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Personnel of Team:

Mr. J. G. Allen (U.S.).

SYNTHETIC LUBRICATING OIL MANUFACTURE
RHENANIA-OSSAG MINERALÖLWERKE A.G.
HARBURG REFINERY.

Introduction.

This report is based on the interrogation of Dr. Karl Zerbe, Research Director, and Alois Becker, Assistant Chief Engineer of Rhenania, at the Shell House, Hamburg, on the 11 October 1945, by Mr. J. G. Allen (U.S.).

Summary of Information.

The interrogation was based on flow sheets of the synthetic lube oil plant at Harburg. These flow sheets and the detailed report which follows cover the design and operation of this plant in its three parts:

- 1) Wax cracking for olefin manufacture;
- 2) Polymerization of olefins and disposal of used aluminum chloride;
- 3) Finishing of raw polymer into lubricating oil.

The Harburg plant had a capacity of 700 T/Mo. lube oil production with a yield of about 54 weight percent of the paraffin wax charged. It is of especial interest in that it operated on wax from natural petroleum refining.

The plant was dismantled late in the war for re-erection on the Harz mountains. The equipment was shipped in two boats, and was last heard of at Magdeburg, on the Elbe River.

Description of Process.

Details are shown in the attached flow sheets. It should be noted that these are primarily design flow sheets, and are not exactly consistent with one another on throughput volumes. The data on yields, as shown on the sheets, may not be exactly consistent with later operating data.

Wax Cracking.

In Figures 1 and 2 are shown the equipment and flow for wax cracking. The use of natural waxes from the manufacture of oils such as spindle oil and heavy machine oil distillate is recommended. These have an average molecular weight of about 500. With heavier waxes, such as wax from cylinder oil, there is difficulty in vaporization in the cracking furnace. It is important that the wax used be deoiled to less than 5 percent content. Otherwise, coking in the cracking furnace and the evaporators takes place.

The wax first receives direct heat exchange in the bottom of the dephlegmator tower, and combines with the recycle there before it reaches the furnace coil. The furnace is divided into two sections: (1) a vaporizer, using convection and radiant heating, and (2) a cracking section, where three parallel coils with radiant heating are used. Intermediate is the first evaporator in which any non-vaporized oil drops out and in which four dry bubble trays serve as a mist extractor to prevent unvaporized oil particles from entering the second section of the furnace.

The division of the flow into the cracking section coils is accomplished by orifices set in the lines. All attempts to use regulating valves for this job were unsuccessful. The injection of steam before the cracking coil controls the cracking time which is normally about 6 to 7 seconds. The degree of cracking is checked by the determination of the bromine number of the cracked distillate product. This value is normally about 120, using the method of McIlheny.

The cracked product from the furnace is immediately quenched with water (condensate) and is then separated in the usual manner into gas, cracked distillate, recycle cracking stock and residuum.

Yields shown on the design flow sheet (Figure 1) compared with actual yields given below. Maximum capacity of the plant was stated to be 60 tons of charge per day.

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Weight Per Cent Yields.

	<u>From Flow Sheet.</u>	<u>Actual.</u>
Gas and Loss	24	30-35
Cracked Distillate	55	60-65
Residuum	<u>21</u>	<u>10</u>
	100	100

Polymerization (Figure 3).

For polymerization, the cracked distillate, average molecular weight 290-300, boiling range approximately 40° to 300°, is used. The process is carried out batchwise in 10-ton lots. The distillate is circulated with continuous addition of a thick aluminum chloride slurry and with controlled temperature depending on the type of oil required. The following variations in operating temperature were noted:

20°C. gives a thick cylinder oil; requires longer polymerization time and gives lower yields.

40°C. usually used for the required aviation oil blending component. Gives a viscosity of about 120E/50° and 5.50E/100°C.

60°C. gives oil with a viscosity of about 40E/50°C.

A minimum circulation rate of about 20 times the charge volume per hour gives sufficient mixing without the use of the stirrer in the reactor.

For the regular oil (5.50E/100°C), a period of 3 to 4 hours is required to add the previously calculated amount of aluminum chloride. Following this addition, the oil is circulated about 2 hours more or until the bromine number decreases to 0. The use of the auxiliary agitators for this latter circulation frees the primary agitators for another fresh batch polymerization.

Following the polymerization, the oil and aluminum chloride were originally separated in a centrifuge, but

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this system was replaced by settling in "tubs" at 30-40°C. for about 12 hours. The raw polymer is separated for further refining in the next step. The sludge is drawn off and decomposed by the addition of warm water, and the "sludge oil" recovered is further polymerized in subsequent batches. No recovery of aluminum chloride is attempted.

It is essential that the sludge oil be absolutely dry to avoid subsequent corrosion difficulties, and more elaborate plans were laid for sludge-oil drying in the relocated plant than were actually used at Harburg.

The polymerization plant, as shown, is considered capable of charging 40 tons/day distillate and yielding 36 tons/day (90% yield) of raw polymer.

Contact Refining (Figure 4).

The raw polymer is mixed with about 4% of clay and enough lime to neutralize its acidity (Note: flow sheet shows 4% lime and 1% clay). This mixture is heated to about 250°C. in a pipe still to decompose aluminum and chlorine complexes still remaining in the oil. A minimum of about 200°C., together with some soaking time, is required for this decomposition. The HCl is then vented from the oil to cut down the corrosion in subsequent distillation steps where steam is present.

The oil is then stripped of its light components by atmospheric and vacuum fractionation. The oil from the atmospheric distillation is filtered through Sweetland filters to remove the clay and lime. The latter residue from the filters contains about 40% oil which is recovered by extraction with gasoline.

The finished oil from the vacuum distillation was used as a blending component for aviation lubricating oil.

Yields from the contact refining and atmospheric distillation were as follows (based on raw polymer charged):-

	Wt. %
Gasoline, 70 Oct. No., Motor Method	5
Gas Oil (Diesel fuel) 40 Cetane No.	15
Lube Oil	.80
	<u>100</u>

Vacuum distillation further reduced the lube oil yield to about 60%, based on the raw polymer charged to the contact refining step.

Capacity of this section of the plant was 50 T/D raw polymer.

<u>Summary of Yields.</u>	<u>T/D</u>	<u>Weight % Yields</u>	<u>Ulti-</u>
		<u>based on</u>	<u>mate.</u>
		<u>Wax Charge.</u>	

<u>Charge to Wax Cracking</u>	60	100.0	100.0
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Yields from Wax Cracking.

Gas and Loss	18	30.0	30.0
Cracked Distillate	36	60.0	
Residuum	6	10.0	10.0
	<u>.60</u>	<u>100.0</u>	

Yields from Polymerization

Raw Polymer (90% of distillate)	32.4	54.0	
Loss	3.6	6.0	6.0
	<u>36.0</u>	<u>60.0</u>	

Yields from Contact Refining & Finishing.

Gasoline	} (40% of Raw Polymer, 13.0	21.6	21.6
Gas Oil (Diesel Fuel)			
Finished Lube Oil (60% of Raw Polymer)	19.4	32.4	32.4
		<u>54.0</u>	<u>100.0</u>

Operating Efficiency of Unit.

The unit was stated to have a normal operating time of 300 days per year or an efficiency of 82 per cent. The normal length of run was 28-30 days, and the principal cause of the shut-down was coking of the evaporators and the tube coil. This major difficulty is tied in with the amount of oil in the wax.

Special precautions in keeping up the operating efficiency were observed in the design of injection nozzles, one of which could be cleaned during operation, and in the design of the heat exchangers on the feed line to the contact-refining furnace which could be segregated and cleaned individually of lime and clay deposits.

Comments on Synthetic Lube Oil Manufacture (by Dr. Zerbe).

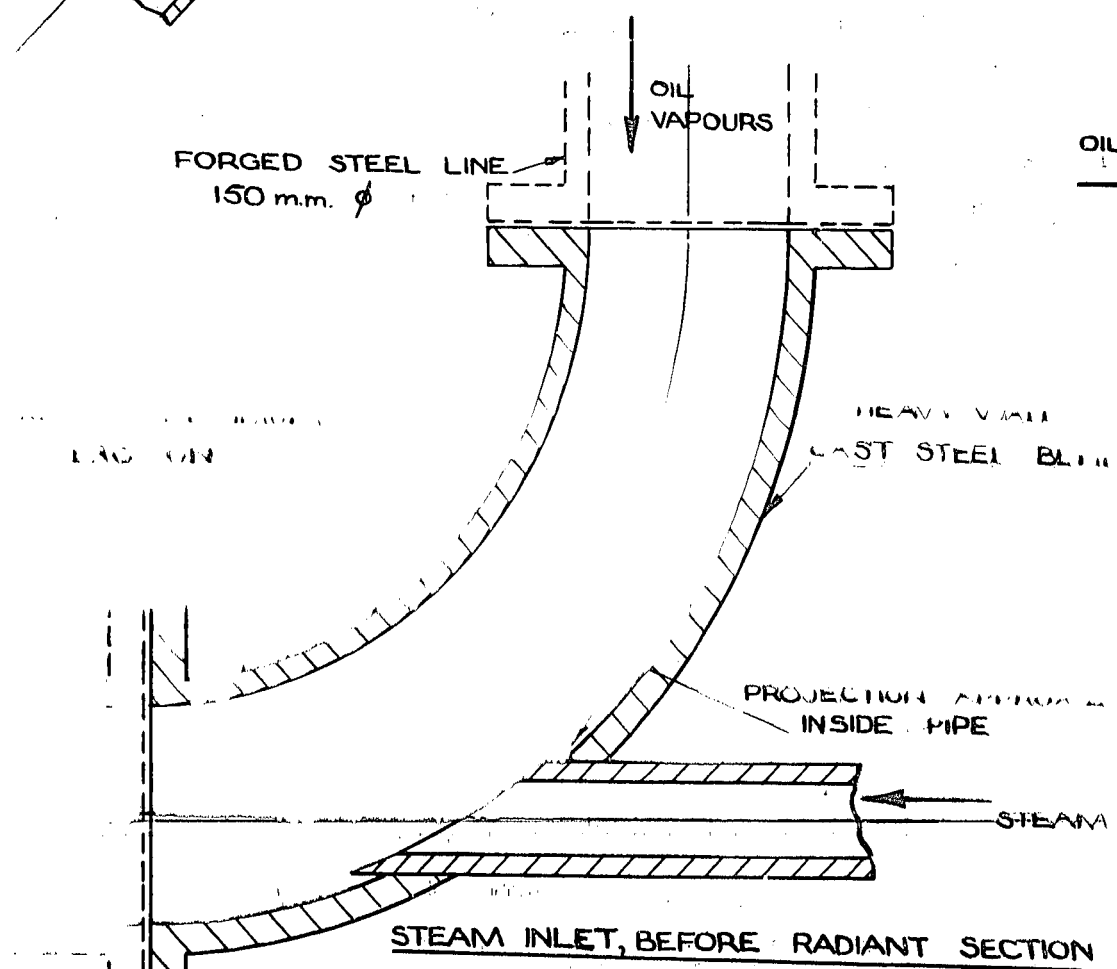
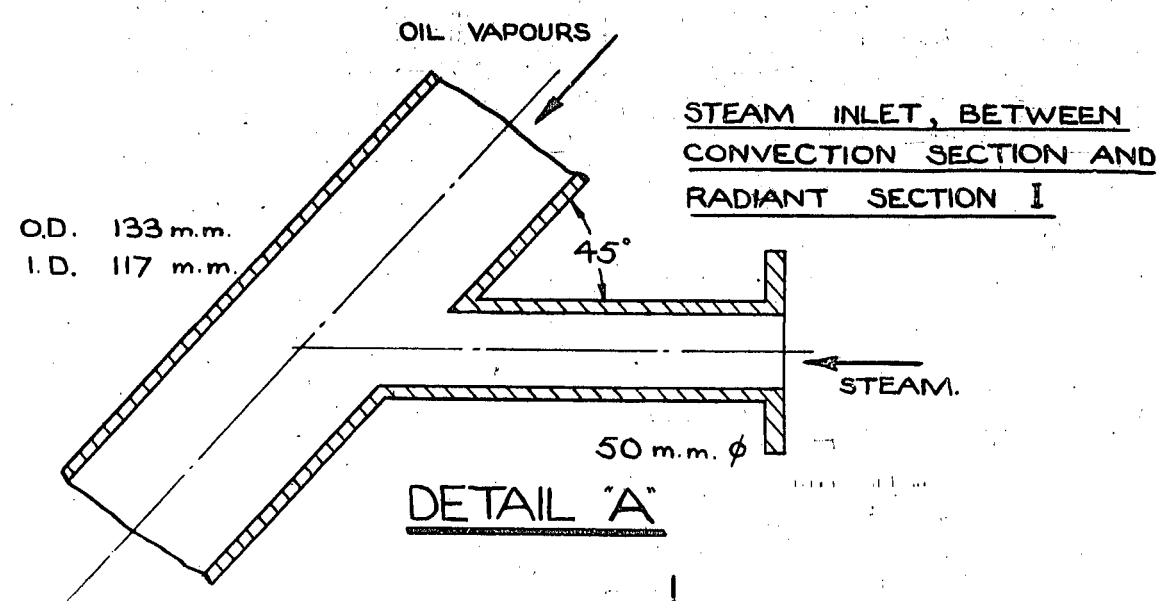
1. Fischer-Tropsch wax is the ideal material for this operation. It contains n-paraffins and gives alpha- and beta-olefins on cracking which polymerize into the best lubricating oil. No distinction is made between alpha- and beta-olefins for this purpose. One plant run was made by Rhénania on Fischer-Tropsch wax from "gatsch" furnished by Ruhrchemie. This gave an oil of 120 V.I., compared with 100-105 normally produced from natural wax. Difficulty was experienced in deoiling the "gatsch". It was necessary to use a two-stage extraction with benzol-acetone, using 300-400 per cent of solvent each time and a temperature of -30°C.

2. Natural waxes contain iso-paraffins and tend to give gamma-olefins which polymerize into poorer lubricating oils. Wax from brown coal tar processing is intermediate in value between Fischer-Tropsch wax and natural petroleum wax as a feed stock for lube oil manufacture.

3. The synthetic lube oil normally produced by Rhénania has an average molecular weight of about 300.

FIGURE 1.
SYNTHETIC-LUBRICATING-OIL-MANUFACTURE.
FLOW SHEET OF WAX CRACKING PLANT,
RHENANIA-OSSAG, HARBURG REFINERY.

FIGURE 1.
SYNTHETIC LUBRICATING OIL MANUFACTURE.
FLOW SHEET OF WAX CRACKING PLANT,
RHENANIA-OSAG, HARBURG REFINERY.



Note:- LOCATION OF FITTING SHOWN ON FIG. 1

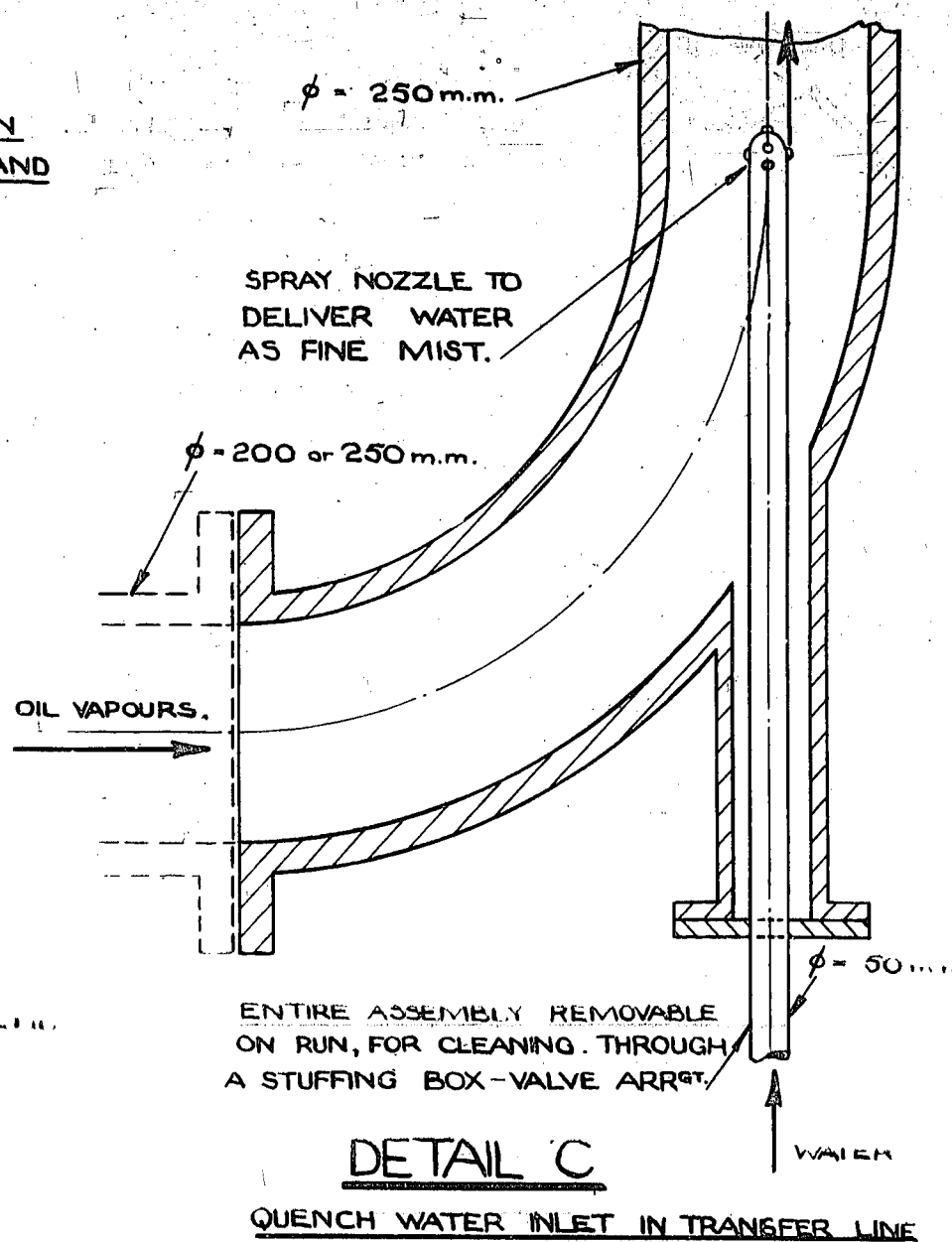
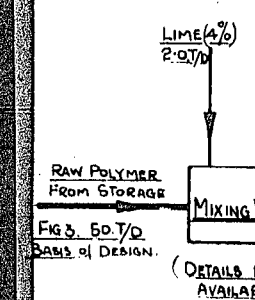
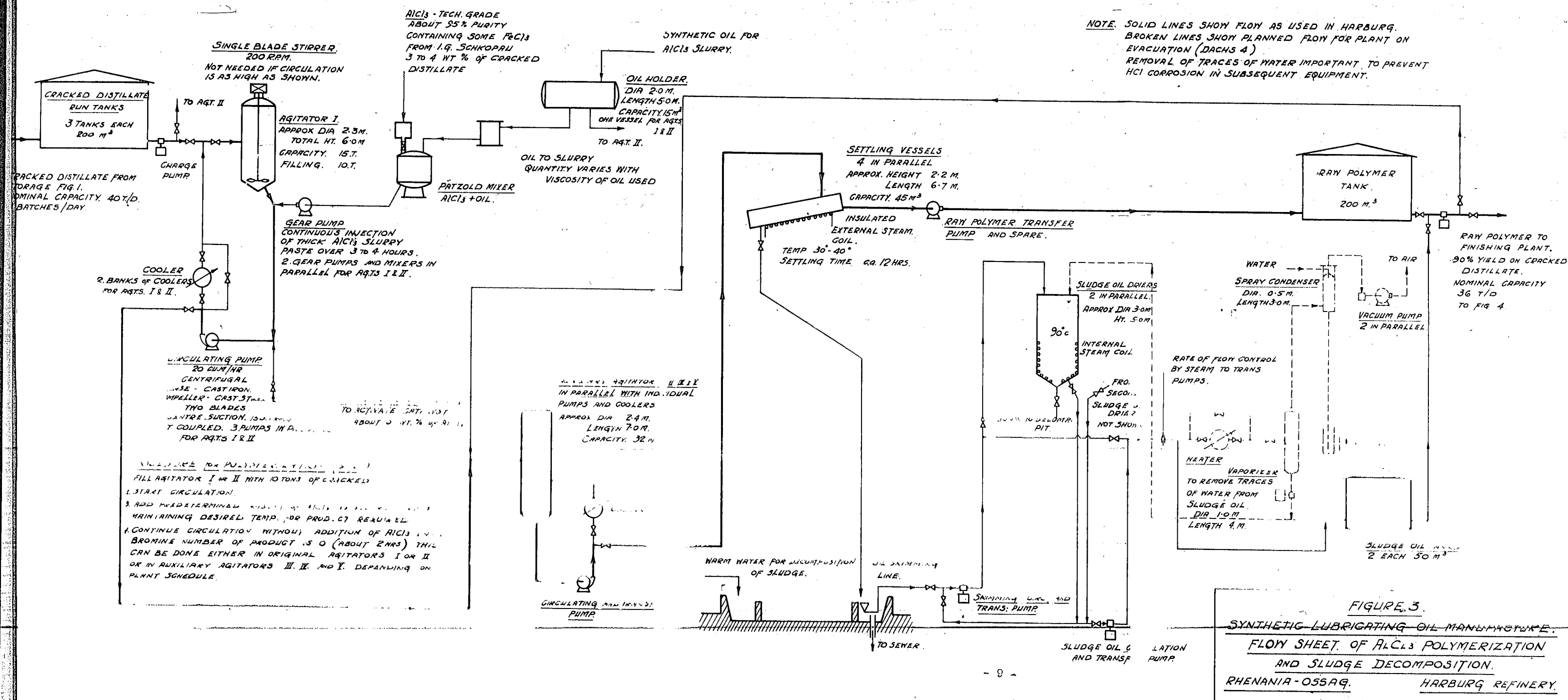
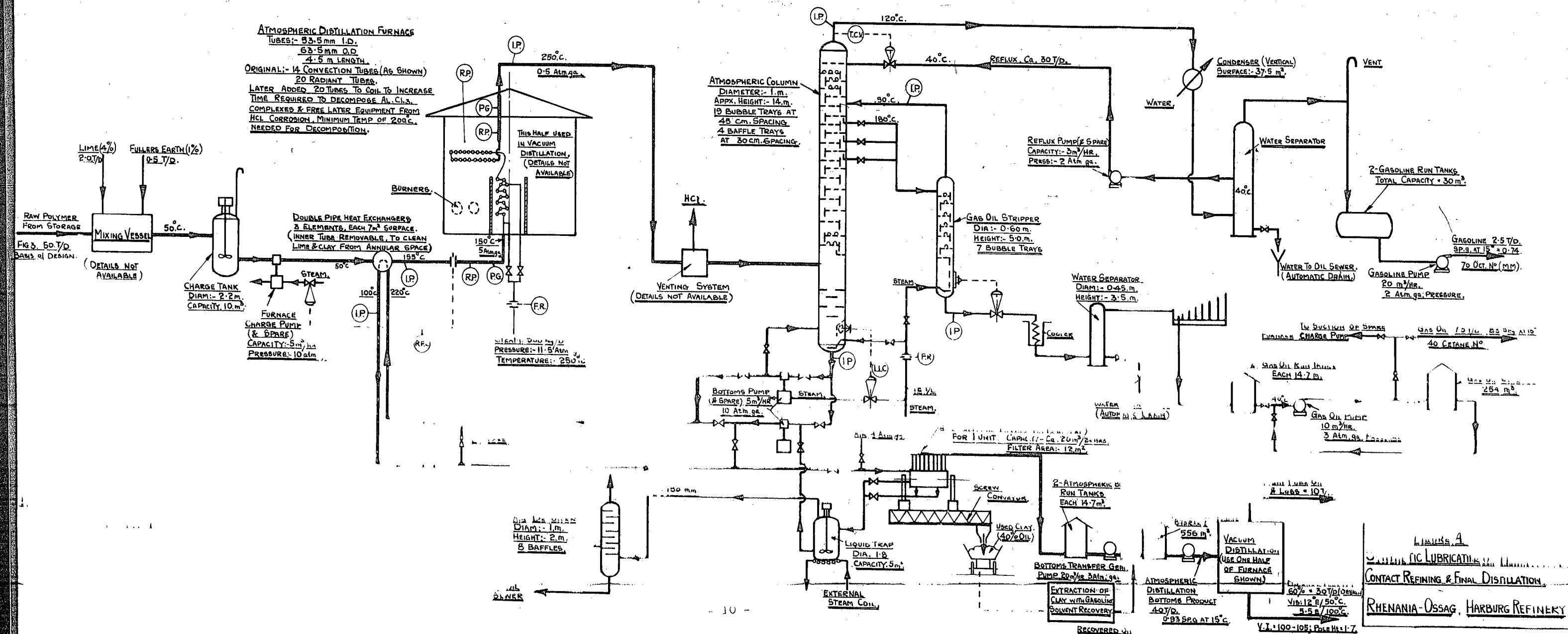


FIGURE 2.
SYNTHETIC LUBRICATION OIL MANUFACTURE
DETAILS OF INJECTION FITTINGS.
WAX CRACKING PLANT
RHENANIA-OSAG, HAMBURG REFINERY





FIAT FINAL REPORT NO. 577

UNCLASSIFIED

SURVEY OF THE LEADING MANUFACTURERS
OF
PRESSURE VESSELS

REC'D. APR 1946

TIIC L.F. & L. S.

