hydrogen decreases. The methane synthesis, however, works best with the greatest possible excess of hydrogen. Consequently, coking gas, which besides 5-8% of CO containsmore than 50% of H_2 can be methanised without further treatment. Town gas containing more than 10% CO (10-18% CO) on the other hand, must have this percentage brought below 10% to avoid trouble from carbon separation, carbonyl formation etc.

The conversion takes place in the same temperature range as the catalytic decomposition of the organic sulphur compounds and brings about such decomposition itself, to a certain extent. This allows both processes to be combined in one step, without enlarging the total catalyst space. It is merely necessary to lead the CO rich gas (carrying the corresponding quantity of steam) first over the conversion catalyst and then, at the same temperature, over the decomposition catalyst. For conversion, one of the known commercial catalysts can be employed. It is used to replace the first half of the decomposition catalyst. The remaining procedure is unchanged.

(d) Catalyst Equipment.

There is only an insignificant heat change during the partial conversion of town gas as described above. The catalytic decomposition of the organic sulphur compounds takes place with absolutely no measurable heat change. Consequently, simple cylindrical containers without any special arrangements for cooling may be used. All that is required is the heating up of the gas, for which heat exchangers may be used and the maintenance of a fixed temperature by means of automatic regulators.

On the other hand, the methane synthesis itself with its great heat of reaction necessitates, like the Fischer-Tropsch synthesis, careful leading away of the heat evolved and temperature regulation within very narrow limits. This did not represent much of a problem for us; we had only to take over the catalyst equipment developed for the Fischer-Tropsch synthesis and modify it to comply with the special requirements of filling station methanisation. The latter applies especially to additional equipment making it possible to stop or start the process at any time as desired, without causing any trouble or change in gas composition.

We used water tube boilers, the nickel catalyst being inside the tubes. The water cycle was heated from outside during shut down periods and cooled during running. Both processes were automatically controlled so that the temperature remained constant, within 1°-2°. The advantage of being able to use comparatively simple catalyst vessels cooled by water under pressure is a consequence of the low working temperature (below 200°) of our nickel catalyst.

(3) Operational Results.

(a) Methanisation Plant.

This can be set up besides existing gas tanking equipment in a comparatively small space. No further personnel are required for its maintenance than the filling station staff already available. Skilled labour is necessary only for changing the chemical fillings. Such labour can naturally deal with a large number of similar plants in turn, one after the other.

Supervision of the process involves merely readings of temperature and pressure and adjustment of a temperature regulator where necessary, as well as control of the water of reaction which runs away. The quantity of the latter immediately gives the output.

The life period given above was far surpassed in practice, indeed it was almost doubled. There was no trouble during a running time of several years, not even when sulphur occasionally came through from the coking plants. The Altenessen plant was one of the few sources of fuel during the heavy air-raids on Essen, when it was working uninterruptedly.

(b) Gas composition.

A coking gas with about 6% CO content was delivered to the Altenessen plant. After methanisation the CO + CO_2 content was certainly less than 1%. Carbon dioxide was thus likewise converted into methane. Sulphur hydrocyanic acid, oxides of nitrogen or other impurities could no longer be detected.

The calorific value rose from 4200 K.cal./c.m. to about 6000 K.cal./c.m.

(c) Compressors and vehicles.

Whereas compressors working with unchanged town gas were always put out of action by piston trouble after short running periods, such stoppages were completely absent with methanised gas. The process was a complete success.

Damage due to corrosion was also no longer met with.

The mixing devices in the vehicles had to be altered to suit the higher C.V. gas. When this was done, complete satisfaction was expressed by all users.

(d) Summary.

The advantages expected from the introduction of filling station methanisation were all realised in practice It was therefore decided in 1944 to provide 120 gas filling stations with the equipment. Immediately a contract was placed for 40 plants, but it was not carried out.

London - Wimbledon. 13.12.45.

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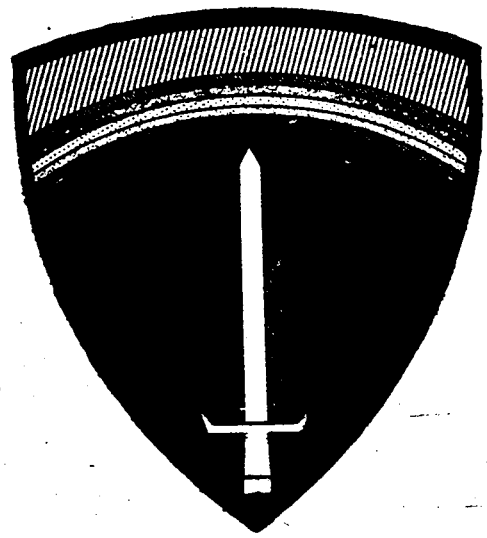
FIAT FINAL REPORT 600

AIR FILTERS
AND
OIL FILTERS FOR ENGINES

Bogue, L.E., Ed Haertz, Norman



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FIAT FINAL REPORT NO. 600 — 12 March 1946

AIR FILTERS AND OIL FILTERS FOR ENGINES

BY

L. E. BOGUE
Norman HOERTZ

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Data on the manufacture of all kinds of filters used on German vehicles to determine whether practice or production was materially different than in the United States. There were only two manufacturers of filters for engines. Principles employed are old but some of the constructions and design are interesting.

INTRODUCTION

An attempt was made to cover the manufacture of filters of all kinds used on German vehicles with the idea of determining whether practice or production was materially different than in the United States. Information obtained indicated that there were only two manufacturers of filters for engines, of any consequence, as covered in this report.

The principles employed are old, but some of the constructions and design are interesting.

PART I

Knecht Kem. Ges. Manufacturers Oil Bath Air Filters and Oil Filters for engines of all types.

Mr.Alfred Knecht, owner, stated that his company and Man & Hummel, Ludwigsburg, were the only manufacturers of filters in Germany.

Figures 7 and 8 show a sectional assembly of their Cyclone (Zyclone) Oil Bath Air Filter used on Maybach Engines in tanks. This filter assembly was on the 300 H.P. engine and two of them were used on the 700 H.P. engine used in the Tiger Tank. Mr.Knecht claims it is 99½% efficient and has a capacity of 750 cubic meters of air per hour.

They made lubricating oil filters with rotatable elements, operated with an external ratchet wrench, connected to any shift lever or other device that is frequently operated by the driver of the vehicle, so it is constantly brushed and cleaned. These elements may be single or in multiple, such as three, geared to one lever. The filtering is between coppered steel wire, wound around a cylinder on threaded vanes, all of which is accomplished in one machine. Space between the wire coils is approximately .004". This is covered by U. S. Patent No. 2,136,853.

Another, later type of Lubricating Oil Filter, while expensive, was 95% efficient, Mr. Knecht claimed. It is built up to

desired length of element by disc assemblies. The disc consists of copper or brass gauze or screen on each side of the disc, supported inside by stronger steel screens and these are spaced apart by a fluted center disc. The five pieces are permanently assembled together by a webbed stamping. The openings in the outside bronze screens were alleged to be .1 m/m for lubricating oil and .06 m/m, for gasoline. The purpose of the larger mesh steel screens inside the finer mesh brass screens was to prevent their destruction, if clogged, up to 20 atmosphere pressure.

Lubricating Oil Filter Elements were also built up from paper discs and the whole element held to standardized dimensions, in line with the national effort to make accessories interchangeable.

The intake air screen used in the automobile engine air filter, is made specially for them and is called "Turbo Metal" for Knecht. It is flat coppered steel ribbon, twisted and woven in one operation. It produces a turbulent effect in the air stream and tends to retain its oil in the surface pockets, and collects the dirt therein, in such a way as to delay a drop in efficiency. Nine layers, normally used, is purported to be 80% efficient.

PART II

Man & Hummel, manufacture air, gasoline and lubricating oil filters for every usage.

Mr. Wilhelm Henzler is the manager.

During the war they manufactured practically the same line of filters, including the tank filter, as the Knecht Co., all as described in Part I.

They also made air filters for the German Luftwaffe with multiple, tubular elements from woven rabbit hair. This material looks like grey felt and is the only animal hair or woven material that will filter air 100% efficiently, according to Mr. Henzler. The tubes are supported on the inside by a wire form and are quite stiff. When necessary to clean them, they may be removed and beaten to knock off the accumulated dirt.

Material Evacuated. The samples referred to herein, and listed below shall be placed at the disposal of American filter manufacturers to examine and test if desirable. They are to be shipped to the Automotive Industries Subcommittee, 15 Canal Street, S.W., Washington, D. C.

1 - Wire Filter Element (Rotatable)

1 - Paper Filter Element

2 - Assembled Discs (Wire Gauze)

1 - Piece "Turbo Metal" Air Screen

1 - LZ-224 Cyclone Filter for Trucks

1 - Rabbit Hair Filter Element

1 - LWR Air Filter for Trucks

Verzeichnis der deutschen Patente der Fa. Knecht-Kom.Ges., Bad Cannstatt

A) Luftfilter u. dgl.

Lfd. Nr.	Pat.Nr.	Gegenstand	erteilt an	läuft seit
1	627 225	Luftfilter (Turbo)	Alfred Knecht	9.2.1934
2	712 491	Vorrichtung zum Reinigen von gasförmigen Stoffen, insbes. Luft (Ablenkring)	Knecht-Kom.Ges.	20.11.39
3	730 175	Vorrichtung zum Reinigen besonders staub-und sandhaltiger Ansaugluft, insbes. für Brennkraftmaschinen (Zentrifugal-u. Luftwaschfilter-Kombination)	Knecht-Kom.Ges.	8.4.41
4	732 494	Vorrichtung zum Reinigen der Luft auf nassem Wege	Knecht-Kom.Ges.	8.10.38
5	734 253	Mit Geräuschdämpfer vereinigter Nassluftreiniger (Drehschieber)	Alfred Knecht	4.2.39
6	736 418	Einrichtung zur Luftreinigung in dem Kühler von Brennkraftmaschinen	Knecht-Kom.Ges.	18.7.40
7	742 825	Nassluftreiniger für Brennkraftmaschinen (kegelförmige Einsätze mit Schlitzen und Leitflächen)	Knecht-Kom.Ges.	24.10.38
8	754 700	Anordnung eines Vergasers und eines Luftreinigers für Brennkraftmaschinen (unter gemeinsamem Schutzgehäuse)	Alfred Knecht	17.7.40

B) Flüssigkeitsfilter u.dgl.

Lfd. Nr.	Pat.Nr.	Gegenstand	erteilt an	läuft seit
9	665 340	Reinigungsvorrichtung für zylindrische Spaltfilter (Drahtspulenfilter m. Bürsteinrichtung)	Alfred Knecht	1.4.36
10	712 433	Spaltfilter für Flüssigkeiten, insbes. f.Schmieröl, Brennstoff o.dgl. (Spaltfilter Kombiniert mit 2 Pumpen)	Knecht-Kom.Ges.	14.6.39

Lfd. Nr.	Pat.Nr.	Gegenstand	erteilt an	läuft seit
11	713 992	Spaltfilter für flüssige Betriebsstoffe (gekürzte Achse u.feststehende Lagerbüchse)	Alfred Knecht	28.4.38
12	761 134	Filterkörper, insbes. für flüssige Brennstoffe, Öle u. dgl.	Knecht-Kom.Ges.	14.7.41

Verzeichnis der Auslandspatente der Fa. Knecht-Kom.Ges., Bad Cannstatt

A) Luftfilter u. dgl.

Lfd. Nr.	Land	Pat.Nr.	Gegenstand	erteilt auf	läuft seit
1	Amerika	2 048 871	Luftfilter (Turbo)	Alfred Knecht	1936
2	England	459 372	Luftfilter (Turbo)	Alfred Knecht	1936
3	Frankreich	792 618	Luftfilter (Turbo)	Alfred Knecht	1935
4	Italien	338 846	Luftfilter (Turbo)	Alfred Knecht	1935

B) Flüssigkeitsfilter u.dgl.

5	Amerika	2 136 853	Drahtspulenfilter	Alfred Knecht	1938
6	England	458 649	Filterwickel-Verfahren	Alfred Knecht	1935
7	England	459 409	Drahtspulenfilter	Alfred Knecht	1934
8	England	495 001	Spaltfilter mit Reinigungsvorrichtung	Alfred Knecht	1938
9	Frankreich	804 928	Filterwickel-Verfahren	Alfred Knecht	1936

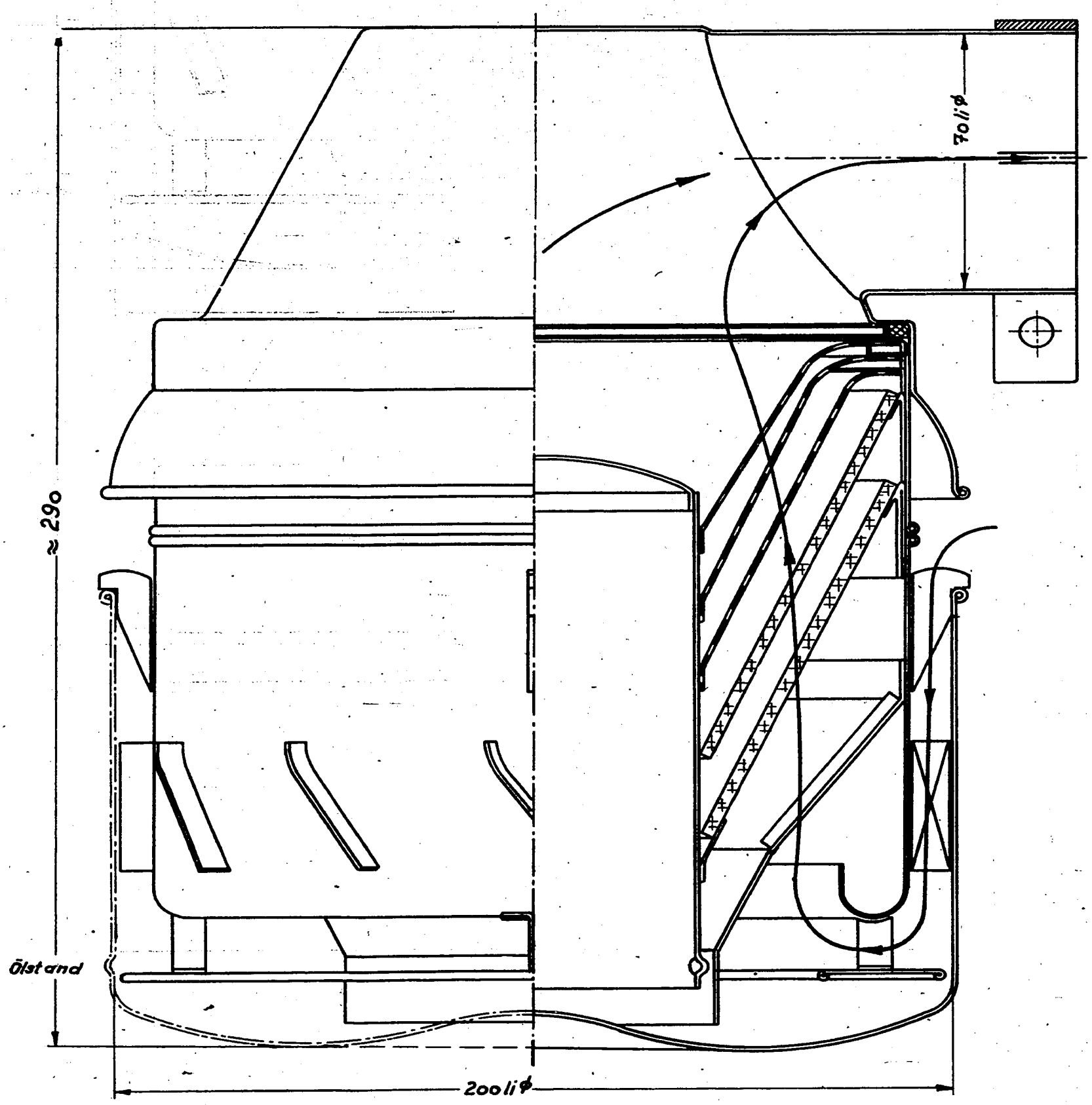
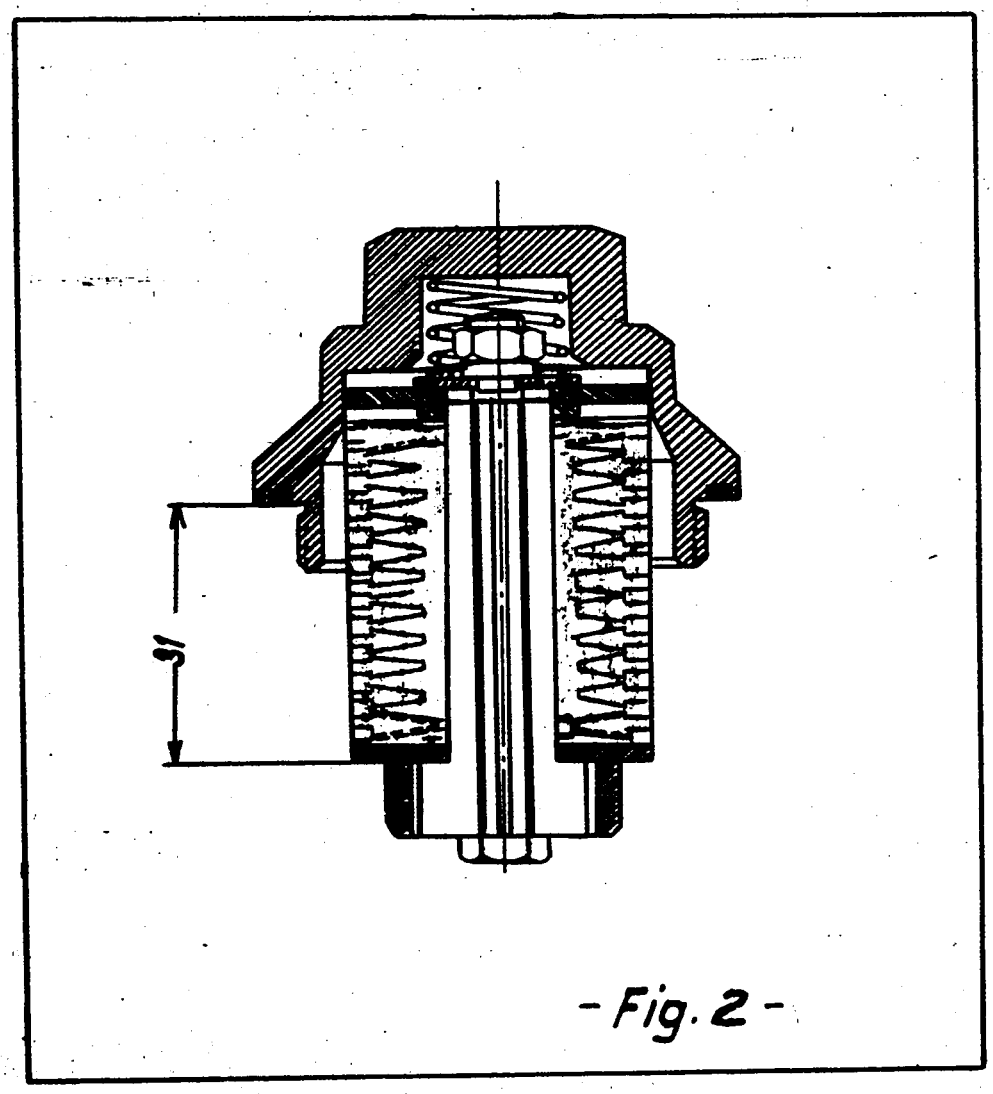
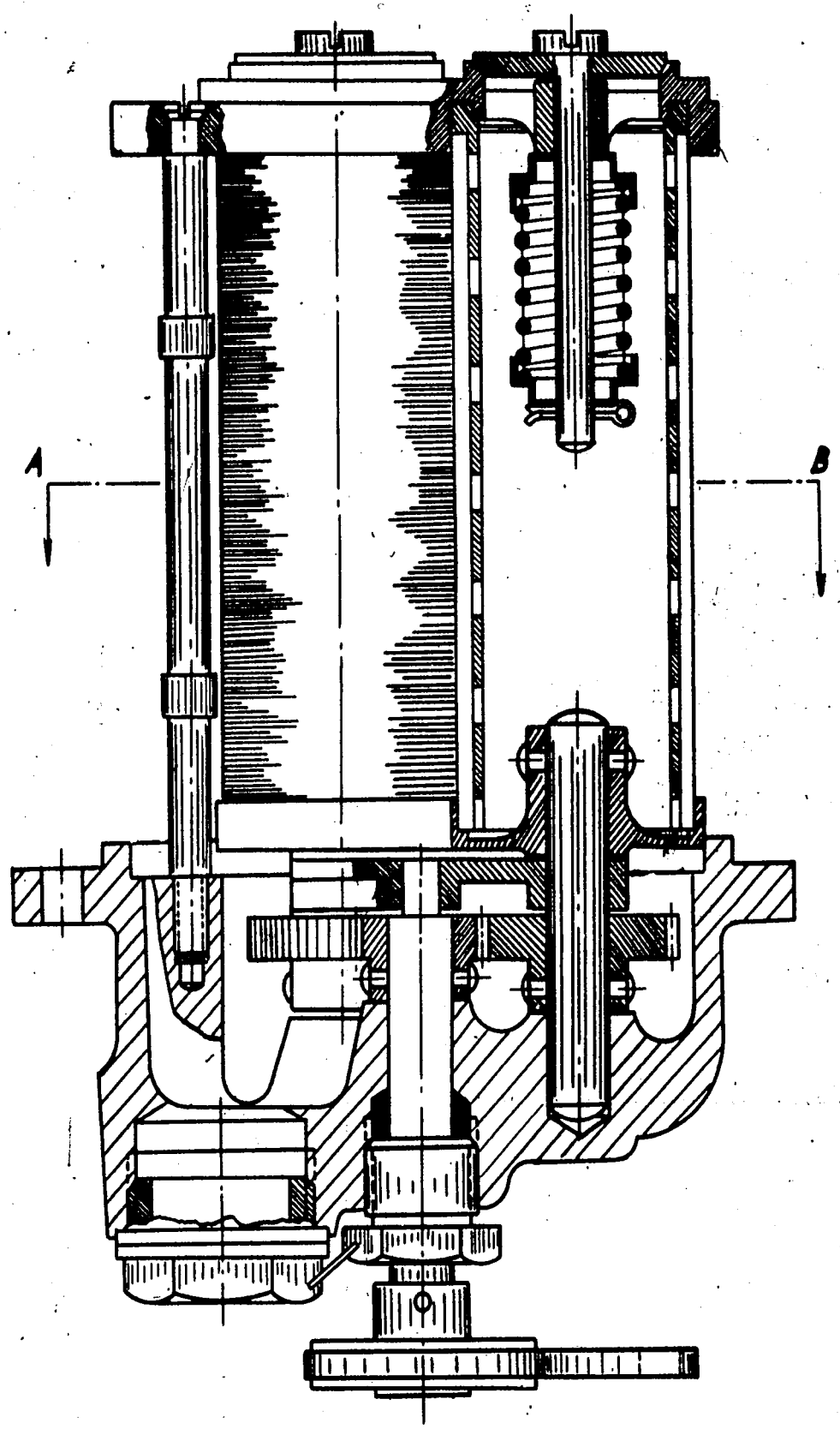
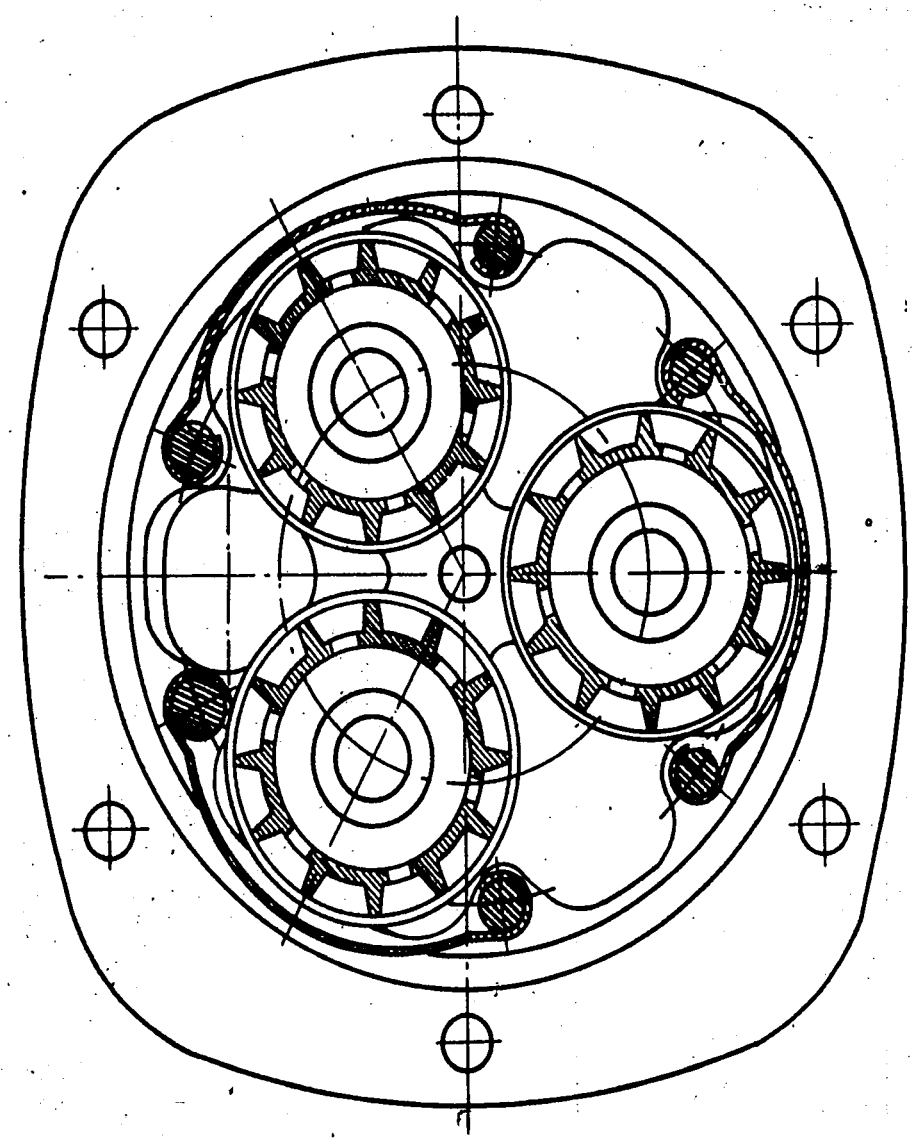