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JOINT INTELLIGENCE OBJECTIVES AGENCY

WASHINGTON, D. C.

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 577

26 December 1945

SURVEY OF THE LEADING MANUFACTURERS
OF
PRESSURE VESSELS

BY

ROY W. CLARK

FOR THE INTELLIGENCE OBJECT

FIELD INFORMATION AGENCY, TECHNICAL

52 p illus

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OBJECTIVE

The purpose of this survey was to investigate and evaluate the leading and most important manufacturers of pressure vessels, in order to determine what innovations had been made in methods or manufacturing technique, in relation to the production of pressure vessels.

To see what new types of vessels, if any, had been evolved, due to scarcity of materials or other causes, through the duration of the war.

To note what progress had been made in the manufacture of clad steels.

INTRODUCTION

The number of pressure vessel manufacturers in Germany, is comparatively large; but the great majority of them limit themselves to one of several classes. In the first class are a relatively small number, which can manufacture vessels of the heavier type, and who have the necessary equipment to properly handle this work.

The second class, contains a number of firms which can manufacture vessels of a medium thickness and length, but who lack certain equipment and are dependent upon one or two of the larger shops to a great extent.

Then, there are quite a large number of shops, which specialize on certain items for the various process industries, and have only the necessary equipment to carry on their own particular work, and, accordingly are a negligible quantity in the industry and not capable of handling the ordinary run of plate work.

Most of the better shops are located in the Ruhr District of the British area, and very few are in either the United States or French areas. There are several large shops located in the Russian occupied area, but these were not considered in this investigation.

The data for this report was obtained in all cases, from discussions with the manufacturers themselves, and from a personal survey of their plants and equipment in conjunction with their technical and operating executives. In all cases a personal inspection of their product was made, whenever such products were available.

DISCUSSION

The P.V. industry as a whole is not a diversified industry. There are a great number of small shops which limit themselves to general repair work or a small specialty which they have developed, perhaps in cooperation with one or another of the manufacturing process companies. These can be discarded as immaterial to this discussion.

The larger and better companies have shown considerable progress and ingenuity, not in new fields of investigation, but rather in perfecting technique in relation to their own particular manufacturing methods.

In their welding practice I saw nothing outstanding in a general way, but a small number of them are doing a very high grade of work. Quite considerable of the work is Oxy-Acetylene welded, but the great majority limit themselves to arc-welding of the hand variety and I saw no automatic machines at all.

One or two of the firms have been doing considerable work with the Union Melt Process and are getting very good results. Two of these firms, Mannesmann, Duisburg and Deutsches Rohrenwerke A.G., Thyssen Werke, Mülheim (Ruhr), have been particularly active in this process and will be discussed briefly in the later reports on individual companies.

Quite a number of pressure vessels in Germany are either forged or of the pressed seamless variety and here they are making an excellent product. In addition, they of course make quite a few under the Roechner Process. Boiler drums are a particular product of either one of these methods and they produce some very fine work.

The cost of these types of vessels is very hard to figure on account of a number of factors, of which forced labor, excessive use of labor, and subsidization of the work in many cases are contributing items. For the sake of a rough comparison of the various types, one firm stated that where the cost of arc welded vessels would run about 700 R.Ms per ton, the vessels manufactured under the Roechner process would run about 800 R.M. per ton and forged vessels approximately 1300 R.M. per ton. This relative comparison was checked with several of the other firms and the proportion of costs seems to be fairly general. No relative costs were obtainable on the banded vessels.

The average good shops manufacture vessels with a plate thickness of 20 mm to 50 mm, but the better shops are producing them up to 100 mm thickness. Of course, in the forged and banded vessels, the thickness of the shells are considerably greater with a limit on the banded vessels of approximately 200 mm.

Their normalizing and stress relieving facilities are not comparable to ours as a great number of them do not have the equipment and if called on to do this, they send the completed vessels to other shops which have the necessary installation.

The largest furnaces are limited to three meter diameter vessels, and a maximum length of eighteen meters. This is roughly nine feet diameter by fifty five foot length and there are only two of this capacity.

In the case of longer vessels they stress relieve each end separately. In many cases only the section in the girth seam is stress relieved and this is accomplished by means of a brick lined sectional portable furnace built around the weld of the vessel to be stress relieved.

In regard to X-raying the welds, only the larger firms go into this very thoroughly, and they report very satisfactory results after the instructional period has been completed.

The outstanding new type of pressure vessel developed is the wrapped band vessel as designed by I.G. Farbenindustrie, A.G. and manufactured by the Deutsches Rohrenwerke A.G.-Thyssen Werke, Mülheim a/Ruhr. A discussion of the manufacture and also a translation of the method of calculating stresses will be submitted in later pages of this report.

The translation of the stress calculations is not the result of a discussion of the vessels by the writer, but is purely a translation of a specification by one of the leading engineers of the I.G. Farbenindustrie, A.G., which was given to the writer by one of the manufacturers.

MANUFACTURE OF PRESSURE VESSELS IN CARBON AND ALLOY STEELS FOR CHEMICAL INDUSTRY IN THE RUHR DISTRICT

Group I

Name and Location	Type of Industrial Plant	Production Capacity	Note
A. Makers of seamless rolled or seamless forged vessels			
1. Deutsche Röhrenwerke A.G. Thyssen Werke Mülheim - Ruhr	Steel works, Drum and Plate Shops	High	Seamless rolled Röhner Process Banded vessels
2. Friedrich Krupp Essen-Ruhr	" "	High	Seamless forged
3. Press-und Walzwerk A.G. Dusseldorf	Press shops Forge shop Steel mill	High	Seamless forged Pressed drums
4. Rohlmittel Duisburg A.G. Dusseldorf-Berlin (Tegel)	Steel works machine, and vessel shop	High	Seamless forged

PRESSURE VESSEL MANUFACTURERS, CONT.

Group I

<u>Name and Location</u>	<u>Type of Industrial Plant</u>	<u>PRODUCTION CAPACITY</u>	<u>NOTE</u>
B. Makers of High Pressure Vessels, Hydrogen Welding			
1. Deutsche Röhrenwerk A.G. Thyssen Werk Mülheim-Ruhr	Steel works, Drum and Plate shop	High	
2. Mannesmann Röhrenwerk A.G. Duisburg-Huckingen	Pipe and Vessel shop	High	
3. Rheinmetall-Borsig A.G. Dusseldorf-Berlin (Tegel)	Steel Works Machine & Drum shops	High	
4. Ruhrstahl A.G. Werke Henrichshütte Witten-Ruhr	Steel Werk Vessel & Drum shops	Medium	

PRESSURE VESSEL MANUFACTURERS, CONT.

<u>Name & Location</u>	<u>Type of Industrial Plant</u>	<u>Production Capacity</u>
C. Makers of High Pressure Vessels Electric Welding		
1. Deutsche Röhrenwerke, A.G. Thyssen Werk Mülheim-Ruhr	Steel Mill Drum and Vessel shops	High
2. Friedrich Krupp Essen-Ruhr	" "	High
3. Mannesmannröhrenwerk A.G. Duisburg-Huckingen	" "	High
4. Rheinmetall - Borsig A.G. Dusseldorf-Berlin	" "	High

All Firms in Group I are expert in vessels, for Chemical Industry.

PRESSURE VESSEL MANUFACTURERS, CONT.

<u>Name and Location</u>	<u>Type of Industrial Plant</u>	<u>Production Capacity</u>	<u>Note</u>
Makers of Medium Sized Plate work and Vessels for Medium Pressure			
1. Deutsche Rohrleitungsbau A. G., Dusseldorf	Machine and Vessel shops	High	Chemical Industry
2. Gutehoffnungshutte Oberhausen-Sterkrade	" "	High	"
3. Dortmunder Union Brückenbau A. G. Werk Orange-Gelsenkirchen Dortmund-Ruhr	" "	High	"
4. Klöckner-Humboldt Deutz A.G. Köln-Deutz	" "	Medium	"
5. Wilke-Werke, A.G. Braunschweig	" "	Medium	"
6. Ewald Borninghaus Duisburg	Boiler shop	Medium	
7. Vereinigte Kesselbau A.G. Dusseldorf	Boiler shop	Medium	
8. Walther & Cie. Köln-Delbrück	Boiler shop	Medium	
9. Wilhelm Küsters Aachen	Boiler & Vessel shop	Medium	

MANUFACTURERS CONTACTED

Vereinigte Deutsche Metallwerke, A.G.	Hesse Strasse, Frankfurt/Heddenheim
Lurgi G. für Chemie und Huttenwesen	Gervinus Strasse, Frankfurt Target - 31/86
"Kühnle, Kopp & Kausch	Frankenthal
Maschinen Fabrik Esslingen	Esslingen/Stuttgart
W. Schiltze Leichtmetallbau	Feuerbach/Stuttgart
M. A. N.	"Nürnberg Augsburg Gustaveburg
Stahlwerke-Rachling-Buderous	Wetzlar
Samebreuther and Co. G.m.b.H.	Butzbach
Wärmefang u. Ventilatorbau	Hackethal Strasse 71 Langenhagen-Hannover
Prometheus Werke G. für Apparatenbau	Mutenfangweg 12 Herrenhausen/Hannover
Erdbeer Werke	Oberhausen
Gutehoffnungshutte	Sterkrade/Oberhausen
Deutsche Kesselwerke	"Mülheim/Khld
Ewald Borninghaus	71 Vulkan Strasse Duisburg Khld.
Gronemeyer u. Bannert	Brackwede - Westp
Schmidtische Meisdam, A.G.	"Wilhelmshöhe" Allee 247 Kassel
Rheinmetall-Borsig A.G.	Ulmen Strasse 125 Grafenburg - Dusseldorf
Walther & Cie.	"Köln-Delbrück

Paul Schutze A.G.

Mannesmann Röhrenwerke A.G.

Press und Walzwerke A.G.

Oggersheim - Palatinate

Huckingen/Duisberg

Reisholz and Düsseldorf

REPORT ON INDIVIDUAL FIRMS

Vereinigte Deutsche Metallwerke, A. G. - Heddenheim/Frankfurt

Director: Herr K. Flesser

Metallurgist: Dr. E. Lay

They make no pressure vessels of any kind. During the war they did make copper wire wound spheroid containers for V1 bombs, but these were very small and they never got into heavy production of them.

Their principal products at this plant were sheets, copper and nickel electroplated, and copper wire. They plate steel sheets with copper, nickel or aluminum for the manufacture of coins.

I was expecting to find that they manufactured clad steels, but their process is strictly an electro-chemical plating process.

At the Altena/Hamm plant they plate with nickel and copper for small chemical containers.

At Duisburg they make condenser tubes of plated material, 70% Copper, 20% Zinc and 10% Tin. Due to the shortage of Tin, they changed the analysis to 76% Copper, 2% Aluminum, 22% Zinc.

Duisburg also makes heat exchanger tubes of 90% Copper and 1% Aluminum.

Dr. Philippi - Dir. Manager - Duisburg Plant

Dr. Baum - Chem. Metallurgist

Lurgi G. für Chemie & Hüttenwesen - Gervinus Strasse 17 - 19 - Frankfurt

Director Behlert

This is an engineering and design firm entirely. They assume the contract and buy all vessels and apparatus from various shops. They do, however, build electric precipitators (Cottrell) for gas cleaning at their Friedberg Plant. They do the erection at complete chemical plants and furnish operating organizations.

The Lurgi Warne subsidiary has offices at Heddenheim with Dr. Danulat as the Chief Engineer in charge. Again they limit their activities to design and operation.

Dr. Danulat stated that all their vessels were built by Mannesmann or M.A.N. at Gustavesburg.

He says that annealing or stress relieving capacity in Germany is limited to 3 meters diameter by 15 meters long, and that there are only 3 firms in all Germany who can handle this class of work.

The limit on their pressure vessels is 50 mm. thickness.

Kühnle Kopp und Kausch - Frankenthal

Director Dr. Winkler

They have made a few pressure vessels for I. G. Farbenindustrie during the war, but pressure vessels are not a standard product with them. Their products are compressors, small steam turbines and axial flow fans.

They have made 8 or 10 agitators of stainless clad steel for I. G. Farbenindustrie. Several of these were still in the plate shop and were 2,800 meters diameter and 2,300 meters seam to seam. The shell was 20 mm. thick with stainless cladding 2 mm.. The clad steel furnished by Deutsches Edelstahlwerke, Krefeld, who are associated with Deutsche Röhrenwerke A.G., Mülheim a/Ruhr.

Kühnle Kopp & Kausch are not a factor in pressure vessel manufacture.

Maschinen Fabrik Esslingen - Esslingen/Stuttgart

Dr. Ludwig Kessler
Dr. Otto Klüsener
Herr Koch
Dr. Klingenstein
Herr Huth

First Director
Second Director (Engineering)
Chief Engineer
Blast Furnace Engineer
Locomotive Department

These people are primarily locomotive boiler and railroad car builders, but they also make steam or gas driven compressors for gas and gasoline plants. They are definitely not a pressure vessel shop, but during the war they did make 3 rivetted towers for I. G. Farbenindustrie on the synthetic rubber program.

W. Schiltze Lechtmittelbau - Feuerbach/Stuttgart

Before and during the war they manufactured air receivers and light containers. The containers were of aluminum and magnesium. They do no pressure vessel work other than this.

The plant is entirely destroyed.

M. A. N. - Nürnberg

This plant has not made any pressure vessels but state that they have been making them at either one or both of their other plants. The works has been about 80% destroyed.

At Nürnberg before and through the war they manufactured coal and ore bridges, cranes, diesel engines, auto trucks and prime movers.

M. A. N. - Augsburg

Chief Director - Herr Otto Myer
Metallurgist - Prof. Dr. E. Sovensen
Acting Director - Herr Meyr

They have made no pressure vessels at Augsburg and informed me that their pressure vessel business was carried on at the Gustavesburg plant.

This plant manufactures diesel engines, heavy machinery for dye plants and breweries, printing machinery and during the war they added guns and heavy ammunition.

M. A. N. - Gustaveburg

Director Reinhart
Director Hübner
Supt. Boiler Shop Herr Silberhorn

This shop produces pressure vessels to a small extent for the chemical industry. They also make waterless gas holders, bridges, pontoons, submarine sections and are the largest producers of roller dams in Europe.

They use electric arc and Union Melt and have been getting very good results with Union Melt up to 50 mm. thickness. They arc weld up to a limit of 105 mm., doing all their scarfing with acetylene torch on the heavy plate.

They have several bending rolls, but the large one - 10 meters long - is a four roll outfit with the top roll adjustable horizontally and vertically. The two outside bottom rolls adjustable vertically. They do all cold rolling and the machine can handle 100 mm. plate not over 800 mm. wide or 50 mm. at a width of 4 meters.

Their X Ray equipment has a limit of 75 mm. above that the results are problematical. They also have one of the largest stress relieving furnaces in Germany and can handle vessels 3 meters diameter with a maximum length of 15 meters.

They have never worked on clad metals and have not been particularly active in pressure vessel production. Their particular specialty is on roller dams and closed gate (double) dams. They have built the great majority of the dams in the Upper Rhine and various other rivers in Germany, others in Norway and Sweden, and one on the Grand River in Colorado for the United States Reclamation Service.

Stahlwerke - Rochling - Buderous A.G. - Wetzlar

Metallurgist - Dipl. Ingenieur Otto Lucas

This plant was supposedly a factor in the chemical industry for towers and vessels, but they have never made any equipment of this kind.

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It is an alloy steel plant specializing on stainless steels and produces about 67,000 tons annually.

They have one analysis of stainless - 18% Chrome, 8% Nickel, 0.08 to 0.15% Carbon - but their normal production is 20% Chrome, 10% Nickel and 1.2 to 2.5% Molybdenum which is very similar to Krupp's Stainless V2A.

Samesreuther and Co. - Butzbach

A small shop doing considerable locomotive boiler repairs, but they do manufacture small heat exchangers with welded tubes and also medium size autoclaves of various pressures. The outer shell has a series of indentations press into it before rolling, and each of the bulbs are welded to the inner shells. Attached illustrations show the construction.

They also make quite a few of these vessels with an alloy lining or the innershell of clad steel. They are, however, a rather negligible quantity in pressure vessel production.

Warmefang u Ventilaforbeau - Langenhagen/Hannover

This firm is entirely out of the vessel business as it is a total ruin from bombs. Their principal product was small heat exchangers of cast iron with rolled tubes and cast iron economizers in banks for stationary boilers.

K. Schmied u. Metallbau - Langenhagen/Hannover

This is a small plate shop doing pressure vessel work of medium size. Their largest capacity is plate of 30 mm. thickness.

They have about 8 welding outfits and one Kjellberg semi automatic welder. They have never worked with clad steels and most of their production is rivetted tankage for petroleum plants.

They have no stress relieving equipment; and if this is called for, they ship the vessels to the Ruhr shops to have it done. There is nothing outstanding in their practice, and they are comparable to our ordinary small shop.

- 15 -

Babcock Werke - Oberhausen

Director - Herr Jantscha

Babcock Werke have limited their production to boilers alone, doing no other pressure vessel work. They can roll plate to 30 mm. thickness, but most of their welding is done on water conditioning and pulverizing equipment. They built economizers of both cast iron and steel pipe in addition to their boiler work.

They buy all their boiler drums from Thyssen Werke and these are seamless 4" thick and 8 meters long for a pressure of 125 Atmospheres. Their headers are bought from Press u. Walzwerke, Dusseldorf, and they weld the ends and forge them to suit in their own shop.

They have one annealing furnace 2 meters by 2 meters, 10 meters long but use it only for tubes and steel castings. They also have one small portable X-Ray machine of 125 volts which is used only on boiler repairs and air-conditioning and pulverizing equipment.

At the present time they are working on boiler repairs for the coal mining industry.

Gutehoffnungshütte - Oberhausen A.G. - Oberhausen/Sterkrade, RHLD

Herr Kollerman	Chief Director
Herr Muhla	Acting Director
Dr. Otto Zechel	Chief Metallurgist
Herr Schulz	Chief Engineer and Manager
Herr Fleischer	Supt. - Boiler Shops

This is a very large plate shop and can handle the heaviest class. The plate and boiler shop is one of the many different manufacturing divisions. As a general manufacturer, they produce heavy machinery of all kinds, boilers, blast furnace plants, coal mining machinery, transmission equipment, bridges of all kinds and complete installations for petroleum, chemical and rubber industries.

In the shop they have a very good line of heavy equipment, such as a four-roll set of bending rolls with a capacity of bending cold plate 50 mm. thick - 6 meters width, a shear with circular knives capacity at 25 mm. plate making the cut either vertical or scarfing, it for welding, and a 1000 ton press made by Ehrhart u. Sehmer, Saarbrücken, Cantilever Herringbone Rack and Gear, operated with electric drive and hydraulic kickout, which is a particularly fast operating close precision press.

Their average welded work runs about 60 mm. in thickness, but they also make quite a large number of vessels up to 105 mm. and any length or diameter required.

Their stress relieving furnace is capable of taking work 3 meters in width, 4 meters in height, and 25 meters in length, with a very close range on the three heat controls. This is the largest and best stress relieving equipment in the entire pressure vessel industry, but it is out of operation and under repair at the present time.

They have 50 Kjellberg 500 KW welders and also 2 Union Melt machines, both of the later temporarily out of operation from bombing. They also have a large number of motor driven trunnions and at least 10 or 12 positioners of various sizes.

I have shown in accompanying pages the class of work that they do and included a cut of a catalyst oven for the Fischer-Tropsch Process of which they have built quite a number. Their heat exchangers are all of the welded tube variety, not being interested in the changeable tube nest type.

The workmanship and product of this firm is of the highest calibre and they rank with the top grade manufacturers in all Europe.

Deutsche Röhrenwerke, A.G., Thyssen Werke - Mulheim a/Ruhr

Herr Ciliac	Director
Dr. Simoneit	Works Director
Herr Paul H. Inden	Ingenieur and Interpreter
Herr Fiene	Supt. Roechner Mill
Herr Gruber	Supt. Plate Mills and Boiler Shop

The Thyssen Werke is one of the outstanding pressure vessel shops in all Germany and makes vessels of all categories, particularly of the seamless and banded varieties.