Fig. 1



- Fig. 2 -





Schnitt A - B

Fig. 3

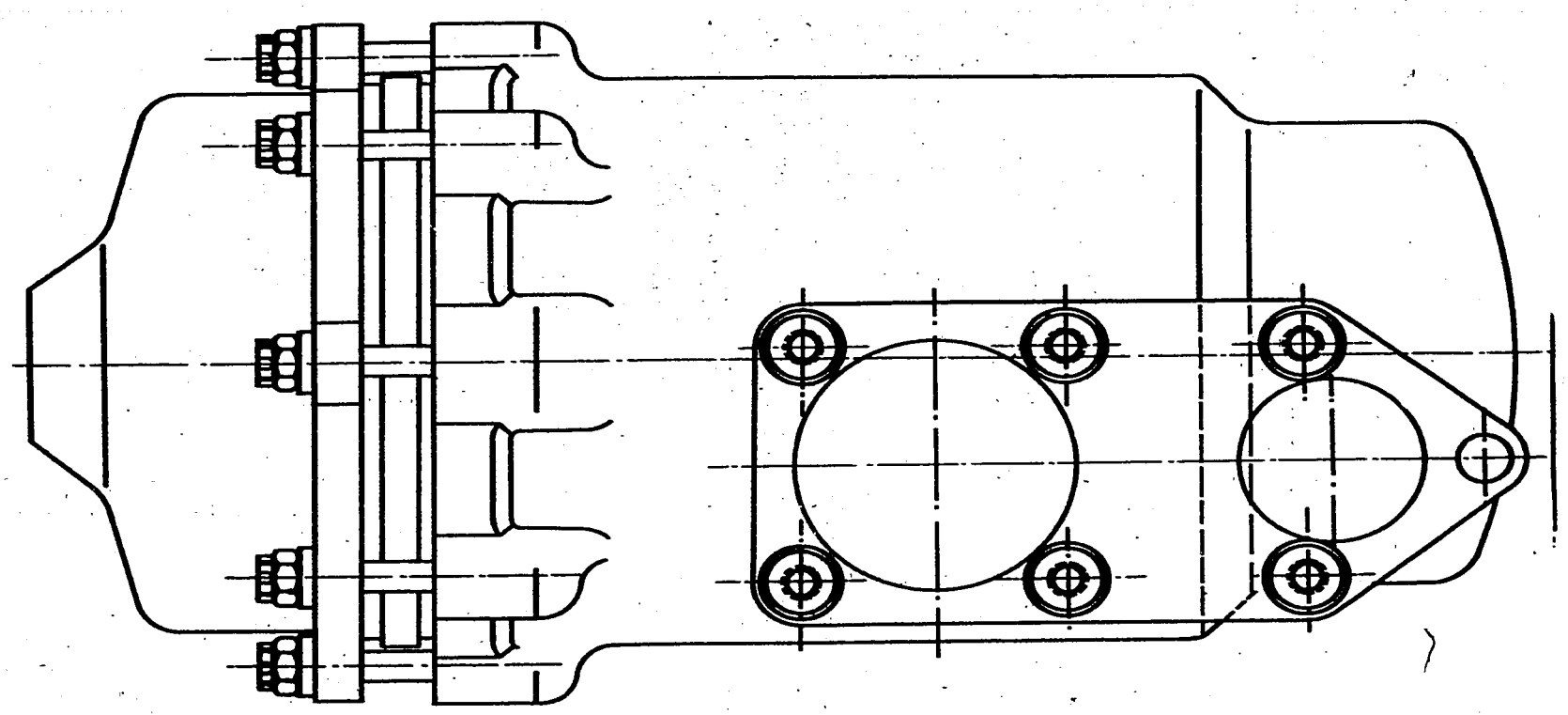
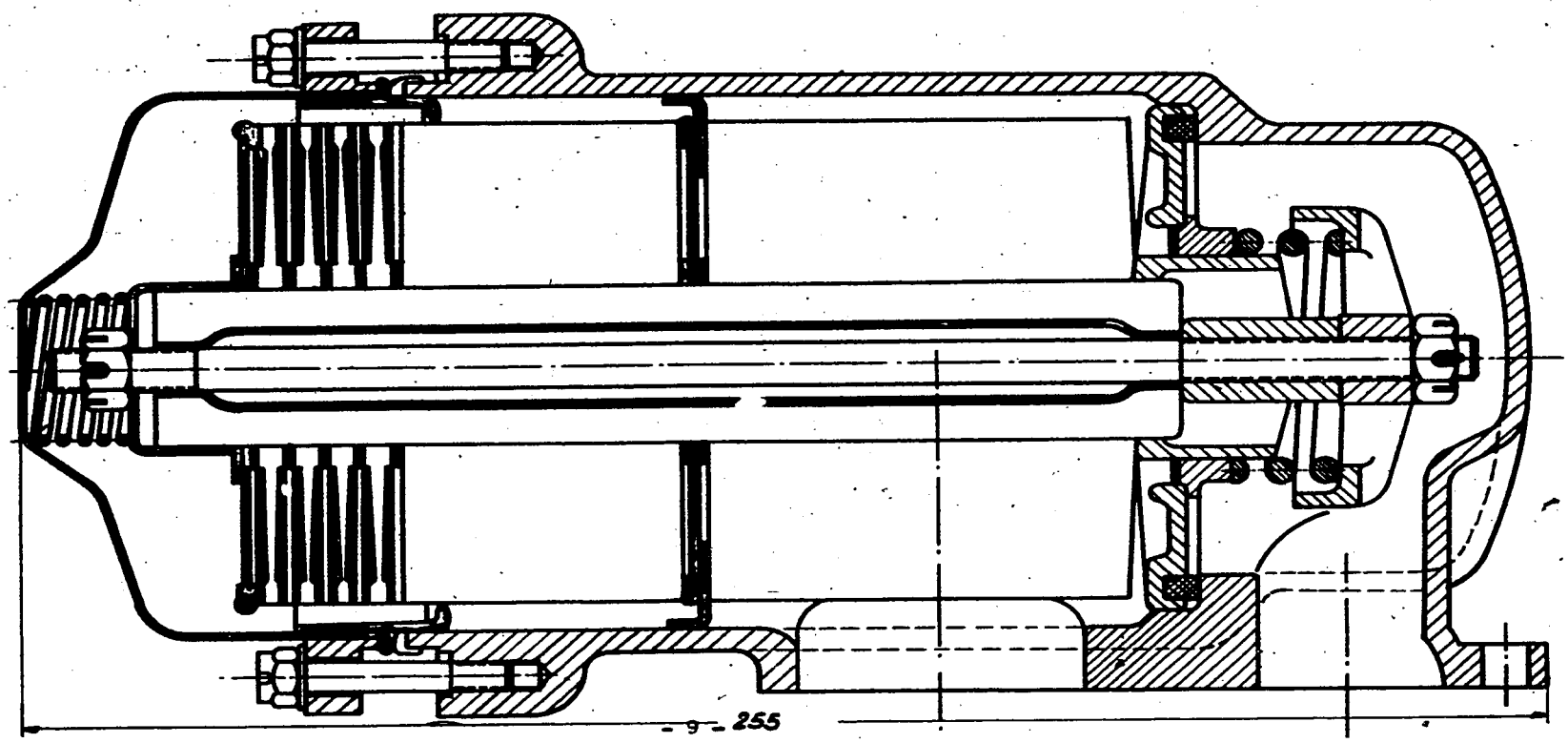


FIG. 4



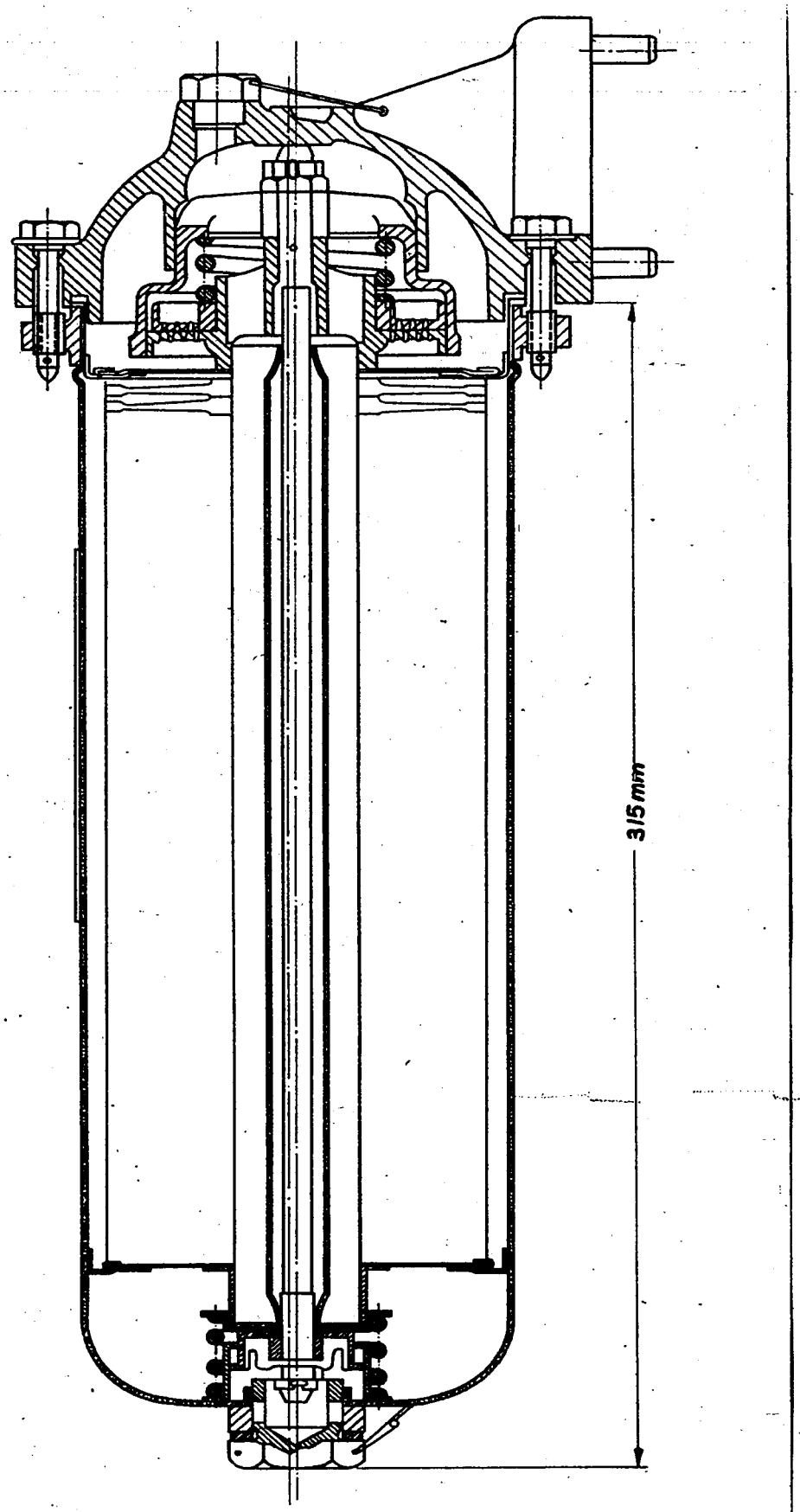
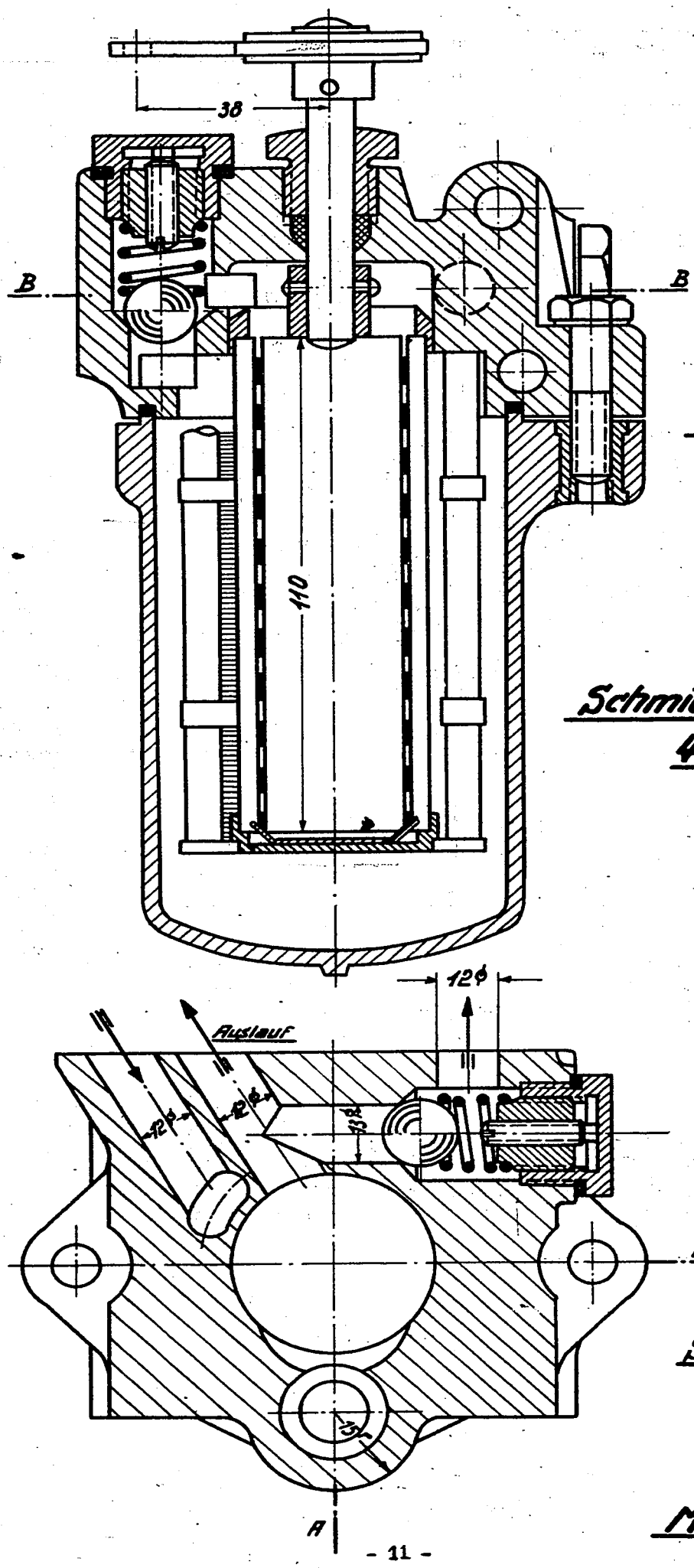


Fig. Nr. 5



SCHNITT A-A

Schmierol-Spaltfilter FOR 429 V/3/110

SCHNITT B-B

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Fig. 6

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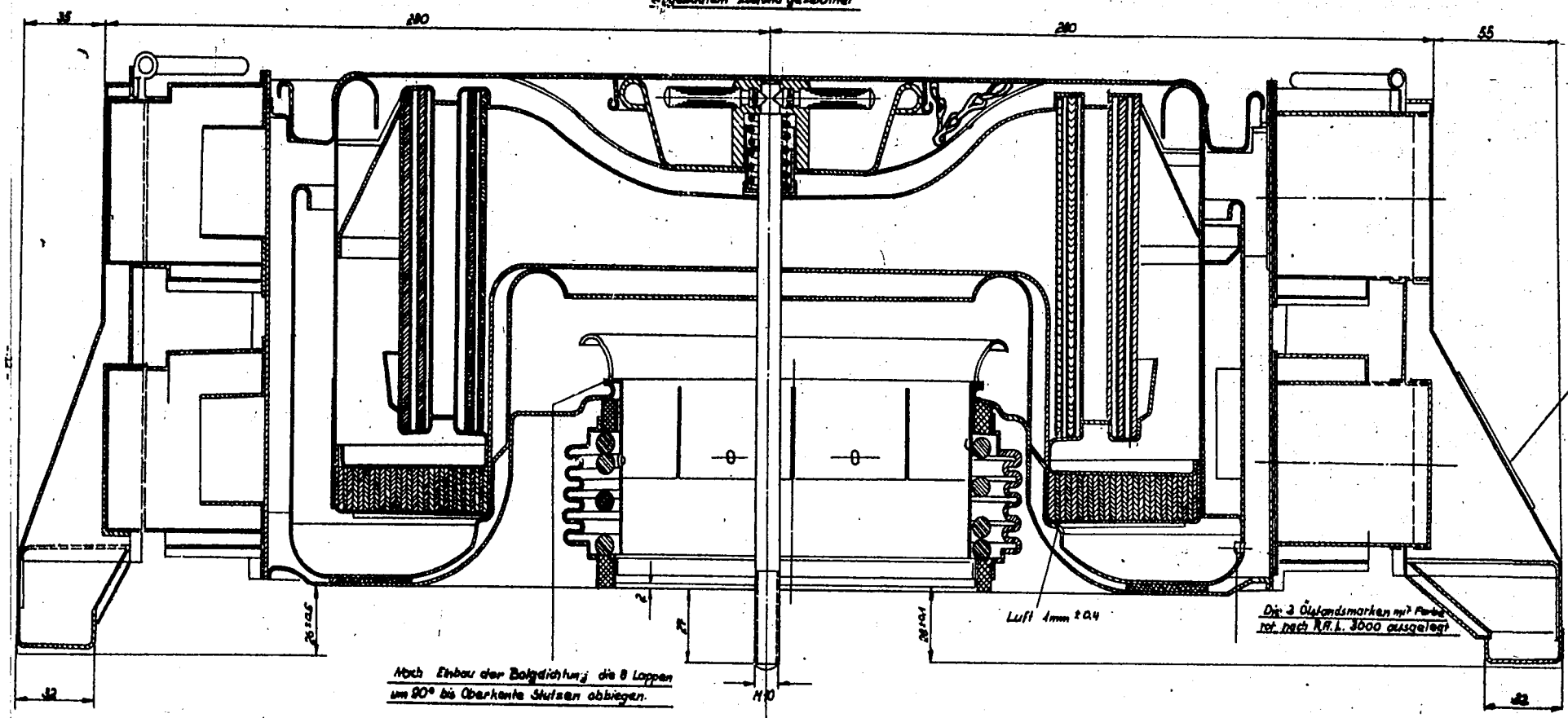

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Fig. 7

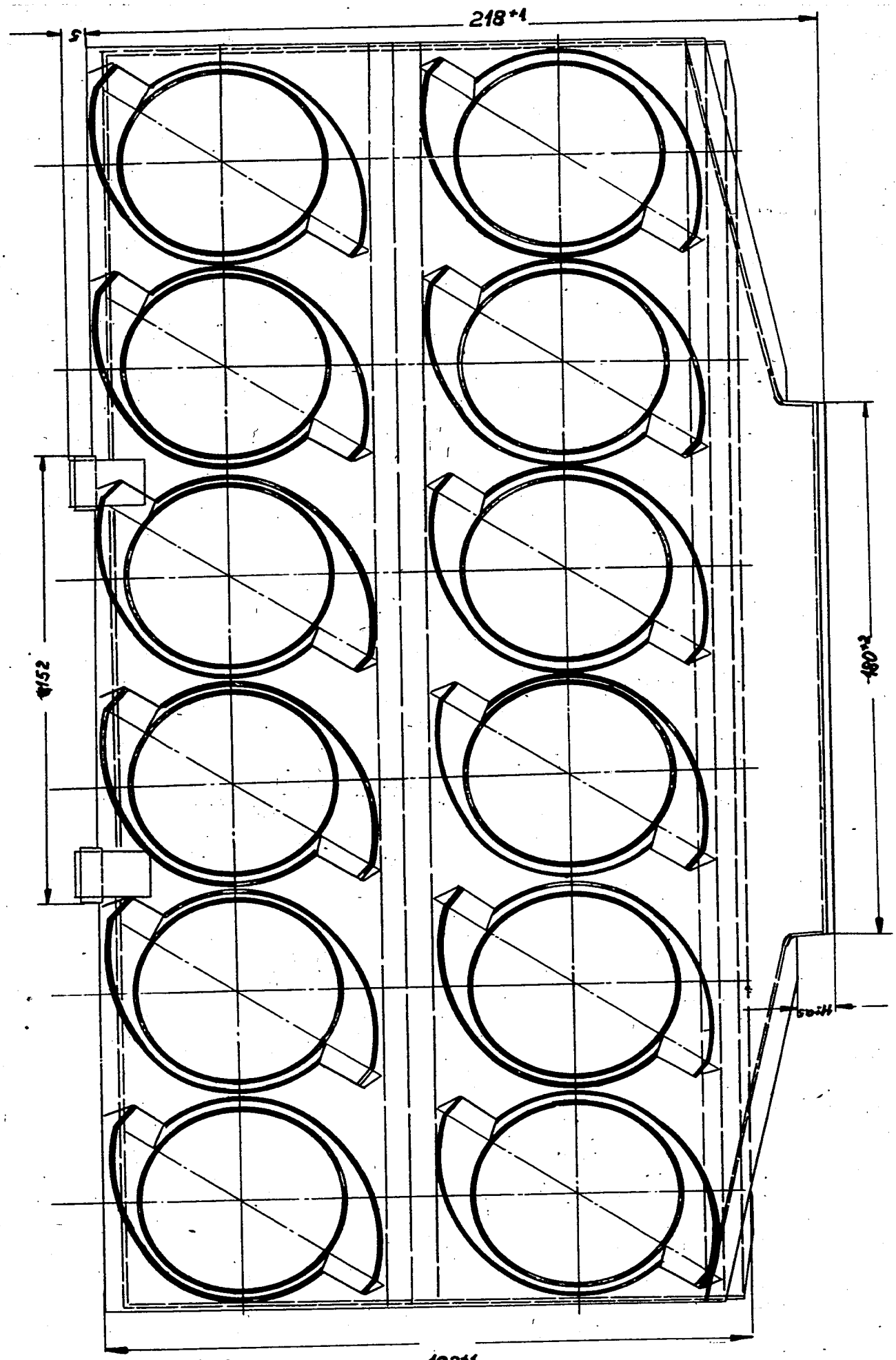

Fig.8

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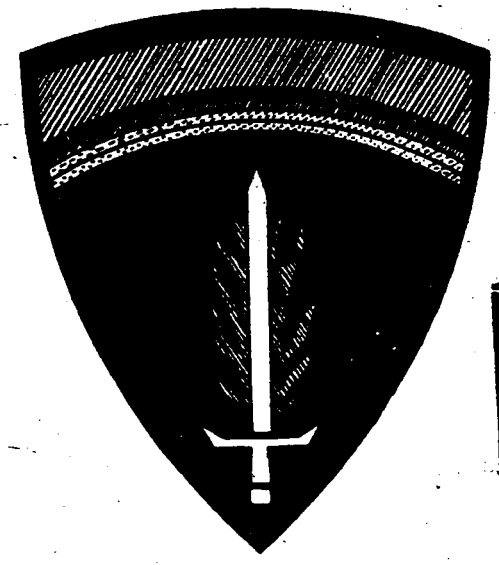
FIAT FINAL REPORT 720

GERMAN TECHNIQUES FOR HANDLING ACETYLENE IN CHEMICAL OPERATIONS



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GERMAN TECHNIQUES FOR HANDLING ACETYLENE IN CHEMICAL OPERATIONS

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FIELD INFORMATION AGENCY, TECHNICAL

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SUMMARY

Acetylene, which could readily be produced from available materials, played a large role in Germany's struggle to become self-sufficient in the chemicals industry, which was vitally necessary to the prosecution of the war. Because of a shortage of petroleum, acetylene was used as the starting material for a large number of chemical products. Many of the processes developed required the use of acetylene under conditions not heretofore considered possible for safety reasons because of the well known tendency of acetylene to decompose with explosive violence under conditions of elevated pressure and temperature.

Considerable research work was done by the I.G. Farben to develop information on the conditions under which acetylene may decompose and the pressures developed as a result of such decomposition. Acetylene decomposition was studied as a function of pressure, temperature, vessel size, moisture content, type of igniter, quantity and kind of diluent gases, etc. The conditions under which acetylene may detonate were also determined, and means to prevent detonation developed. The remarkable success achieved by the Germans in the handling of acetylene is due to a considerable extent to this careful study of its behaviour under various conditions.

By the end of the war the Germans were carrying out a number of processes which are very interesting from the standpoint of acetylene handling technique and had developed considerable know-how from such operation. Among the processes which are interesting because of the rather drastic conditions under which acetylene is handled are the following:

1. The purification and concentration of arc acetylene at Huels by absorption in water at 18 atm pressure.

2. Manufacture of butinediol on a large scale using acetylene in the presence of copper acetylide (usually considered a good detonator) at a pressure of 6 atm and a temperature of 110°C.

3. Production of Koresin, a tackifier used in building of tires of Buna rubber, by the condensation of acetylene and p-tertiary butyl phenol at 20 atm and 200°C.

4. Production of vinyl pyrrolidon, the polymer of which was used by the Germans as a substitute for blood plasma. This involved direct vinylation at a pressure of 20-25 atm and a temperature of 150°C.

5. Vinyl ether manufacture utilizing pressures of 20 atm and reaction temperatures of 150-170°C to react C_2H_2 with alcohols.

INTRODUCTION

The purpose of this report is to present the advances made in recent years by the Germans or, more particularly, the I.G. Farben in the technique of handling acetylene in chemical operations. This includes the research work done to establish the conditions under which acetylene undergoes explosive decomposition, how these data were used to design plants and set up operating conditions, and subsequent experience in these plants. Most of the processes described herein have been discussed in other reports so that they will be considered here primarily from the point of view of acetylene handling techniques. Some of the older and better known processes have not been included.

The present report is concerned only with the handling of acetylene in chemical processes; German practice in generation, bottling, etc., has already been amply covered by other investigators.

Acetylene will under certain conditions decompose explosively to carbon and hydrogen with release of considerable energy, viz., 53,000 kg. cal/mol. of gas. It has been known for a number of years in a qualitative way that decomposition is affected by a variety of factors the principle ones of which are as follows: Pressure, temperature, type of ignition, concentration of the gas, size of the containing vessel, etc. Because of the increased tendency toward decomposition with increased pressure and temperature, chemical operations utilizing acetylene have always heretofore been carried out at moderate temperatures and pressures. For the same reason acetylene generators are in most countries not operated over a pressure of 1.5 atm gauge (higher pressures usually forbidden by law), because of the number of explosions which resulted at higher pressures. Decomposition in such generators is caused by local overheating of the carbide.

Acetylene may decompose in essentially two different ways. The spread of decomposition may be relatively slow and the resulting pressure rise gradual as in the usual processes of explosion or combustion or it may be extremely fast, i.e., a detonation. Actually, the latter represents the limiting speed of the former. The maximum final pressure (assuming no heat loss) in the case of the slow type of decomposition can be calculated from the energy released and is approximately 12 times the original. In the case of a detonation the ratio of final pressure to initial may be many times this factor. Equipment can be designed to withstand pressures developed by slow decomposition, but it is usually impractical except for very small vessels to design equipment to withstand detonations.