I have submitted separate reports in the following pages which cover their activities in these lines. They are the only shop manufacturing the banded vessels; they also manufacture vessels under the Roechner Process, and they make clad steel for corrosion resistance, all three of these items being covered under separate reports later in the text.

Their welded pressure vessel shop is well equipped, but this is the minor one of their activities. All of their products are of a high grade and they are considered a potential unit in the steel as well as the pressure vessel industry.

Ewald Berninghaus, 71 - 73 Vulkan Strasse, Duisburg, Rhld.

Ewald Berninghaus Director
Dr. Greve 2nd Director

This firm is primarily a marine boiler and shipbuilding organization; but, as a fill-in, they manufactured pressure vessels of medium size.

About the only equipment they had at this plant were 10 or 12 welding machines as they sent the plates to another shop for scarfing and rolling.

This plant is a negligible quantity in pressure vessel production, but they informed me they had another plant in Herne a little better equipped.

The Duisburg shops were 90% destroyed and the Herne plant about 65%.

Gronemeyer u. Banck Kesselsmeide - Brackwede-Westf.

This firm is a very small outfit doing nothing but stationary boiler repair work.

They have made in the past a few pressure vessels of light plate and some heat exchangers with tubes welded in. They have very little equipment, and what they have is very old.

These people are builders of small marine boilers for pressures of 50 and 150 ATM pressure. They had light equipment and have never been considered in the pressure vessel category.

The plant is 90% destroyed.

Krupp - Borsig, A.G. - Ulmen Strasse 125, Grafenbourg/Dusseldorf

Borsig at this works was formerly fairly active in pressure vessel manufacture of the forging class. They are primarily an artillery and high speed tool steel production firm, but all the equipment for pressure vessels and artillery had been evacuated to Berlin and Eastern Germany in the summer of 1943.

They have a larger plant in Berlin which I expect to visit later on.

Walther and Cie. - Köln/Delbruck

Herr Wolfram Ahn - Commercial Director

Walther is strictly a boiler shop and has never manufactured pressure vessels of any other class. They do, however, have a very complete plant for the manufacture of boilers, but they buy their drums from Thyssen and Mannesmann.

Paul Schutze, A.G. - Oggersheim - Palatinate

Director - Herr Schulte

This company is a small repair shop but has made a number of small pressure vessels during the war. They also have worked on clad steels to a small extent.

The principal products are small lead lined tanks and kettles and also enameled kettles.

They definitely are not a factor to be considered in the pressure vessel industry.

Mannesmann Röhrenwerke - Huckingen/Duisberg

Works Manager - Herr Ing. Otto Weinrich
Director of Research - Dr. Buckholtz
Asst. Manager of Works - Dr. Knapp

Mannesmann are one of the most important units in the manufacture of pressure vessels in all Germany. Their pressure vessel work is carried on at Huckingen and Berlin.

The principal products at Huckingen are pipe, boiler drums and pressure vessels welded by either water gas, electric arc, or Union Melt process. They have the shop laid out on a production basis - and they have the necessary equipment for any type of pressure vessel up to a plate thickness of 104 m.m. The great majority of their work averages about 60 to 75 m.m. thickness.

Their equipment is excellent and they have plenty of everything. They cold roll plates to 60 m.m. thickness and have several other rolls which will handle 40 to 50 m.m. plate. They have a considerable number of driven trunnions and positioners of all kinds.

They have progressed farther in the use of Union Melt than any other firm in Germany. In fact, they are the pioneers in this process in Germany. Their set up at the Union Melt process is particularly flexible as they have a very well designed outfit to handle work of at least 4 meters diameter and 18 meters long.

There are three separate installations for Union Melt, two of which are used for pressure vessel manufacture and the other one for pipe welding. They also use a small portable outfit on rails to weld the inside seams.

Their heat treating and normalizing equipment is one of the best in Germany being able to handle 3 meters diameter by 18 meters length. They handle considerable of the work of this type for many of the other pressure vessel manufacturers.

Mannesmann are considered in Germany, as the top rank of pressure vessel manufacturers and their executive and research personnel is of high calibre; their product is very high class and I would rate them as the leading manufacturer with Thyssen Werke as a close second.

Press Und Walzwerke A.G. - Dusseldorf

Managing Director - Rudolph Krautheim
Director - Wilhelm Martin

This firm is not particularly active in pressure vessel manufacture with the exception of boiler drums. They have two methods of manufacture; first, the extrusion of boiler drums and second, the forging of some few vessels.

They make a very fine product under each method but are known particularly for the pressed boiler drums.

PRELIMINARY RULES FOR CALCULATING BANDED HIGH PRESSURE VESSELS

Banded high pressure vessels are manufactured, according to Dr. Schierenbeck of I. G. Farbenindustrie A.G., by rolling profiled steel bands in several or more layers, in a spiral with a width of the various steps in the cross section of the band, similar to the spiral grooves turned on the corepipe, which has a relatively low wall thickness. The bands are rolled on a red heat, varying as to the use of the vessel (hot or cold use), and shrink tight to the corepipe when cooled. The thrust edges of the winding bands of the consecutive layers are staggered and the bands have a profile that grip into one another of two positions. The corepipe also has grooves turned on the outside, spirally, with width and pitch conforming to that of the band, thus allowing the first layer to get a firm grip on the corepipe.

Through this rolling of the profile bands together and also with the clamping action obtained by shrinkage of the outer layer on the corepipe and the succeeding layers on each other, a very homogenous structure results, which allows the transmission of axial forces with safety.

This band construction has been proven by various tests. Compared with plain wall vessels, a higher strength is obtained, which is a result of better elaboration of material and a more even distribution of tension. The superiority of the banded vessel even allows us to exceed the elastic limit in some places, either in the manufacturing process or in the operation; whereas with plain wall vessels, this condition must strictly be avoided. Naturally, a loosening of the band from any manner of working influence must also be avoided. This may be taken care of either by including the calculation of additional stresses (perhaps heat) beforehand or by close supervision of temperature while the vessel is in operation (safety against overheating and any other causes).

I. Calculating The Wall Thickness

According to tests, the distribution of the stresses and strains raised by internal pressure, corresponds to those of Liners or Cores with plain walls. Whereas with plain wall liners, the longitudinal stress is $\frac{\sigma_t + \sigma_r}{2}$ at any place, this value is exceeded with the banded

at the liner. The rolled up band, however, on account of a greater flexibility has a much lower value. The rolling up process brings the inner forces of the liner or core in the circular direction under compression preload, the outer forces under tensile load.

As the value of this preload and that of the longitudinal stress is not exactly laid down, the stress calculation may only be done with the mean strength by internal pressure figured out with the help of the

shearing stress hypothesis. This is

$$\sigma_{vm} = 0.5 \frac{P}{100} \times \frac{d_1 + s}{s}$$

in which - P = Internal Pressure - K_g/cm^2 (1)
 d_1 = Inside Diameter of Vessel - mm
 s = The Whole Wall Thickness - mm

As with banded vessels, a 1.6 times safety against deformation of larger scale is sufficient on account of better elaboration of the band material, the wall thickness of the vessel should be made to suit the following condition

$$\sigma_{vm} \text{ (is less than) } \frac{\sigma_{0.2}}{1.6} \text{ (or equal to)} \quad (2)$$

in which $\sigma_{0.2}$ = yield point of original material respectively of band at working temperature. (Calculation should be based on a yield point 0.7 times the value of stress.)

The necessary wall thickness is:

$$s = \frac{d_1}{2 \times \sigma_{vmzul} \times \frac{100}{P} - 1} = \frac{d_1}{2 \times \frac{\sigma_{0.2}}{1.6} \times \frac{100}{P} - 1} \quad (3)$$

A careful production process with regard to the wrapping of the bands will secure the complete compactness of the individual layers. Any allowances do not seem, therefore, to be required.

The yield point should only be inserted into calculation as a maximum value of 0.7 of the stress.

As already mentioned, the stressing in axial direction of the liner wall, as well as in the core liner, cannot be determined accurately by calculation. However, actual tests have indicated that this axial stressing is considerably less than the tangential stressing. An after calculation of the safety in axial direction is, therefore, not necessary with regard to the wrapped body, as well as the full walled body and the core liner.

In order to avoid too high longitudinal stresses in the pipe core, its wall thickness should not be less than 10% (an in case of interlocking, 15%) of the total wall thickness. The 15% takes into account the grooves turned in the core outer shell. The yield point of the core liner should not be lower than that of the wrapping material. Assuming "a" % of the wall thickness, consisting of material with yield point of $\sigma_{0.2I}$, the remaining "b" % of a material with yield point $\sigma_{0.2II}$ then

Equation (2) will have the following form:

$$\sigma_{vm} = \frac{1}{1.6} \left(\frac{a}{100} \times \sigma_{0.2I} + \frac{b}{100} \times \sigma_{0.2II} + \dots \right) \quad (4)$$

If the core liner has a longitudinal seam, the yield point must be multiplied by a weakening factor, $V = 0.9$. Calculation of the wall thickness according to equation (3) has to be performed with this new value.

As the preloads resulting from wrapping up and also the thermal stresses of vessels working at higher temperatures rise with an increasing of the wall thickness, it is recommended to limit the wall thickness of wrapped vessels to not more than approximately 200 mm. as long as we do not have enough experience available as to the effect of the aforementioned stresses. At the same time only wrapped vessels for wall temperatures not exceeding 350° should be used. The material used for the wrapping bands must be less sensitive to ageing from fatigue and a minimum elongation, $\delta_5 = 15\%$, following the heat treatment required in the wrapping process.

II. Testing The Stress of Heat Tensions

Under the influence of stresses evoked by internal pressure and heat on vessels working at higher temperatures and on account of a decrease in the yield point, a diminution or lessening of the shrinkage will take place. In order to leave a sufficient pre-tension after diminution of shrinkage and still have a good compactness of the wrapping after taking away the internal pressure, it is necessary that on the outside the sum of the circular tension evoked by the working pressure -

$$\sigma_{t_1} = \frac{K}{100} \cdot \frac{D}{D_1} - 1$$

and the heat tension which corresponds to the prevailing temperature drop D_t , then σ_{t_1} is approximately $0.2 \times D_t$ (6)

and is not higher than 75% of the yield point of the material at working temperature.

At wall temperatures up to 350° it has to be figured with a temperature drop

$$D_t = 0.2 \times S \quad (\text{with } S \text{ in mm.}) \quad (7)$$

provided it cannot be proven that a lower temperature drop is prevailing.

As the pre-tension and the working stress at the inside of the vessel work in opposed directions, it is not necessary to test the stresses.

III. Transmission of Forces at the Ends

In order to get a good transmission of the longitudinal forces from the flanges to the bands, the shrunk ring or rolled up flanges have to have at least such a height that the shearing area (product of number of actual grooves, times groove width, times circumference) equals the area of the wall of the vessel

If

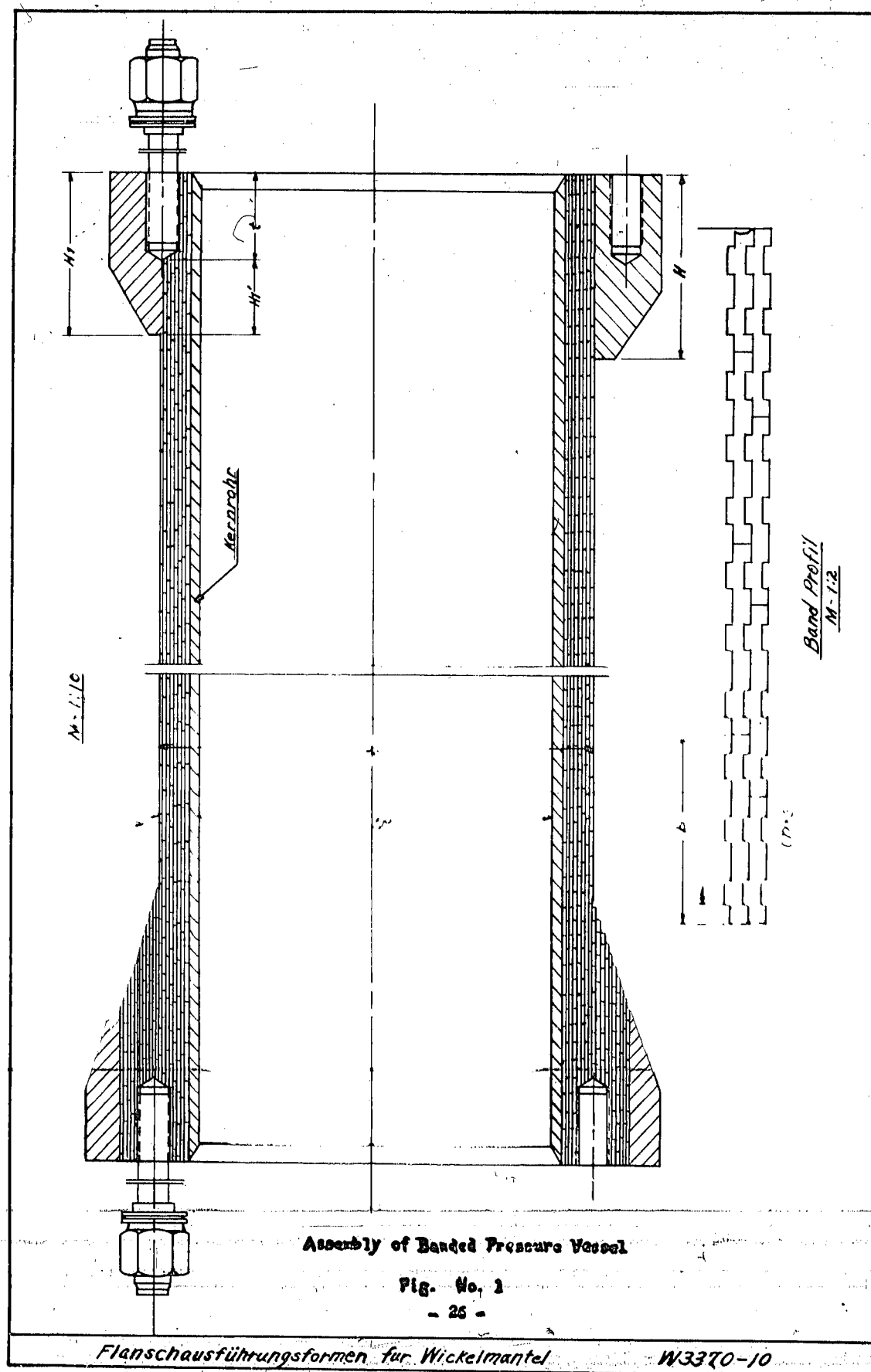
- B = band width in mm.
- b = groove width in mm.
- n = number of grooves in band width
- d_a = outside diameter vessel in mm.
- F = area of wall of vessel in mm²

the necessary number of grooves in

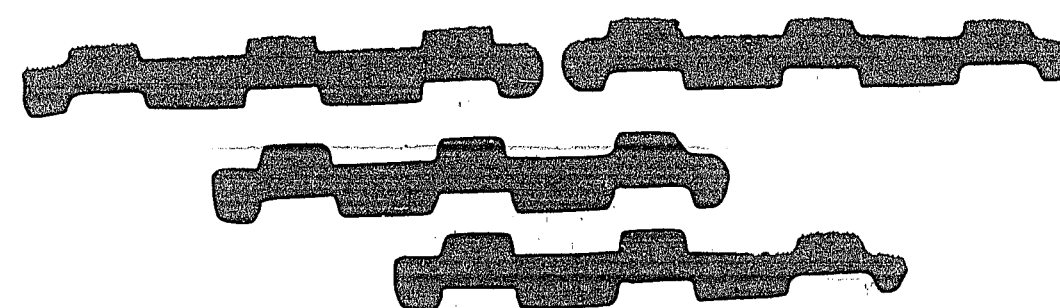
$$Z = \frac{F}{3.1416 \times d_a \times b} \quad (8)$$

and the height of the flange is:

$$h = \frac{Z \times B}{n} = \frac{F}{3.1416 \times d_a \times n \times b} \quad (9)$$



Section of Band
for
Wrapped Band Vessel



Assembly of Bands (Spread) for
Wrapped Band Vessel

MANUFACTURE OF BANDED VESSELS

The wrapped band vessel was first brought out in 1940 by I. G. Farbenindustrie, A. G., in order to relieve heavy forging and pressing equipment to some extent for work in the production of other war materials. Actually, it was designed, not so much to relieve heavy equipment, but rather to increase facilities for the production of high pressure vessels. The shops capable of making vessels for high pressures were scheduled to capacity and very few, if any, quit production of vessels for the manufacture of other war items. It was an additional facility to increase the production of pressure vessels which were sorely needed for the chemical, rubber, and petroleum industries. This is the general consensus of opinion of most of the pressure vessel manufacturers.

The banded vessel did relieve to a certain extent the pressure on the production capacity of the heavy plate mills, but this was counter-balanced by the load thrown on the smaller bar mills.

The entire production of banded vessels was concentrated in one plant, the Deutsches Röhrenwerke, A. G., Thyssen Werke, Mülheim a/Ruhr.

The vessel, as designed by I. G. Farbenindustrie, is shown in the accompanying drawing, Figure No. 1, Page 10 of this report, shows a central core pipe 20 mm. thick with a series of bands about 8 mm. thick by 79 mm. wide, wrapped spirally around the core pipe.

The successive bands are interlocked in the spiral. The wrapping is stepped forward one or two steps in order to straddle the gap of approximately 1 mm. which occurs in each wrapping on each layer.

In order to give the first band wrapped the proper grip on the core pipe, it is necessary to machine turn an exactly similar spiral groove the complete length of the core pipe. The core pipe, as originally designed by I. G. Farbenindustrie, had a minimum thickness of 20 mm., but in subsequent practice they found a core pipe of 25 mm. a better pipe to use, mainly from the fact that 25 mm. pipe was available more often than the 20 mm. pipe and also allowed the groove turning without reducing the thickness of shell too much. Core pipes of various thickness to a maximum of 40 mm. have been used.

The vessels were all built in standard sizes and lengths, and the specifications of steel analysis had a wide range, dependent upon whether or not it was for hot or cold use and other varied local conditions in the plant in which it was to be used.

The standard diameters were 600 mm., 800 mm., 1000 mm. and 1200 mm., and the standard lengths - 6 meters, 8 meters, 10 meters, 12 meters, 14 meters and maximum 18 meters. The ends were always covered, without exception, with a bolted blind plate cover through which all connections and openings were made. They had been unable up to the present time to take any connection of any size through the side wall, as any hole drilled through the side wall would cut through the open space between bands at some level of the wrapping bands. They had in mind making connections through the side walls by drilling and inserting nozzles and welding these inside and outside but had not produced any in this manner at the Thyssen plant. They had no knowledge of I. G. Farbenindustrie attempting this at the operating plants.

The vessels were constructed for two operating pressures. One, to operate at 325 atmospheres, was tested at a pressure of 425 ATM. and the other class at operating pressure of 700 ATM. to be shop tested at 925 ATM.. The "hot use", or as they express it "hot going", vessel operated at a temperature of 350°C and the "cold use" vessels at 20°C. All vessels were reactors and regenerators for "hot going" and washers for "cold going".

Their standard specifications required core pipe tests of "cold going" vessels with a tensile strength of 50-60 KG/mm² and a yield point which must be above 30 KG.; while the "hot going" vessels required T.S. of 40 KG/mm² and a Y.P. above 20 KG.. The wrapping bands required a T.S. of at least 50 KG. with a minimum Y.P. of 32 KG. for "hot going" vessels. The specifications for the "cold going" vessel bands were about the same as the "cold going" core pipe specifications.

In explaining the manufacture of the vessels, I ask your tolerance, as it may be necessary at various times to break the continuity of the technique, to pick up some point farther back in the manufacturing method.

The principal pieces of equipment are: first, a coiling machine with an electric heating element, and second, a heavy machine lathe which has an unwinding machine with electric heating element to heat the bands before application

to the core pipe.

The bands are produced on the bar mills with a section as shown in the upper corner of Figure No. 1, Page 27 and are delivered to the vessel shop in 35 to 40 meter coils. The bands are specified 80 mm. wide with an 8 mm. standard thickness but an overall thickness dimension of 10.8 mm.. This would give a depth of groove of 2.8 mm. with an approximate width of the groove of 15.5 mm.. You will note that one end of the band has a square vertical with very small fillets top and bottom, while the other end has a semicircular section. It was intended that both ends have the square vertical section, but difficulties in the rolling of the bar dictated the round end on one end. The bars, when rolled to a square vertical on both ends, seemed to form a small projection of excess material on the top or laying side of the band which prevented a closely wrapped vessel. It was, therefore, decided to accept the band with the rounded edge as the lesser of the two evils. Unfortunately, this gives a gas leak as each successive ring is wound, which extends the entire spiral length of the vessel in each layer; this, however, has no effect on the vessel itself.

As stated, the bands are delivered in coils of 35 to 40 meters, and they are immediately placed in the coiling machine to be unwound and recoiled in larger coils of 3500 meters.

The band is unwound in the coiler and runs through an electric heater element which heats it to a temperature of 950°C for annealing and recoiling. The successive coils are flash welded to the ends to produce a continuous band. The heater element is a resistance heater with 25 volt 3500 AMP 300 KVA current and is 3½ meters long. The band travels through the heater at a speed of 0.1 P.M.; and if it is to be used for "cold going" vessels, it is immediately recoiled without any tempering of the band.

If the bands are to be used in fabricating "hot going" vessels, immediately after leaving the heating element they are tempered over an air-cooled jet system, 1½ meters long, to a temperature of 600°C and then recoiled.

The recoiling is necessary for two reasons: first, annealing, and second, to get a coil long enough to make at least one or more complete wrapping of the vessel being fabricated. Some of the largest vessels require as high as 21000 to 22000 meters of bands.

The core pipe, which has previously been turned in another shop with a thin skin turning inside and outside full length and the spiral turned to match the grooves in the band, is always about 500 to 800 mm. longer than required dimension. The grooves on the pipe are an 80 mm. spiral pitch which allows for any variation in the 79 mm. width of the band. The core pipe may be either electric or water gas welded or of the seamless variety.

The wrapping machine is a lathe without a tool carriage. On the back of the lathe, a travelling carriage is attached which carries the entire wrapping and heating mechanism.

The core pipe is chucked in the lathe and the band is fed through the electric heater which heats it to approximately 850°C for "cold going" and slightly less for "hot going" vessels. The hot band is attached to the core pipe by tack welding, while the machine is turning, the lugs of the band fitting into the grooves turned into the outer surface of the core pipe. As the band progresses around the spiral grooves, the entire carriage with coil and heater travels ahead on the lead screw of the lathe.