In the early history of acetylene production, many accidents occurred until proper techniques of compressing and storing the material were developed. It can be compressed in slow-moving reciprocating compressors by stages with proper intercooling up to 15-20 atmospheres. The

storage cylinders are filled with a porous material, for example, Kieselguhr, and the acetylene is absorbed in acetone which is also added to the cylinder. Small lines are employed for the most part. Most of the present technique has been developed on a rule of thumb basis over a period of years, and the knowledge so accumulated has been of limited assistance to the chemist or chemical engineer desiring to use acetylene as a raw material under wholly different conditions.

Since Germany did not have petroleum resources, acetylene, which could be produced from raw materials readily available, played a large part in Germany's program of self-sufficiency in the chemicals industry and was used as the starting material for many organic compounds. Work on acetylene chemistry was intensified just prior to the war and during the war. Many of the processes developed required the use of acetylene under conditions not heretofore considered possible for safety reasons.

PERSONNEL INTERVIEWED

Griesheim	
Dr. Holler	Tests at Griesheim on acetylene decomposition.
Dr. Maier	
Friedrichsdorf	
Ing. Schnedler	Formerly at Griesheim. Interviewed at his home on Griesheim test work.
Berlin	
Dr. Rimarski	Desensitizing of liquid acetylene.
Dr. Konschak	Acetylene decomposition.
Huels	
Dr. Baumann	Acetylene production, concentration and purification.
Dr. Haberl	
Dr. Harand	
Dr. Kraus	
Dr. Dietrich	
Dr. Grunert	
Ludwigshafen	
Dr. Pistor	Butinediol manufacture.
Dr. Steinhofer	
Dr. Dorrer	
Dr. Christ	Korsin, vinyl pyrrolidon, vinyl ethers.
Dr. Alt	
Fechenheim	
Dr. Reppe	Acetylene handling, Reppe laboratory, cyclooctatetraene, etc.

DEVELOPMENT OF FUNDAMENTALS

The best known prewar work on the conditions under which acetylene will decompose was done by Dr. Rimarski of the Chemische Technische Reichsanstalt at Berlin. A considerable portion of this was published before the war. Most of the work was directed toward the technique of generating, and storing acetylene.

Outside of the foregoing, the most important earlier work on fundamentals was that by Dr. Boesler of I.G. Farben, which is decidedly more from the chemical point of view. This work was not published and therefore deserves considerable discussion in this report. It seems to have had considerable influence on the thinking of I.G. Farben's technical people on the subject of acetylene handling.

Decomposition of Acetylene by Initial Ignition--Dr. Boesler

Exhibit A includes a translation of this report. The purpose of this investigation was to determine the pressure at which acetylene could be decomposed by the action of a strong igniter as a function of vessel diameter, moisture content, temperature, composition (and hence temperature) of the igniting wire, and of diluting gases such as N_2, H_2, CH_4, C_2H_4, CO, (N_2 plus H_2), and (H_2 plus CH_4). After considerable experimentation, it was decided to use a platinum wire of 0.5 mm diameter and 10 mm length for ignition. This wire was fused instantaneously through proper choice of current. The fallacy of using an incandescent wire as had been done by some previous investigators was pointed out.

The decomposition pressure (i.e., the pressure above which acetylene can undergo decomposition) for pure, dry acetylene at 15°C decreases with increasing vessel diameter. The decomposition pressures at 50 mm and 200 mm diameter are 1.80 kg/cm^2 and 1.40 kg/cm^2 respectively. Above 200 mm further increase in diameter has no effect.

For pure, dry acetylene the decomposition pressure was determined as a function of igniter temperature in a large chamber. With wires of melting points more than 1700°C (Pt. and Mo.) decomposition pressure is constant at 1.40 kg/cm^2. With fusion temperatures decreasing to 660°C, the pressure rises slowly to 2.65 kg/cm^2 and then more rapidly as the temperature is further dropped so that at 330°C (Pb) it amounts to 7.50 kg/cm^2.

It was found that the decomposition pressure decreases slowly with rising temperature; at 15°C, it is 1.40 kg/cm^2, and at 180°C, only 1.06 kg/cm^2.

The presence of water vapor raises the decomposition pressure. However, it should be noted that the actual partial pressure of acetylene is practically constant within the range tested (up to 100°C).

The decomposition pressure of acetylene mixed with other gases was determined at various temperatures. The acetylene content necessary for decomposition increases at a rate depending upon the gas. With H_2 the C_2H_2 content was the least and with CH_4 the highest.

It will be noted that the translation of Boesler's report includes some notes by him on earlier work of Rimarski.

Experiments on the Detonability of Acetylene in Long Pipes--Dr. Rimarski

In 1940, the I.G. Farben was planning installation of a synthetic rubber plant in Bavaria (later given up) which would have required piping large quantities of C_2H_2 a distance of 83 km. Because of the background of experience of the Chemische Technische Reichsanstalt, they were called in by the I.G. Farben to assist in an experimental investigation to determine what pressure might be used in such a line before a detonation would be possible. As a result large scale experiments were carried out at the Griesheim plant.

Prior to this time Dr. Weissweiler of the Ludwigshafen plant had been doing certain experimental work for Dr. Reppe primarily directed at safe methods of handling acetylene for the butinediol process. He accordingly took part in the Griesheim experiments as originally planned and then later extended the work with the application to plant equipment in mind.

A summary of the C.T.R.'s portion of the work is as follows: A complete translation is included in the Appendix of this report, Exhibit B.

These experiments led to the conclusion that acetylene in pipes sufficiently long and of large diameter undergoes detonation at low pressures (1.4 kg/cm^2 absolute), without there being any pressure region within which the decomposition progresses slowly. With detonations the resulting pressures amount to several hundred atmospheres. The starting distance required for transition to a detonation is rather long and is greater the lower the initial pressure. With weaker ignition the pressure limits lie higher. (Fusion of platimum was used in these experiments). Also it is possible that with higher initial temperatures the pressure limits would be somewhat lower.

With the admixture of N_2 with the C_2H_2 the pressure limits are raised. Small percentages of N_2 up to 25% do not have much effect in preventing detonation but perhaps shift the starting point slightly. A real increase in pressure limit is obtained only by using large quantities of

N_2 (50%). It appears that with C_2H_2 - N_2 mixtures in a ratio of 1:1 a small pressure range exists, within which no detonation takes place even with strong ignition or at least the starting distances fof such mixtures are so long that the 30 m pipe used in these experiments was not enough for development of a detonation.

On the basis of these experiments it was concluded that a pressure of not more than 0.3 kg/cm^2 gauge should be used in long pipes of large diameter for transfer of acetylene or 3.0 kg/cm^2 gauge for an acetylene-nitrogen mixture of a 1:1 ratio. The Reichsanstalt considered it necessary to undertake some control tests in this pressure range on hot summer days, to determine whether such temperatures appreciably affect the results obtained.

Experiments on Acetylene Decomposition--Dr. Weissweiler

As mentioned above, Dr. Weissweiler's original work at Ludwigshafen was started before the experiments at Griesheim and was directed towards developing safe handling methods for the butinediol process. Using pipes of 1.0 m length x 90 mm I.D. and 5.5 m length x 120 mm I.D., he measured decomposition pressures as a function of gas temperature, etc. He demonstrated that the copper acetylide catalyst, deposited on silica gel, is not an igniter (while on the silica gel) and acts as an arrestor if it fills the entire pipe cross-section. He also investigated various devices as explosion arrestors such as plugs of steel wool, porous filters, etc. Earlier favorable results at Ludwigshafen on this type of arrestor were later invalidated at Griesheim, and the idea of developing an arrestor capable of stopping any and all decompositions were given up.

Experiments were made in which the large pipe at Griesheim (100 mm I.D.) was filled with a bundle of small tubes ($\frac{1}{2}$" and 3/8"). At lower acetylene pressures (up to 3.4 kg/cm^2) this arrangement stopped decomposition altogether and at higher pressures prevented detonation. Additional experiments on a $\frac{1}{2}$" pipe 60 m long showed that detonation was prevented up to 10 kg/cm^2. The necessity of avoiding large empty spaces was demonstrated by use of an entrance chamber which greatly diminished the effectiveness of the small pipes.

As a result of the foregoing work the following specifications were laid down for the first butinediol plant at Schkopau:

1. All pipelines carrying acetylene under pressure are filled with small tubes of $\frac{1}{2}$" maximum diameter.

2. Elbows are also to be filled with such tubes and when this is not possible with steel Raschig rings.

3. All large empty spaces are to be strictly avoided. Dished heads of vessels, etc., are to be filled with Raschig rings.

In December 1941, the safety of the butinediol process was discussed by the I.G. with representatives of the Reichswirtschaftsministerium (from whom permission to operate must be secured) and the C.T.R., who were acting as technical consultant to the latter bureau. A further series of experiments were agreed to and carried out. These involved further and more drastic experiments on tube bundles and Raschig rings. In general earlier work was corroborated but the importance of avoiding open spaces was emphasized. Following this work the Reichswirtschaftsministerium and the C.T.R. were satisfied as to the effectiveness of safety measures planned for inclusion in the butinediol installations.

A translation of Weissweiler's report is included as Exhibit C.

Desensitizing Liquid Acetylene - Chemische Technische Reichsanstalt

The authors had been advised that the C.T.R. in Berlin had been doing some work on the desensitizing of liquid acetylene. Dr. Rimarski and Dr. Konschak were interviewed on this subject, but very little real data was obtained inasmuch as it was claimed that all their records had been destroyed or otherwise lost during the siege of Berlin. They had run some experiments to determine the amount of CO_2 required in liquid acetylene to make it stable. Various amounts of CO_2 were added to acetylene in a small bomb containing both liquid and gaseous acetylene at various temperatures. A platinum wire located in the gas phase was then fused, and the bomb examined to determine whether decomposition of the liquid had occurred. It was stated that as the temperature was raised, the amount of CO_2 required for stabilization became less, presumably due to the increase in the CO_2 content of the gas phase with increasing temperature. By the same token low temperatures favored decomposition. Up to 30% CO_2 was tried. It was stated that a C_2H_2 - CO_2 mixture of this composition is stable at room temperature and 70 atm pressure.

It was claimed that the purpose of the experiments was to develope new methods for the transportation of large quantities of acetylene. It was stated that the work was not carried far because of war time difficulties.

APPLICATIONS

Concentration and Purification of Arc Acetylene at Huels

An excellent overall picture of operations at this plant has been given in other reports, e.g., CIOS Report, Item No. 22, File No. XXII- 21, by Handley et al. Therefore the present report will be concerned only with acetylene concentration and purification. In Exhibits D and E are

listed prints, and copies of process write-ups obtained at the Huels plant. These will be on file with the Rubber Sub-Committee of the J.I.O.A. in Washington.

Fig. 1 shows a block flow sheet of the acetylene manufacturing operations with material flows involved. The quantities given are for operation primarily on refinery gas, which is the preferred raw material. Additional quantities of hydrocarbons for feed to the electric arcs are obtained from coke oven gases, after removal of ethylene, and from natural gas from the Bentheim wells. Raw gas from the arcs contains 13-16% of acetylene depending upon the feed gases.

Typical analysis of raw gas from the arcs is given below:

CO_2	0.0%	CH_4 + Homologues	25.1%
C_2H_2	16.2%	N_2	3.4%
Olefine	3.6%	HCN	1/3 g/m^3
O_2	0.2%	Naphthalene	1/3 g/m^3
CO	1.0%	Benzene	1/6 g/m^3
H_2	50.5%	Diacetylene	15 - 30 g/m^3

After separation of carbon black, which is present to the extent of 20-25 g/m^3, the gases are scrubbed with oil to remove higher boiling aromatic and aliphatic compounds, and with water to remove HCN. The gases are then treated with iron oxide to remove H_2S.

The gases, treated as above, at normal temperature and slightly above atmospheric pressure pass to the suction side of the compressors for compression to 18 atmospheres. The compressors, 6 in all, operate in parallel; a gasometer is provided on the suction side to take up surges. The compressors are reciprocating type, 4 - stage, with a rated capacity of 13,000 m^3/hr at a power input of 1900 kw. They operate at a speed of 125 r.p.m. Stroke is 850 mm and piston diameters for the four stages are 1290 mm, 900 mm, 615 mm, and 440 mm. Water coolers are provided after each compression stage. The normal temperature leaving each stage is about 60° - 70°C, although if a cooler becomes dirty this will rise considerably. Temperatures up to 110°C have been observed on the last stage. Pressure ratios vary somewhat with the condition of the coolers and the load on the compressors, but the compression ratio on each stage is normally not far from the expected 2.06.

According to the Germans there are no design features especially provided in the compressor because of the nature of the gas handled except for the fact that four stages were employed to avoid high temperatures whereas only three would be more usual for ordinary gases. Apparently very little trouble has been experienced with these compressors. No fires or explosions have as yet occurred in these units. All such difficulty, which will be discussed later, took place further on in the

system. The compressors are taken out of service every six months to clean polymers from the valves and passages.

The fourth stage cooler is the most troublesome part of the compressor system as it becomes plugged with polymers in a relatively short time and is extremely difficult to clean. Life of these coolers is variable but is usually 4-6 weeks. Cleaning of the coolers is one of the most laborious tasks of the whole operation. Plans had been made to replace these tubular coolers with a water spray type, but the installation was never made. For a time two compressors were operated without any final cooler. This was not satisfactory because (1) the pipes leading to the water scrubbers became clogged and (2) the temperature of the gas in the header system was so high that the effectiveness of the alarm system which signals a rising temperature, denoting an acetylene decomposition, was considerably reduced.

Originally, the gases from the compressors were scrubbed with oil to remove higher acetylenics and then were passed to the water scrubbers for removal of the acetylene. However, considerable difficulty was encountered with this arrangement because of polymer formation in the oil which after a short time was unfit for use. It appeared very likely that this polymer formation was catalyzed by water carried over from the compressors inasmuch as good means of water separation had not been provided. Accordingly, proper separators were installed immediately following the compressors. A few days later the first of several acetylene decompositions occurred, in a manner hitherto unobserved by the Germans. An elbow in the gas line began to heat up, became red hot, and in a few minutes burst open. The pipe was not shattered; it appears to have been softened from intense heat, and then split open by the system pressure. Fifteen or twenty minutes apparently elapsed from the time the heating up was first observed to the bursting of the pipe. This was the first of several such incidents all of which followed about the same pattern, viz., started at an elbow, comparatively slow local heating of the pipe, a marked temperature rise of the gas beyond this point, no particular pressure rise. Many theories were advanced by the Germans as to the cause of the trouble. It seemed very apparent that the sudden appearance of the difficulty was associated with elimination of water from the lines through installation of the separators. It was observed that polymer deposit inside the lines could at times decompose with explosive violence if dried and sufficiently disturbed. However, it was not understood how the acetylene decomposition could proceed so slowly. The reason for the difficulty apparently being associated with elbows was not clearly understood. It was pointed out that the polymer deposit was thinnest at the elbows. The theory was advanced that some catalytic effect of the pipe material might be involved which in effect lowered the temperature required for acetylene decomposition.

For a discussion of details of the explosions refer to J.I.O.A. microfilms, Reel O-15, which include the Huels files on the subject.

In view of the above difficulties it was decided (1) to pass the gases directly from the compressors to the water scrubbers (2) to remove the acetylene homologues following concentration (3) provide water sprays at several points to keep the piping system wet at all points from the compressors to the water towers (4) to avoid elbows as much as possible (5) install a temperature alarm system to signal local high temperatures anywhere in the piping system. Later a pressure alarm system was added to indicate failure of any spray due to pluggage. After final installation of the foregoing items, no further difficulty with acetylene decompositions was encountered.

The gas from the compressors passes to six water absorbers which operate in parallel and are each equipped with flash chambers. The absorbers themselves are sieve plate columns (66 plates) approximately 2.5 m in diameter and 30 m high. There appears to be nothing particularly unusual in their design. The sieve plates themselves have holes 4 mm diameter on 10 mm centers. The sieve area is a rectangle 606 mm wire and extending for the full diameter of the column. As shown on the flow sheet the water flow for 9500 m^3/hr of fresh gas is a nominal 750 m^3/hr, which is varied depending upon the water temperature. Acetylene is stated to have solubility characteristics similar to those of carbon dioxide. It was stated that the scrubbers were designed using the following data which are those given by Vogel, "Das Acetylen", and refer to 760 mm pressure (gas volume at 0°C.)

t°C	Liters C_2H_2/Liter H_2O	t°C	Liters C_2H_2/Liter H_2O
0	1.73	16	1.13
2	1.63	18	1.08
4	1.53	20	1.03
6	1.45	22	0.99
8	1.37	24	0.95
10	1.31	26	0.91
12	1.24	28	0.87
14	1.18	30	0.81

The gas leaving the towers passes to the Linde plant for separation of the H_2 and ethylene after which the residual gases are recycled to the arc. It is essential that all traces of C_2H_2 be removed in the water scrubbers since its presence causes freeze-ups in the Linde system. Each water scrubber is provided with a water separator consisting of a tower filled with Raschig rings. We were given to understand that these towers were not especially designed for this purpose but were salvaged from another operation.

The water leaving the tower passes through a turbine which supplies part of the energy to pump the feed water into the tower. Turbine, pump,

and a motor are all mounted on a common shaft. The water carrying the C_2H_2 then passes to the first flash chamber at a pressure of 2.62 atm. The flash chambers are all essentially towers packed with 2" Raschig rings to an effective depth of approximately 3 m. They are all 2500 mm in diameter except #5 which is 2700 mm. The flash gases from the first chamber contain approximately 45% C_2H_2 and are recycled to the compressors. The pressure on this chamber is maintained at the desired figure by means of a pressure controller operating an automatic valve in the gas line.

The water from the first flash chamber discharges into the second which is exactly similar to the first except that the pressure is 1 atm; which is held by a gasometer. Originally it was planned to have the relative levels of the flash chambers such that water levels would be self regulating. However, this was not attained, and it is necessary to throttle manually to maintain proper water levels. The gas leaving the #2 flash is 92% C_2H_2 and goes on to the final purification step.

The water is flashed again at approximately 0.15 atm in #3 flash chamber and again to 0.05 atm in #4. These gas streams join that from the other flash chambers to give a raw acetylene of 96% concentration. Vacuum is supplied by pumps arranged as indicated on the flow sheet. These so-called K.S.B. pumps consist of a cylindrical rotor mounted in a housing in which it is set off center. The rotor carries spring loaded plates mounted in slots cut parallel to the axis of the rotor. The design is very similar to that of the most common type of small laboratory vacuum pump used in the United States. It is interesting to note that there is a metal to metal contact in these pumps and that at times plates have been sheared off during operation but that no explosion or decomposition has been ever noted. This fact was ascribed to the low absolute pressure of the C_2H_2 and its consequent decreased tendency to decompose. These are relatively high speed pumps, viz., 370 - 585 r.p.m. and were not considered safe by the Germans for use on acetylene of this concentration at normal pressures.

The vacuum pumps at one time had been equipped with automatic controls but these were found unnecessary and discarded; the vacuum on the chambers is determined by pump capacity.

Flash chambers #1 - #4 are equipped with cyclones. Also they are equipped, as indicated on the flow sheet with water seals which act to relieve the pressure in case the water absorber should lose its seal. This is to avoid the necessity of designing the flash chambers for absorber pressure, viz., 18 atm.

As shown on the flow sheet the water from #4 flasher was intended to be pumped up to atm. pressure and then to be stripped in #5 flasher by means of re-cycle gas for further removal of acetylene and homologues which would be returned to the arc. Actually, this stripping operation was found

ineffective and is no longer carried out. The last traces of organic are removed in large Demag towers of conventional construction.

No special materials of construction are used in the foregoing equipment, steel and iron being employed throughout.

Except for difficulties in the lines leading to the absorption towers as previously described, no decompositions or explosives have been noted in the rest of the equipment.

The raw acetylene from the flash chambers is treated to remove higher homologues of acetylene either by oil scrubbing or by low temperature cooling. Oil scrubbing which was the system originally used was not too satisfactory in that a gas containing only 96% acetylene was obtained and difficulty was encountered in obtaining a proper oil. The oil scrubbing system is no longer used except for standby purposes. When it is in operation, the raw gas is scrubbed counter-currently at atmospheric pressure. The oil is stripped with a small amount of re-cycle gas to remove acetylene, and this gas (50% acetylene) is returned to the compressors. The oil is then scrubbed with a larger quantity of re-cycle gas for removal of higher acetylene and this gas returned to the arc. Actually, both stripping operations are carried out in one tower. An upper part of 10 bubble caps is for acetylene removal, and a lower part of 30 bubble caps is for removal of higher homologues.

The low temperature system of removing higher acetylenics is interesting for the rather elaborate safety precautions found necessary after an earlier plant had blown up presumably due to explosive polymerization of higher acetylenics. A flow sheet of this system is shown in Fig. 3.

The acetylene produced is stated to have the following analysis C_2H_2 97%; CO_2 1%; other hydrocarbons + N_2 2%.

The raw gas is compressed by Elmo pumps, a water sealed pump very similar to the Nash, to a pressure of 1.4 atm and cooled with water in a packed tower. It is then fed to two finned coolers which are operated alternately. The first cooler is being thawed by the feed gas and the second cooler is cooled by means of pure gas from the low temperature cooler. The gas leaving this set of coolers is at a temperature of about -15°C and passes to the ammonia pre-coolers. The condensate from the aforementioned finned coolers is considered dangerous and is diluted immediately upon leaving the cooler with benzene and water (to aid polymerization). The higher acetylenics are caused to polymerize, the remaining organic is steamed off and partially recirculated.

The gases are cooled to -55°C in two ammonia coolers operating in series. The ammonia is cooled by means of an ethylene refrigerating system.

The gases pass on to another double exchanger where they are cooled by re-cycle gas and by means of ethylene to -78°C.

The condensate from the final coolers, which is 40% acetylene (-65°C) is heated immediately to -40°C to remove the acetylene down to 5%. The mixture containing 40% acetylene is considered very dangerous and so every effort is made to keep the quantity present at this concentration to a minimum. The liquid is then stripped in a packed column (10 m high x 1 m I.D.) by means of gas from the Linde plant which has been pre-heated to 100°C. The top gases from this stripper are returned to the arc.

The gas from this installation is scrubbed with NaOH to remove CO_2 and is then ready for acetaldehyde manufacture as 98% gas.

Each low temperature installation is located in a "box" of steel reinforced concrete some 1-1.5 m thick and open at the top. Nobody is allowed in the box during operation. All necessary valve movements, etc., are carried out from the operating floor outside the box.

It should be helpful to compare the experience at Huels with what would have been expected based on some of the fundamental data as developed by Boesler. Fig. 9 of this report shows the partial pressure of acetylene, in a mixture of acetylene with CH_4 and H_2, necessary for decomposition to start as a function of total pressure. Ignition was with a fusing platinum wire. At a total pressure of 18 atm corresponding to that following the compressors at Huels, this curve shows that an acetylene content of 40% is necessary before decomposition occurs. Compare this with the 16% actually obtaining in the operation. On this basis the Germans felt that the process was safe. At a gas temperature of 100°C the composition would have to be 32-33% before a fusing platinum wire would cause decomposition. What actually occurred has already been described.

Some of Boesler's results give a clue as to what might have happened. He found that at fairly low temperatures, e.g., 200°C, for some mixtures partial decomposition took place before actual ignition had occurred. Also, soot deposits were found on the wires at fairly low temperatures. Boesler in his summary of Rimarski's work of passing acetylene through hot tubes indicates that partial decomposition can take place at fairly low wall temperatures.

It seems not too difficult to postulate conditions of velocity and heat transfer where if a moderate decomposition is started at one point in a pipe line, the wall temperature at that point can continue to rise. If the operating pressure is high, the pipe may be weakened to the bursting point before really rapid decomposition occurs. An analogy might be drawn between the behaviour of acetylene in this case and that

of a gas of high ignition temperature which can be burned if contacted with a hot surface and once the combustion is started will keep the surface hot.

Although the cause of the decompositions at Huels was not determined it seems undoubtedly to be tied up with the presence of higher acetylenics which might supply heat on polymerization or form explosive peroxides with the oxygen in the gas. Once decomposition was started, catalytic action of the pipe wall may have played a part in causing the decomposition to continue. Wetting the pipe wall was effective apparently purely because of its cooling effect in preventing hot spots from developing and in keeping the polymers or peroxides insensitive. There is no evidence of any kind that water exerts any catalytic effect against the decomposition of acetylene.

Butinediol Manufacture

The process for butinediol, operated at Ludwigshafen, has been covered in some detail in a previous report, Hopkinson et al., CIOS Report, Item 22, File No. XXII-7. The present investigation was primarily concerned with the hazards involved and correlating operating conditions with the basic research on acetylene decomposition. As mentioned previously, Weissweiler's work on acetylene decomposition was directed primarily toward making this process safe.

The synthesis of butinediol is briefly as follows: C_2H_2 and 15% aqueous formaldehyde are fed to the top of a 1.5 m diameter by 18 m high steel reactor lined with V4A stainless steel. Normally, two reactors are operated in series. The reactors contain a Cu-Bi acetylide catalyst supported on silica. Operation is at about 110°C and at a pressure of 5 atm gauge. The crude product leaves the bottom of the last reactor and enters a separator. The gas from this separator (110°C) is cooled to 30°C and enters a second separator. The gas from this separator (30°C) is 99% C_2H_2 which is mixed with the fresh C_2H_2 feed, compressed to 5.5 atm gauge and re-cycled.

The liquid from the 30°C separator contains about 6% propargyl alcohol, 10% methanol, 5% formaldehyde and the balance water. This is fed to the methanol still.

The liquid from the 110°C separator contains about 1.5% formaldehyde, 32% butinediol, 15% propargyl alcohol, and the balance water with a very little C_2H_2. This stream is withdrawn at a rate of 13 cubic meters per hour and divided into two equal streams. 6.5 cubic meters per hour are filtered through cloth to remove acetylides and added to the reactor feed tank, together with about 4 cubic meters per hour of 30% formaldehyde as fresh feed plus about 0.5 cubic meters of a 6% methanol-6% propargyl alcohol solution from the methanol still.

The other 6.5 cubic meters per hour of crude butinediol is likewise filtered, passed through a steam stripper to remove C_2H_2 and sent to the butinediol distillation.

The purpose of filtration is to remove copper acetylide washed off the catalyst. Cleaning of these filters is one of the most hazardous steps of the operation. The filters are perforated pipes about 0.5 inches I.D. by 6 ft. long with cloth wrapped on the outside of the pipe. They are arranged in bundles and the flow is through the cloth into the pipes. Periodically these filters must be cleaned. The pipes are removed from the bundle and immersed as rapidly as possible in an aqueous HCl bath to decompose the acetylide. Although some workers have been burned, it was stated that there had been no fatalities.