The band moves at a speed of 5 meters per minute and the heater element is about 4 meters long. The uncoiler has an adjustable brake which holds just enough tension on the band and core to insure a tight contact and at the same time allow no deformation or elongation to the band during the winding process. The band, as stated before, is heated to a temperature of about 850°C; and experience has proven that, in order to get the correct and complete shrink fit, it is necessary that each separate ring around the vessel have a definite close range of cooling temperature as the wrapping progresses.

The core pipe is water cooled, having a running stream ranging from one quarter full at the start of the wrapping to a full pipe as the outer layers are applied, preventing collapse of the core pipe, and cooling the band. They claim that the band leaves the heater at 850°C and it is necessary that 4 complete rings have heat enough for shrinking at all times. The first or youngest of the 4 bands with shrinkage carried a temperature of 600°C, the next one runs close to 500°, the third one 450°C and the last of the four rings about 400°C. From that ring on, the temperature drops so rapidly, due to the inside cooling, that they are not concerned about its temperature. It is claimed that no shrinkage of any great amount is secured after the completion of the fourth ring from the coiling machine.

The carriage progresses to the head end of the lathe; and at the end of the core pipe, the band is clamped, cut off and tack welded. The successive bands are applied in the same manner until the desired thickness of the vessel is acquired.

The application at the present time is about 5 meters per minute and they have been working on the possibility of speeding it up to 10 or 12 meters per minute. The entire problem hinged on the design of a heating element and the necessary investigation and experimentation in regard to the cooling of the bands after they have been wrapped on the core pipe.

Referring again to Figure No. 1, Page 26 of the completed banded vessel, please note that they have several methods of end construction. If the vessel had a shell thickness sufficient to allow for tapped steel stud holes, the ends were not built up with wrapped material on the first few vessels. This, however, was discarded and the practice adopted as shown in Figure No. 1. The most popular form was that showing the wrapped buildup with a machined forging shrunk on the outside, all of the stud holes being in the wrapped section of the end. The other two sketches, showing the studs in either the entire reinforcing ring or half in the ring and the other half in the banded vessel, were used to some extent with the preference shown to the half and half construction. Thyssen were of the opinion that the band build-up without any reinforcing ring was entirely adequate, eliminating the expense of the forging and the necessity of machining the vessel for the shrink fit of the collar.

Due to the fact that the band ends stop and start at various points, the vessels are always made long enough so that each end is machine cut far enough to assure a complete ring on each and every layer at each end. In fact, in all cases the ends so cut off are used as test specimens. As the successive layers are simply tack welded at the start and finish, it is evident that as soon as this cut-off has been made, the vessel would immediately release all tension.

In order to prevent this, the last three rings on the top layer are welded completely around the circumference on each end, thus allowing them to make the cut to trim up the ends. After trimming the ends, the tongue ends of the bands on the face of the cylinder often show loose, and it is standard practice to weld these tongues in. The vessels

were drilled and tapped; and it was my thought that in the drilling and tapping, the tool hitting the joints of the bands would be likely to break or chip. I am informed that they have never broken either a drill or tap from this cause. The only danger to a drill or tap is in the start of the hole, where the loose tongues might break them.

The reinforcing ring on the outside is an unnecessary expense, according to the fabricator, as the vessel is strong enough and as the last three rings are welded together, there is no likelihood of it releasing tension.

The time factor in manufacturing is an important item. I have been told that after the material, such as core pipe and coiled bands are ready, a complete wrapping can be made of a vessel 800 mm. in diameter and 14 meters long with a wall thickness of 150 mm. in 5 to 6 days of 20 hours each -- this at their present speed of 5 meters per minute, and they were hopeful of increasing that speed to a maximum of 12 m. per minute. Even if they only increased it 8 or 10 M.P.M., you can readily see the decrease in manufacturing time.

They have produced only between 60 and 70 of these vessels, all of them, of course, being for the I. G. Farbenindustrie A. G..

Several of the vessels have had bomb hits and the damage showed only through the outer layer and in no cases beyond the second layer. The layers affected were immediately welded to each other and to date they have had no failure of any vessel.

I saw a test cut-out section of one of these vessels and each and every layer could be definitely seen. The layers in some cases showed open spaces between each other, which while small, still were definitely not steel-to-steel contact. This specimen also gave a very clear demonstration of the open gap between the successive layers in each wrapping, where the rounded end of the band would not fit up to the square end of the next band, giving a spiral gas leak the entire length of the vessel in each layer. The vessel is figured evidently to take care of this discrepancy which after all is probably immaterial to the strength of the shell.

In many of the vessels, they fitted an alloy lining after the wrapping and blew it up to fit the shell, saving the cost of clad steel.

As stated earlier, this is the only new type of pressure vessel brought out by the Germans during the course of the war.

MANUFACTURE OF PRESSURE VESSELS BY ROECHNER PROCESS

The Deutsche Röhrenwerke, A. G., Thyssen Werke, Mülheim a/Ruhr, in addition to the wrapped band vessel, also produce seamless vessel shells under the Roechner Process.

They have two mills, the large one for vessels 300 mm. to 1800 mm. dia. and the small mill which can roll cylinders from 400 mm. to 1000 mm. diameter.

The large mill rolls shells of any thickness from 40 mm. to 200 mm., but the average runs 150 mm. with a maximum length of 18 meters. The small mill can roll cylinders from 40 mm. to 150 mm. with an average of 100 mm. to 120 mm. and a maximum length of 15 meters.

The Roechner Process, in a few words, consists of a series of inside and outside rolls working on an ingot at the same time rolling and drawing out the steel to required sizes. The large mill has a mandrel holding 7 rolls that are adjustable but which are idlers. The outside rolls are 7 in number also and are, of course, adjustable, but these rolls are the driving rolls, being driven through pinions by two 7000 H.P. electric motors.

The Trunnion wheels carrying the ingot are movable both ways, vertical and horizontal, and are also motor driven.

The ingots are bored before being sent to the mill. They are heated and twelve passes are made on them through the mill on the first heat. Ordinarily two heats are required to finish an ordinary sized vessel, but often more are required depending on the size and shell thickness of the desired vessel.

All vessels are stress relieved as Thyssen Werke has one of the few large annealing furnaces used in pressure vessel fabricating shops. Their furnace will handle 2 meters width, 2 meters height and 18 meters length.

For some reason, I. G. Farbenindustrie has always specified that these vessels have a light cut taken over both inside and outside surfaces.

Thyssen were opposed to machine turning the shell inside and outside as they were able to hold the diameters and thickness to a very close margin under this process.

Here again they often fit alloy linings inside

the completed vessel and blow them up to conform to the finished vessel, plug welding them to the outer shell if necessary.

The maximum size ingot the mill can handle is 110 tons. The cost of these shells is approximately 30 per cent higher than welded vessels.

MANUFACTURE OF CLAD STEEL

The manufacture of clad steel, or Plattierte Bleche as it is known in Germany, is of several varieties, of which the method employed by the Deutsches Röhrenwerke A. G. - Thyssen Werke, Duisburg a/Ruhr is probably the best.

There is no knowledge of any practice of electric welding alloy sheets cold to carbon steel plates. There is, however, the practice of forming alloy linings to suit the individual vessel, fitting the lining to the vessel and blowing it up to set it in place. More often than not, these linings are then plug welded in spots, the plugs being spaced about one-half meter to a meter apart. Some operators claim that they do not even go to the trouble of plug welding as they think it entirely unnecessary. In these cases, various alloys are used but the most important ones are stainless steel, nickel and copper.

The process employed by Thyssen is an hydrogen welded process, the plates being assembled and then rolled in the plate mill. They have a very wide range of combinations, plating either one or both sides and use almost any alloy, but principally copper, stainless steels of several varieties, nickel, chrome, chrome molybdenum; silver and under special circumstances brass.

Their process is as follows. The pack is made up of carbon steel plates on the outside. These plates have a strip of strip welded around the four sides. This strip is to be used as the seal and the size varies in accordance with the sizes of the pack to be made up. The pack is always made to clad two plates at least with each rolling. Frequently when they have requirements for plates to be clad both sides, the pack will be built with the double clad plates on the inside of the sandwich.

After the plates have been prepared with the alloy strip, the alloy cladding is laid inside and covered with a magnesium oxide paste. The second alloy cladding is laid on top of the paste and the top carbon steel cover closes the pack.

Pipe inlets and outlets for hydrogen are fitted into two opposite sides with about 10 foot leads. The sealing edges of the plates are then welded all around and the pack is ready for heating and rolling. The thicknesses of the carbon steel plate and alloy cladding set up in the

pack depend entirely on the thickness requirements of each after the plate has been finished-rolled. There is no reasonable limit to the thicknesses required although the great majority run about 1 to 2 mm. thickness of alloy. Again the size of plates has no limit, except the limit of furnaces and mills. The rolling of clad steel is done at Thyssen only on the 3½ meter mill as the furnace and rolling crews on this mill are the only ones competent to handle it.

The packs are charged into the furnace and the hydrogen fed through the lead pipes. The hydrogen is fed at a very low pressure, just a few ounces above atmospheric pressure. The pack is heated to required heat, the hydrogen being fed during the heating until it comes out in flame at the open end of the outlet lead pipe.

The packs are rolled at different temperatures, dependent on the alloy to be clad. Copper pack rolled at 1000°C, nickel pack at 1200°C and remanit or stainless pack at 1280° C.

When the pack is drawn from the furnace at the correct heat, the lead pipes on each side are broken off and the pack is shunted to the mill. The pack is rolled to the desired thickness, sheared and stripped.

The variation of thickness of the cladding is, of course, dependent again on what thickness had been ordered, but I am told it will vary only 2 to 4% on the widest plate. If the pack has been built of two one-sided and one plate of both sides, the thickness variation of each cladding is greatly reduced.

Thyssen are making an investigation of the quality of the product. I am informed that no loose spots are encountered and no laminations have been found after forming and welding in the pressure vessel shops.

For the sake of clarity, I am inserting a sketch showing the lay up of the pack of two varieties under Figures 1 and 2, Page No. 37A of this report.

Their capacity is about 1000 tons monthly on any particular product.

CLAD STEEL PACKS

as set up by

DEUTCHES ROHRENWERKE A.G.