There is also a tendency for acetylide to build up at times in the 110° separator prior to entering the lines to the filters. Although there have been explosions at this point that have shaken the building, no serious damage has resulted up to this time.

The acetylene used is treated with active carbon to remove phosphorous and arsenic compounds. It was said to contain 15 mg. of sulfur per cubic meter. Feed of fresh acetylene is at the rate of 300 cu. meters per hour. The fresh acetylene at slightly above atmospheric pressure is compressed in two stages by means of Elmo pumps to 4.0 atm gauge. Then it is compressed by another Elmo, together with the re-cycle gas from the 30°C separator to 5.5 atm gauge.

The catalyst is composed of 12% Cu, 3.5% Bi. as acetylides formed in situ on silica which is about 85% by weight. The preparation has been described in the Hopkinson report. A grain of dry catalyst will give tiny local explosions when hammered. However the Germans use reamers to remove spent catalyst and even in bulk it seems to be fairly safe. It is said to be extremely inert when moist. Considerable work had been done on catalyst supports before choosing silica. Bi is supposed to reduce C_2H_2 polymer formation but even with Bi, care must be taken to avoid overheating which gives cuprene and other polymers. The life of the catalyst is about three months. Formation of the catalyst and starting the reaction with formaldehyde are hazardous, and considerable care must be exercised. Silica grains are treated with Cu and Bi nitrates, dried and heated to 500°C in a muffle. The final catalyst has a grain size 2 mm diameter and 6 mm long. Each tower contains 15 tons of this material.

After the towers have been filled with catalyst, the reactors are swept with N_2, and N_2 and water are circulated through the system. The temperature is gradually raised to 70°C. The N_2 is slowly replaced with C_2H_2, and formaldehyde is then carefully added until the feed is about a 15% solution. The feed of C_2H_2 is judged by temperature control, i.e.,

the temperature is raised to the desired 110°C, by control of the C_2H_2 feed.

According to Dr. Reppe, who was interviewed by the authors, the heat of "wetting" of the catalyst with acetylene is very great. This factor makes startup especially difficult.

Rather elaborate methods are used to control catalyst temperature, i.e., to eliminate hot spots which promote cuprene formation or may cause acetylene decomposition. First of all, a minimum liquid flow of 60-70 kg per sq. decimeter is specified to keep the packing wet. This liquid is carefully distributed at the top of the tower by means of an annular distributor. The short distance between the distributor and the catalyst is filled with Raschig rings to aid in distribution and to minimize free space. At various points throughout the catalyst mass are arranged 50 thermal elements to make possible careful checking of the catalyst temperature. At four different levels along the reactor are provided annular distributors for introducing "dry" acetylene. If a hot spot is noted, dry acetylene is fed in just above the hot spot. The C_2H_2 so introduced causes additional evaporation of water with consequent cooling.

All pipe lines, including elbows, were filled with multiple pipes as recommended by Weissweiler to prevent detonations. All empty spaces throughout the system which could not be filled with such tubing were filled with steel Raschig rings, generally 50 x 50 mm. The separators, dished heads of the towers, etc., were all so filled.

The tube size used for filling pipes was 14 mm I.D. with a thin wall. In general this tubing was merely held in place by friction, a section of large pipe being prepared by filling it with tubes of the same length and hammering in the last few to hold the whole bundle in place.

Dr. Pistor and Dr. Steinhofer, in charge of the operation, stated that on six different occasions decompositions had occurred which filled the lines with carbon and even melted the pipes in spots. Pistor described having been at the top of the reactor on one occasion when the acetylene inlet pipe became red-hot. One of the plant operators told us that one night an entire reactor started to glow. Everybody ran for the air raid shelter except one man who knew the system thoroughly and stayed to shut off the acetylene. In none of these cases did a detonation occur. It should be mentioned here that the equipment is designed to withstand 100 atm pressure. No equipment has ever been actually blown open by an explosion although pipes have burst after having been softened by the intense heat.

The authors were shown discarded lines filled with carbon and showing signs of fusion of the metal.

The reactors themselves are separated from the control room by a concrete wall, which however, it was stated, was not designed to take heavy explosions. The separators were in separate rooms from the towers and fairly well protected by heavy concrete walls.

The measures developed by Weissweiler seem to have been very satisfactory in preventing the development of a detonation. There seems little doubt that without these devices the installation would have been completely destroyed. If one again inspects Fig. 2 of Boesler's report it is seen that at the pressure used in the butinediol process a decomposition could be caused by a hot surface of 300-400°C. In this particular case there are acetylides present, which can serve as igniters, and also by the nature of the process hot spots can occur in the tower which may cause decomposition. The Germans felt that in such a process decomposition could hardly be avoided at all times, but that if detonation could be prevented, the equipment could be designed to withstand any pressures developing, i.e., a maximum of 12 times the operating pressure. A decomposition would then cause no damage; the equipment could be cleaned out and the operation started again.

Koresin

The manufacture of Koresin at Ludwigshafen has been well outlined in a previous report, Hopkinson et al., CIOS Report, Item 22, File No. XXII-7.

The process consists of treating 800 kg p-tertiary butyl phenol plus 68 kg zinc naphthenate with C_2H_2 in a horizontal agitated steam jacketed autoclave operated up to 16 atm gauge and at a temperature of 180-230°C. After about 200 kg C_2H_2 have been reacted which requires 12-16 hours, the product is discharged. Formerly the melting point of the resin was followed but now the operator judges the state of the reaction by the C_2H_2 consumption and the pressure.

The autoclave is lined with stainless steel (V4A) and has a volume of 1500 liters. The agitator is steel, and presumably of the paddle type, although no blueprints could be found. Dr. Christ, who is in charge of this process which started about 1939, had never seen the autoclave opened since 1940 when he became connected with the operation. The speed of agitation was about 45 r.p.m. This autoclave was built to stand 300 atm and has a steam jacket carrying steam at 20 atm. The agitator stuffing boxes at both ends of the autoclave are water cooled and an asbestos-graphite packing is used. A new piece of packing is put in every 48 hours.

The process is carried out as follows: The mixture of p-tertiary butyl phenol and zinc naphthenate is melted in a jacketed agitated kettle heated with steam at 2-3 atm and any water removed at a pressure of

100-200 mm Hg. It is important to prevent water from being added since the catalyst activity is reduced, and the product becomes opaque.

The above dried mix is fed into the autoclave which is filled 2-3 times with N_2 to 3-5 atm and vented to remove air. The autoclave pressure is then raised to 3 atm with N_2 and the autoclave temperature brought up to 100-120°C. Acetylene is then added until the total pressure is about 15 atm, and the temperature is further raised to 180°C. The C_2H_2 reacts readily; the temperature rises to about 220°C and the pressure falls to about 8 atm gauge. C_2H_2 is fed at full compressor capacity, during this period until a temperature of 220°C is reached. The C_2H_2 feed is then reduced to 10-12 m^3/hr to prevent the temperature going too high. Feed of C_2H_2 is continued until the pressure which fell within the first hour to 8 atm reaches 15 atm gauge. This takes about 14 hours. Examination of the pressure charts showed the following:

Time in hours approximate	Pressure atm gauge
0	3 atm gauge N_2
0.5	16 total N_2 - C_2H_2
1	8 "
7	10 "
12	12 "
14-15	15 "

When 15 atm is reached, the gas in the autoclave, it was stated, contains about 50% C_2H_2 due to buildup of inerts from the C_2H_2. N_2 is now added to give 25-30 atm to aid in blowing out the charge. After discharge, a fresh batch of p-tertiary buty phenol and catalyst is added to the hot autoclave; 3 atm N_2 are added, and the cycle repeated as above. C_2H_2 feed is measured by a gas meter on the low pressure side of the compressor.

The C_2H_2 used is ordinary 99% welding grade from Oppau wet carbide generators and has been water washed but not specially purified. No arrestors or precautions are taken on the low pressure side, which is at a pressure of 270 mm H_2O.

The compressor used was of standard construction and had no novel features. Three stages were employed with intercooling.

In the line between the compressor and the autoclave, there was provided an explosion arrestor consisting of a porous filter stone approximately 70 mm long by 38 mm diameter. This device was considered by Dr. Christ to be an effective arrestor but of limited applicability because of the high pressure drop at appreciable gas flows. At one time a check valve had been used in connection with the filter but since discarded

because of deterioration of the rubber parts.

In spite of the rather drastic operating conditions involved in this process no trouble from decomposition of acetylene had been encountered to date. No special precautions were taken to protect the operators from possible explosions.

It is extremely interesting to compare the operating conditions obtaining in this process with the fundamental data as developed by Boesler. It is at once apparent that the success in running this operation has been the judicious use of nitrogen. Fig. 2 of Boesler's report shows the pressure at which pure, dry C_2H_2 will decompose as a function of the igniter temperature. At a pressure of only 7.5 atm decomposition can be brought about by use of a fusing lead wire of 300-330° melting point. The curve for pressure vs, temperature is rising rapidly in this range so that extrapolation is difficult, but it probably can be assumed that at 15 atm. the temperature to bring about ignition might be in the range 200-250°C. Of course the limitations of the experiments as pointed out by Boesler, viz. that there is a spark as the wire fuses should not be forgotten. At any rate the data indicate that it would be foolhardy to run without nitrogen and that trouble would be expected.

Figure 6 of Boesler's report is also interesting in evaluating the probable margin of safety of the Koresin process. This figure shows the pressure necessary for decomposition of mixtures of acetylene with nitrogen. In this case the igniter is a fusing platinum wire. At 200°C such a mixture will decompose if the acetylene concentration is 30%. Of course, this ignition is undoubtedly more drastic that what might occur in the Koresin operation. It is probably significant that agitation of the autoclave is good so that local hot spots cannot build up to give trouble.

In consideration of the foregoing discussion, it seems rather remarkable that no decompositions have occurred.

Vinyl Pyrrolidon

The preparation and use of Vinyl Pyrrolidon at Ludwigshafen was covered in CIOS Report XXVII-85, Item 22, by Kern, Murray and Sudhoff. This process was examined again from the viewpoint of hazards in handling acetylene. The production of gamma butyrolactone by dehydrogenation of 1-4 butandiol and the formation of pyrrolidon by reaction of the lactone with NHg were discussed in the above report and were not studied further. Additional information on the polymerization of the vinyl pyrroliden was obtained and is included here.

Dr. Christ supplied the following information on the vinylation which is in substantial agreement with that obtained by earlier

investigators. The vinylation is carried out in a vertical steel reactor 16 m high and 200 mm in diameter which was built to stand a pressure of 200 atm. The lower third of the reactor is jacketed with steam at 20 atm. The upper two thirds is oil jacketed for heating or cooling with a circulation of 10-20 m^3/ hour of oil.

The reactor is fitted with base inlets for the feed of a solution of pyrrolidon-KOH and a mixture of C_2H_2-N_2. The gases leave the top of the reactor through a cooler and separator. The C_2H_2-N_2 is recirculated by a pump through a steam jacketed line while the crude vinyl pyrrolidon is run to a small receiver from which it is withdrawn to crude storage.

In starting the operation, the apparatus is swept with N_2, then a pressure of 10 atm. of N_2 applied, and the reactor heated to 140°C. 200 kg of a pyrrolidon-KOH mixture (about 3-4% KOH) is pumped into the reactor and a feed of 5-10 liters per hour of KOH free pyrrolidon started into the base of the reactor through the steam jacketed C_2H_2-N_2 preheater. The pyrrolidon-KOH mix is prepared by adding 100 kg powdered KOH to 2000 kg pyrrolidon at 40-50°C and distilling under vacuum until about 300 kg of distillate are removed. The mix is then cooled to about 50°C.

Pyrrolidon is fed with the C_2H_2 to prevent C_2H_2 from ever contacting dry KOH which to date fortunately has caused only a vigorous slow C_2H_2 decomposition accompahied by the melting of the inlet line. This is an important point in all C_2H_2 processes using KOH at high temperature. One contact point with KOH could conceivably serve as the source of ignition leading to a detonation if the conditions were right.

The pressure is now raised to 20-25 atm with C_2H_2 and the temperature adjusted in the reactor to 150-160°C. A 60% C_2H_2-40% N_2 composition is maintained in the recycle gas which is circulated at a rate of 5 m^3/ hour, by a pump built for 200 atm.

The following conditions are now observed in normal operation:

Reactor Base	150-155°C
Reactor Middle	160-170°C
Reactor Top	150-160°C
Inlet Gas	90-100°C
Circulating Gas	60% C_2H_2
Pressure	22-25 atm
Fresh C_2H_2 Feed	10-15 m^3/hour

After about 45 m^3 C_2H_2 are fed, the vinylation is continued feeding 30 liters of the pyrrolidon-KOH mixture per hour to the reactor base. The feed of 5-10 liters/hour of pyrrolidon to the gas preheater and 15-20 m^3/hour fresh C_2H_2 are continued.

The gas stream off the top of the reactor is cooled to 40-50°C, the gas recirculated and the crude vinyl pyrrolidon collected in a 200 liter receiver from which it flows to a larger receiver of about 2 m^3 volume where it is kept at atmospheric pressure.

The crude product is distilled at a rate of 50-100 liters per hour at 5 mm/Hg, at which pressure the main production of pure vinyl pyrrolidon distills at 70-80°C. There is a small foreshot and the main fraction is followed by a binary of vinyl pyrrolidon-pyrrolidon. The yield of vinyl pyrrolidon is 60% theory based on the pyrrolidon.

Dr. Fikentscher supplied the following information on the polymerization of vinyl pyrrolidon for Periston, the synthetic blood plasma. A 300 kg batch of a 30% water solution of vinyl pyrrolidon is prepared. Half this batch is put in a kettle at 80°C and the remainder is added step wise. Polymerization is catalyzed with 0.05-0.2% H_2O_2 using half as much NHg as an activator. About 2-3 hours is required for polymerization. The H_2O_2 also controls the molecular/weight of the product. It is probable that the Germans had specifications on the mol. wt. for plasma use but these were not available.

In this process as in the Koresin process, the secret of successful operation is the proper use of nitrogen and a knowledge of just how much nitrogen is necessary to make the process safe. The same comparisons with the Boesler data can be made as were considered under the Koresin process. In this case trouble was at one time encountered due to acetylene being decomposed by contact with dry KOH. Such possibilities of ignition due to some abnormal process conditions should always be considered in setting up such processes.

Vinyl Ethers

The method of making vinyl ethers at Ludwigshafen has been outlined in a previous CIOS Report, Item 22, File No. XXVII-85 by Kern, Murray and Sudhoff.

The vinylation of alcohol is carried out by contacting a solution of KOH in the alcohol with acetylene at temperatures of 150°C to as high as 175°C depending on the alcohol. The pressure varies from about 22 atm for methanol down to zero for a high boiling alcohol such as octadecyl.

The reactor is a steel tower with a volume of 4.7/m^3, 700 mm diameter by 10 m in height and is normally operated with 2.5/m^3 of solution. Temperature, pressure, feed rates, etc., for the production of the isobutyl, ethyl and methyl vinyl ethers are given in the attached table.

KOH solution in the given alcohol is introduced at the base of the reactor which contains a steam heating coil, the C_2H_2-N_2 feed is preheated by steam in a heat exchanger with a portion of the alcohol feed and likewise introduced at the base of the lower. The alcohol prevents dry KOH

contacting C_2H_2 at the gas inlet. This is Very Important. Before this was done, several C_2H_2 decompositions occurred. Acetylene should NEVER be allowed to contact solid KOH under these temperature conditions. The inlet of V2A steel and the reactor base were melted by C_2H_2 decompositions before these precautions were taken.

The mixture of C_2H_2, N_2, alcohol, ether and acetal leaves the top of the reactor through a partial condenser and passes through a gas-liquid separator. The liquid phase enters the first heated stripper which is fitted with a partial condenser. The liquid discharged from this stripper normally has the following approximate composition:

500 kg vinyl ether/hr
300-400 kg alcohol/hr
10-15 kg C_2H_2/hr
15-25 kg acetals/hr

The N_2 plus C_2H_2 from the gas-liquid separator and from the first stripper is mixed with fresh compressed C_2H_2 feed and recirculated.

The mixture of ether, alcohol, C_2H_2 and acetal is now fed into an acetylene stripper at reduced pressure as shown in the table. The 10-15 kg/hr C_2H_2 from this stripper is returned to the C_2H_2 gasometer.

The ether is separated from most of the alcohol and acetal by distillation. The conditions are also given in the table. Alcohol-acetal separation is then carried out in another column.

The crude ether usually 500 kg/hour, stored under N_2, is purified by a continuous water wash, separated, and the ether dried with solid KOH. The alcohol-water from the ether washer is then distilled to recover the alcohol which is returned to the alcohol storage.

An important feature of the process is the continuous withdrawal and purification of about 100 kg/hour of the mixture in the reactor. This is necessary to prevent the build up of salts. The mixture which may have about the following composition: 60 kg alcohol, 20 kg acetal and ether, 15 kg KOH and 5 kg salts is mixed with water in an agitated kettle and distilled off. The distillate, 80 kg/hour of ether-alcohol-acetal, goes into the feed to the ether still.

Dr. Christ stated that alcohol stabilized the ether against polymerization and therefore there were no difficulties prior to isolation of the alcohol free ether.

TABLE

VINYL ETHER MANUFACTURE SUMMARY

Product	Iso Butyl Vinyl Ether	Ethyl Vinyl Ether	Methyl Vinyl Ether
Feed kg/hr ROH	900	800	700
KOH	12	20	25
Reaction Temperature	150-155°C	155-160°C	160-165°C
Pressure atm.	4-5	18-20	20-22
% N_2 in C_2H_2	90	60	55
ROH fed with C_2H_2 kg/hr	100	100	100
Approx. % of KOH maintained in reaction mixture	12-15	20	22
Operating pressure atm final C_2H_2 stripper	0	4	6
Ether crude still temp.	82°C	approx. 45°C	approx. 45°C
Pressure atm	0	1	4
Approx. feed/hr to still	500 kg ether 300-400 kg alcohol 15-25 kg acetal		
% overall yield ether	92	90	85-90
Approx. production tons/month	50 for Oppanol * 75 adhesives 50-100 oils for leather	50 adhesives	10-20 for textile finishes, latex heat sensitization **

(*) Polymerized in propane at - 30°C with BF_3

(**) They were considering expanding this for CH_2CHO production with MeOH re-cycle, thus avoiding Hg catalyst for CH_2CHO.

The C_2H_2 used for vinyl ethers was the same as that used for butinediol production. Dr. Christ said they could use the same welding grade C_2H_2 used for Koresin.

The following information was obtained on the C_2H_2 compressors.

Cylinder Diameter	1st stage 370 mm 2nd stage 210 mm 3rd stage 120 mm
Stroke	300 mm
Pulley Wheel	Diameter 2500 mm
Fly Wheel	Width 350 mm Speed 65-85/RPM
Capacity	100-130 m^3/hour
Final Pressure	30 atm
Power Requirement	28-36.5 H.P.
Cooling Water	1.6-2.1 m^3/hour
Manufacturer	Sulz Wurzen 25-4-41

The high pressure C_2H_2 line was 40 mm i.d. and was supposed to stand 200 atm. Close to the compressor in this line were a check valve and an explosion arrestor of large pipe filled with raschig rings.

So far as acetylene handling techniques are concerned, here again the importance of using sufficient nitrogen is emphasized and the necessity of preventing contact between acetylene and dry KOH pointed out again.

Reppe Laboratory

The I.G. Farben Company built a laboratory at Ludwigshafen devoted to acetylene research under the direction of Dr. Reppe. In this laboratory acetylene gas is piped at a pressure of 30 atmospheres to the various laboratory benches where autoclaves are located. The acetylene supply is compressed to this pressure in a three stage compressor of usual design for acetylene. The acetylene is circulated through the piping system and what is not used is re-cycled to the supply side of the compressor through an automatic valve. All piping is 40 mm in size.

The supply manifold is protected from each branch line by means of a so-called Magin check valve so named after the person who invented it. The purpose of the valve is to prevent decompositions originating at the point of consumption from propagating back to the manifold and the rest of the system. This valve works somewhat on the principle of a bicycle valve. Gas can pass through it in one direction only. A number of rubber bands are held in place over numerous holes in the core of a device looking somewhat like a strainer. The gas pressure pushes the rubber off the holes for flow in one direction, but the rubber snaps the holes shut if the downstream pressure rises above supply pressure. Such an arrangement having very little inertia is said to be very fast acting and capable of reacting to the pressure rise occurring from decomposition before the actual flame front reaches the valve. Other types of check valves were stated by Reppe as being too slow acting.

The Magin valve so far has not been adapted to any but small size pipes.

The autoclaves are of such a size that they can withstand any decomposition including detonation. Hence experiments under any reaction conditions desired can be carried out.

Cyclooctratetraene

The preparation of cyclooctatetraene is cited as an example of the type of work done in the Reppe laboratory. This involves contacting a nickel cyanide catalyst suspended in tetra hydrofurane at 70°C with acetylene at 15-20 atm pressure. Although this synthesis is only in a laboratory stage it presents many interesting possibilities. The original work was done with ethylene oxide in an attempt to react that with acetylene. Careful observation of the results led to a concept of the possible reaction mechanism and the choice of tetra hydrofurane which gave improved yields of cyclooctatetraene.

Laboratory directions for the preparation of this material as obtained from Dr. Reppe are given below:

20 g. nickel cyanide (see below)
50 g. calcium carbide powder are suspended in 2 liters of tetrahydrofurane and put in a 4 to 5 liter container. The autoclave is purged of air as usual with nitrogen and under a N_2 pressure of 5 ata is heated to an inside temperature of 60-70°C. The contents are kept in motion through agitation or by rolling. After the reaction temperature is reached, the pressure is raised with C_2H_2 to 15-20 ata until the solution is saturated and the consumption falls off markedly. After this, acetylene additions are made only hourly to maintain the pressure.

One can also hold an agitated autoclave under constant acetylene pressure, if it is provided with a Magin check valve.

If the reaction is stopped after 60 hours, one obtains a brown solution, in which cuprene is suspended. The cuprene and catalyst are filtered off. For best yield the filtrate is given a preliminary distillation at reduced pressure. When the solvent and the benzene resulting from the reaction have been largely removed, an exact distillation is carried out at 14-20 mm Hg. One obtains in this way the cyclooctatetraene (separated from residue), which is subjected to rectification under normal pressure. Under these conditions 320 - 400 g of cyclooctatetraene are obtained, 30-50 g of resin and approximately 50 g benzene.

Nickel cyanide has been shown to be the most effective catalyst, which gives a good conversion of acetylene with comparatively little resin

and benzene formation, especially when it is made from nickel chloride and HCN. To do this, nickel chloride is dissolved in denatured alcohol, cooled to 0 to 10°, and treated with an approximately 10% alcohol solution of HCN. It is allowed to stand for 12 hours at this temperature, treated again with alcoholic HCN solution to complete precipitation, and then after another 12 hours the precipitated nickel cyanide is filtered off. After washing with water until neutral, the light blue nickel cyanide is converted at 175° into the yellow brown anhydrous salt. Other nickel cyanide is inferior in effectiveness to salt produced in this way. If one uses an acid free and dry nickel cyanide produced in this way and a completely anhydrous tetrahydrofuran, it is possible to obtain a satisfactory yield of cyclooctatetrane without addition of calcium carbide, provided of course that the acetylene is not too moist.

If one works under the conditions given, higher boiling hydrocarbons as well as at times azules (only traces) are produced. The formation of these hydrocarbons is very much dependent upon the temperature. If the reaction temperature is raised to 110-130°, higher boiling oils are obtained, besides larger amounts of resin and cuprene, accompanied by a decrease in formation of cyclooctatetraene. These oils are generally colored blue from the azules. Especially suited for the formation of higher ring homologues of cyclooctatetraene are nickel salts such as the carbonate and formate, also, the substitution of ethylene oxide for the calcium carbide has a favorable effect. The concentration of this material should not exceed 5% based on the tetrahydrofuran used. Copper powder has been shown to be effective as a catalyst for the formation of these C_{10} and C_{12} hydrocarbons. After 60 hours, in addition to 200 g cyclooctatetraene, approximately 50-100 g higher boiling hydrocarbons are obtained.

Miscellaneous

Several interesting processes, carried out on a plant scale, using acetylene, not covered in detail in this report, are as follows:

At the Hoechst plant is located the largest vinyl acetate installation in Germany, viz., 1000 tons per month. Details of this process are given in CIOS Report, I.G. Farben Industrie, A.G., Hoechst am Main, Item No. 22, File No. XXVI-11, by Richardson et al. In this process, C_2H_2, containing 23% acetic acid is steam heated to 170°C and passed through catalyst beds of activated carbon impregnated with zinc acetate and held at a temperature of some 200°C by electrical heating. Pressure is slightly over atmospheric.

At Huels acetylene is hydrogenated to ethylene in a process involving passing an acetylene-hydrogen mixture at 200°C over a palladium catalyst suspended on silica gel. Details are given in CIOS Report, Plant of Chemische Werke, Huels, Germany, File No. XXVI-51, by Haensel and Cotton.

At the Leverkusen plant, vinyl cyanide is manufactured by reacting acetylene and HCN in the presence of a cuprous chloride catalyst. For details see CIOS Report, Item No. 22, File XXIII-25, by Curtis and Fogler.

At Ludwigshafen vinyl benzoate is produced by passing an acetylene gas stream carrying benzoic acid (ratio of about 10 cbm of acetylene per kg of benzoic acid) over a catalyst of mixed cadmium and aluminum oxides suspended on activated charcoal at a temperature of 250-300°C. Details were not obtained.

Also, vinyl carbazole is produced at Ludwigshafen by the action of acetylene on carbazole under pressure in a process similar to that for vinyl ether production.

Details on the two foregoing processes as well as other Reppe processes are to be given in a book now being prepared by Reppe under the direction of U. S. military authorities.

DISCUSSION AND CONCLUSIONS

It is believed that the information presented in this report will be useful in planning new processes where acetylene is used and in estimating in a qualitative way the probable hazards of existing ones. Although the handling of acetylene for chemical operations, unfortunately, is not yet an exact science, some general principles can be enunciated. The first consideration is of course the normal pressure and temperature of operation, and the acetylene concentration involved. If these are outside of the limits given as subject to decomposition by Boesler, the process probably is reasonably safe. However, further consideration must be given to the possibility of these conditions being changed through accident or misoperation until they lie within the decomposable range. Also, the possibility of an igniter being present cannot be overlooked. The Huels installation seemed safe enough judging from the Boesler data so far as normal operation was concerned. However, apparently an unexpected igniter was present.