Thyssen Werke - Mulheim a/Ruhr

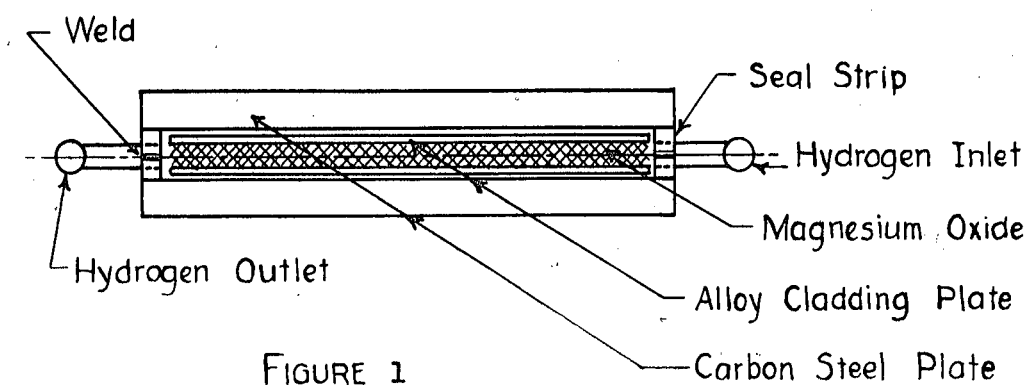


FIGURE 1

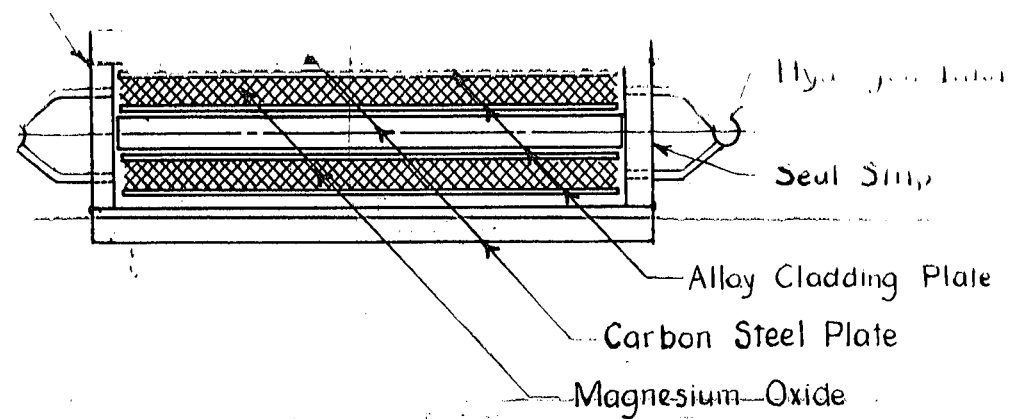


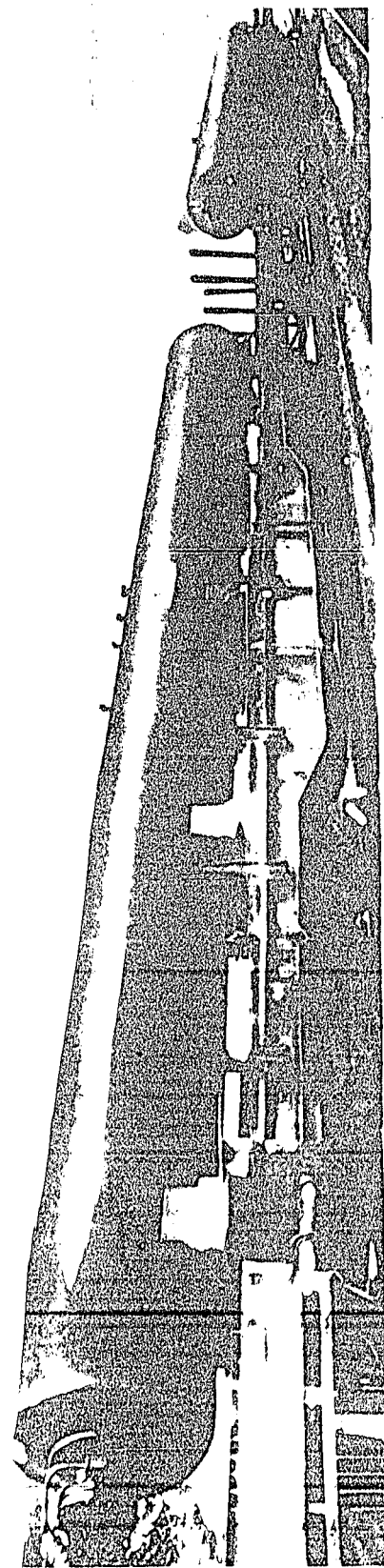
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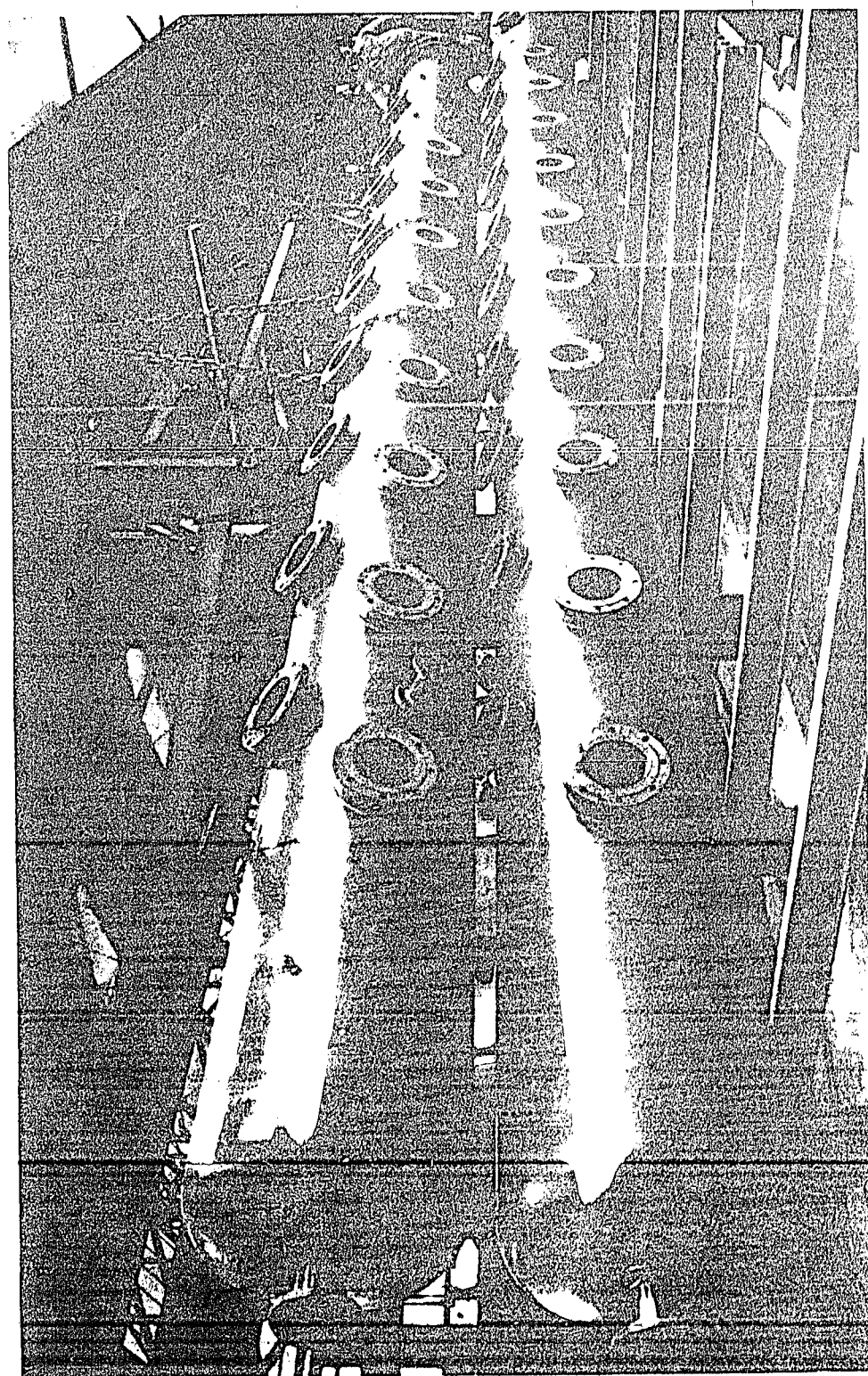
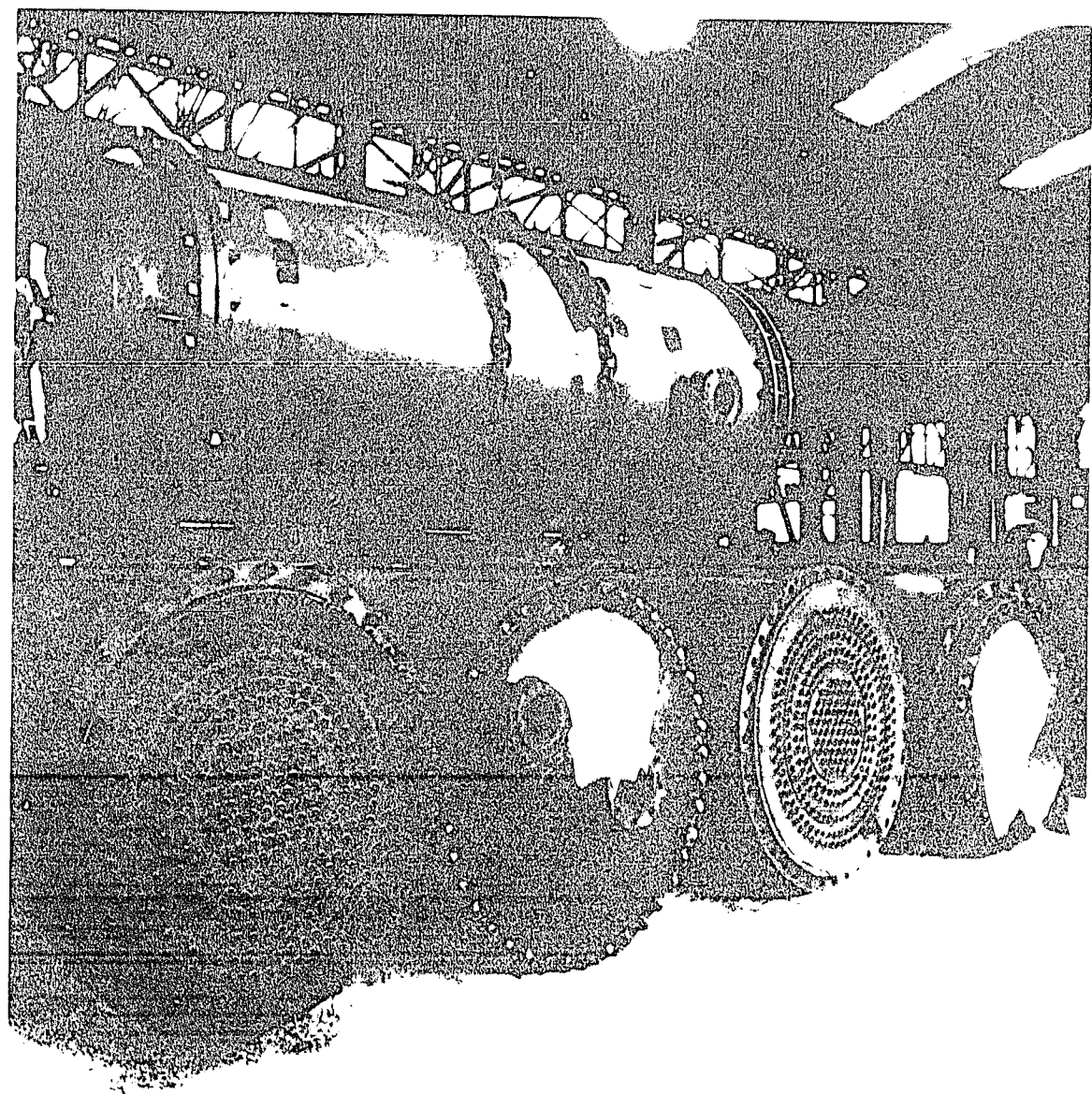
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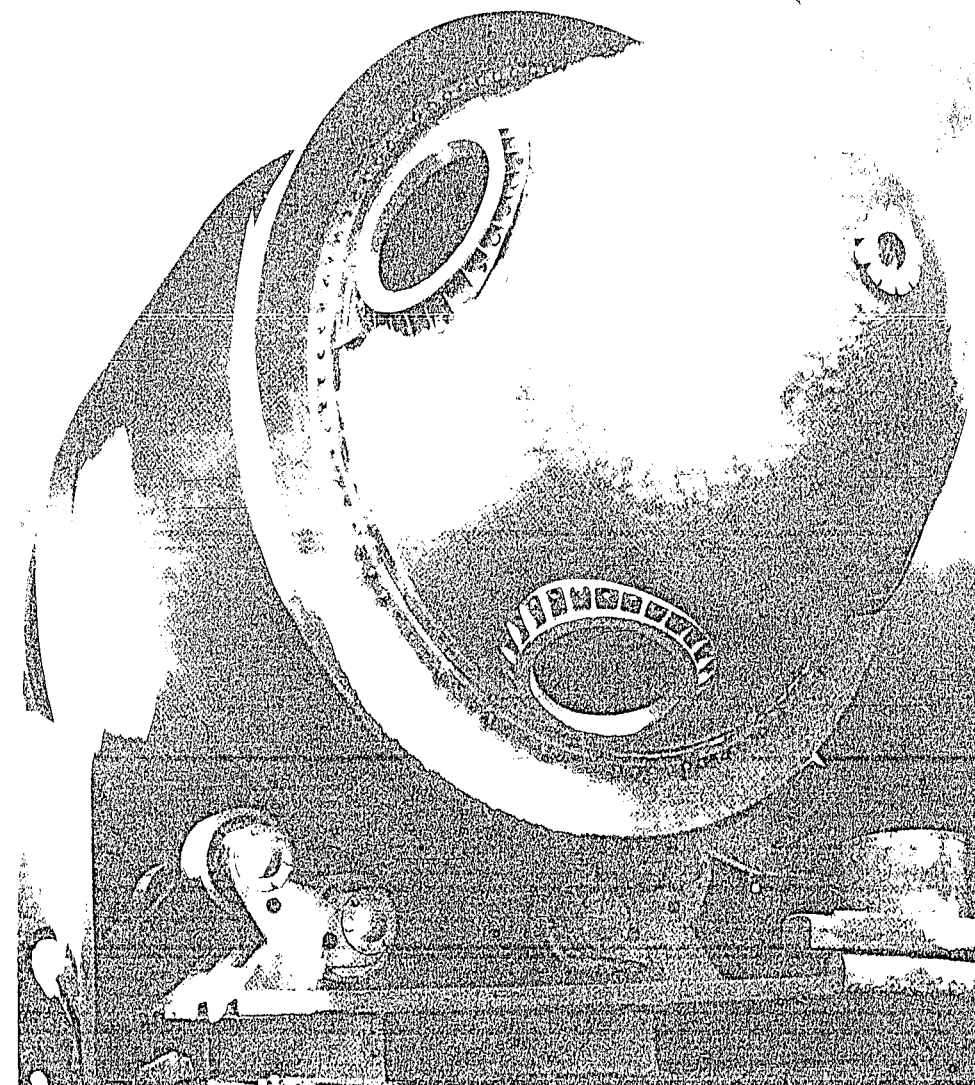
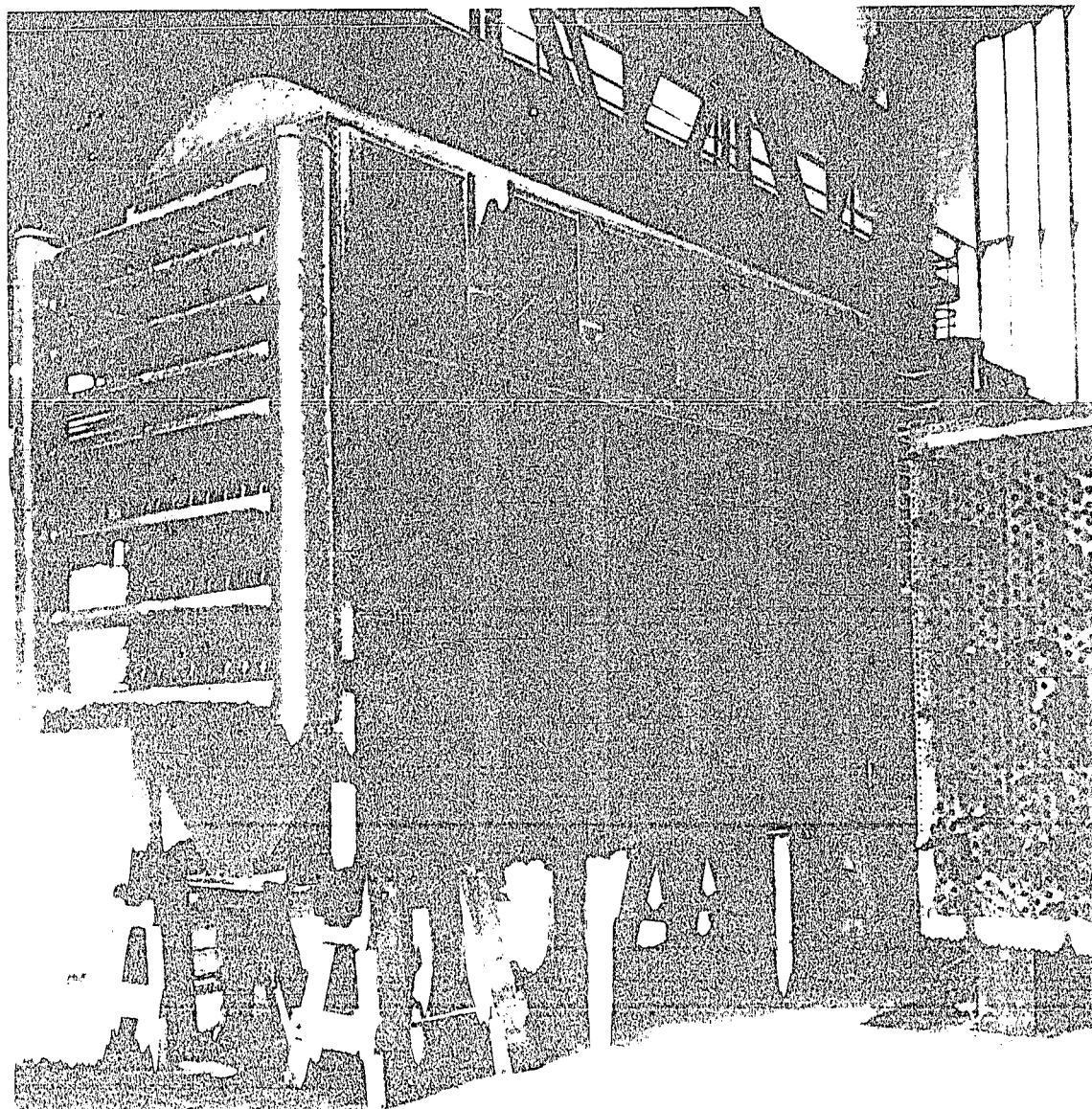
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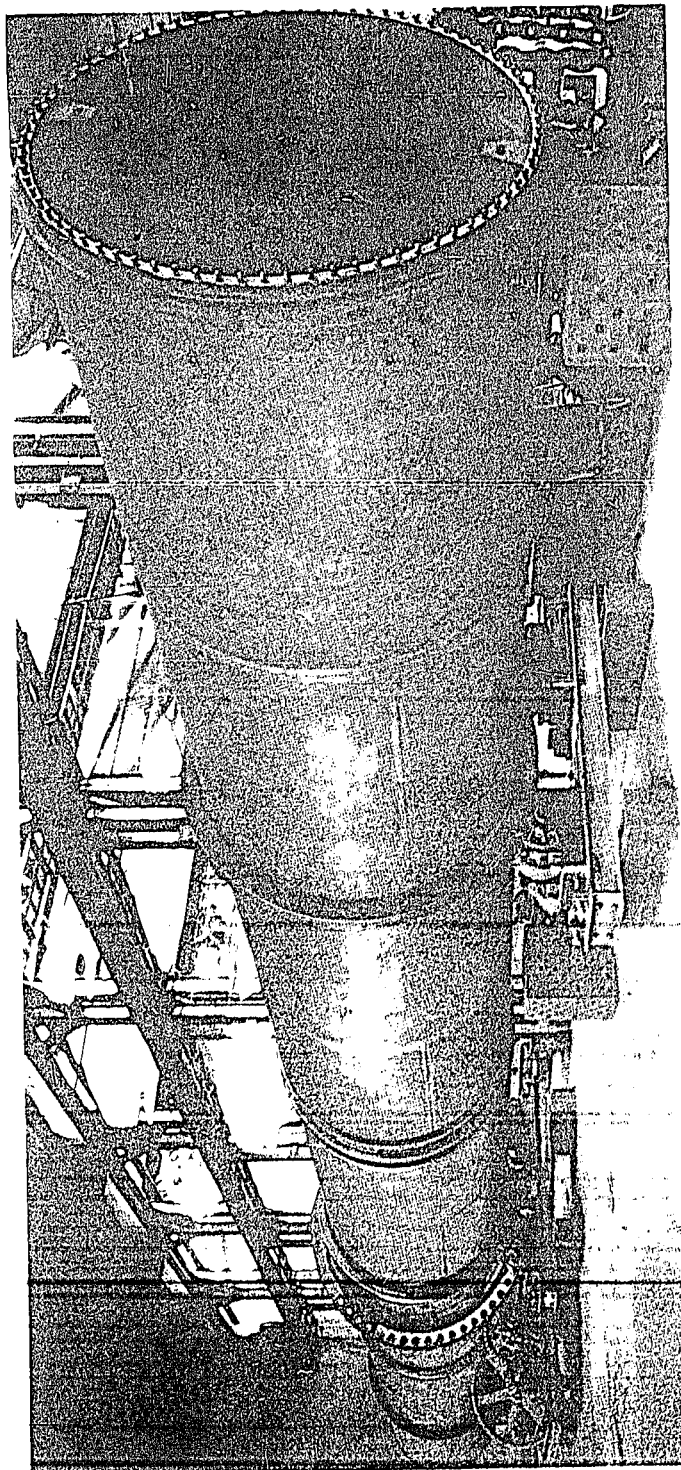
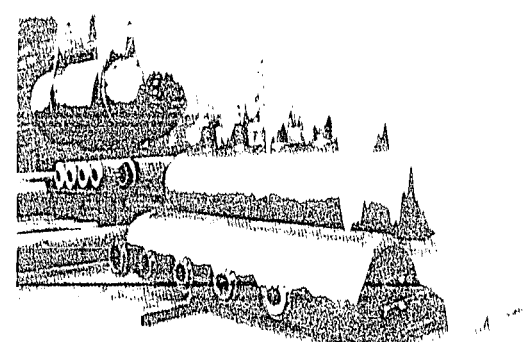
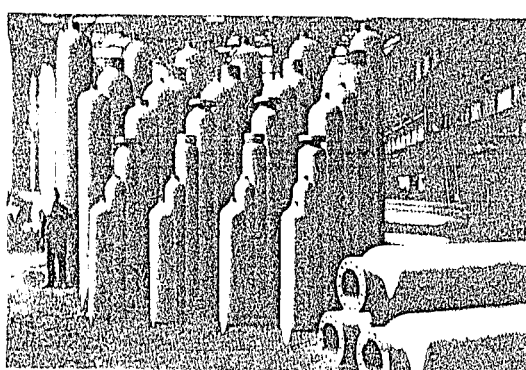
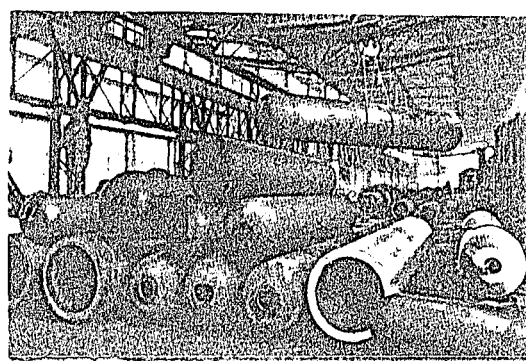
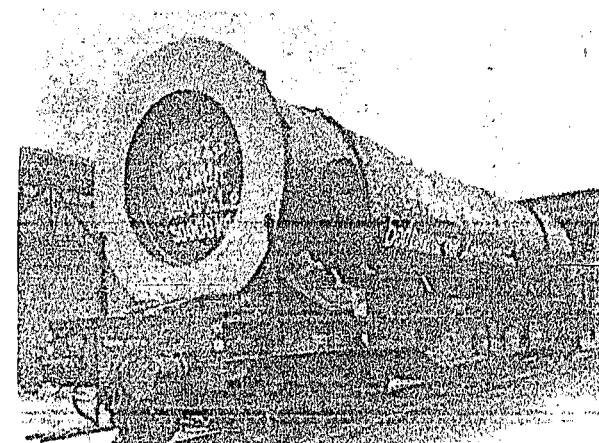
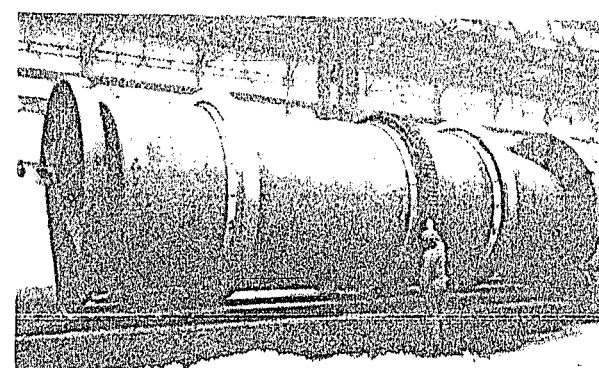
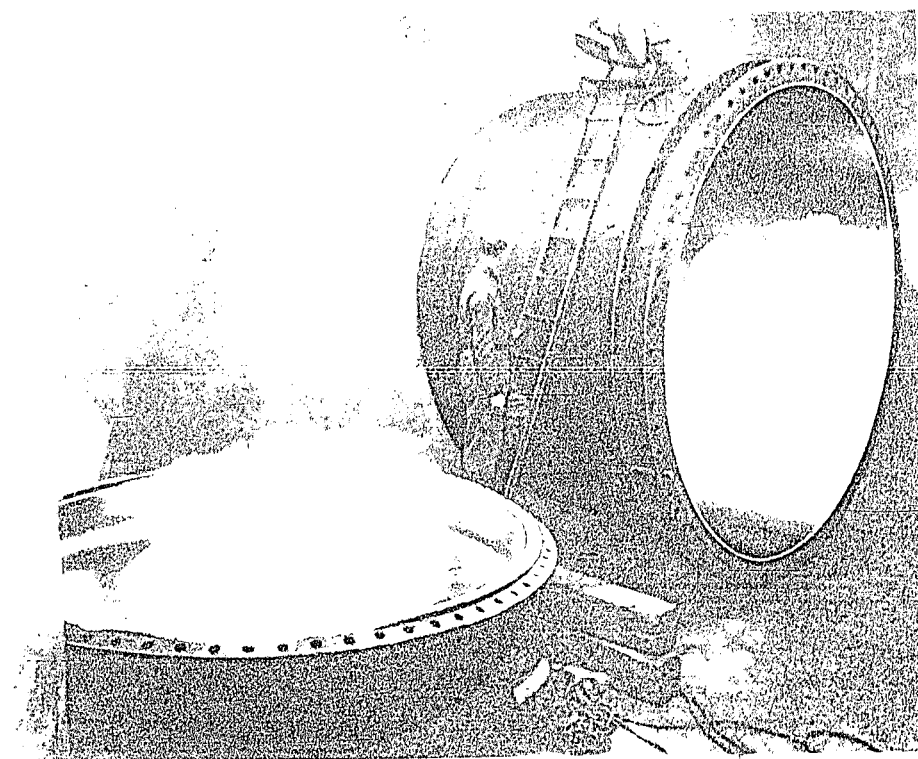
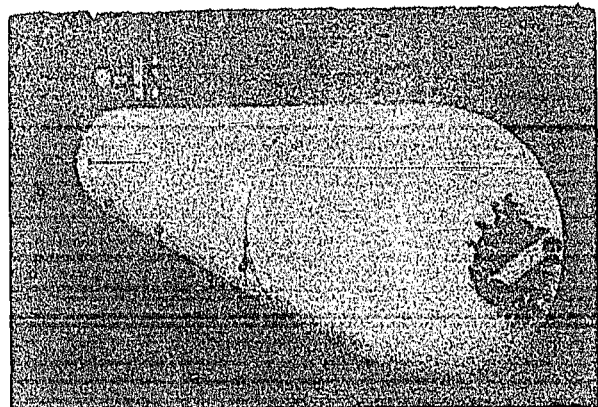


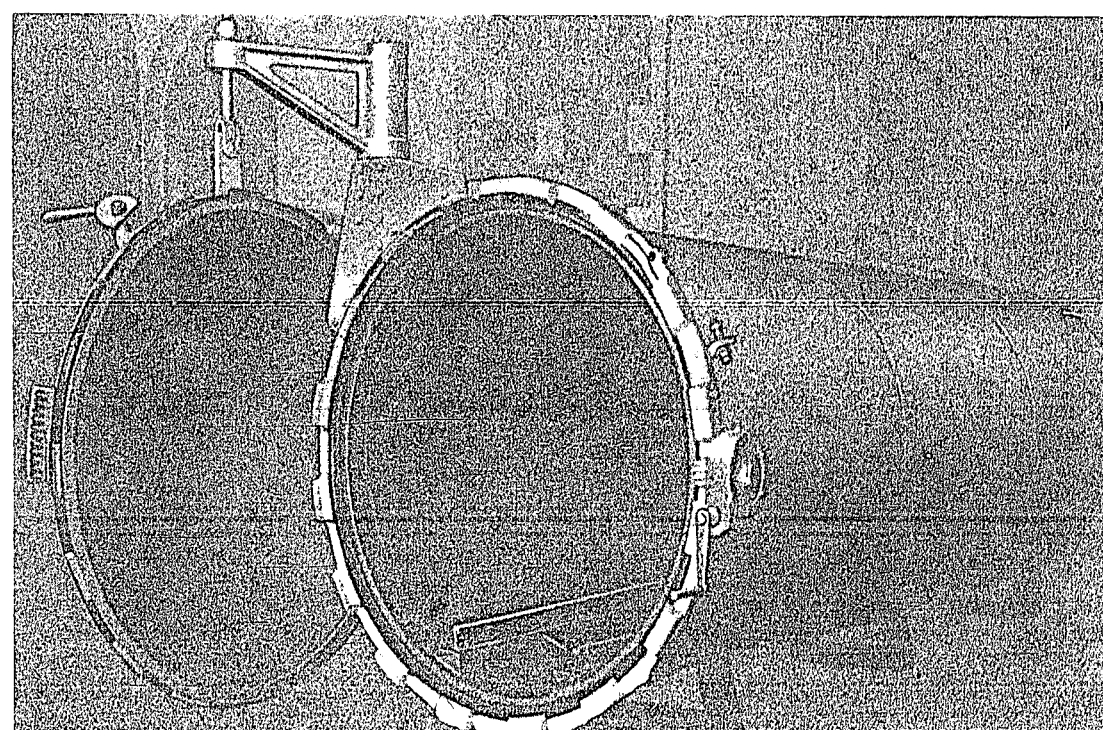
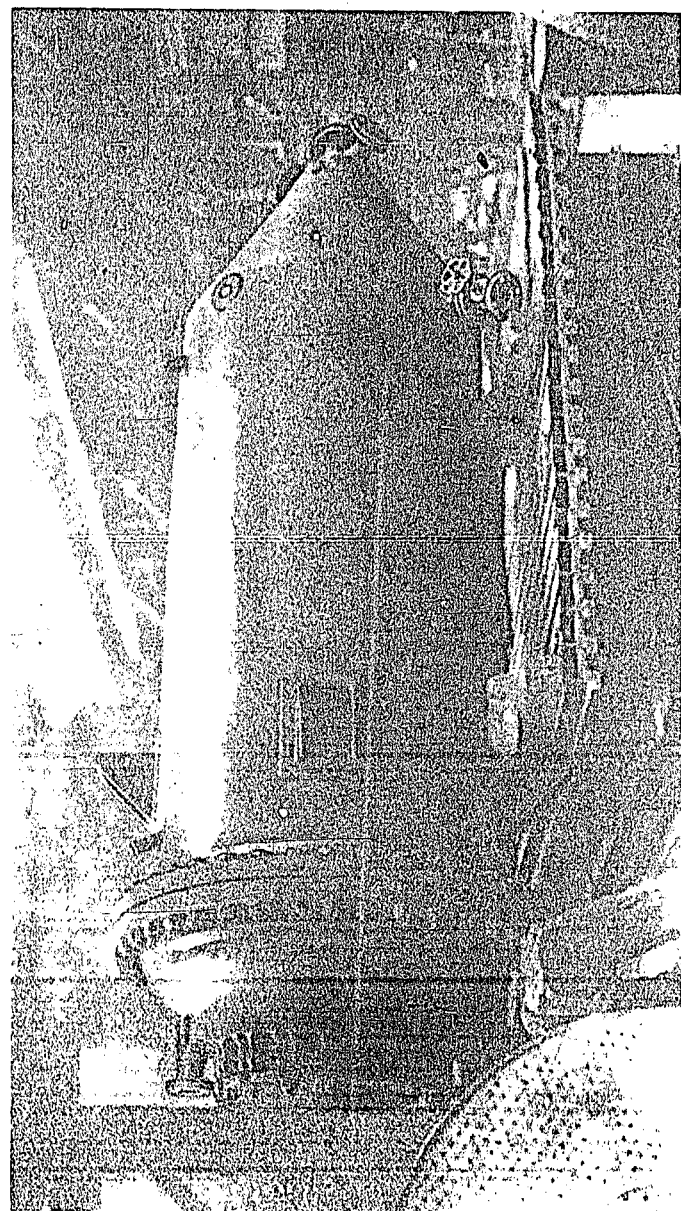
Figure 11
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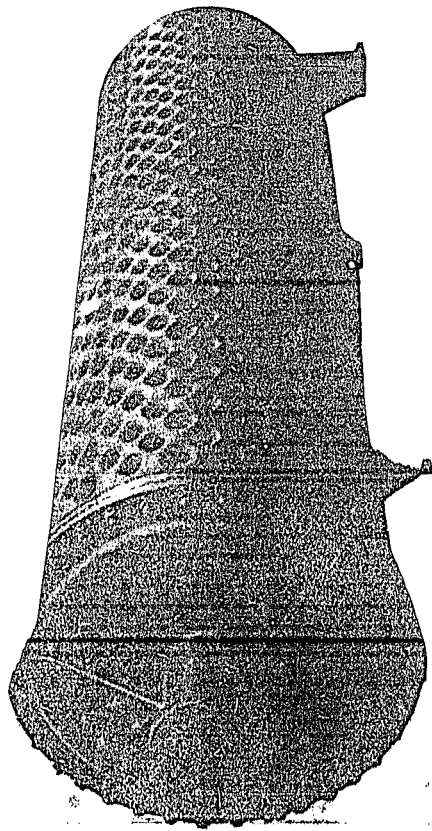
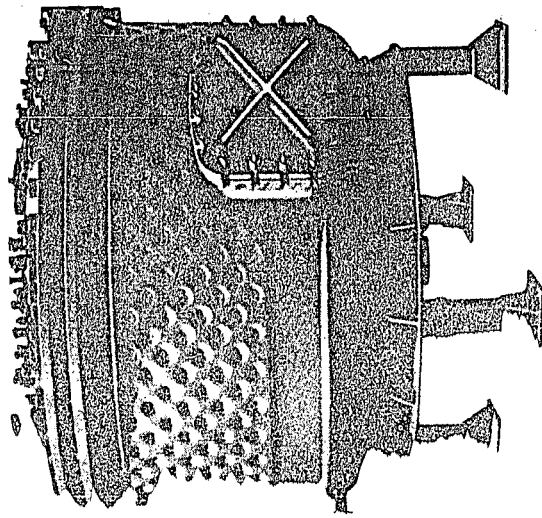
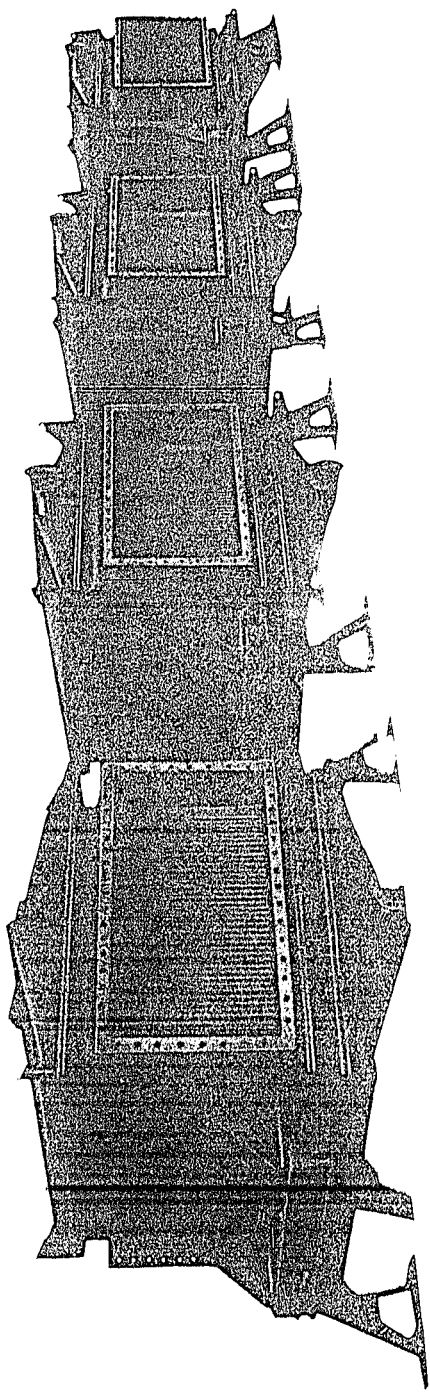


High Pressure
Containers and
Steam Receiver









FIAT 422

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U. S. GROUP CONTROL COUNCIL, GERMANY
OFFICE OF THE DIRECTOR OF INTELLIGENCE

MANUFACTURE AND REGENERATION OF CATALYSTS

AT I. G. FARBENINDUSTRIE LUDWIGSHAFEN/OPPAU

(Supplement No. III to C.I.O.S. Report No. 1-XXX-103, by Holroyd, R.)

Reported by

DR. W. F. FARAGHER (U. S.)

DR. W. A. HORNE (U. S.)

TARGET NO. 30/4.03

Report on Investigations by the
LIQUID FUELS AND LUBRICANTS SUB-COMMITTEE OF THE
TECHNICAL INDUSTRIAL INTELLIGENCE COMMITTEE

Prepared by Direction of
FIELD INFORMATION AGENCY, TECHNICAL (U. S.)

USFET (MAIN)

INDUSTRIAL BRANCH

APO 757

NEW YORK, N. Y.

DATE OF TRIP

28th AUGUST - 1st SEPTEMBER 1945

PUBLISHED by the BUREAU of MINES, UNITED STATES DEPARTMENT of the INTERIOR

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Personnel of Team:

Dr. W. F. Faragher, U. S.
Dr. W. A. Horne, U. S.

MANUFACTURE AND REGENERATION OF CATALYSTS AT
I.G. FARBENINDUSTRIE, LUDWIGSHAFEN-OPPAU
(TARGET 30/4.05)

I. INTRODUCTION

The principal equipment in the catalyst plants at Ludwigshafen-Opbau was inspected and is presented in the form of flow sheets for the manufacture of four of the principal catalysts. The equipment is in many cases of special design rather than stock items that was built by the company and modified in the course of the growth of the high-pressure synthesis of hydrocarbons in Germany. It is believed that if the manufacture of catalysts were to be undertaken elsewhere, the selection of equipment for the operations involved could be made successfully from the guidance furnished by this rather general report. Five additional catalysts are described, also.

II. CATALYST 5058 FROM FRESH TUNGSTIC ACID

In a supply tank of about 2,000 liters capacity, 500 kg. of tungstic acid ($WO_3 \cdot H_2O$) that contains about 92-93 percent of WO_3 is dissolved at 60-70° C. in 1,500 liters of mother liquor. The solution is effected by stirring for about 1-1/2 hours. The mother liquor is obtained from a previous lot of catalyst and is first adjusted to a concentration of 13 percent NH_3 by passing in gaseous ammonia. The solution is allowed to stand without stirring for 1 hour, then is pumped into the saturating vessel through a cloth filter (three-quarters hr. to one hr.). The saturator is purged with H_2S and thereafter the solution, which has been cooled to about 55°C., is heated in an atmosphere of hydrogen sulfide with stirring to about 70°C. This charge is slowly cooled to 50°, and then more rapidly to about 20°C. (time of cooling 6-7 hours).

The precipitate of yellow salt ($(NH_4)_2WS$) is fed to the suction filter while stirred.

Nitrogen under pressure of 1/2 atm. is used in the filter. The mother liquor is collected in a stirred storage vessel and is used subsequently as mentioned above. The decomposition of the yellow salt is carried out in a screw-conveyor furnace in a stream of hydrogen at 400-430°C. The black powder (WS_2) is cooled at the end of the furnace by a stream of nitrogen. The capacity of the furnace is 1.2-1.5 tons per day. The black powder is then ground in a hammer-mill until 70-80 percent passes through a 100-mesh screen. (Important not to grind too fine.) 10 mm. pellets are then made in a Kilian press flushed with nitrogen. The sharp corners of the pellets are removed in a rotating screen drum, and the finished catalyst is packed in barrels that are flushed with nitrogen.

Catalyst 5058 from Regenerated Tungstic Acid.

The used catalyst is crushed to pieces of about 2-5 mm. and calcined in a revolving oven that is heated externally. The product is ground and dissolved in the supply vessel in mother liquor that is then discharged into a settling vessel. Further operations are the same as in the method of preparation from new tungstic acid. The crushing strength of the pellets is 250-300 kg. per sq. cm.

Regeneration of Catalyst 5058.

The pellets are ground, together with the dust that had been removed by screening, and are calcined at 600-800° in a stream of air in a gas-heated furnace. The calcined material is processed in the same way as yellow earth.

III. METHOD OF PREPARATION OF CATALYST 6434

500 kg. of Terrana A extra (Degendorf) is etched with 344 kg. of 8 percent hydrofluoric acid in a stirred pan for about 15-20 minutes at ordinary temperature. 500 liters of a 10 percent solution of yellow salt (ammonium thiotungstate) is added slowly, and the pan is heated with steam. In 8-10 hours, the charge is dry. During a further two hours, it is cooled. The cooled product is broken up in a special hammer-mill fitted with a 5 mm. screen (Schlagkreuzmühle) and is then decomposed in a screw-conveyor furnace at 400-450°C. in the presence of hydrogen and hydrogen sulfide. The discharge end of the furnace is cooled with nitrogen. The capacity of the furnace is 1-1/2 tons/day. The cooled product is again ground in a hammer-mill, passing out through a 1 mm. screen. The ground product is wetted in an Birich mixer, each 20 kg. of product receiving 6.2 to 7 liters of water. The mass is then pressed through a 3 mm. screen. This product is fed to the Kilian press, where it is made into 10 mm. pellets (capacity 700 kg. per day). The pellets are allowed to stand in the air for several hours, are tumbled in a screening apparatus and then dried in a drying oven or an electrically-heated vertical furnace (up to 200°C.). The final operation is calcining at 450°C. in a treating furnace in the presence of hydrogen and hydrogen sulfide. The finished catalyst is cooled with nitrogen and packed in drums under nitrogen.

Regeneration of Catalyst 6434.

The used catalyst has been regenerated only in a few instances by very careful roasting at 550-600°C., impregnating with a solution of yellow salt (1 percent WS_2) and sulfurizing at 450°C. The greater part of this used catalyst (several hundred tons) was worked up electrothermally into ferro-tungsten at Bitterfeld. In this operation, the catalyst is roasted and then reduced electrothermally, alone or after admixture with ore.

IV. CATALYST 8376

Commercial aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) that contains about 18 percent Al_2O_3 is dissolved in water at 50-70°C. to an almost saturated solution (about 10 percent alumina in the solution). This solution is allowed to flow simultaneously with a 20 percent ammonia solution into a steam-jacketed stirred vessel to precipitate aluminum hydroxide. Solutions are so added to the vessel that there is always a small excess of ammonia in the mixture, which is controlled by an antimony electrode (pH between 8 and 10). 20 cc. of the filtrate requires about 10 cc. of N/10 H_2SO_4 . The precipitate is pumped from a storage vessel into the filter press and washed sulfate-free with weak ammonia solution (0.1 percent). The filter cake (about 19 percent solids) is dried in a drying oven or a rotating-tube dryer until the ignition loss of the product is 15-20 percent. The dried

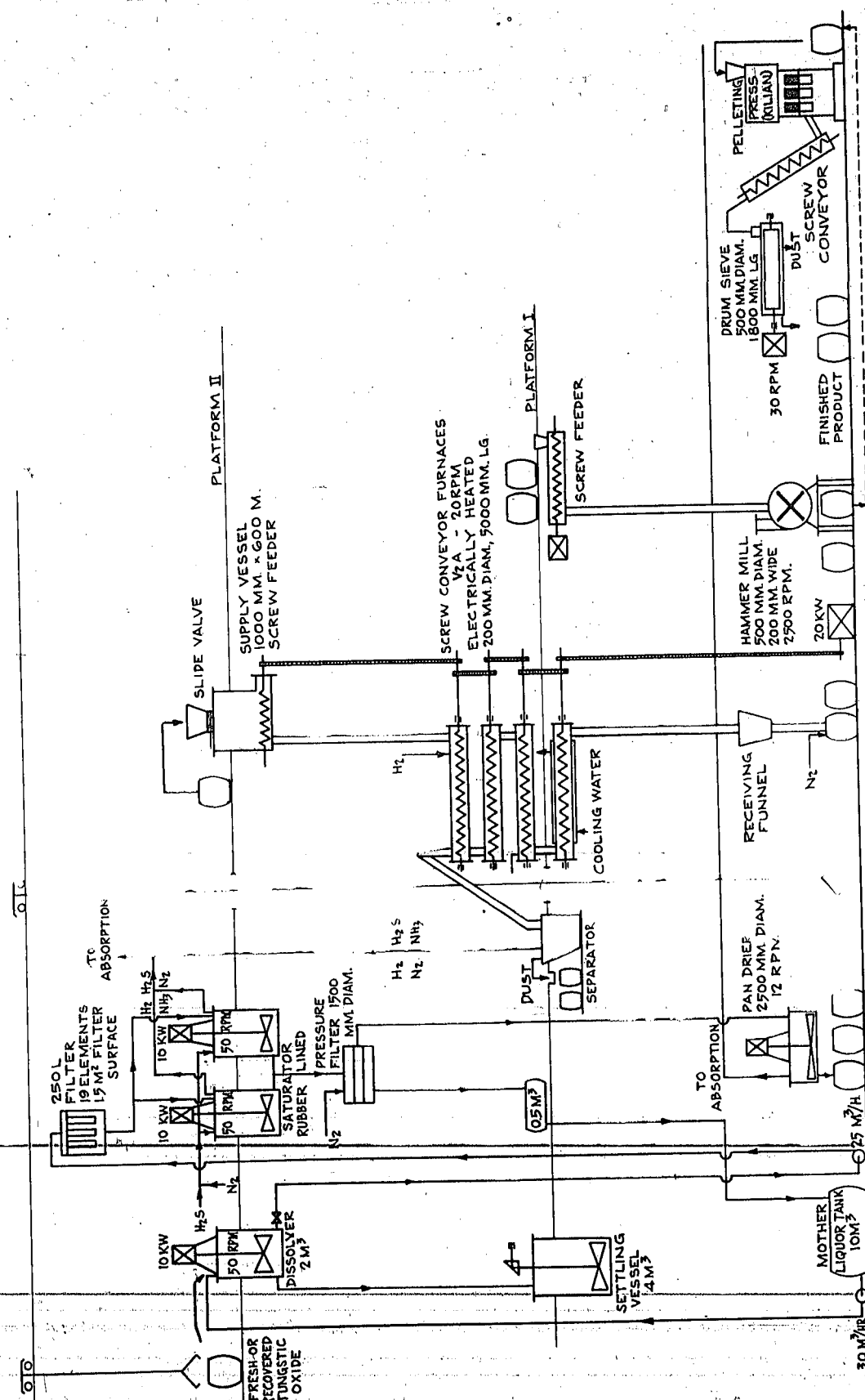


FIGURE 1. DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 5058 (1 TON/DAY).

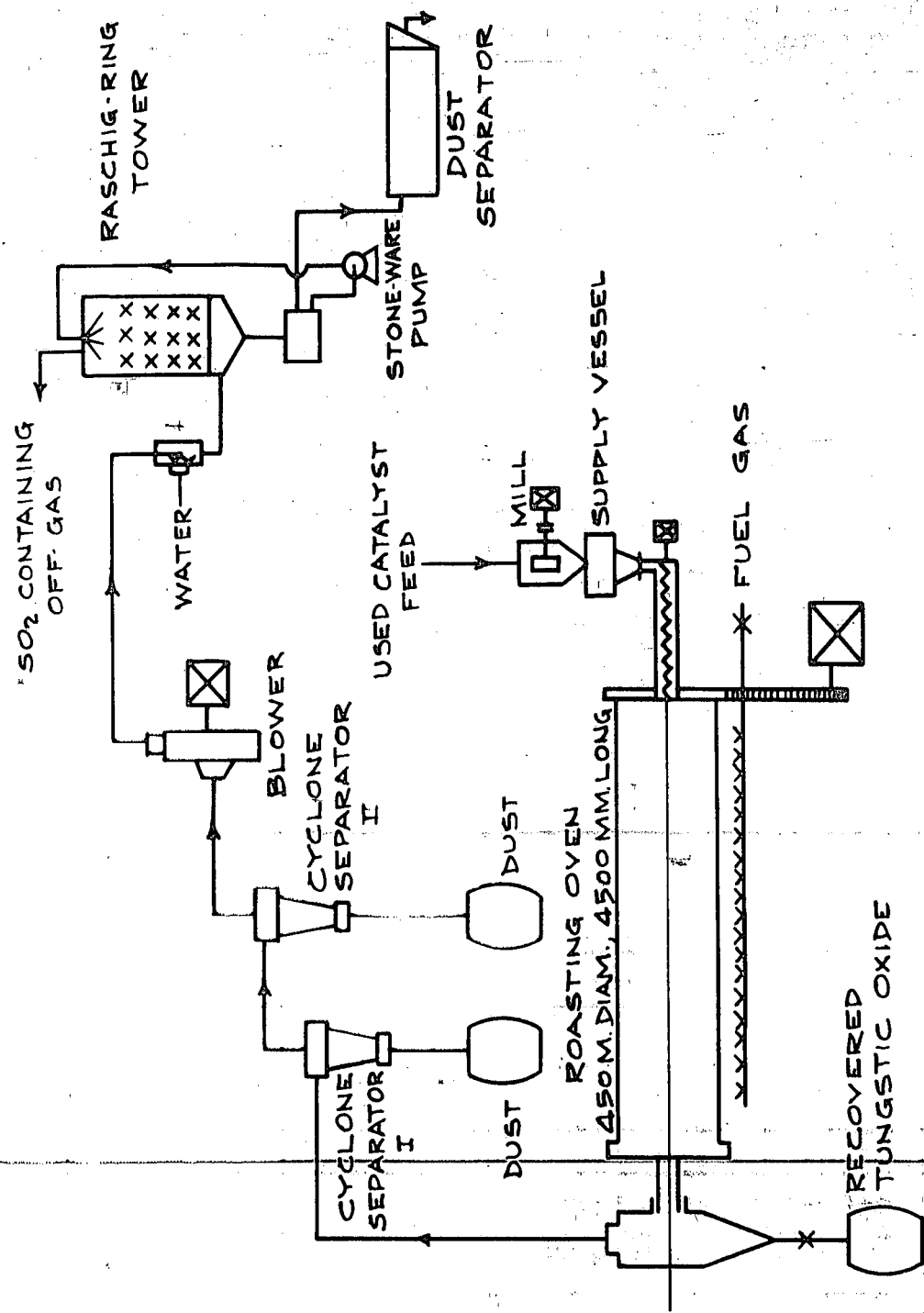


FIGURE II. DIAGRAM OF ROASTING APPARATUS FOR RECOVERY OF TUNGSTIC OXIDE FROM USED CATALYST 5058.

TUNGSTIC OXIDE FROM USED CATALYST 7070.

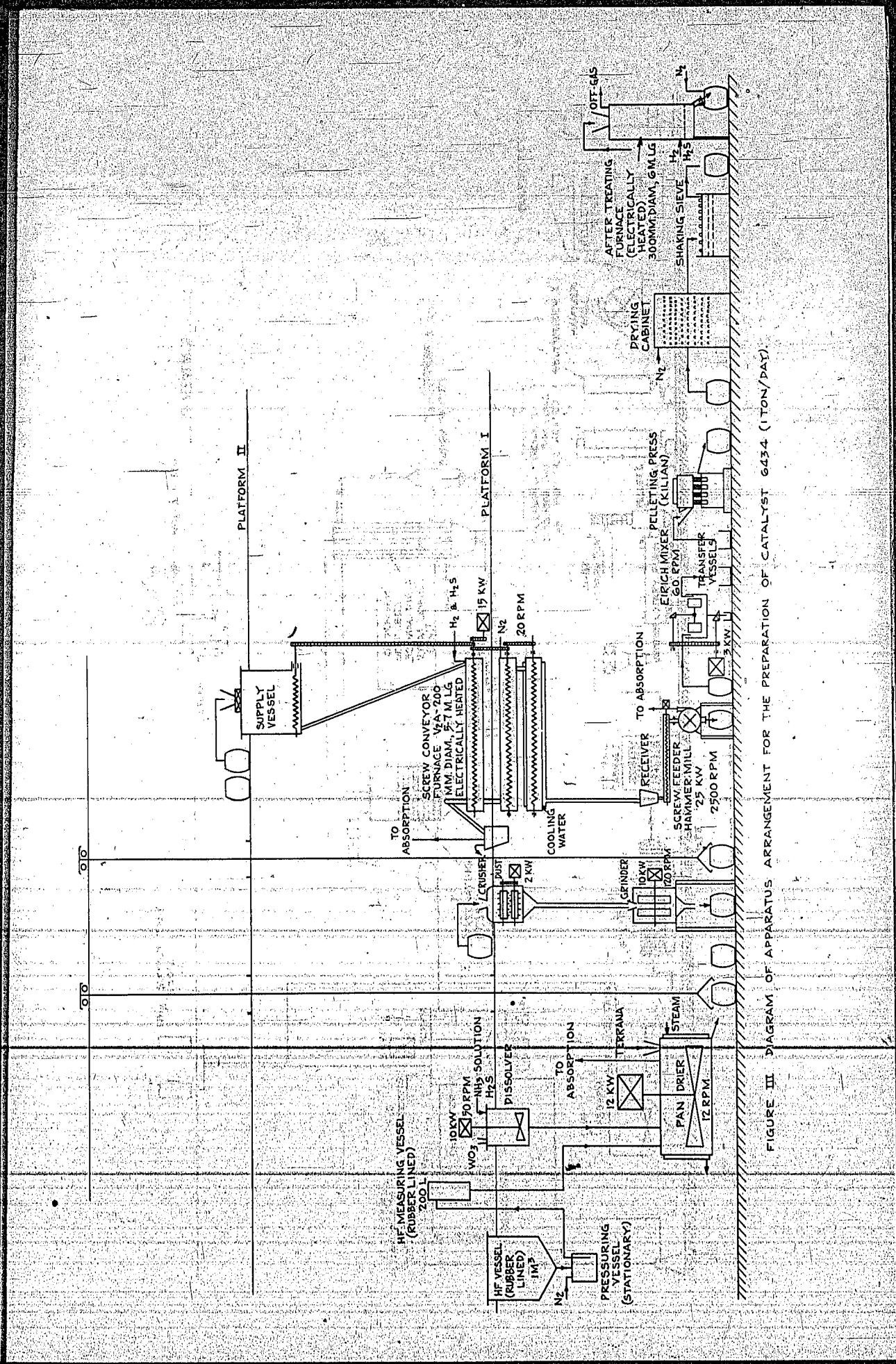


FIGURE III. DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 6434 (1 TON/DAY).