In the various operations at Ludwigshafen, i.e., Koresin, vinyl ethers, and vinyl pyrrolidon, the Boesler data indicated how much nitrogen was necessary. Here, however, the possibility that acetylene could be decomposed by contact with KOH at elevated temperatures was overlooked in the last two processes.

The presence of water or other liquid is highly desirable because of the cooling effect exerted by evaporation of the liquid in case of a local decomposition which may prevent propagation. The liquid also makes initial ignition more difficult, and may prevent development of a local hot spot sufficiently high in temperature to cause ignition. The butinediol and Huels processes are good examples.

As mentioned previously there is no evidence that water has any special catalytic effect on the decomposition of acetylene.

Long lengths of large diameter pipe under pressure are to be avoided so far as possible because of the possibility of detonation. Use of tube bundles within large pipes is an effective way of avoiding detonations with resultant high pressures. If detonations can be avoided by proper equipment design, viz., keeping down empty spaces, a process can be operated safely within the decomposable range since final pressures resulting from decomposition will not exceed 10-12 times the initial pressure which can be provided for in the design.

Packed lengths of pipe filled with raschig rings make effective explosion arresters if used properly and can be used to isolate various pieces of equipment. Also detonations can be prevented by filling empty spaces with raschig rings.

Exhibit A

The Decomposition of Acetylene By Initial Ignition

Dr. Ing. Boesler, Oppau
May 8, 1930

1) Goal and Purpose of Experiments:

The experimental results on the decomposition of acetylene published by Bertholet for the first time have been recently reviewed and considerably extended by Rimarski of the Phys. Techn. Reichanstalt. His results were published in a special booklet by the V.D.I. in 1926. In addition there are available some results of laboratory experiments of the I. G. at Griesheim (Lab. Ber. 228/1926). These experiments have to do primarily with pure acetylene; part are directed towards the needs of welding technique. They also deal with mixtures of acetylene with gas oil and H_2.

In considering the behaviour of $C_2 H_2$ in the presence of different gases, the constituents of coke oven gas namely H_2, CO, and CH_4 seemed most important. Certain experiments were planned to determine the decomposition pressure under the following conditions: With pure $C_2 H_2$ as a function of (1) vessel diameter, (2) moisture content, (3) temperature, (4) the composition of the igniting wire. With gas mixtures as a function of the gas added, viz., N_2, H_2, CH_4, $C_2 H_4$, CO, (N_2 + H_2), (H_2 + CH_4) and as a function of temperature.

In all cases initial ignition was accomplished by fusion of a platinum wire.

2) Apparatus

The experiments were carried out in a bomb (see sketch), of a diameter and height of 270 mm. In order to determine the effect of different vessel diameters on the resulting decomposition pressure cylindrical liners (a) of 100, 150, and 200 mm. diameter were used; also for preliminary experiments a smaller bomb having a diameter of only 50 mm. was used. The gas inlet and outlet are located in the cover as well as the igniting apparatus (b). In the bottom are an opening (c) for a sight glass for observation of the igniting process,

and two openings for a thermo couple (d) and the electric leads (e) of the electric heater (f). This last consists of resistance wire which was wrapped around an insulator and was provided on the inner side with an asbestos cover to eliminate effect of radiation on the thermo couple. For determination of the pressure in the bomb, manometers were provided in the inlet and outlet gas lines. These manometers were always calibrated after the completion of a series of experiments. In order to fill the bomb with gas in the dry state, vessels filled with calcium chloride were provided in the gas supply line. In preliminary experiments in which this procedure was not followed, especially with a mixture of H_2, an appreciable scattering of data occurred.

3) Experimental Procedure

After being well swept with gas, taken from a cylinder, the bomb was filled with gas to a pressure approximating the decomposition pressure expected, and the ignition brought about. If a decomposition did not occur, the pressure would be raised 0.1 to 0.2 ata* for another trial at the same temperature, until a decomposition took place. In order to ascertain the point accurately, two additional experiments were always carried out at a slightly higher and lower pressure. This procedure was advantageous, although it could be dropped, after a general pattern had been established, inasmuch as it was very time consuming. In the case where C_2H_2, saturated with water vapor was being investigated, water instead of calcium chloride was put in the vessels, so that the gas passed through it. Also a certain amount of water was sprayed into the bomb. In order to make certain that saturation had been reached, the gas was allowed to stand for a time before ignition.

The mixing of the gases was accomplished in the bomb itself. After filling, a certain time was allowed to permit complete mixing.

The heating of the contents of the bomb by electrical means through a resistance lying in the explosion chamber, which was operated at intervals to obtain a certain temperature, was not an ideal method. It had to be used, however, since heating from the outside would have taken too long.

(*) 1 ata = 1 kg per sq. cm. absolute

To avoid great loss of heat, the bomb was covered with an asbestos sheath and heated from the outside with steam. Furthermore, before beginning an actual experiment, the bomb was filled with H_2 and held for some hours under high temperature in order to heat the walls of the vessel. In the case of an inside temperature of 100°C, an outer wall temperature of 85°C was observed; in the case of 200°C on the inside, a temperature of 130°C was measured on the outer wall.

The intermittent heating proved necessary because of the lag in the thermo couple. This was of normal construction and contained in a pipe of 3.5 mm. I.D., and 5.0 mm. O.D. As a result of the large heat capacity of the soldered joint, a lag in the temperature measurements could be observed. In order to determine the size of this error, heating experiments, independent of the actual experimental program were carried out, in which a second thermocouple was introduced, consisting only of the bare iron-constantin wires. Also to avoid flow of heat to the bomb wall, the wires were looped several times. In rapid heating, this thermocouple showed on the average a temperature 4° to 6° higher than the first couple. With short interuptions in heating, equalization of the two readings occurred immediately. Since the thermocouple could not follow the rapid temperature changes taking place during a decomposition, no measurements of this kind were undertaken.

The decomposition pressure was measured by means of manometers. It would have been very interesting to have measured the actual pressure rise during decomposition, which might be done by means of an optical indicator. In the absence of such equipment only relative values were observed. (Furthermore observation of the decomposition was made through the sight glass). This could be done better than had been expected. The highest pressure reached cannot be determined accurately in this way, since in the comparatively long and narrow lines to the manometers a certain amount of throttling occurs, which distorts the readings. Also the manometers because of inertia probably register high. As a comparison, the final pressure developed was determined by calculation from the heat released and the specific heat of the gases.

The construction of the igniting apparatus and the investigation of the influence of ignition were the subject of special experiments. As Rimarski states, he used a platinum wire of 0.15 mm. diameter, which by regulation of the current he could bring to different temperatures or to fusion. He also made use of a Bosch spark plug. This latter method was

rejected by us after some experiments, which showed it to be unsuitable. At higher pressures when a higher voltage was required to make a spark, breakdown of the insulation occurred. Of course it would have been possible in order to work with lower voltages to have reduced the spark gap, but this would have meant an unnecessary complication in carrying out the experiments. When a pressure of 10 ata is exceeded, this arrangement is no longer usable since even at a very short spark gap the insulation breaks down. Also near the decomposition pressure, a partial decomposition of acetylene takes place whereby soot deposits between the electrodes and acts as a conductor.

The difference between an incandescent and a fusing wire already observed by Rimarski was substantiated by us. It was shown that with use of a fusing wire, decomposition occurs at a lower pressure than with an incandescent wire. For example, with pure acetylene decomposition was observed at 1.40 ata with the former, and 1.60 ata with the latter. For this reason a series of experiments was carried out with different wire temperatures (see Fig. 2). Of course, it is obvious that if trends are to be determined, a definite type of ignition must be used throughout. Also, according to the experiments performed thus far, the speed of ignition was also important, i.e., a fast or slow fusion of the igniting wire. It was observed that, with pure acetylene and more especially with mixtures of C_2H_2 and CH_4, in the neighborhood of the decomposition pressure, products separate out on the glowing wire and cover it with a carbide like layer, so that the wire requires a longer time for fusion. There were even instances in which the current was on for such a long time that complete decomposition took place without actual fusion of the wire having occurred, whereas under similar conditions rapid fusion would not have caused decomposition. From this it appeared that the decomposition pressure was dependent not only upon the temperature of the igniter but also upon the time during which it is hot. This kind of slow ignition was especially noticeable at a comparatively small bomb volume, which for the small bomb used for preliminary experiments amounted to only 250 cc. The decomposition pressures determined in this way show considerable scattering and are by no means reproducible with great exactness. In contrast, the quick fusion of the igniting wire proved to be a reliable method and gave results which could always be reproduced.

The material of the igniting wire is extremely important, and for this reason, this point was especially investigated for pure acetylene.

In order to carry out all experiments under constant conditions, the following were held fixed:

1. The igniting apparatus was always in the cover of the vessel.

2. The igniting wire was of platinum of 0.5 mm. diameter.

3. The wire length was 10 mm.

4. The igniting current was such as to cause an instantaneous fusion of the wire.

The following experimental results are valid only for the above conditions.

Experiments

4) Pure Acetylene

4a) Relation between Decomposition Pressure and Vessel Diameter; Magnitude of Explosion Pressure.

First of all, the decomposition pressure of pure, dry, acetylene at various vessel diameters was determined at a gas temperature of 15° - 17°C. The experimental results of Rimarski served as a starting point for this work, although his values throughout, lay somewhat higher than ours as already mentioned above. This discrepancy is probably due to the unavoidable differences in igniting methods. The curves, which show the decomposition pressure as a function of vessel diameter (Fig. 1), are exactly similar in the two cases.

The following table shows values determined (see Fig. 1).

Vessel Dia. in mm.	Decomposition Pressure in ata Our Experiments	Vessel Diameter	Decomposition Pressure in ata (Rimarski)
50	1.80	38	2.1 to 2.3
100	1.60	66	1.80 to 1.85
150	1.45		
200	1.40		
270	1.40	250	1.50 to 1.55

The three points determined by Rimarski are not sufficient to give a good picture of the dependence of decomposition

pressure on vessel diameter. However, the intermediate values determined by us at 150 and 200 mm. diameter show that the decomposition pressure approaches the value 1.40 ata asymptotically and as a matter of fact reaches this value at a diameter of only 200 mm., so that above this there is no further influence of diameter. The cause of the different pressures with different diameters is explained by the so-called "wall effect". It is probable that dissipation of heat through the wall at ignition has an influence on the progress of the decomposition. This theory is supported by the fact that with dilute acetylene no dependence of decomposition pressure on vessel diameter could be observed, because the dissipation of heat through the walls of the bomb is small compared to the heat taken up by the gas mixture.

At low acetylene pressures, the ignition wire fuses readily. The closer the decomposition pressure is approached, the more soot and polymerization products are found on the wire. With smaller vessel diameters, furthermore, a thin coating of soot is formed on the vessel walls, so that at least a partial decomposition must have taken place, although on so small a scale that a pressure rise in the bomb from the heat so released cannot be determined.

The spark occurring as the wire separates becomes brighter as the decomposition pressure is approached, which means that in the immediate vicinity of the igniter there is a zone of decomposition, which with increasing pressure becomes larger and at the actual decomposition pressure is suddenly distributed over the entire bomb, the contents of which become almost incandescent.

The pressure rise caused by the decomposition of pure acetylene takes place very rapidly, and at a vessel diameter of 270 mm. and an initial C_2H_2 pressure of 1.40 ata, the final pressure amounts to 13 ata, i.e., approximately 9.5 times the initial pressure. Rimarski obtained 15 ata final pressure with an initial pressure of 1.80 ata. From the heat of decomposition of C_2H_2 (53,000 K Cal/mol) and the specific heat of C and H_2 a final temperature of 3100°C would be obtained neglecting heat transmitted by the walls. This corresponds to a pressure rise of 12 times. This value checks satisfactorily with the measured value. (With a bomb diameter of 50 mm. a final pressure of only 6 ata was observed in spite of the higher initial pressure (1.80 ata) because of the larger rate of heat transfer to the walls).

4) Dependence of Decomposition Pressure on Igniter Temperature (Composition of the Igniting Wire)

Sufficient electrical energy was used on the wires of various materials (molybdenum, platinum, iron, copper, aluminum and lead) to cause instantaneous fusion. With the exception of the lead wire, which had a diameter of 1 mm, only wires of 0.5 mm diameters were used.

For the different materials the following decomposition pressures were obtained for pure, dry acetylene.

Melting Point °C		Decomposition Pressure ata
Mo	2550	1.40
Pt	1760	1.40
Fe	1530	1.71
Cu	1080	1.84
Al	660	2.65
Pb	330	7.50

The results are shown graphically in Fig. 2. Particularly noteworthy is the sharp rise of decomposition pressure in the low temperature region.

Although the melting points of the materials cannot be regarded as a direct measure of ignition temperature, one sees a definite relationship between the melting points of the material and the decomposition pressure. It can be assumed from this, that to bring about a decomposition, a certain energy is necessary. Since this is small with a lead wire, the corresponding decomposition pressure is very high and for platinum and molybdenum is very low. Whether the decomposition pressures with platinum and molybdenum are absolutely equal could not be determined exactly. It is hence understandable, that with the use of incandescent wires (not fused) the diameter of the wire (surface) plays an important role, and it is to be expected that use of thin wires, because of the lower energy involved, would result in higher decomposition pressures than with thick ones. Investigation with a copper wire of 0.1 mm diameter corroborated this assumption. A decomposition pressure of 2.1 ata was obtained as compared to 1.7 ata with a diameter of 0.5 mm.

4c) Relationship between Decomposition Pressure and Gas Temperatures

The dependence of decomposition pressure on the gas temperature was determined for pure dry acetylene in a bomb of 270 mm diameter. The ignition was by means of the instantaneous fusion of a platinum wire of 0.5 mm diameter.

The following table shows the results:

Temp. °C	Decomposition Pressure ata (Our Observations)
15	1.40
100	1.25
150	1.13
180	1.06

Temp. °C	Decomposition Pressure ata (Rimarski)	
15	1.60	(1.45)*
50	1.48	(1.40)*
100	1.33	
140	1.10	

The results are shown graphically in Fig. 3. There are some differences between our values and those of Rimarski, which can only be explained by the fact that Rimarski used an incandescent platinum wire. The inaccuracies of this method have already been mentioned, especially the fact that the time of ignition cannot be controlled. According to Rimarski decomposition at a pressure of 1.0 ata must occur at a temperature of 150°C, whereas we found that at 1.06 ata complete decomposition first took place at 180°C, and even then at such a slow rate that only a very small pressure rise resulted. The reasons for this have already been discussed above. One experiment with a gas temperature of 200°C gave no rapid decomposition at higher pressures, although the gas had broken down to some extent. The gas, which was 96% acetylene at room temperature, contained after heating to 200°C only 70-80% C_2H_2; also a tarry deposit appeared on the walls of the bomb, but was too slight to be collected. Also traces of soot were found on the heating element.

*The values shown in parentheses were determined by fusion of platinum wire, the others by means of an incandescent wire.

4d) C_2H_2 Saturated with H_2O

The determination of the decomposition pressure of acetylene saturated with water vapor lay beyond the scope of this investigation as originally visualized. However, individual values were determined in order to make a further comparison with Rimarski's results. With acetylene saturated with water vapor at 15°C, a curve of decomposition pressure vs vessel diameter was obtained which was parallel to that for dry acetylene; the decomposition pressures for moist C_2H_2 are some 25% higher than those for dry acetylene (Fig. 1).

For moist acetylene, the curve of pressure vs temperature is the reverse of that for dry gas. (Fig. 4). The reason for this is that with increasing temperature the water content of the gas increases appreciably, so that the C_2H_2 is diluted. The same phenomenon appears here as was noted later in experiments with mixtures with other gases. Also, the presence of H_2O has some effect on the type of decomposition. The relatively high specific heat doubtless serves to hinder the progress of the decomposition. Our experiments do not indicate, that after dissociation of the water vapor, some sort of reaction with decomposition products takes place, which, as reported by Rimarski causes an especially powerful decomposition. Even if the measured values of the decomposition pressures had checked those of Rimarski's we could detect only a decrease in the power of the explosion. This decrease became greater with increasing temperature (and consequently water content).

The values observed are as follows:

Temp. °C	Decomposition Pressure ata (Our Values)	Rimarski*
15	1.75	---
50	1.80	1.70
80	2.10	2.40
100	2.80 (Uncertain)	---

5) Decomposition of Pure C_2H_2 as Effected by Pressure and Temperature Without Ignition.

Without a source of ignition, pure acetylene, both dried and saturated with water vapor can be compressed to 60 ata

(*) With incandescent platinum wire.

at 18°C or to 50 at. at 97°C without decomposition taking place. This can be accomplished by means of a Hg. receiver.

6) C_2H_2 Mixed With Gases

The determination of the decomposition pressures of C_2H_2 in gas mixtures was the chief object of this work and was carried out keeping in mindmixtures occurring in industry. Data in the literature are very meager, and experimental conditions are not given. Results of a very recent investigation by I. G. Griesheim (Lab. Ber. 228/1926) which was carried out with a mixture of C_2H_2 and gas oil is reproduced in Fig. 12.

With the results of the Griesheim work on mixtures of acetylene with gas oil (chief constituents C_2H_4, C_2H_5, C_3H_8) decomposition pressures of mixtures, it was thought, could be predicted for this type of mixture, while for C_2H_2- H_2 mixtures decomposition occurs when the partial pressure of C_2H_2 in the mixture amounts to 2.0 ata. With the foregoing information the decomposition of mixtures of C_2H_2 with other inert gases presumably could be predicted.

It was desired to corroborate and extend this information. Also the curve shown in Fig. 12, which is taken from the Griesheim report, is somewhat in doubt, since the value found by Rimarski for pure acetylene is shown as 0.8 ata (atm. absolute) whereas it apparently should be 0.8 atü (atm. gauge pr) to judge by comparing Fig. 1 with Fig. 12. Furthermore, the decomposition pressures as determined by Berthelot for C_2H_2 - H_2 mixtures, so far as can be judged from the literature indicated an increasing partial pressure of C_2H_2 with increasing total pressure. A few preliminary experiments on our part with C_2H_2 - N_2 mixtures did not support the contention that the decomposition pressures with admixture of inert gases was independent of the nature of the gas added. Of course to what extent H_2 should be regarded as inert in this case is open to question.

For the individual experiments it appeared necessary to investigate binary mixtures with C_2H_2. H_2, N_2, CH_4, CO, and C_2H_4 were chosen.

Since with gas mixtures the effect of vessel diameter is very slight, all experiments were carried out in the largest bomb of 270 mm diameter.

It was not planned to investigate the effect of moisture in gas mixtures.

6a) C_2H_2 - H_2 Mixtures

After a few preliminary experiments, it was apparent that the assertion that the decomposition pressure of the mixture corresponded to an acetylene partial pressure of 2.0 ata was definitely false. Actually the partial pressure of acetylene increases with increasing total pressure, although slowly, as can be seen from the following data:

Total Pressure Of Mixture	15°C % C_2H_2 in Mixture	15°C Partial Pressure of C_2H_2 at Decomposition	100°C Partial Pressure of C_2H_2 at Decomposition	100°C % C_2H_2 in Mixture
3.0	66	2.0	1.7	57
5.0	48	2.4	2.3	46
10.0	33	3.3	2.7	27
15.0	24	3.6	3.5	23
20.0	20	4.0		
25.0	16	5.8		

The values are shown graphically in Fig. 5.

All experiments were carried out with fusion of platinum wire of 0.5 mm diameter. It was observed again that with very low pressures a decomposition can be brought about if the heat source causing the decomposition is strong enough. Of course the power of the explosion decreases greatly at these low pressures. This decrease was especially noticeable in all experiments with 25% C_2H_2 and less. The dilution of the C_2H_2 is then so great that the decomposition is very slow and not explosive in character. The pressure rise is very gradual. The flame decreases greatly in intensity and spreads slowly as can be readily observed through the sight glass.

The following remarks can be made in comparing our results with data appearing in the literature:

Abegg's data (Handbuch der Anorg. Chemie III, 2) on the decomposition pressures of C_2H_2 - H_2 mixtures likewise indicate

an increasing C_2H_2 partial pressure with increasing total pressure. For example, with a total pressure of 4 ata the partial pressure of C_2H_2 is 2.0 ata; with 7.0 ata total pressure the partial pressure is 2.3 ata; and with 10.0 ata total pressure, the partial pressure is 2.5 ata. The foregoing correspond to concentrations of 50; 33 and 25% respectively. The values are throughout lower than ours, which is presumably due to different experimental conditions.

Berthelot and Vielle state that the pressure limit at which a decomposition of acetylene takes place increases with increasing H_2 partial pressure. With a mixture of 33.3% C_2H_2 and 66.7% H_2 a decomposition occurs at an initial pressure of 10.8 ata. (Compt. Rendu 128,782). These data agree exactly with ours.

With respect to temperature, it is to be noted that, as would be expected, at 100°C the decomposition pressure is lower than at 15°C.

Experiments with temperatures in excess of 150°C could not be carried out. At this temperature, without ignition, other products (tar) were formed so that the C_2H_2 content of the mixture could not be controlled.

If these experimental results are judged in light of earlier results and theories, the following might be said: If the decomposition pressure were reached when the partial pressure of C_2H_2 reached two ata, the simple rule would hold that the product of the C_2H_2 concentration in the gas and the gas pressure should be always constant. Actually on the basis of the present experiments, the partial pressure of C_2H_2 in the mixture at decomposition pressure is an exponential function of the gas pressure. The curve of Fig. 5 is calculated on this basis. Except for two points agreement of the experimental data is excellent.

6b) C_2H_2 - N_2 Mixtures

Work was undertaken on these mixtures, even though they would not be often encountered, in order to determine whether it was correct to assume that the decomposition pressure of mixtures of inert gases with C_2H_2 was independent of the actual gas. A few experiments quickly showed that the

decomposition pressure was dependent on the C_2H_2 concentration in the mixture. Also mixtures with N_2 gave in all cases decomposition pressures higher than those found with H_2. With respect to the actual process of decomposition little can be said. It appeared that deposition of polymerization products on the ignition wire was less than with H_2. Also, with N_2 mixtures it was possible to make determinations at 200°C inasmuch as decomposition did not take place before ignition. Also in this case the values of the C_2H_2 partial pressures are an exponential function of the total pressures.

The experimental results are shown in the following table and also graphically in Fig. 6.

	15°C				200°C	
Total Pressure ata	Partial C_2H_2 Pressure ata	% C_2H_2	Partial C_2H_2 Pressure ata	% C_2H_2	Partial Pressure ata	% C_2H_2
3.0	2.3	76.5	2.0	66.5	---	---
5.0	3.2	64.0	---	---	2.4	48.0
10.0	4.8	48.0	4.0	40.0	3.6	36.0
15.0	6.4	42.5	5.0	33.3	4.5	30.0
20.0	7.5	37.5	---	---	---	---

The above were carried out in a bomb of 270 mm. diameter.

As proof of the statement that with dilute C_2H_2 mixtures, the vessel size has little effect, the following data are given for a bomb of 50 mm. diameter.

Total Pressure ata	% C_2H_2 at 15°C	Partial Pressure C_2H_2 ata
1.8	100	1.8
3.0	76.5	2.3
4.0	67.5	2.7
8.0	56.5	4.5
12.5	48.0	6.0
17.0	41.5	7.1

6c) $C_2H_2 - (50\% H_2 + 50\% N_2)$

The addition of a gas mixture to acetylene, consisting of half N_2 and half H_2, gave decomposition pressures, which were somewhat lower than

those for addition of N_2 alone. In experiments at a temperature of 200°C and a total pressure of 5.0 ata a decomposition could still be obtained with an C_2H_2 partial pressure of 2.2 ata. With higher total pressure tar formation started and the series could not be carried further. Also nothing new was noted in the behaviour of the decomposition.

The experimental data are given in the following table, and shown graphically in Fig. 7.

	15°C		100°C	
Total Pressure ata	Partial Pressure of C_2H_2 ata	% C_2H_2	Partial Pressure of C_2H_2 ata	% C_2H_2
5.0	3.0	60.0	2.4	48.0
10.0	4.2	42.0	3.8	58.0
15.0	5.4	36.0	4.6	30.5
20.0	5.8	29.0	---	---

6d) C_2H_2 - CH_4 - Mixture

The behaviour of this mixture is primarily the same as that of the C_2H_2 - N_2 mixture. However, polymerization products were found on the igniting wire and connections to a much greater extent, which is attributed to the decomposition of the CH_4. In fact, before the decomposition pressure was reached the deposit at the ignition zone, which heretofore had consisted of a light soot, became a very hard mass, which caused a short circuit and to some extent prevented fusion of the wire. Therefore, in order to obtain suitable initial ignition the same as in the other experiments, it was often necessary to check the points obtained and at times to increase the current.

The high proportion of C_2H_2 in the mixture, necessary for an explosive decomposition is explained by the decomposition of the CH_4, which is "heat absorbing". In all cases decomposition is more gradual. The progress of decomposition can be observed very well through the sight glass. The final pressure reached is considerably lower than with other mixtures.

The experiments with these mixtures at higher temperatures gave values for decomposition pressures which agreed fairly well. To judge from the appearance of the inside of the bomb and of the heating element, a change in composition of the mixture (as was true with the C_2H_2 - N_2 mixtures) had not taken place before ignition. An analysis of the contents of the bomb after heating showed no change in composition. Griesheim

asserts, based on experimental results, with C_2H_2 in gas-oil mixtures (see Fig. 12), that for mixtures with exothermic gases (that is decompose endothermically) the decomposition pressures should be approximately equal regardless of the kind of gas. The decomposition pressures for CH_4 mixtures as determined by us are considerably lower. The experimental technique does not seem to be the only factor involved.

Of the various constituents of gas-oil, C_2H_4 decomposes exothermically whereas C_2H_6 and C_3H_8 require heat for decomposition. The amount of C_2H_2 necessary in the mixture for an explosive decomposition depends upon the heat requirements. However, the amount of heat required for decomposition of the mixture is not so important as pressure and temperature.

The following table shows the experimental results which are shown graphically in Fig. 8.

	15°C		100°C		200°C	
Total Pressure ata	Partial Pressure of C_2H_2 ata	% C_2H_2	Partial Pressure of C_2H_2 ata	% C_2H_2	Partial Pressure of C_2H_2 ata	% C_2H_2
3.0	2.45	81.5	2.12	71.0	---	---
5.0	3.35	67.0	3.20	64.0	3.0	60.0
10.0	5.70	57.6	5.10	51.0	4.5	45.0
15.0	7.40	49.5	---	---	6.1	40.5
20.0	9.30	46.5	---	---	---	---

6e) C_2H_2 - (50% H_2 + 50% CH_4)

With these mixtures, because of the influence of the H_2, the decomposition pressures are somewhat lower than with the C_2H_2 - CH_4 mixtures. In spite of the equal proportions of the H_2 and CH_4 the influence of the latter is greater. The same behaviour is noted with these mixtures as with the mixtures C_2H_2 - N_2 on one hand and C_2H_2 - (50% N_2 + 50% H_2) on the other. The investigations at higher temperatures again gave tarry residues in the bomb at 200°C before ignition as had already been found with the C_2H_2 - H_2 mixtures. This series of experiments was therefore not carried further.

In general the mixture showed no special behavior as compared to the others. The results are shown graphically in Fig. 9.

	15°C			100°C	
Total Pressure ata	Partial Pressure of C_2H_2	% C_2H_2	:	Partial Pressure of C_2H_2	% C_2H_2
5.0	3.4	68.0	:	2.8	56.0
10.0	5.0	50.0	:	4.2	42.0
15.0	6.4	42.5	:	5.4	36.0
20.0	7.4	37.0	:	6.4	32.0

6f) C_2H_2 - CO

With these mixtures the decomposition pressures are somewhat lower than with C_2H_2 - CH_4 but approximately the same as with C_2H_2 - N_2.

A proper determination of the decomposition pressures at higher temperatures could not be carried out above 100°C. The influence of temperature was not quite the same as would have been expected from the results with the other mixtures. At 200°C a definite change in the composition of the mixture took place. A deposit of a brownish powder formed on the heating element similar to that observed with the C_2H_2 - H_2 mixture but somewhat lighter. Also the heating element showed some corrosion which was not observed in the other experiments.

The process of decomposition with this mixture was fundamentally different than heretofore observed. Whereas in the other experiments either an explosive decomposition or a gradual pressure rise took place depending upon the C_2H_2 concentration, with these experiments using CO, the pressure rose very slowly to a value roughly half the final pressure and then rose suddenly. Although the final pressure as measured checked very well with the calculated value, there appeared to be some special process of chemical nature taking place at least at the beginning of decomposition. This will be discussed later.

The following table gives the experimental results which are shown graphically in Fig. 10.

Total Pressure ata	15°C Partial Pressure of C_2H_2 ata	% C_2H_2	100°C Partial Pressure of C_2H_2 ata	% C_2H_2 in Mixture
5.0	3.0	66.0	2.8	56.0
10.0	4.6	46.0	4.1	41.0
15.0	6.0	40.0	5.5	36.5

6g) C_2H_2 - C_2H_4

The decomposition pressures with these mixtures were approximately equal to those with C_2H_2 - N_2. The final pressure is high apparently as a result of the decomposition of C_2H_4 which releases heat. Also, this causes a higher decomposition velocity than with the other mixtures. With this mixture experiments at 100°C and 200°C were successfully carried out which fit the general pattern of results very well. A change in the composition of the mixture during heating could not be observed.

The decomposition values obtained are given in the following table and shown graphically in Fig. 11.

15°C			100°C		200°C	
Total Pressure ata	% C_2H_2	Partial Pressure of C_2H_2	% C_2H_2	Partial Pressure of C_2H_2 ata	% C_2H_2	Partial Pressure of C_2H_2 ata
5.0	62.0	3.1	60.0	3.0	50.0	2.5
10.0	46.0	4.6	41.0	4.1	38.0	3.8
15.0	39.5	5.9	34.5	5.2	31.5	4.7

7) The Nature of the Decomposition Process as Judged by the Final Pressure.

In addition to observing the process of decomposition through the sight glass, which gives only qualitative results, the comparison of the final pressure, as measured, with the calculated value offers a possibility of studying the decomposition process and the behavior of the various mixtures. Since a measurement of the rate of pressure rise could not be undertaken, at best only an approximate picture can be obtained in this way.

For comparison purposes the following values obtained for a total pressure of 10 ata are presented.

With a heat of decomposition for C_2H_2 of 53,000 Kcal/mol, a final pressure 11.8 times the starting pressure will be obtained with complete decomposition. With pure C_2H_2 at a starting pressure of 1.4 ata, a final pressure of 13 ata was measured which is 8.0 times the initial pressure. This can be explained, of course, by the transfer of heat to the walls of the vessel. An exact calculation of this heat loss is not possible because of the effect of soot on heat transfer rates. If the C_2H_2 is diluted with N_2, a decomposition takes place at 10 ata total pressure when 48% C_2H_2 is present. The final pressure amounts to 7.5 times the initial pressure. This corresponds to a calculated value of 9.0 times. With a mixture of C_2H_2 - H_2, the measured final pressure is 7.6 times the initial pressure. With the C_2H_2 - N_2 mixture the thermal conductivity is greater than with the C_2H_2 - H_2 mixture. Therefore, the heat dissipation rate is greater, and the measured final pressure is relatively smaller than the calculated value. If complete decomposition of the CH_4 in a C_2H_2 - CH_4 mixture is assumed, which would be expected at high temperatures, and with a heat of decomposition of 20,000 Kcal/mol, a pressure rise with 58% C_2H_2 in the mixture of 5.2 times is obtained. From the increase in volume, an additional pressure increase of 1.43 times is to be expected, i.e., a final pressure 7.2 times the initial pressure. As compared to this actual measurement gave 7.5 times. Since the decomposition took place very slowly, during which time a considerable amount of heat must have been lost, the fact that the measured final pressure was so high can only be explained if some of the methane did not decompose or if it otherwise reacted. In recognition of this it seems futile to seek a relationship between decomposition pressure and decomposition heat of the mixture as was done at Griesheim.

To consider again the process of decomposition with the C_2H_2 - CO mixture, a final pressure of 8.6 times the initial pressure is obtained by calculation with 44% C_2H_2 in the mixture, assuming that the CO remains unaltered, whereas a value of 8.5 times was actually observed. From the fact that these values are essentially the same, it is to be concluded that side reactions of some kind have taken place in such a way as to give off additional heat. The following observations were made during the course of decomposition: The pressure rose comparatively slowly, after decomposition started, to roughly 5 times the initial pressure, and then suddenly rose to the final pressure while a noise similar to a detonation could be heard. Of course, an exact measurement of the final pressure cannot be made with the manometer. Nevertheless, the occurrence of a reaction in the last stage of decomposition seems definite.

8) Influence of the Type of Gas on the Decomposition Pressure.

From the foregoing experiments it follows that the kind of gas has a very considerable influence on the final pressures reached.

The process of decomposition is not completely understood even for pure C_2H_2. Explosive decomposition takes place at a pressure of 1.40 ata or over. However, at lower pressures partial decomposition takes place which does not progress beyond the proximity of the igniter. An attempt has been made to explain this phenomenon by saying that the increase in pressure pushes the molecules closer together and in this way a decomposition started at one point progresses further. As evidence favoring this theory is the fact that liquid acetylene in which the molecules are very close together can be detonated at ordinary temperature with incandescent platinum wire, fulminate of mercury, or by the heat of compression or friction. On the other hand with dilute acetylene where the molecules are further apart a higher pressure is required than with pure acetylene in order to get the same action. However, according to our experiments as well as many earlier experiments, the type of initial ignition, the size of the ignition wire, as well as its temperature have considerable effect on the decomposition pressures so that the above theory is not the complete explanation.

If this theory were correct, the assertion made by Griesheim that the decomposition pressure is independent of the type of inert gas would be correct. Since, however, this is by no means the case, other factors must influence the progress of the decomposition. It is a fact that in initiating ignition in all cases even though the conditions for an explosive decomposition are not realized at least a partial decomposition in the immediate vicinity of the ignition zone takes place. The heat set free in this way must be the ignition means for the decomposition of the rest of the gas. The manner in which this heat is transferred to the balance of the gas must be the deciding factor in the progress of the decomposition wave. It can, therefore, be assumed that possibly the heat conductivity of the gas should have some relation to the decomposition pressure of gas mixtures containing acetylene.

It also appears that the gas mixture under the conditions prevailing at the ignition point may undergo a change or may form a compound with the decomposition products of the acetylene. It is possible that, with a mixture of C_2H_2 and H_2, compounds result in the immediate vicinity of the ignition point under the influence of the pressure and temperature brought about by the partial decomposition of the acetylene which may cause a change in the amount of heat resulting from the decomposition. Under these circumstances it appears questionable that H_2 should be called an inert gas in this connection. If one studies the experimental results for a C_2H_2 - H_2 mixture, it is evident that there is a relationship between the partial pressure of the acetylene in the mixture and the

decomposition pressure up to 10 ata. At higher pressures, the experimental pressures lie somewhat lower than the established trend. This variation was shown by repeated experiments to be real.

The above considerations are even more valid for other gas mixtures with which it is certain that their composition is changed with the initiation of acetylene decomposition. However, there is a fundamental difference whether the heated gas undergoes a change at the same time the acetylene decomposition starts or whether this change takes place only after the decomposition has gone far enough that it will become complete regardless. In the first case, the conditions are not controllable and therefore results may not follow any particular rule. In the second case the heat conductivity of the gas should be important (compare later CO and CH_4 mixtures).

The experimental values obtained show an exponential relationship between the partial pressure of the acetylene in the gas and the total pressure at decomposition. This relationship was used in drawing the curves, which fit the experimental values very well. The data show little scattering and primarily only in those cases where a considerable deposition of polymerization products took place on the igniting wire and interfered with ignition.

If we designate p as the partial pressure of acetylene in the mixture in ata and P the total pressure, we can write:

$$p \cong 1.21 \times P^{0.436} \text{ for } H_2$$
$$p \cong 1.13 \times P^{0.637} \text{ " } N_2$$
$$p \cong 1.19 \times P^{0.598} \text{ " } CO$$
$$p \cong 1.10 \times P^{0.715} \text{ " } CH_4$$
$$p \cong 1.14 \times P^{0.616} \text{ " } C_2H_4$$

The above is valid for a gas temperature of 15°C. The same relationships can be developed for other temperatures in which case the exponent would be different. Since for practical purposes calculation is too tedious, special charts have been designed for mixtures containing CH_4, C_2H_4, and N_2 which were investigated to a temperature of 200°C. These charts show the acetylene concentration of the mixture subject to decomposition as a function of total pressure and temperature (Fig. 13 to 15).

The above relationships hold only for initial ignition by means of the instantaneous fusion of a platinum wire 0.5 mm diameter and 10 mm long. Because of the important effect of experimental conditions on the decomposition, a universally valid relationship cannot be developed. However, from the foregoing experiments, it can be concluded that the type of ignition used is very effective in causing decomposition. It means the presence of a heat source at 1700°C aside from the spark which occurs as the wire melts. Since through higher temperatures, the

decomposition pressure is not greatly lowered, for practical purposes, for example, the compression of a mixture of gases, it can be concluded that danger of explosion does not exist if the values determined here are not exceeded. On the other hand, it should be mentioned that the different gas mixtures at temperatures of 150°C to 200°C may undergo decomposition or reaction which, however, can occur without a pressure increase.

As has been stated above with the mixture of such gases with acetylene which are not inclined to react at the start of ignition, there should be a relationship between decomposition pressure and heat conductivity of the gas. In establishing such a relationship, it is not a question of determining absolute factors but a matter of comparing the behavior of the various gases. If in the above equation, one eliminates the constant and determines the ratio of the exponents the following results:

$$\frac{N_2}{H_2} = 1.46 \quad \frac{CO}{H_2} = 1.37 \quad \frac{H_2}{CO} = 1.06$$

These values correspond with good approximation to the square root of the ratio of the product of the molecular weight and the heat conductivity of the respective gases.

Heat conductivities are: $H_2 = 0.144$; $N_2 = 0.020$; $CO = 0.0195$

Whence

$$\frac{N_2}{H_2} = \left(\frac{28 \times 0.02}{2.0 \times 0.144}\right)^{\frac{1}{2}} = 1.40; \quad \frac{CO}{H_2} = 1.38; \quad \frac{N_2}{CO} = 1.02$$

These last ratios check very well with the ratios of the exponents so that an influence of heat conductivity of the mixture on the magnitude of the decomposition pressure is definitely shown. However, for CH_4 - C_2H_2 mixtures no such relationship holds which is undoubtedly explainable by the fact that these gases at the very start of ignition change their composition, that is, apparently themselves undergo decomposition.

The gas mixture C_2H_2- (H_2 + N_2) cannot be compared in this way since determination of the heat conductivity of a gas mixture from the values for the individual gases is not possible theoretically. Also it is not possible to develop a general rule for the decomposition pressure of acetylene in all mixtures since the fundamental theory necessary for the determination of the exponent is lacking. Hence, such determinations must be made by actual experiment. The fundamentals are completely lacking for mixtures of gases which take part in the decomposition.

A P P E N D I X

The Decomposition of Acetylene

Short Review of Experiments to Date

The most important results to date are from the experiments of the Chem. Techn. Reichsanstalt under the direction of Rimarski. This work was published in: Autogene Metallbearbeitung, 1925 and 1926, of which a summary is given in the special publication "Schweisstechnik" of the V.D.I., 1926, and also in Autogene Metallbearbeitung 1929, Vol. 10. Other publications, namely those of Vogel, are only repetitions of the above.

Rimarski investigated the limits under which acetylene decomposes explosively under different experimental conditions. Variables investigated included the type of ignition, the diameter of the explosion bomb, the temperature of the gas, and the moisture content.

For ignition, fusion of platimum wires of 0.15 mm diameter was used. Also in order to simulate the conditions of glowing carbide incandescent wires were also used. In the first case, the pressure at which decomposition set in, 1.45 ata, was somewhat lower than in the second, which was 1.60 ata. All other conditions were the same. The diameter of the vessel is of influence to the extent that with increasing vessel diameter, decomposition starts at lower pressures, for example at 2.0 to 2.3 ata with 38 mm diameter as compared to 1.5 to 1.55 ata with 250 mm diameter under conditions which are otherwise the same. Further increasing the diameter would have little additional effect.

With increased gas temperature, the decomposition pressure is likewise decreased. For example, 1.60 ata at 15°C as compared to 1.10 ata at 140°C.

The presence of water vapor in the gas increases the decomposition pressure somewhat according to the amount present.

The first experiments of Rimarski with respect to the type of ignition represent especially severe conditions, more so than normally encountered in industry, with the exception of those in an acetylene generator in the presence of incandescent carbide. However, these latter conditions cannot be reconstructed exactly for experimental purposes. Consequently the high pressure generators can be operated at 2.5 ata even though on the basis of the experiments the possibility of a decomposition is present at 1.6 ata. Actually statistical methods show that operation of a generator at 2.5 ata is undesirable.

The latter experiments of Rimarski have to do with the determination of the influence of velocity on the temperature necessary for the initiation of an explosive decomposition. In contrast to earlier experiments, a type of ignition more closely approximating industrial conditions was used in that in place of a single ignition point (a short platinum wire brought to fusion or incandescence) in the cold gas. The walls of the bomb were heated to a definite temperature. In these experiments the explosion vessel consisted of a pipe 25 mm in diameter and 650 mm long which was provided with electrical heating. Rimarski altered the temperature of the surface of the pipe and the velocity of the gas and determined the pressure at which an explosive decomposition of acetylene occurred. It was determined that with increasing temperature as would be expected the decomposition pressure at a given velocity was lowered. With increasing velocity at the same temperature the decomposition pressure became higher, with the exception that at temperatures above 600 to 800°C with increased velocity a pressure decrease occurred. If the decomposition pressure is plotted as a function of velocity for constant temperatures, the curves converge at velocity equals zero (that is, a gas at rest), to a value of 2.34 to 2.39 ata. That is a value appreciably higher than the 1.60 ata obtained with electrical ignition. The essential conclusions of these experiments is that for a gas at rest in the temperature range investigated (500 to 900°C) the decomposition pressure is constant and independent of temperature. Rimarski states definitely that under the conditions described the decomposition is more than local and is actually explosive. This can be demonstrated by the quantity of soot involved which makes difficult the progress of decomposition. However, in none of the experiments did an actual detonation take place. The heating of the acetylene had to be very rapid as otherwise the acetylene decomposed slowly without violence.

This fact was also demonstrated in our experiments. It is possible to heat acetylene at rest in a closed bomb to a temperature of approximately 200°C whereby the temperature of the heating element is 400°C without an explosion taking place in the acetylene. However, depending upon the duration of the heating, a decomposition takes place with formation of tar. Also the influence of the type of ignition was investigated by us in that various materials were used for ignition purposes. Although the temperature of the igniter cannot be considered in any way equal to the melting point of the wire since as the wire breaks a spark occurs which must play a roll in starting ignition. Nevertheless, a definite influence of the ignition temperature on the decomposition pressure can be demonstrated in this way. This pressure amounted to 1.40 ata for platinum as compared to 7.50 ata for lead.

Rimarski calculated from the temperature of 510°C corresponding to the temperature of the wall necessary for decomposition, the pressure of adiabatic compression necessary to reach this temperature. He arrived at a value of 170 ata. Apparently there is either a misunderstanding or mistake because it must have been 117 ata. According to this the possibility that pure acetylene can be brought to decomposition in poorly cooled

compressors is very small, if no other means of ignition are present because of this consideration.

A summary of Rimarski's conclusions are as follows:

1. Below 500°C and with pressures up to 3 atu (gauge pressure) no explosive decomposition takes place.

2. Explosive decomposition was first observed at 510°C and 2.05 atu (gauge pressure) and a velocity of 0.4 m per minute (vessel diameter 25 mm). From this point on the temperature and pressure limits increased with increasing velocity. At higher temperature and velocity, the pressure limit decreases.

3. By extrapolation to zero velocity the pressure limit for a temperature in the range 540 to 900°C is 1.37 atu (gauge).

4. The pressure calculated as being necessary to cause explosive decomposition by adiabatic compression is around 170 ata (actually this must be 117).

Further work of Rimarski has to do with determination of the explosion pressures for pure acetylene and also saturated with water and acetone. It has been reported that Rimarski calculates an explosion temperature of 3180°C for pure acetylene from which an explosion pressure of approximately 11 times the initial pressure follows. Practically, of course, explosion pressures are below the theoretical values because of heat losses. Higher pressures may be obtained if a detonation takes place.

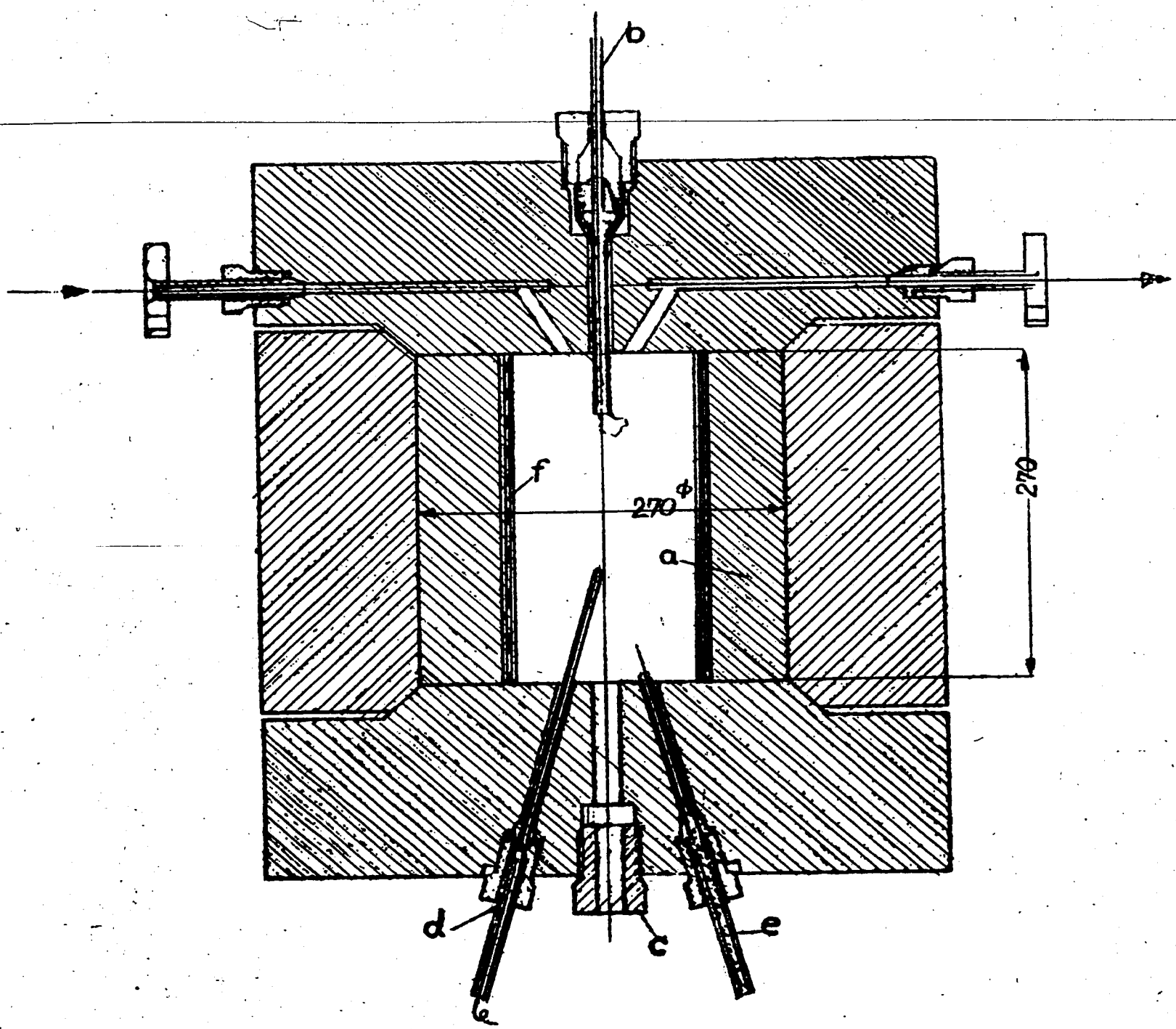
Rimarski writes the following:

1. The explosion pressure for pure acetylene up to 9 ata initial pressure amounts to approximately 11 times the initial pressure. The values agree very well with the calculated values.

2. The explosion pressures measured in larger vessels (40 liter vol.) are not higher than those taken from the older literature sources obtained with much smaller vessels. The decomposition products consisted almost exclusively of H2 and C except at higher pressures when condensation products are formed.

3. Water vapor and acetone vapor decrease the explosion pressure. The difference however is not great. The production of H2 is smaller than with pure acetylene.

4. These experiments do not reproduce conditions in very long and wide pipes.



Maßstab 1:5

Bombe für Zerfallsversuche

Fig. 1

Zerfallsdruck für trockenes gereinigtes C_2H_2
in Abhängigkeit vom Gefäßdurchm. bei 15°C
(Initialzündung)

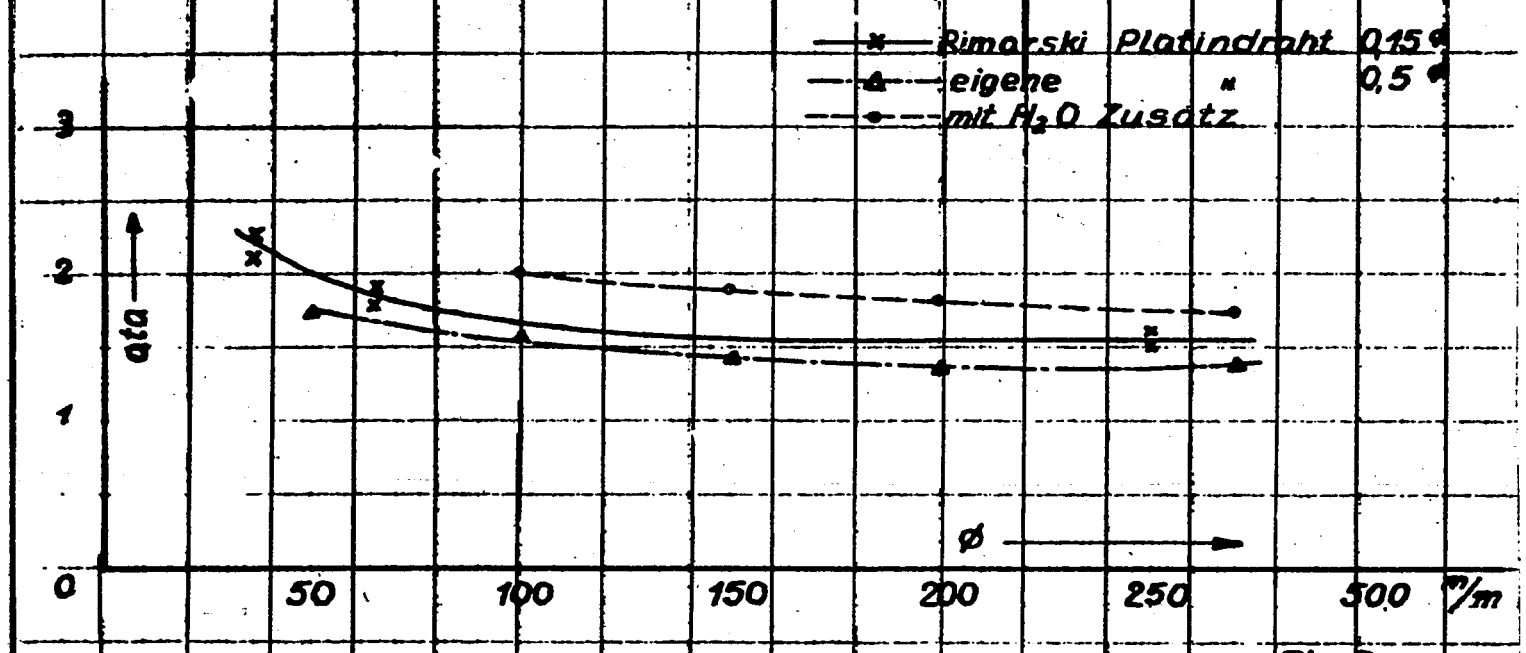


Fig. 2

Zerfallsdruck von reinem getrocknetem C_2H_2
in Abhängigkeit von der Schmelztemperatur
des Zünddrahtes