3KW
50 RPM
NH₃ SUPPLY TANK
SOLUTION OF WO₃ & NI SO₄

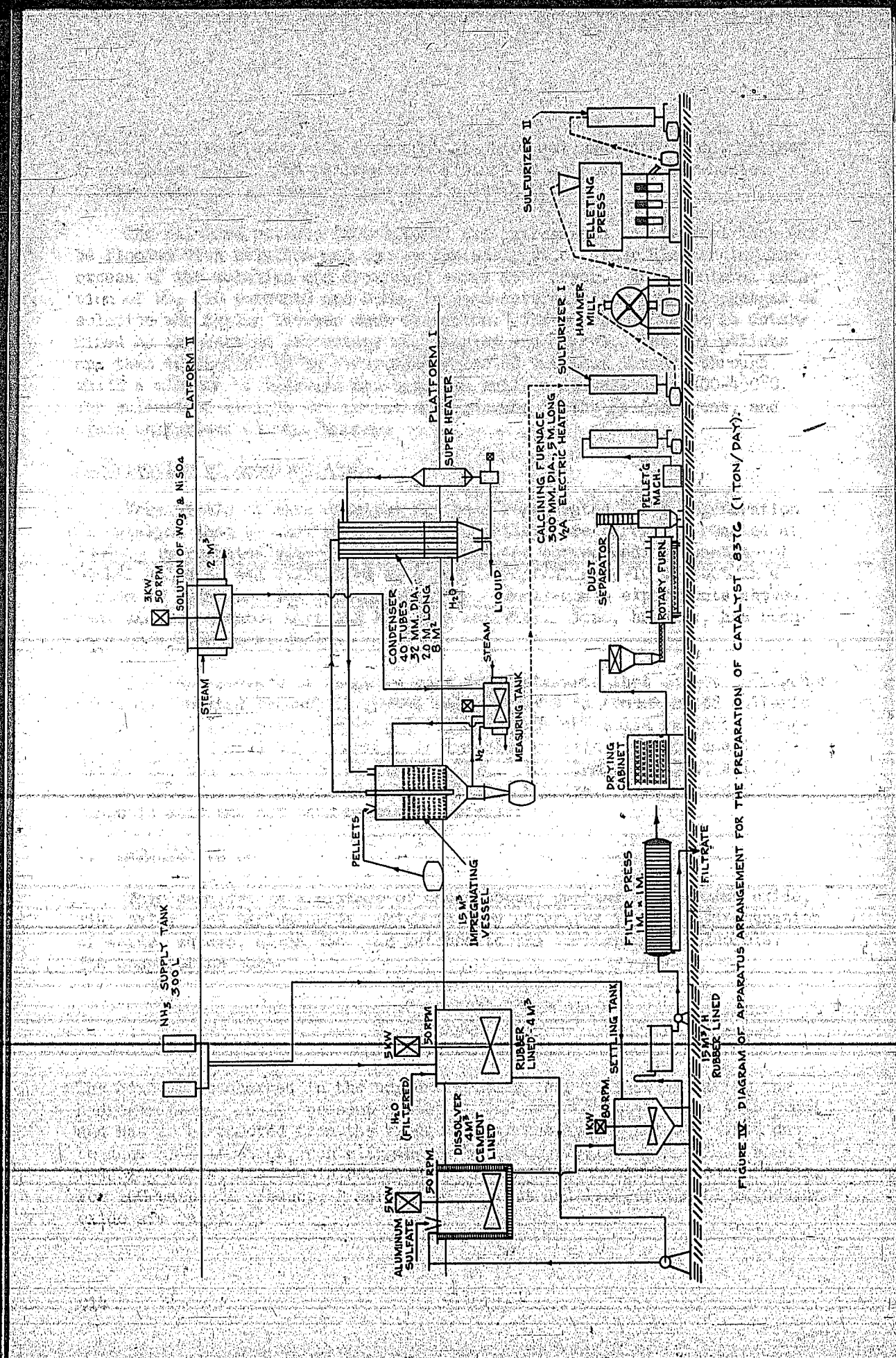


FIGURE IV. DIAGRAM OF APPARATUS ARRANGEMENT FOR THE PREPARATION OF CATALYST 837C (1 TON/DAY).

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Regeneration

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V. CATALYST

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product is then ground with 1 percent graphite and made into 10 mm. pellets in a Kilian press. The pellets are calcined in an electrically-heated vertical furnace in the presence of air at 450°C.

The calcined pellets (800 liters) are impregnated in a vessel that can be flooded with solution and can subsequently (i.e. after discharging the excess of the solution and draining) serve as a dryer. An ammoniacal solution of WO_3 (20 percent) and $NiSO_4$ is used several times with discharges of solution and drying between each operation. The number of stages is determined by the desired percentage of tungsten and nickel. The dry pellets are then sulfurized in an electrically-heated vertical furnace through which a mixture of hydrogen and hydrogen sulfide is passed at 400-450°C. The sulfurized pellets are ground and reformed in the Kilian press, and again sulfurized in the furnace.

Regeneration of Catalyst 8376.

Very little of this catalyst has been regenerated. For regeneration of catalyst that has had normal use, the pellets are carefully roasted at 600°C., impregnated with 1 percent WO_3 and the corresponding quantity of nickel sulfate, and sulfurized to a sulfur content of 9-10 percent in a stream of hydrogen plus hydrogen sulfide. Small-scale experiments showed that the regenerated material had good activity. None, however, has been used on a commercial scale.

For the recovery of tungstic acid from catalysts that cannot be regenerated, the roasted product is ground and dissolved in concentrated sulfuric acid. The solution is diluted and filtered from the solid residue. Tungstic acid is dissolved in ammonia or ammonium sulfide solution and is used either for the preparation of 5058 or 8376. The aluminum sulfate solution can be used for the preparation of activated alumina. This recovery of tungstic acid has not been made commercially.

V. CATALYST PH 36

This catalyst is a mixture of basic copper carbonate, chromium oxide, zinc oxide, and barium oxide, which is very effective for the hydrogenation of acids, esters, aldehydes, and ketones to the corresponding alcohols. Its composition is:-

45 percent copper
2 percent chromium
2 percent zinc
2 percent barium.

The contact is charged in the unreduced state, but is reduced during the hydrogenation. In its present state, it can be used only in the sump oven and has to be removed from the product after the hydrogenation. This can be done by filtration, centrifuging or by decomposition with acid. When reducing acids, its use is recommended in conjunction with magnesium oxide. For 100 parts of product, 2 percent of contact and 1.8 percent of magnesium oxide are required.

The hydrogenation with this catalyst is carried out at temperatures between 230 and 270°C. and at a pressure of 250 atm. of hydrogen.

The catalyst has the great advantage of not forming any paraffin, even at higher temperatures.

Method of Preparation of Catalyst PH 86.

Materials for 100 kg. of catalyst:

105-108 kg. of sodium carbonate
56-59 kg. of copper, equivalent to 497 kg. of copper nitrate solution containing 11.8 percent of copper.
4.17 kg. of barium nitrate
3.53 kg. of zinc nitrate (6 mols of water of crystallization)
5.93 kg. of chromium nitrate
15.5 kg. of sodium bicarbonate.

Procedure for 632 kg. of catalyst:

7000 l. of sodium carbonate solution (12.5° Be') is diluted with water in a stirred container to a specific gravity of 8.5° Be' (final volume is about 10,800 l.). Into this solution is introduced (at room temperature) 3,150 kg. of copper nitrate solution (content of copper is 11.8 percent). The temperature should not be higher than 30°C., and the Ph between 6.5 and 7.5. The mixture is stirred for about 30-40 hours (sic), until the blue color changes to green. The precipitate is then washed by decantation (12 times with 10 m³ of condensate) until diphenylamine shows the absence of nitrates. After settling, about 5,700 l. of the clear solution is discharged.

The remaining solution (about 5,100 l.) is provided with a stirrer, in 650 l. of water. The zinc nitrate (2 kg) is added to this solution and after it has dissolved, the chromium nitrate (57.4 kg) is added. The chromium nitrate used is the anhydrous triple purified grade.

The suspension of copper solution to (5,700 l.).

In the meantime, a solution of 10 kg. of sodium bicarbonate in 100 l. of water is put into a stirred vessel. This solution is added to the named mixture of copper carbonate and metal nitrates until no further precipitate forms. The filtrate from the finished mixture is weakly alkaline. Washing by decantation is carried out until diphenylamine shows the absence of nitrates (about eleven washings). The filtrate must be neutral towards litmus and phenolphthalein. Only when a sample is boiled should the filtrate turn litmus blue and phenolphthalein red.

After washing has been finished, the precipitate is allowed to settle and the clear liquid above the precipitate is discharged. The remainder is centrifuged, and the solid dried at 120°. The product is ground in a hammer mill (Schlagkreuzmühle).

VI. PREPARATION OF METHANE-SPLITTING CATALYST

The catalyst splits methane in the presence of steam at about 700-750°C. into CO₂, CO and H₂. Its composition is approximately:-

SiO ₂	20-21 percent
Al ₂ O ₃	17-18 percent
Fe ₂ O ₃	5.0-5.5 percent
NiO	19-20 percent
CaO	10-11 percent
MgO	8.5-10 percent

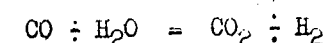
The specific gravity is about 1.0.

For the preparation of the catalyst, 184 kg. of nickel powder as a 14.5 percent nickel-nitrate solution is diluted with 1,000 liters of water, and is precipitated at 65-70°C. with 340 kg. of sodium carbonate (as a 10.5 percent solution). A slight excess of sodium carbonate should be present. The total contents of the precipitation vessel is separated in a filter press and the cake washed free from carbonate and nitrate at about 40°C. The filter cake is blown dry with compressed air for about 15 minutes.

To about one-third of this filter cake (about 360 kg.), in a kneading machine, is added 178 kg. of kaolin, 76 kg. of magnesium oxide and 36 kg. of nickel powder (as about a 15 percent solution). After kneading, the mass is spread about 20 mm. thick on plates and ignited for about 7 hours at 500°C. The ignited material is ground to powder. Fifty kg. of this powder is mixed with 23 kg. of alumina cement in a mixer, with the addition of 12 liters of water, screened through a 2 mm. mesh sieve and pressed in a tableting machine to Raschig-ring shapes (16-18 mm. diameter and 12-14 mm. long). These rings are piled up and sprayed with water twice a day for three days to set the cement. They are then packed.

VII. PREPARATION OF BROWN OXIDE CATALYST

Brown oxide is a CO-conversion catalyst and works according to the following equation:-



It contains approximately:-

Fe ₂ O ₃	86-87 percent
Cr ₂ O ₃	7-7.5 percent
Sodium and Iron Sulfate - Balance	
(approximately 1 percent SO ₄)	
Specific gravity is about 1.17.	

The preparation of this catalyst is divided into three operations:-

- Preparation of the iron oxide
- Preparation of the chromium nitrate solution
- The further working up of both products.

For the iron oxide preparation, iron sulfate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) is dissolved in water to give a 20-percent solution and the solution is pumped into a storage vessel. Sodium carbonate (10-12 percent solution) is put into the precipitation vessel, and the iron sulfate is added with stirring at about 30-35°C. Quantities are adjusted to give a slight excess alkalinity at the end of the precipitation. The iron carbonate precipitate is allowed to settle and is then well washed on a rotary filter with warm water (60-70 percent). It is then dried in a rotary kiln and decomposed in an annealing furnace. The iron oxide formed (about 95 percent Fe_2O_3) should have a weak red glow on leaving the furnace. It is then cooled in a screw-propeller cooler and stored in bunkers.

The chromium nitrate solution is prepared by dissolving a 34-40 percent wet slime of chromium oxide in nitric acid at about 70-90°C., with stirring. The nitrate solution should contain a minimum of 15 percent Cr_2O_3 .

The further working up of the catalyst consists in filling a kneading machine with the previously prepared iron oxide and adding, with kneading, enough chromium nitrate solution to give the desired composition of the finished catalyst (86-87 percent Fe_2O_3 , 7-7.5 percent Cr_2O_3). The product from the kneader is pressed into cakes (10-12 mm. thick) and is roasted on plates in a tunnel kiln at 500-550°C. The dried cakes are broken in a cylindrical crusher. The fines (under 5 mm.) are screened out and the material above 5 mm. size is again calcined in a furnace at 550°C. It is then screened into small-kernal size (5-10 mm.) and large kernel-size (over 10 mm.) and packed in barrels.

The fines mentioned above (under 5 mm.) after a fine-grinding can be used when kneading up a new batch.

VIII. CATALYSTS 7935 AND 7360

7935

The activated alumina is prepared as described for catalyst 8376. The calcined pellets are treated in the combination impregnating and drying apparatus in batches of 800 liters with an ammoniacal solution of MoO_3 (about 5 percent of ammonia and 12-15 percent MoO_3) until the finished catalyst contains 15 percent MoO_3 . After drying in the apparatus at 190°, the catalyst is calcined in an electrically-heated vertical furnace in a stream of air heated to 400°C.

7360

Activated alumina is prepared in the form of cubes by the aluminate process, and the cubes treated in the same way as for catalyst 7935, until the finished catalyst contains 10-12 percent MoO_3 .

Regeneration of catalysts 7360 and 7935.

The used catalyst is roasted and ground. The powder is then moistened and dissolved in concentrated sulfuric acid; the solution is diluted and saturated with hydrogen sulfide. The impure precipitate of molybdenum sulfide is filtered, roasted and dissolved in ammonium hydroxide.

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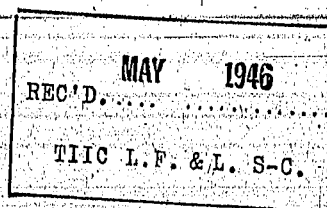
**SUPPLEMENTAL REPORT ON THE RUHROL
HYDROGENATION PLANT, WELHEIM, RUHR**

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OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 299

8 October 1945

SUPPLEMENTAL REPORT
ON THE RUHROL HYDROGENATION PLANT
WELHEIM, RUHR.

BY

Dr. W. F. FARAGHER
Dr. W. A. HORNE

Technical Industrial Intelligence Committee

FIELD INFORMATION AGENCY, TECHNICAL

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PERSONNEL OF TEAM:

Mr J.G.Allen, U.S.
Dr.G.S.Bays, U.S.
Dr.W.F.Faragher, U.S.
Dr.W.A.Horne, U.S.
Mr.B.L.MacKusick, U.S.

SUPPLEMENTAL REPORT ON THE RUHROL HYDROGENATION PLANT WELHEIM

INTRODUCTION

This target was revisited to obtain further information concerning the development and preparation of the 700 atm. catalyst. Some data was also obtained on production.

The information presented herein is in addition to and supplements that previously reported in CIOS report dated 8 August 1945 "Botrop-Welheim Hydrogenation Plant" by C.Cockram.

PRODUCTION

The Welheim plant charged 263,000 tons per year of a 70% bituminous coal tar pitch, 30% heavy tar oil mixture and 32,000 cu.m. of hydrogen per hour. The production was approximately as follows:

120,000 tons per year of marine fuel oil
60,000 " " " " aviation gasoline
18,300 " " " " liquid gas (propane and butane)
36,000 " " " " pitch stall residues (for briquetting)

In addition the following by-products were supplied monthly to neighboring plants:

70-80 tons of ammonia
120-150 " " sulfuric acid
10 " " phenols and inhibitors for gasoline
About 400,000 cu.m. of gas containing 45-50% ethylene
About 100,000 cu.m. of oxygen.

The hourly utilities requirement for this hydrogenation were as follows:

Electrical energy	32,000 KWH
Steam at 3 atm.	65 tons
Steam at 15 atm.	35 tons
Make-up water	600 cu.m.
Cooler water	5,000 cu.m.

CATALYST DEVELOPMENT

Hydrogenation in both phases is performed in the Welheim plant at a pressure of 700 atm. In the last few years, newly-built hydrogenation units at Wesseling, Nordstern, Pöhlitz, Brück and Blechhammer have been put into operation also at a pressure of 700 atm. for the sump phase. In all these plants, however, the hydrogenation in the gas phase was conducted at 300 atm. since at higher pressures, formerly known catalysts produced a gasoline that was too strongly hydrogenated.

The gas phase unit at Welheim was the only one operating at 700 atm. at the end of the war; it has the advantage that, by virtue of a newly-developed catalyst, the production of aviation gasoline (C₃ quality) is effected in one step, while in these units

operating at 300 atm., three operating steps with three completely separate units (5058, 6434, DHD) are required to make aviation gasoline from middle oil. There is moreover, the advantage that, in the operation at 700 atm. used in the Welheim unit, the sump phase and the gas phase chambers have a common gas recycle circuit.

This Welheim catalyst was fully developed in Feb. 1938, after four and a half years of research work in a semi-commercial plant.

In the course of this work, 536 different catalysts were made and investigated for their suitability in a 50 c.c. oven. Those that appeared to be favorable were then used in 5 and 8-liter ovens, and the best of these were then tested in the Welheim gas phase chambers that had a catalyst capacity of 12-16 cu.m.

The best cracking component found after extensive experimentation was the bleaching clay "Terrana" and the closely related AD5 paste marketed by the Süddeutsche Mächen. Molybdenum and tungsten are most suitable as the hydrogenation components. Since, however, the molybdenum compounds were more easily procurable, experiments were limited to them.

In the course of these extensive investigations, the following essential points were established:-

1. An improvement of the cracking action of Terrana and AD5 paste is obtained if the clays are etched with dilute hydrofluoric acid;
2. The hydrogenating component is strongly activated by the addition of small quantities of chromium. The hydrogenating activity of the mixed catalyst (molybdenum and chromium) is considerably greater than that of molybdenum alone.
3. If the finished catalyst is activated in a stream of H₂S or mixed H₂S and hydrogen rather than in hydrogen alone, an important increase in the charging rate and in the reduction of phenols is obtained without great sacrifice of aromatics. Therefore 5-10% of elementary sulfur is added to the catalyst which is evolved as hydrogen sulfide during the activation in the hydrogen stream at 350-400°C. Catalysts so prepared

allow higher throughputs and give essentially better reduction of phenols and bases.

4. The sulfurizing of Welheim middle oil that contains less than one-tenth percent sulfur gives only a small increase in permissible charging rate and in the extent of reduction of bases. Simultaneously, the reduction of phenols and the aromatization are impaired.

The composition of the most important catalysts used commercially are as follows:-

	K.157	K.413	K.534	K.536
Cr (as oxide)	-	2%	2%	2%
Zn (as oxide)	1%	5%	5%	5%
Mo (as oxide)	1%	0.4%	0.6%	0.7%
S (evolved as hydrogen sulfide during activation).	-	-	5%	5%

All these catalysts contain, as support and cracking component, a mixture of 60% AD5 paste and 40% Terrana which, beginning with catalyst K 346, has been etched with hydrofluoric acid. These catalysts were developed principally for the hydrogenation of pitch middle oil; with other charging stocks, a small decrease in quality of the gasoline results.

CATALYST PREPARATION

The following materials are required for the preparation of 60 Kg. of finished K-534 or K-536 catalyst:

90 kg. of AD5 paste (average water content is 60%; therefore, 56, kg. of dry material).

24 Kg. of Terrana

4.1 kg. of hydrofluoric acid (70-72%)

3.7 kg. of zinc oxide

3.0 kg. of sulfur (flowers of sulfur)

2.3 kg. of chromic acid anhydride (CrO_3)

1.4 kg. of ammonium thiomolybdate $(\text{NH}_4)_2\text{MoS}_4$.

16.0 kg. of ammonia solution (sp.gr. = 0.910)

About 90 kg. of AD5 paste (exact composition unknown) is mixed for a half hour in a kneading machine with 4.1 kg. of hydrofluoric acid. After adding 10 kg. of Terrana, the kneader is operated for a further 10 minutes. The zinc oxide (3.7 kg), sulfur (3.0 kg) and chromic acid anhydride (2.3 kg), with an equal weight of water, are added and the mixing continued for 10 minutes more. A further portion of Terrana (10 kg) is added, and the mixture is neutralized with 9 kg. of technical ammonium hydroxide. Finally, the thiomolybdate (1.4 kg) dissolved in 7 kg. of the ammonia solution is added, together with the remaining Terrana, and mixing is continued for a further 20 minutes. The finished mass is then made into cylindrical pills of 10 mm. diameter and dried in an oven at 70-75°C. for four days.

Activation with dry hydrogen is effected by reduction according to the following schedule:

Increasing temperature to 350-360°C	-	8 hours
Maintained at 350-360°C	-	4 "
Cooling to atmospheric temperature	-	10 "

The catalyst is then placed in barrels. Contact with air does not decrease the activity but moisture does.

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I. G. FARBENINDUSTRIE - LEVERKUSEN, GERMANY

WARNING: Some products and processes described in this report may be the subject of U.S. patents. Accordingly, this publication cannot be held to give any protection against action for infringement.

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MAY 1946
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OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
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3 October 1945

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BY

W. F. FARAGHER
C. C. CHAFFEE
H. SCHINDLER
D. A. HOWES

Technical Industrial Intelligence Committee

FIELD INFORMATION AGENCY, TECHNICAL

11 p. diagrs.

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Personnel of Team

Dr. W.F. Faragher	U.S. Petroleum Administration for War
Dr. Hans Schindler	
Capt. C.C. Chaffee	U.S. Ordnance Department
Dr. D.A. Howes	British Ministry of Fuel and Power

RECOIL FLUID

Summary

The mixture of triglycol, ethylene glycol and water used regularly by the German Army as recoil fluid was found unsuitable in the winter campaign in Russia. The addition of a sulfonamide of low molecular weight eliminated the difficulty since, in this way, it was possible to obtain a recoil fluid of not too high viscosity at low temperatures and still to maintain the high specific gravity necessary for satisfactory brake action.

Information was obtained by interrogating Dr. Detlef Delfs, on July 5 and 6, 1945.

Details of Formulation.

The composition of the German recoil fluids is given in the following tables. The addition of K_2F_2 prevents corrosion of light-metal alloys, whereas mercaptobenzo-thiazol was added for rust prevention. The mixture of sodium and potassium salts of phenylglycine served as anti-oxidant. The code name "Methanamid" is used at Leverkusen for the monomethylamide of methane-sulfonic acid, $CH_3SO_2NHCH_3$, whereas "Sulfoethan" stands for the methyl-hydroxyethylamide of methane-sulfonic acid, $CH_3SO_2N(CH_2CH_2OH)$. The figures in the table give the composition as per cent by weight.

COMPOSITION OF RECOIL FLUID

	Bremsflüssig- keit. Braun (old formula)	Bremsflüssig- keit Ark*	Bremsflüssigkeit Braun Up to 1944	Bremsflüssigkeit Ark Since 1944
Triglycol	34	-	17	17.3
Ethylene glycol	34	51	42.5	42.3
Methanamid	-	5.0	2.5	3.0
Sulfoethan	-	8	4.0	3.5
Water	28	32	30.0	31.4
K_2F_2	2	2	2	-
Mixed Na and K salts of phenyl- glycine.	1.9	1.9	1.9	-

*See page 2.