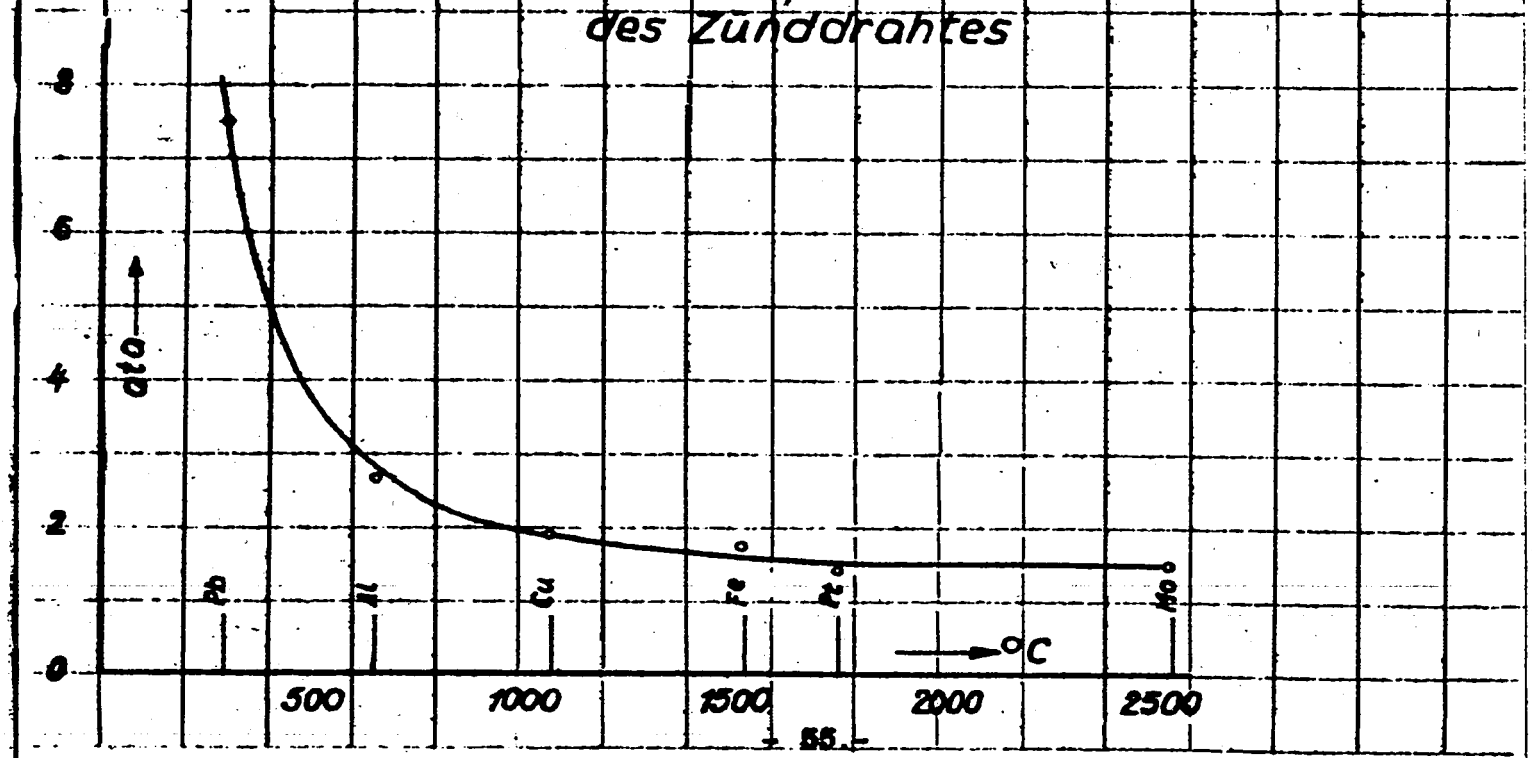


Fig. 3

Zerfallsdruck für trockenes gereinigtes C_2H_2 in Abhängigkeit von der Temperatur

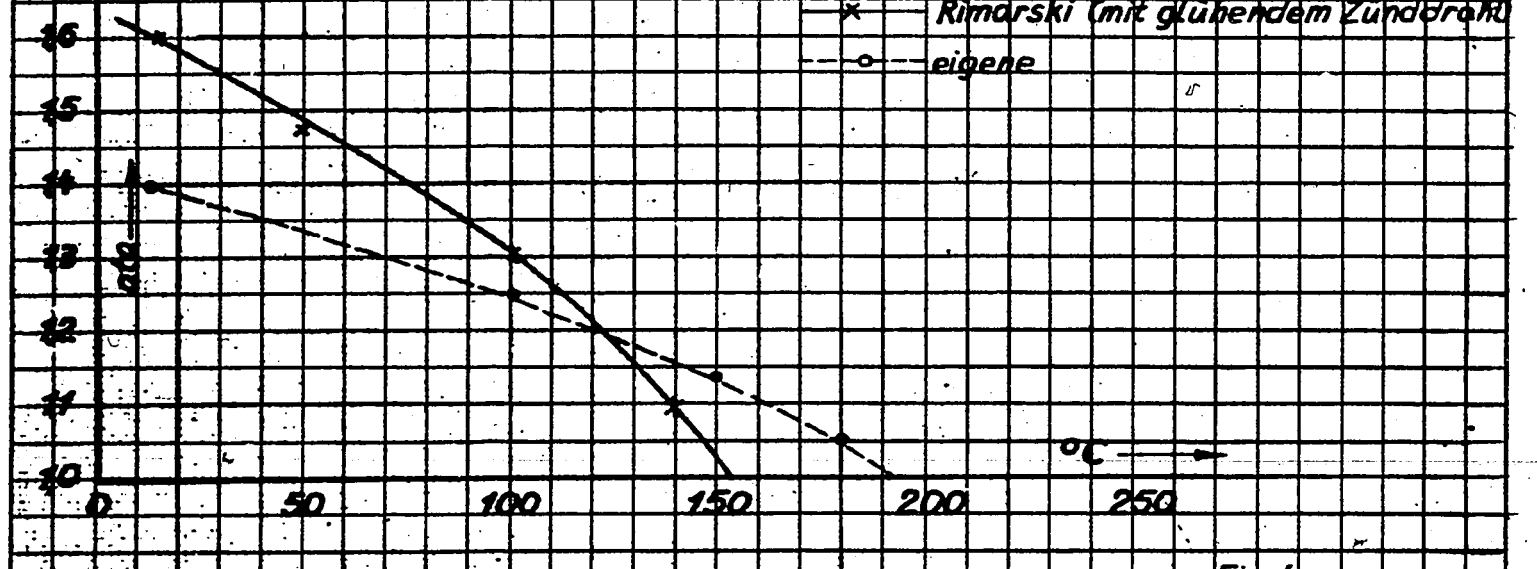
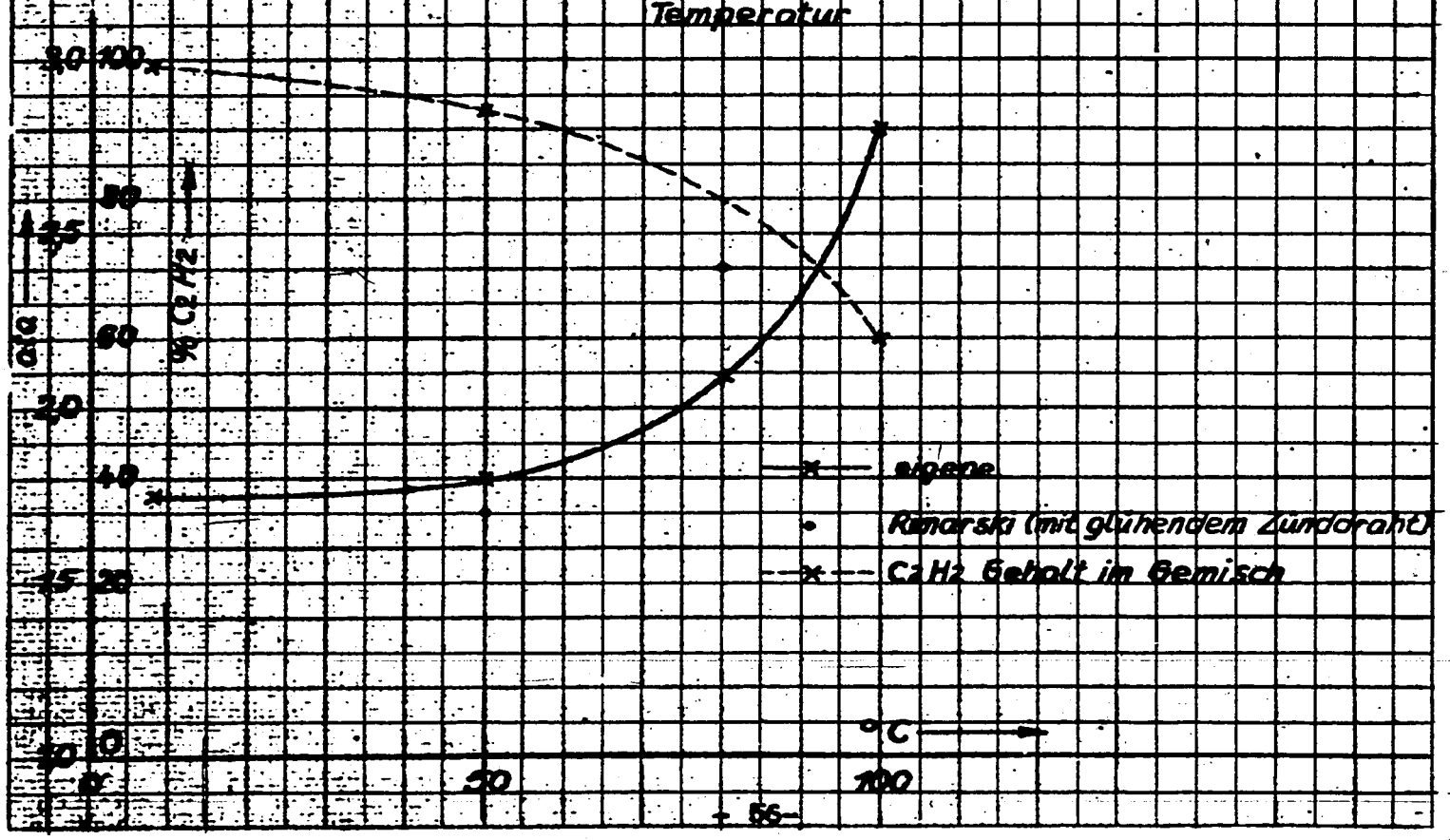
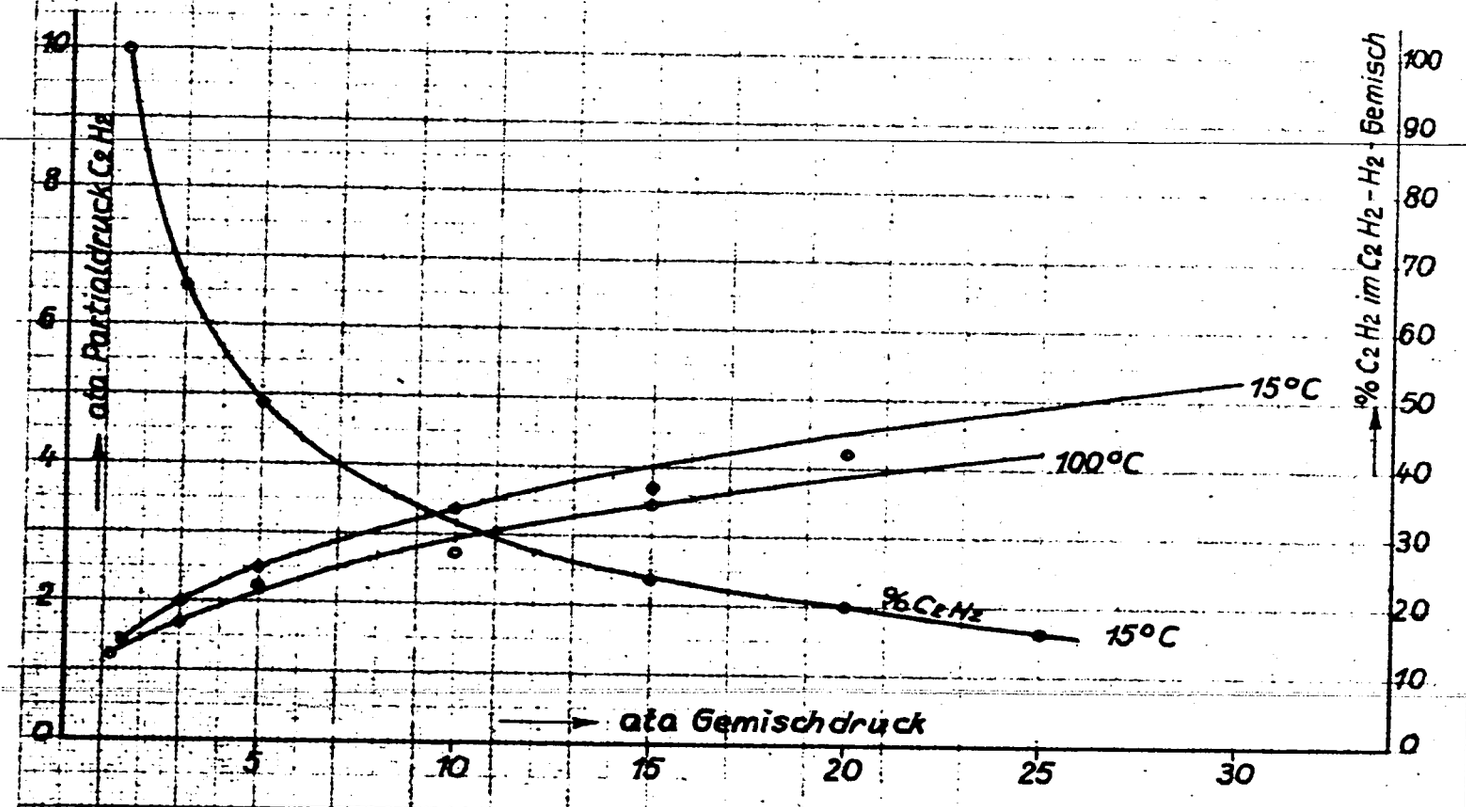


Fig. 4

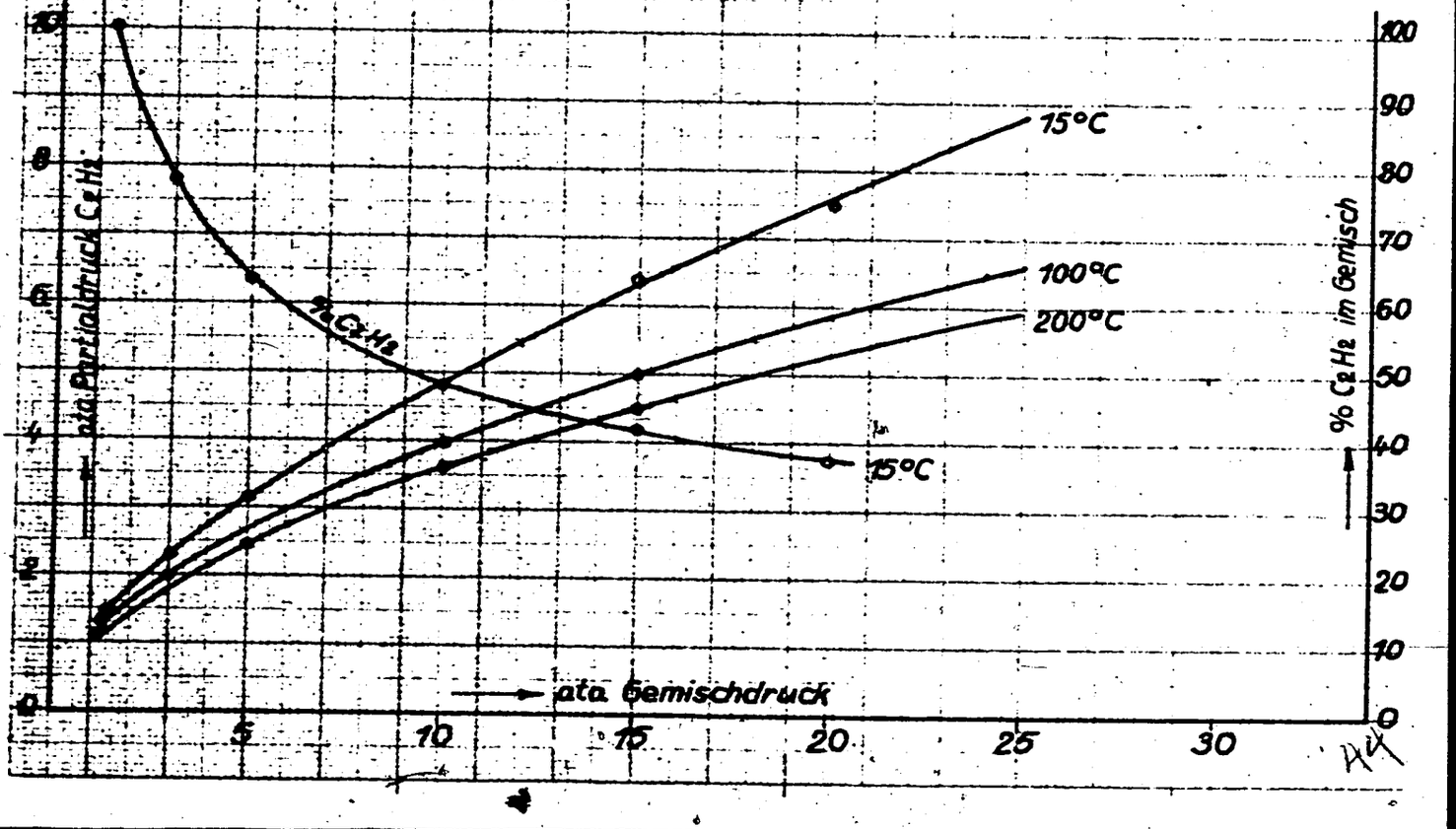
Zerfallsdruck des mit H_2O gesättigtem C_2H_2 in Abhängigkeit von der Temperatur



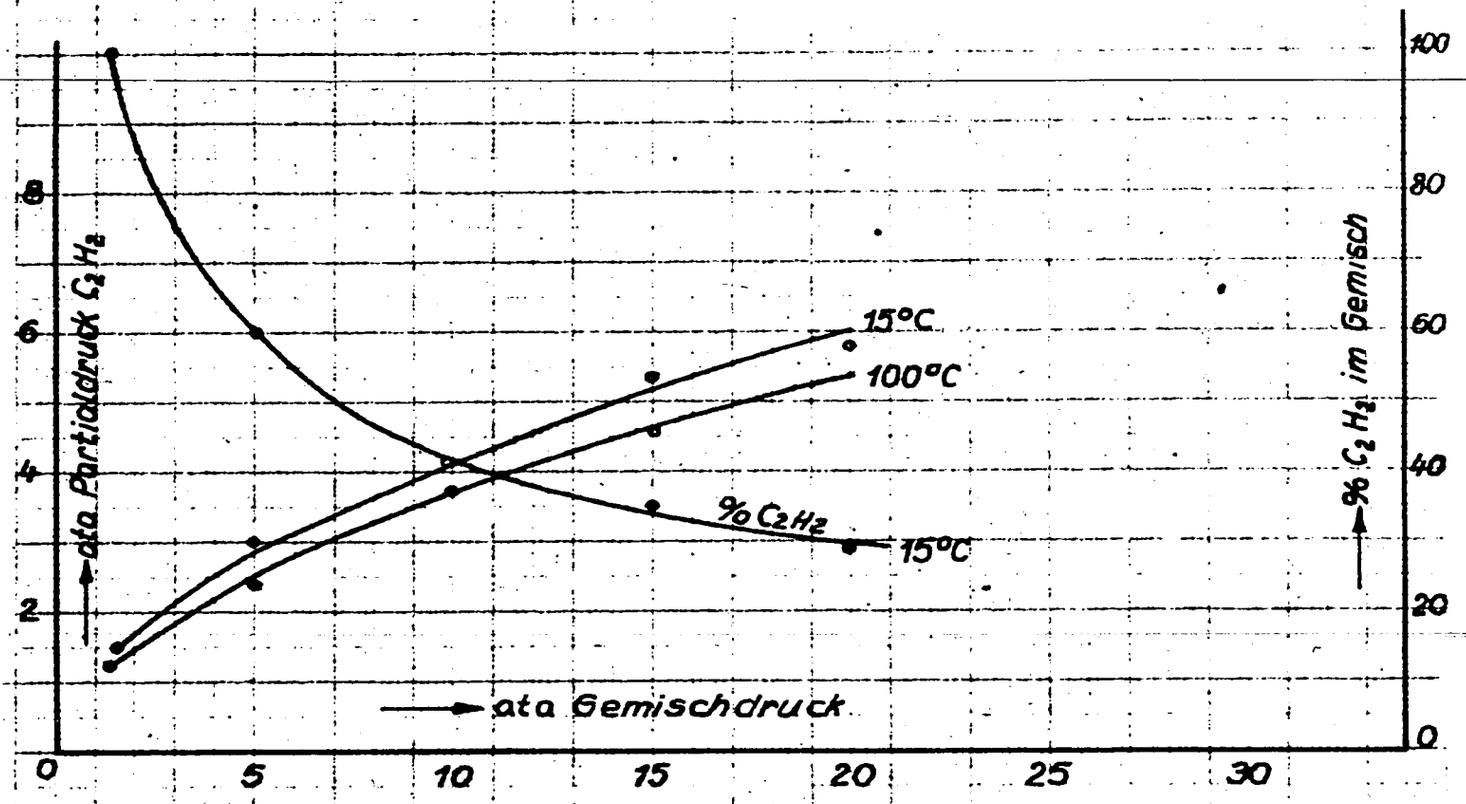
Zerfallsdrücke eines C_2H_2 - H_2 Gemisches Fig. 5



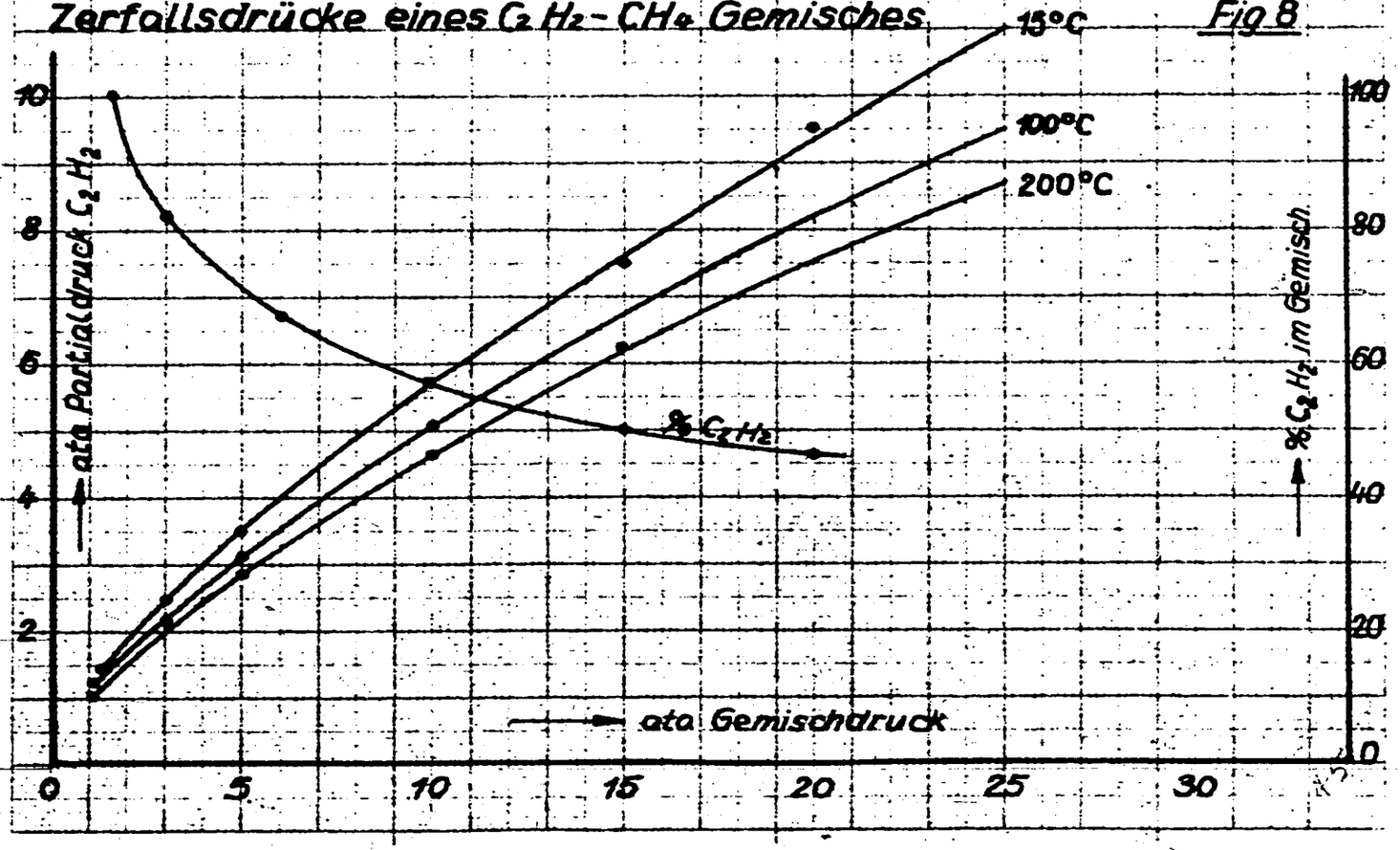
Zerfallsdrücke eines C_2H_2 - N_2 Gemisches Fig. 6



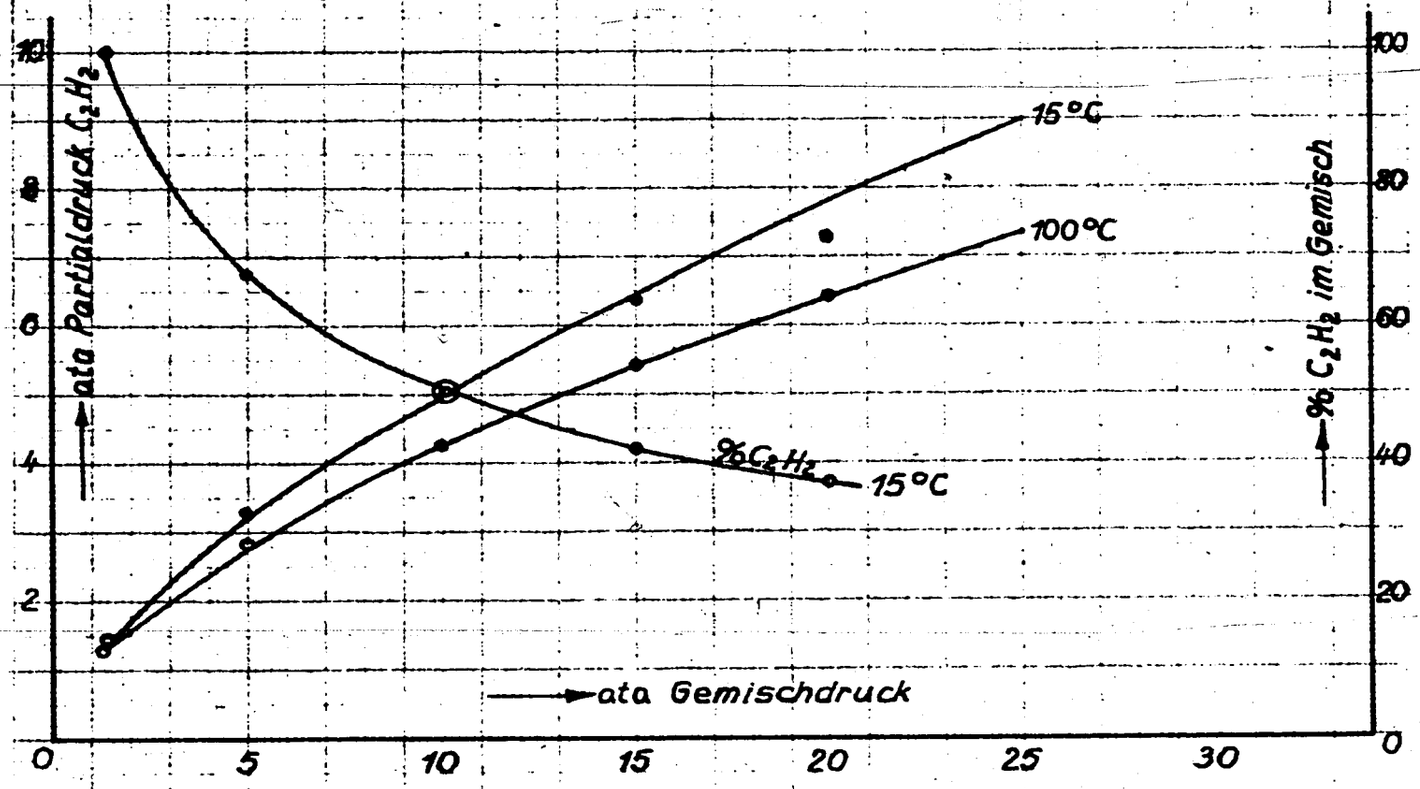
Zerfallsdrücke eines C_2H_2 – 50% H_2 – 50% N_2 Gemisches. Fig. 7



Zerfallsdrücke eines C_2H_2 – CH_4 Gemisches. Fig. 8



Zerfallsdrücke eines C_2H_2 – 50 % CH_4 – 50 % H_2 Gemisches Fig. 9



Zerfallsdrücke eines C_2H_2 – CO Gemisches Fig. 10

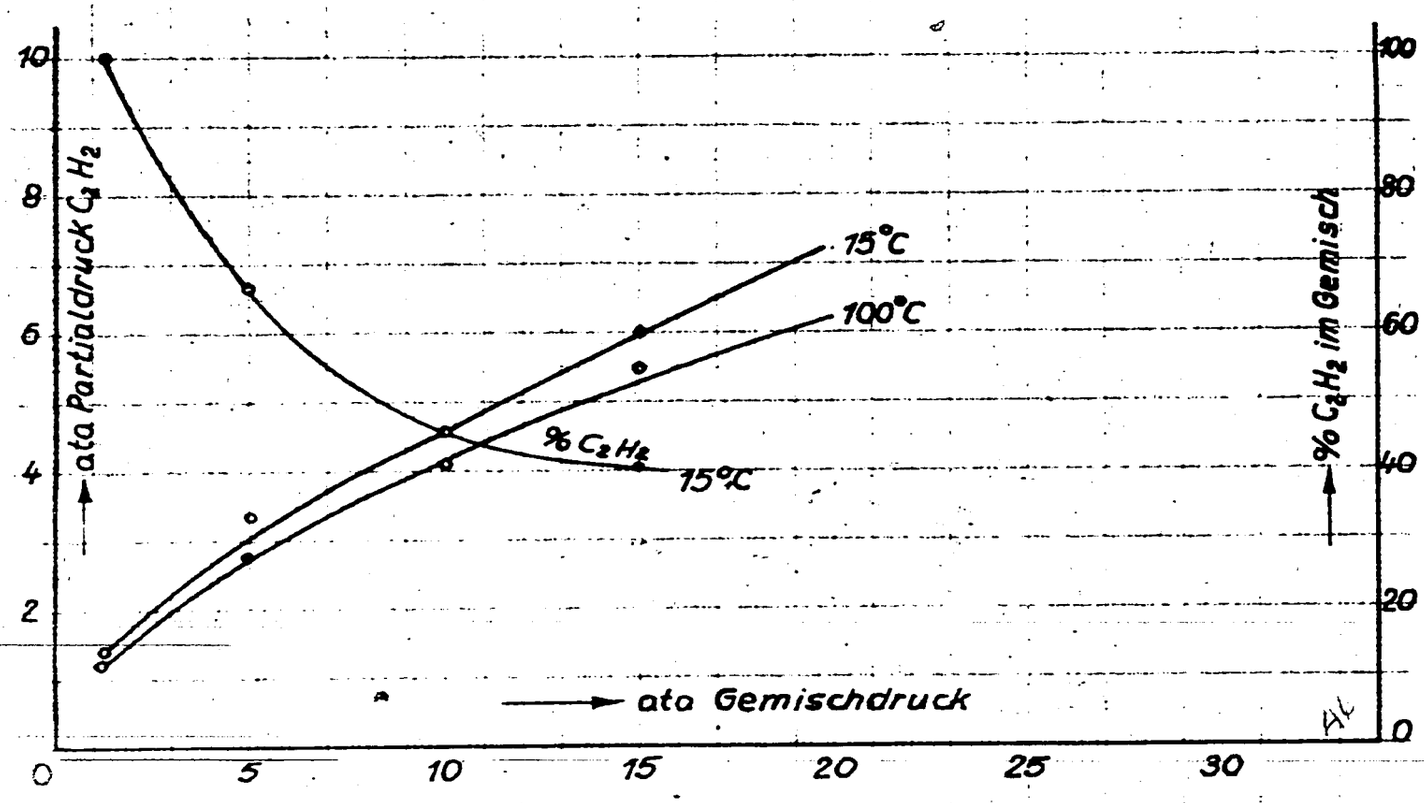
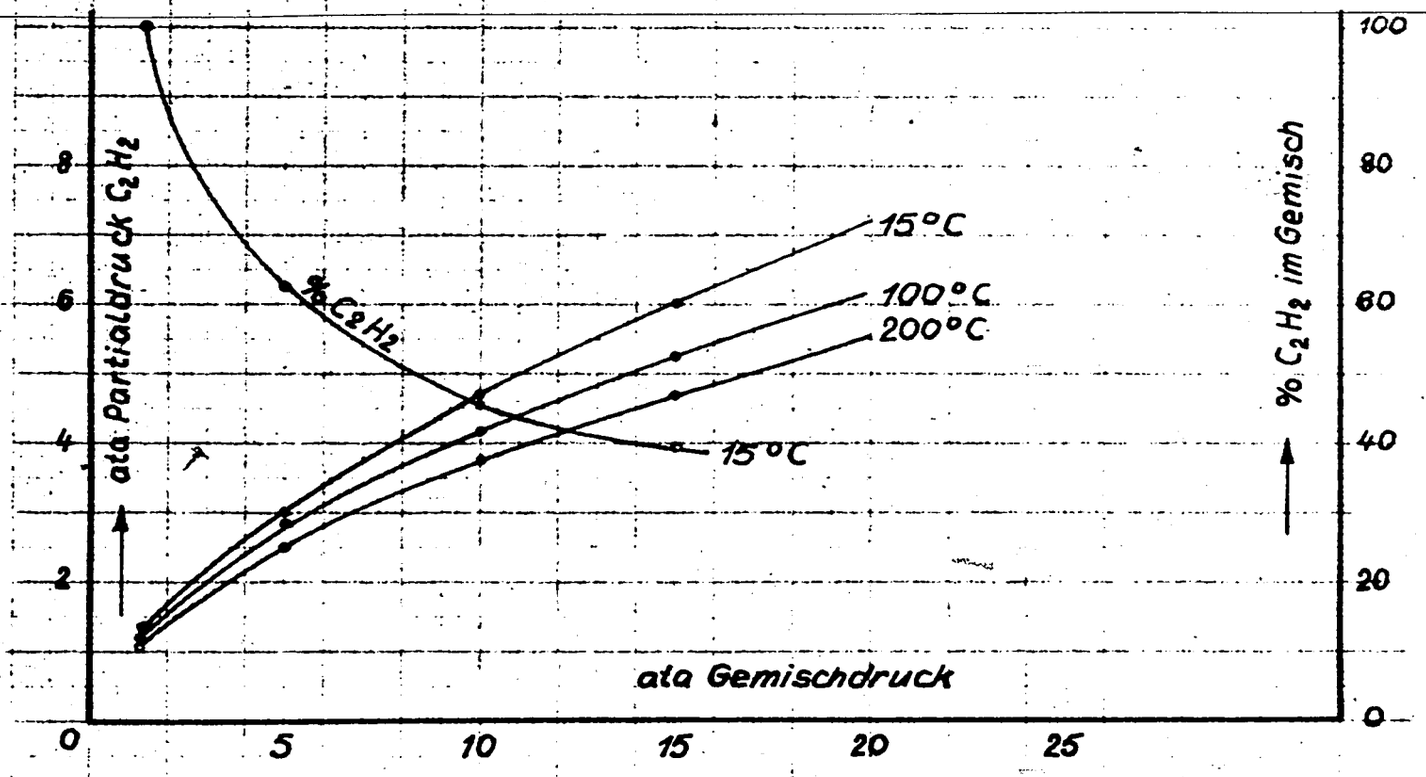
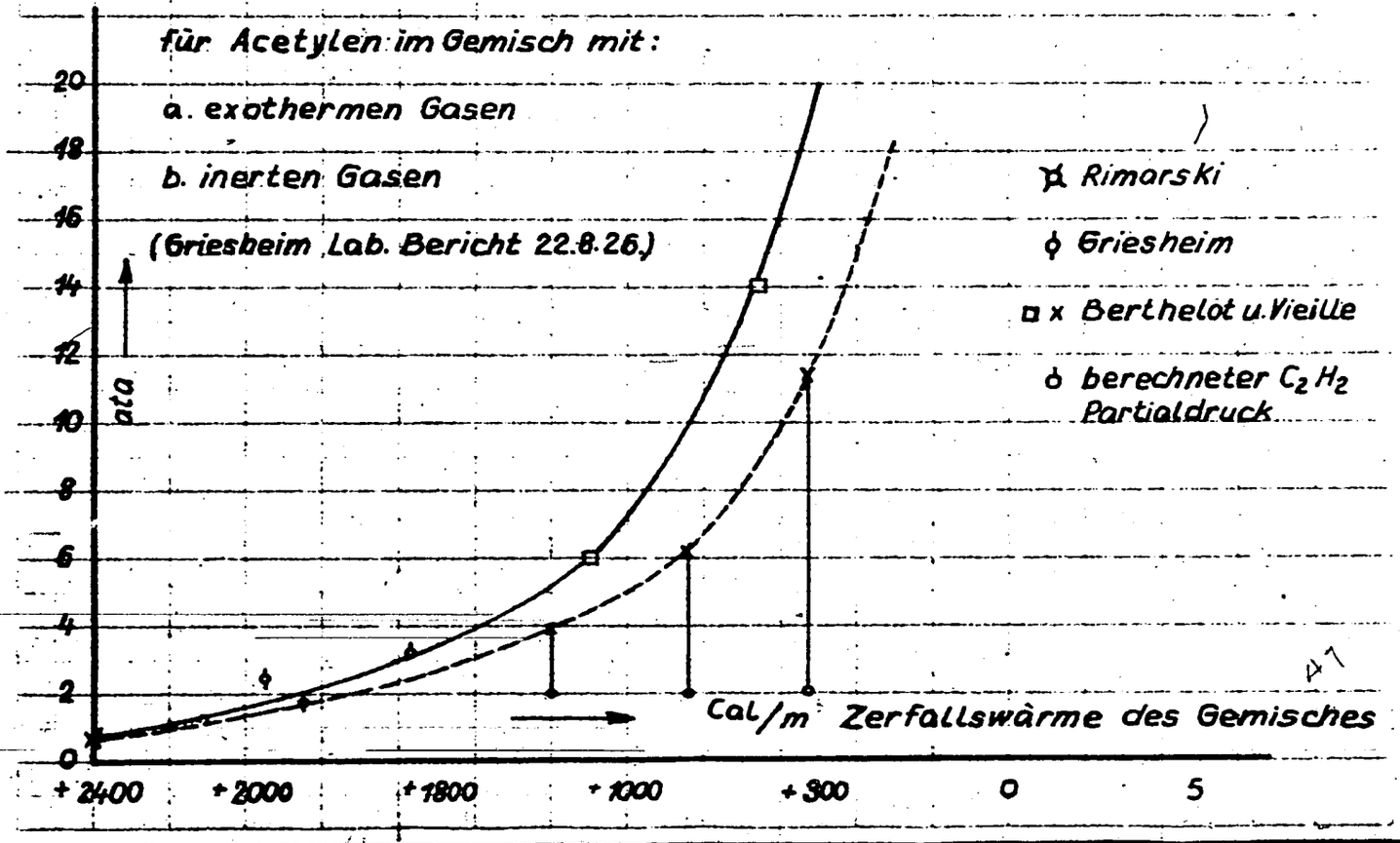


Fig. 11

Zerfallsdrücke eines C_2H_2 - C_2H_4 - Gemisches



Zerfallsdruck u. Endothermie bei Glühdrahtzündung Fig. 12



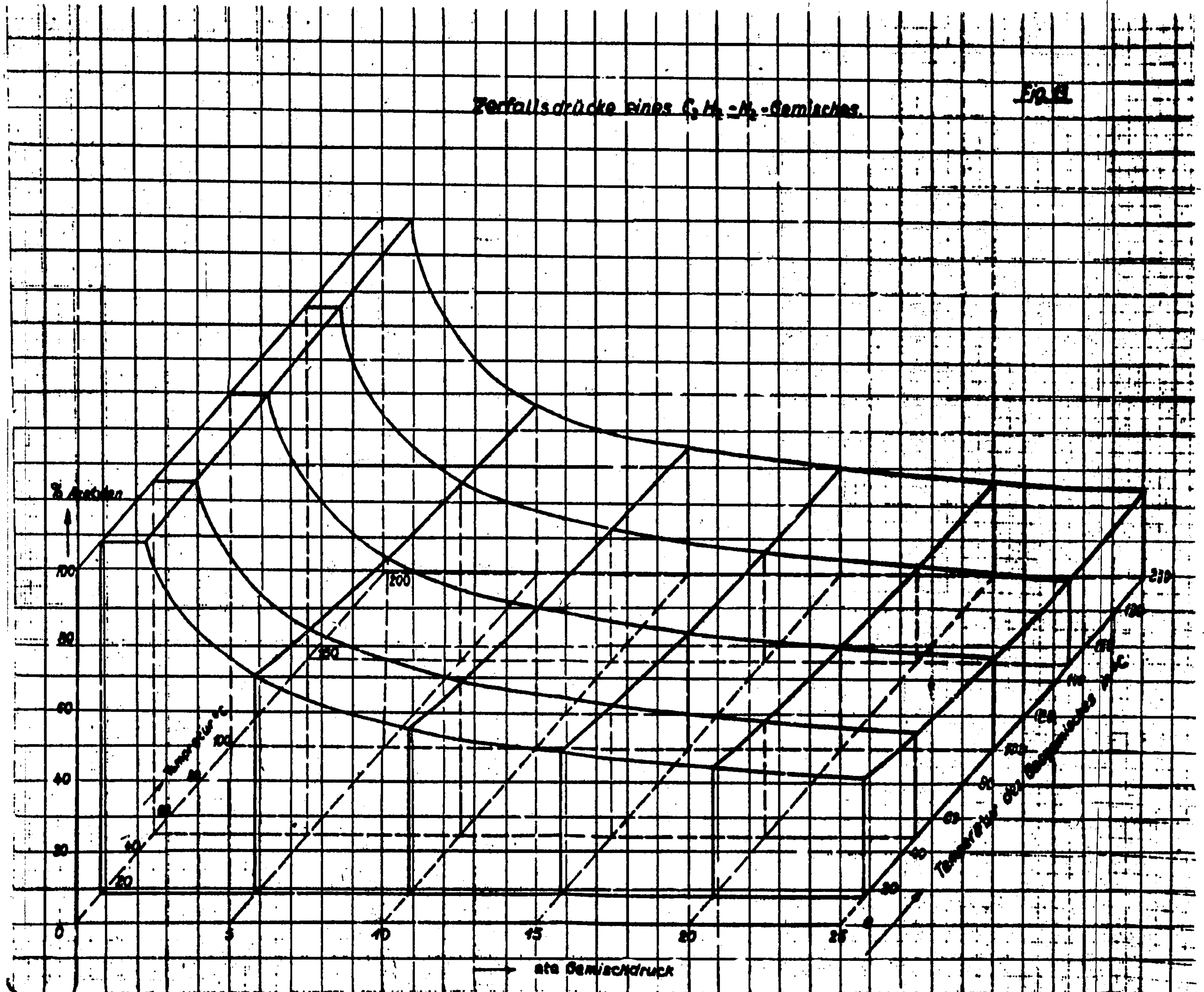
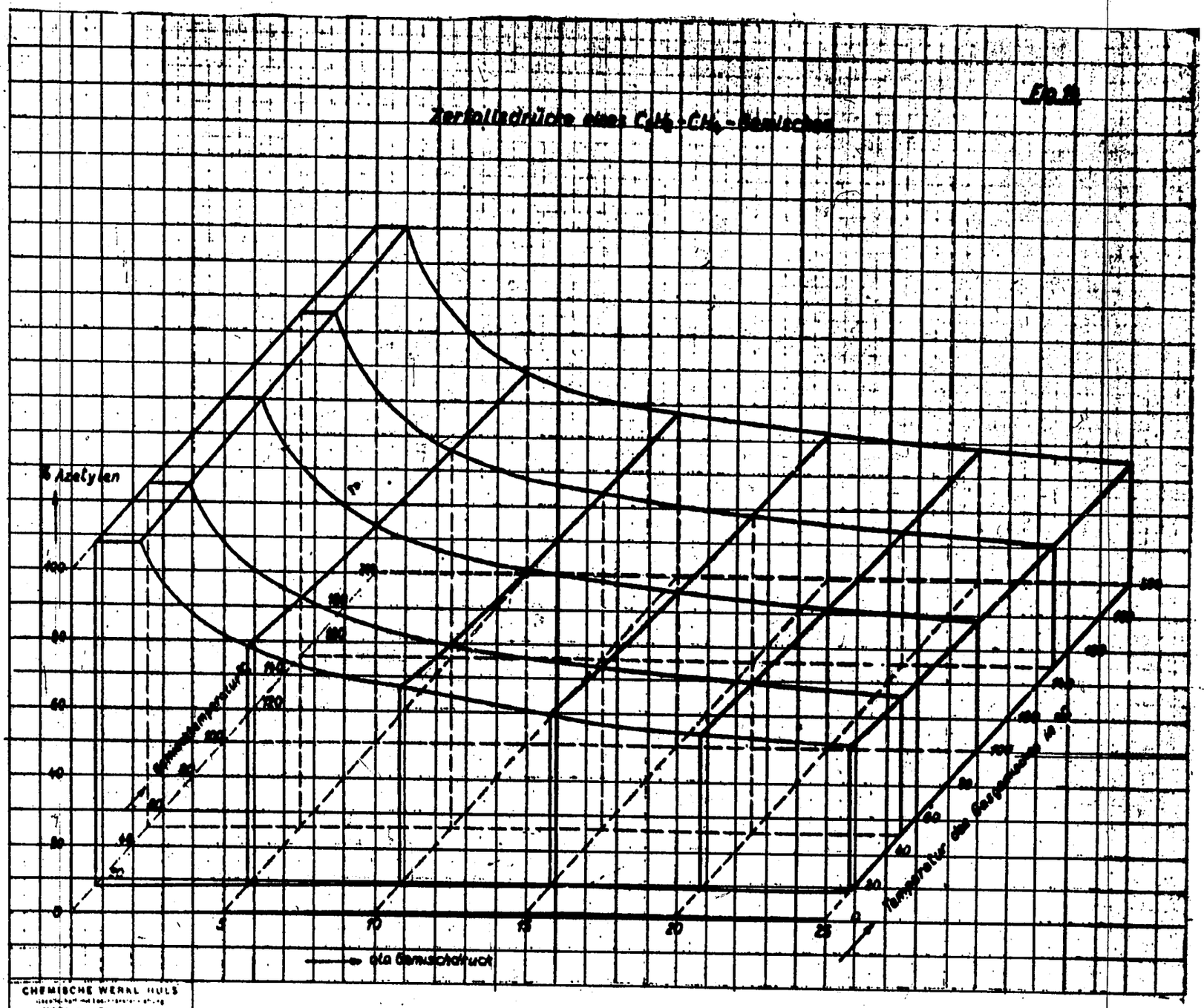


Fig. 8

Zerfalldrücke eines C_2H_2-CH_4-Gemisches



CHEMISCHE WERKE HÜLS

Abb. 61
Partialdruckdiagramm C_2H_6-C_6H_6-Gemische
Partialdruck C_2H_6 in Torr
Partialdruck C_6H_6 in Torr
Gesamtdruck in Torr
CHEMISCHE WERKE HÜLS

EXHIBIT B

Chemisch-Technische Reichsanstalt — Berlin 2-5-41
Department for General Chemistry
Dr. Rimarski

Experiments Over the Detonation of C_2H_2 in Long Pipe Lines

In the report of the Reichsanstalt dated 12-7-39 in which data on the decomposition pressures of C_2H_2 are given and the question of transfer of C_2H_2 over long distances in pipes was discussed, it was recommended that experiments on the decomposition of C_2H_2 in long pipe lines of various dimensions be carried out. The Autogen Works of I. G. Farben at Griesheim offered to place at our disposal their experimental area and to provide the pipe and necessary additional apparatus as well as to take care of other preparations. The Reichsanstalt agreed to furnish the actual pressure measuring equipment and to develop the experimental program.

The experiments were carried out with the cooperation of the Autogen Works from 10-11 to 11-27-1940.

Experimental Equipment

In the report of the Reichsanstalt of 12-7-39 the question of what pressure would be developed in pure C_2H_2 under conditions of strong ignition, large vessels, and a vertically directed decomposition was considered. The question was still open as to what decomposition velocity would occur in large vessels and what pressures could develop in the most unfavorable cases. Since on the basis of earlier experience, it must be assumed that C_2H_2 decomposition requires a long starting distance in order to develop into a detonation, a steel pipe 30 m long was chosen as the experimental vessel. The internal diameters were 25, 50, 100, 200, 300 and 400 mm, with wall thicknesses of 2.5; 3.4; 5.5; 7.75 and 10 mm, respectively.

Flanges were welded to the ends of the pipe to accommodate pressure tight covers. The covers were held on in the case of the small pipes by 8 and in the case of the large pipes by 12 and 16 bolts which were pulled up tight enough to hold a vacuum of a few mm of mercury. The covers were provided with nipples for two gas inlet valves arranged in series, an opening to receive the ball pressure measuring device for the measurement of the decomposition pressures as well as openings for spark plugs. In place of a spark plug, a quartz transmitter could also be inserted, if it was desired to compare the values obtained by the ball device with those of a cathode ray oscillograph.

Immediately next to the first flange a half inch pipe was in-

stalled which led to an oil pump by which the pipe could be evacuated. This pipe had further connections for vacuum and pressure guages and for taking samples before and after firing.

The experimental pipes were also provided at a distance of 5 and 15 m from the first flange with two additional connections for insertion of a second and third spark plug. These were provided in case it became necessary to ignite the C_2H_2 at an intermediate point. Actually this did not prove necessary.

After preparation of the experimental pipes they were buried in parallel trenches 80 cm wide, 30 m long, and 1 to 1½ m deep, which were located at 4 m intervals. The pipes up to 200 mm I.D. were buried 1 m deep and the pipes with 300 and 400 mm I.D. were buried 1.5 m deep. In order that the covers could be worked on, the trenches at each end were lengthened by 3.5 m, widened by 1 m and deepened 2.2 m. The ends of the pipe which contained the valves and pressure measuring devices extended into these enlarged trenches and could be tended from there.

After the pipes were put in place the trenches were filled and the header trenches covered with railroad ties.

A battery of C_2H_2 cylinders with appropriate piping and regulating devices, some 20 m away, a transformer for the necessary igniting current as well as a blower with necessary piping for removal of soot were provided.

Some illustrations in the appendix of this report serve to explain the apparatus.

Illustration I shows the welding of the flanges.

Illustration II shows a pipe being transported to the experimental area.

Illustration III and IV show the experimental area and the trenches with pipes in place.

Illustration V and VI show the blower with blower piping.

Illustration VII shows the 40 mm pipe with cover before the trench was ready for use.

In Illustration VIII and IX the fore parts of the 50 mm and 200 mm pipe are shown extending into the end trench.

The tables contain the following data: Experiment number, date, initial pressure in the pipe in kg/cm^2 gauge, type and strength of ignition, time of ignition (time between turning on the current and the melting of the wire), duration of decomposition (time from turning on current to the arrival of the explosion wave at the forward cover), temperature of the gas (5-11°), purity of the gas, pressure at the different points of measurements, as well as remarks. Ind. (indicators) means that the quartz transmitter, which, as already mentioned, was screwed into the forward cover at a distance of 30 m, from the point of ignition, was used.

The measurement of the ignition time and duration of the explosion was only possible after installation of the oscillograph and could only be carried out a few times.

The results, which were obtained with the different pipes are as follows:

-5-

Experiments in the 25 mm Pipe (Table I)

Up to a pressure of 2.5 kg./cm^2 ignition of the acetylene took place, but propagation stopped at a distance of 1 m from the point of ignition. From 2.75 kg./cm^2 on up the decomposition traversed the entire pipe and in fact became a detonation starting at a point 20 m from the point of ignition as shown by the high pressures (150 and 200 kg./cm^2). It should be mentioned that with small pipes the bar carrying the ball pressure devices could not be installed. For pressure measurements there were only two devices available which were located at 20 m and 30 m from the point of ignition.

With the use of 25.0 mm pipe, which was bent in the form of two S's, to determine whether elbows played a part in the propagation of a decomposition, no break-through was observed up to 2.75 kg/cm^2. Soot lay only 8 m from the ignition point. At 3.0 kg/cm^2 a detonation occurred immediately.

Experiments in the 50 mm Pipe (Table 2 and 3)

With use of a short spark plug, which was installed at the back flange next to the cover and on the other side, (see Table 2) no decomposition took place at 0.4 kg/cm^2. In the range of 0.6-1.75 the acetylene decomposed but the explosion wave did not reach the front end of the pipe. The ball device did not show an appreciable indentation, which is indicated with an X. With two kg/cm^2 detonation occurred immediately with a pressure rise at a distance of 5 m from the ignition point. Whereas the pressures before detonation started amounted to only 19-27 kg/cm^2, at detonation they were in the range 100 and 200 kg/cm^2.