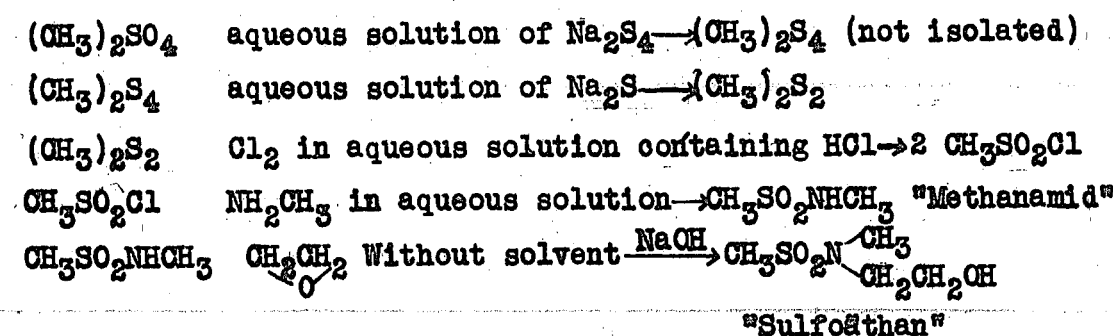
COMPOSITION OF RECOIL FLUID (Cont)

	Bremsflüssig- keit Braun (old formula)	Bremsflüssig- keit Ark*	Bremsflüssigkeit Braun Up to 1944	Ark Since 1944
Mercaptobenzo- thiazol NaOH	0.1 -	0.1 -	0.1 -	- 2.0

*Formulated tentatively to save triglycol.

Manufacture of Sulfonamide.

The manufacture of "Methanamid" and "Sulfoathan" is carried out according to the following scheme:



W.F. Faragher.
C.O. Chaffee.
D.A. Howes.
H. Schindler.

SYNTHETIC LUBRICATING OILS FROM TETRAHYDROFURAN.

Summary.

Synthetic oils of good viscosity index but poor thermal stability have been prepared at Leverkusen by copolymerization of tetrahydrofuran and ethylene oxide in the presence of FeCl_3 and SOCl_2 . Engine tests with an oil of a viscosity of about 83 SUS at 210°F resulted in ring sticking after short running time and indicated that the piston was not properly lubricated, probably because of decomposition of the lubricant. The synthetic product is not miscible with petroleum oil. It has been used as gear oil and for the lubrication of machinery operating at temperatures below 280°C . Production of the material was irregular and on a small scale (maximum 1-2 tons a month).

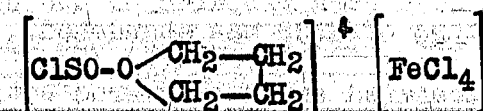
Information on the subject was obtained by interrogation of Dr. Otto Böhme, manager of the dyestuff intermediates department, and especially Dr. Detlef Delfs, head of the research laboratory of the intermediates department, on July 5 and 6, 1945.

Theory of Polymerization of Tetrahydrofuran.

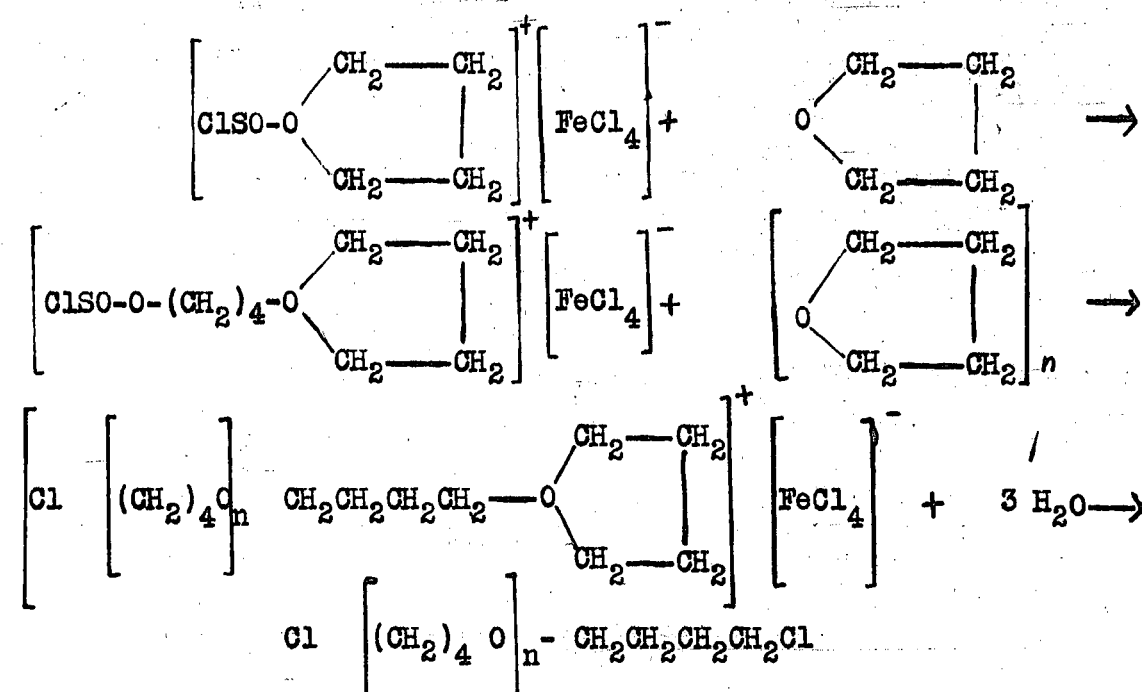
The ability of tetrahydrofuran to polymerize in the presence of oxonium salts was discovered by H. Meerwein and his collaborators, and the possibilities of the reaction were investigated by the I.G. at Leverkusen. A comprehensive patent application by the I.G. covering the present state of the chemistry of this field has been obtained.

The oxonium salt which serves as catalyst is formed directly in the reaction mixture from tetrahydrofuran, SOCl_2 and FeCl_3 . Other catalyst combinations are mentioned in the patent application.

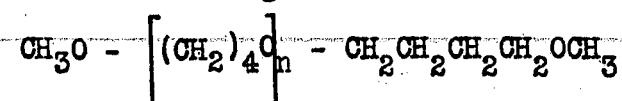
Reaction of tetrahydrofuran, SOCl_2 and FeCl_3 leads to the formation of a tertiary oxonium salt of the following structure:



This compound reacts with tetrahydrofuran according to the following scheme:



To eliminate the chlorine present in the molecule, the polymerizate is reacted with methanol to give the final product that has the following structure:



The above compound is a solid and is not suitable as a lubricant. In order to obtain liquid products, copolymerization with ethylene oxide or a similar compound is necessary. Copolymerization with propylene oxide, e.g., leads to synthetic oils with a pour-point of -60°C . Instead of methanol, it is of course possible to use other compounds; e.g., phenol.

Manufacturing Details.

Two grades of oil, M620, about 83 SUS at 210°F , and M586, about 256 at 210°F , have been prepared on the semi-plant scale. The manufacture of M586 was abandoned.

The catalyst can be prepared separately from tetrahydrofuran, FeCl_3 and SOCl_2 , which makes it possible to

operate the polymerization process continuously. Additional thionyl chloride is added in that case together with the reactants.

For the manufacture of M620, the molar ratio of tetrahydrofuran to ethylene oxide is 2:1 and the catalyst requirements are 0.1 mol FeCl_3 per 100 mols reactants and 5 mols SOCl_2 per 100 mols reactants. The polymerization temperature is $25-35^\circ\text{C}$. The polymerizate is left standing for several hours; the FeCl_3 is washed out with water, and water and unreacted tetrahydrofuran are removed by distillation. Chlorine is removed by reaction with methanol and NaOH at $90-100^\circ$ in a closed vessel; excess methanol is distilled off; the mixture is neutralized with HCl and the NaCl formed is washed out. After the addition of 0.5% by weight of iso-octylphenol (as stabilizer), the product is dried and filtered.

The ratio of tetrahydrofuran to ethylene oxide is 4:1 for the manufacture of M586. The catalyst requirements are 0.1 mol FeCl_3 per 100 mols of reactants, and 2.5 mol SOCl_2 per 100 mols of reactants. The polymerization temperature in this case is about $25-30^\circ\text{C}$. The polymerizate is left standing for several days and neutralized (Congo Red) with NaOH . The unreacted tetrahydrofuran is distilled off, phenol and caustic are added to the polymerizate and the mixture is heated to 165°C until no organic chlorine can be detected. The reaction product is then treated with water and neutralized with HCl . After the addition of 0.3% by weight (calculated on finished product) of iso-octylphenol, the water is removed by distillation, the product is diluted with naphtha, filtered and freed from the solvent.

Inspection Data of Synthetic Oils.

Inspection data of the synthetic oils from copolymerization of tetrahydrofuran and ethylene oxide are given as follows:

Oil Grade	20		Pour		Kinematic Viscosity (cStokes)						Pole Height
	4		OC		20°C	50°C	80°C	99°	150°	200°	
M620	1.024	-25	16.4	25.4	62	221					1.1
M586	1.014		1032	244		55.3	22.4	11.2			1.1

	% Chlorine	Conradson Carb.Res.	Flash °C	%Ash	Noack Evap. Test. (1 hr, 230°C, 20 mm.Hg)
M620	0.02	0.2			
M586			262	0.07	3.3%

Both oils are not miscible with paraffin hydrocarbons, but are soluble in alcohols, ethers, ketones, esters and aromatic hydrocarbons.

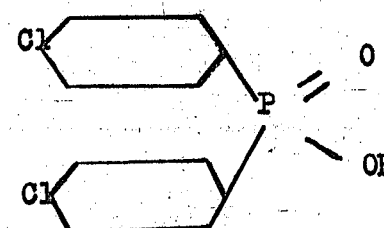
W.F.Faragher.
C.C.Chaffee.
D.A.Howes.
H.Schindler.

ADDITIVE FOR BREAK-IN OIL

Summary.

An additive for the lubricating oil used during the break-in period of engines, mainly aircraft engines, has been developed at Leverkusen. By the use of the additive it was possible to reduce the break-in time of German aircraft motors from 70 hours to 20 hours and to eliminate rejects.

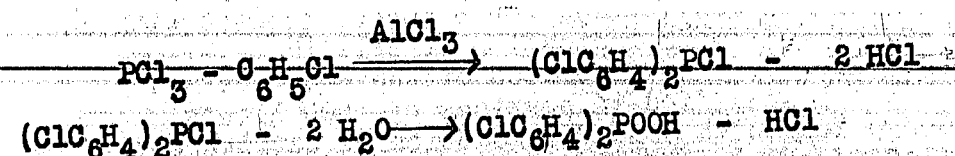
The effective compound in the additive is dichlorodiphenylphosphorous acid ("Product 891")



To increase the solubility in oil, the compound is used in the form of its stearylamine salt and to further increase ease of handling the additive was distributed as a solution in alcohol-benzol (50:50). The solution which contains 50% by weight of the stearylamine salt of Product 891 was termed J7. The break-in oil for aircraft engines consisted of Rotring Oil (Red Band) with 2% by weight of J7. The information was obtained by interrogation of Dr. Berthold Wenk, manager of the dyestuff department, on July 5 and 6, 1945.

Preparation.

The preparation of the additive is based on the following reactions:



To 1240 kg. of chlorobenzene and 760 kg. of PCl_3 is added, with stirring, 372 kg. of AlCl_3 . Since no reaction takes place in the cold, the temperature is rapidly brought to

70-75°C. Development of HCl begins, and heating is continued according to the following schedule:

In 2 hours to	80-90°C.
" 2 "	" 100-105°C.
" 4 "	" 107-109°C.
" 4 "	" 110-112°C.
" 4 "	" 113-116°C.
" 4 "	" 117-120°C.
" 4 "	" 121-124°C.
" 6 "	" 125-127°C.
" 6 "	" 128-131°C.
" 8 "	" 132-134°C.
" 28 "	" 134-136°C.

Total 72 hours

Excess PCl_3 and some chlorobenzene are distilled off at atmospheric pressure until no PCl_3 can be detected in the overhead product; the residue is cooled to 70°C and distilled under vacuum at 81-136°C during 7-8 hours. Of the chlorobenzene charged, about 800 kg. is used in the reaction and 400 kg. is recovered. The distillation residue is cooled to 50-55°C. and passed by N_2 pressure into 2000 liters of water and 2,500 kg. of ice. The yield of the crude moist product "Product 891" is 1200-1250 kg.

The following procedure is used for the purification of the crude product.

1200-1250 kg. of Product 891 is pasted with about 4000 liters of water, brought to the boiling point with direct steam, made weakly alkaline (phenolphthaleine) by the slow addition of about 250-300 kg. of Na_2CO_3 and boiled with direct steam for about 20 hours. The solution, whose volume is now about 7000 liters, is treated with about 250-300 kg. of concentrated HCl (technical) until it is barely alkaline (Brilliant Yellow indicator) and is then filtered at about 90-95°C. The residue is again pasted with 3000 liters of water, made alkaline (phenolphthaleine) with about 60 kg. of Na_2CO_3 , boiled for 6 hours, treated with about 40 kg. of HCl (weak indication of brilliant-yellow paper) and filtered. The filtrates of the two treatments are combined and acidified in portions of 1500 liters (strong Congo Red) with HCl; the reaction is carried out in an enamelled vessel of 2500 liter capacity. The total consumption of HCl is about 400 kg. Product 891 separates out as a viscous oil, which settles to the bottom of the vessel and the supernatant solution is drawn off.

If the product still does not give a clear solution in a Na_2CO_3 solution, it is necessary to repeat the soda treatment. The total product obtained is dissolved in about 1000 liters of water, together with about 40-50 kg. of Na_2CO_3 (weakly alkaline towards phenolphthalein), boiled for 1/2 hour, made weakly alkaline toward Brilliant Yellow by means of HCl and filtered; the solution is again acidified in an enamelled vessel. The separated oil is repeatedly washed with water at 50-60°C. and the product is finally dried under vacuum at 135-140°C. Yield: 500-550 kg. of pure Product 891.

The preparation of the stearylamine salt and solution of the salt in alcohol and benzol is carried out in one step as follows: 800 kg. of pure Product 891 is heated to 60°C., 500 kg. of benzol is added with stirring and after complete solution 500 kg. of alcohol (94%) is added. The temperature has sunk to 40°C. by this time, and 200 kg. of stearylamine (well broken up) is added within about 1 hour. The temperature is maintained at 40-45°C. by cooling during this period. After complete solution has taken place, stirring is continued at 40-45°C. for 2 hours. The solution is allowed to stand undisturbed for 24 hours and is then filled into glass containers. Yield: 2000 kg. of J7.

Iron drums as well as galvanized or lead lined drums are not suitable for shipping the product.

Specifications for J7.

The following specifications have been proposed by the I.G. Leverkusen for the additive J7 for use by the German Air Force:

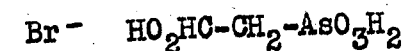
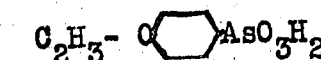
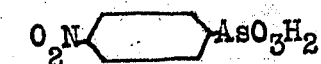
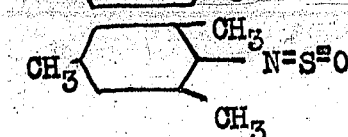
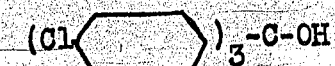
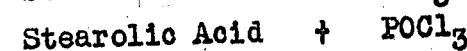
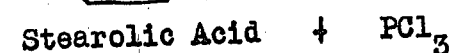
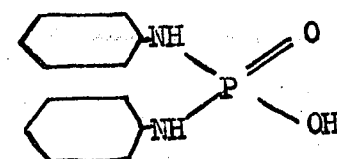
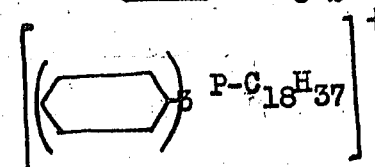
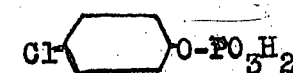
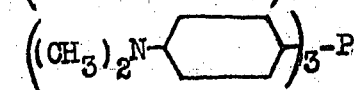
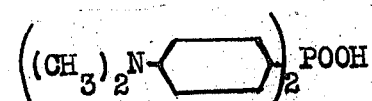
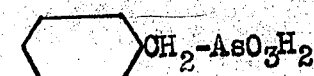
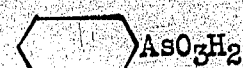
- | | |
|---------------------------------------|---|
| 1) Density $\frac{20}{4}$ | 1.004 - 1.015 |
| 2) Refractive Index N_D^{20} | 1.491 - 1.494 |
| 3) Phosphorus content | 4.5 - 5.0% |
| 4) Solubility | A 2% solution in Redring (Red band) oil must show no residue and no separation must take place on cooling to 17°C. Opalescence on cooling is permissible. |
| 5) Performance | Rotring oil containing 2% J7 when tested on the Wieland Machine shall give no seizure at a load of 1500 kg. |

6) Identification of J7

A red color appears when 5 cc. of J7 are mixed with 5 cc. of a solution of 0.5 g. of chloranil in 100 cc. of dichlorobenzene.

Development Work.

In the course of the laboratory work to find a suitable additive for break-in oil, the following compounds were tested and found unsuitable:



1.) Diphenylphosphinic acid

2.)

3.)

4.)

5.)

6.)

7.)

8.)

9.)

10.)

11.)

Diphenylphosphinic acid

Dinitrodiphenylphosphinic acid

Bis - (2-Chlorophenylphosphinic acid

- N - propylamide

- N - propylamine

- N - butylamine

- Triethanolamine

- Stearylamine

- N - butylamide

- dodecylamine

- paraffinamine

- Stearylamine

- Stearylamine

W.F. Faragher.

C.C. Chaffee.

D.A. Howes.

H. Schindler.

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FIAT FINAL REPORT NO. 478

COAL TAR CREOSOTE FOR WOOD
PRESERVATION IN GERMANY
DURING THE WAR PERIOD

REC'D. APR. 1946....

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

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 478

6 NOVEMBER 1945

COAL-TAR CREOSOTE FOR WOOD-PRESERVATION
IN GERMANY DURING THE WAR PERIOD

BY

F. W. GOTTSCHALK

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

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Personnel of Team

F. W. Gottschalk, U. S.

COAL-TAR CREOSOTE FOR WOOD-PRESERVATION IN GERMANY DURING THE WAR PERIOD

Introduction

Object

An investigation was made of the principal creosote distillation firms in Germany to establish whether there had been any improvements or technical developments for the preservative during the last several years. This report is one of a number that has been prepared on forest products; related information will be found in the following FIAT reports:

German Wood-Preservatives, other than Coal-Tar Creosote, for the War Period, by F.W. Gottschalk (1)

Wartime Operation of Pressure Wood-Preserving Plants in Germany, by F.W. Gottschalk (2)

Firms Investigated

The following companies, selected because they were the largest and most typical, were investigated:

<u>Name</u>	<u>Location</u>
Aktiengesellschaft der Kohlenwertstoff-Verbände	Bochum (near Essen)
Gesellschaft für Teerverwertung m.b.H.	Meiderich (near Duisburg)
Rutgerswerke A. G.	Rauxel-Castrop (near Dortmund)

The investigations were made during the period June 29, 1945, to October 1, 1945, by F.W. Gottschalk, U.S.

Summary

Inasmuch as several developments with coal-tar creosote during the past half-century came from Germany, and as this preservative was the principal one used in Europe prior to the war, it was anticipated that the

carried on in Western Germany at the following plants:

<u>Name</u>	<u>Location</u>
Gesellschaft fur Teerverwertung m.b.H.	Meiderich (Duisburg)
Gesellschaft fur Teerverwertung m.b.H.	Alsdorf
Gesellschaft fur Teerverwertung m.b.H.	Rauxel-Castrop
Rutgerswerke A.G.	Rauxel-Castrop
Rutgerswerke A.G.	Wanheimerort (Duisburg)
Chemische-Fabrik A. G.	Waldhof (Mannheim)
Saargruben Kokereien und Chemische Werke	Saarbrücken

Of these firms, Gesellschaft fur Teerverwertung m.b.H. and Rutgerswerke A.G., can produce up to 60 to 80 per cent of the coal-tar distillation products required in Germany; the first one is probably capable of at least 50 per cent of the total Germany output. Besides these plants there are a number in eastern Germany in Russian territory.

It was reported that the total coal-tar distilled by the two leading producers, Gesellschaft fur Teerverwertung m.b.H. and Rutgerswerke A.G., is as follows (the last firm, having plants on the Ruhr and also eastern Germany, is shown as a western and eastern group):

Tons of Distilled Coal-Tar

Year	<u>Total for Firm - All Plants</u>		<u>Total Both Firms</u>	
	Teerverwertung	Rutgerswerke West East		
1938	677,160	219,020	-	-
1939	728,271	216,425	-	-
1940	750,286	205,374	136,144	2,101,166
1941	772,130	219,601	153,154	2,267,017
1942	775,385	224,623	153,689	2,293,636
1943	806,737	234,048	156,633	2,288,728

The theoretical total distillation capacity for Gesellschaft fur Teerverwertung m.b.H., and Rutgerswerke A.G.

in the west was claimed to be 850,000 and 300,00 tons per year, respectively. However, during the last stages of the war, Allied aerial bombing reduced the production at the Meiderich plant of Gesellschaft fur Teerverwertung m.b.H. from 50,000 tons to 10,000 tons per month and at the Rauxel plant of the Rutgerswerke A.G. from 18,000 tons to 3,600 tons per month. The first of these plants only received a few scattered hits with several very large bombs which turned buildings into craters. The second plant had 250 direct hits by explosive bombs of all sizes. Yet, both distilleries were in actual operation and each expected to be able to exceed over 50 per cent by the end of July (if authorized by the Military Government and if coal-tar was available).

Source of Coal-tar

The crude coal-tar is a product of many coking plants which, in most cases, are separate from the distilleries. The tar is brought to the distilling plants by railroad tank cars, except in several cases where pipelines are used.

Distillation of Coal-tar

Distillation is controlled so as to produce the most desirable fractions according to governmental directives and, secondly, sales outlets. For the many products that can be produced from crude coal-tar, the German plants obtained from as little as 10 per cent to over 30 per cent of the total as creosote. However, during the war, the economic requirements for fuel, oil for hydrogenation, marine oils, and special lubricating oils had priority over wood preserving needs; in fact, the 1938 directive by the Reich Government that controlled distribution of creosote was strictly enforced so that by 1940 no German treating plants could receive creosote. In 1943 the total creosote supplied to German plants was 1,864 tons (about 2 per cent of prewar requirements); this 465,000 gallons may have been used for impregnating wood for marine structures. During this same year, exports were limited to 30 tons to Denmark and 103 tons to Hungary. It is doubtful whether any creosote for wood preservation will be available for many years for treatment in Germany or exportation.

Exports of coal-tar creosote by the firm of Gesellschaft fur Teerverwertung m.b.H., to the United States amounted to 38,774 tons in 1937, 34,088 tons in 1938, and

15,844 tons in 1939.

Prewar Production of Creosote

There is no reliable source for data as to the actual amount of creosote used in the years immediately prior to the war. Various German experts place their total creosoted volume at 35,000,000 cubic feet of wood in 1938 which could be considered an average year. This is mostly in the form of railroad cross-ties, and it is the production of the 35 major plants which account for at least 90 per cent of Germany's treating. Comparatively, the number of plants and treated volume for Germany in 1938 is approximately the same as for the United States in 1904. (By 1938 the 230 treating plants in the United States impregnated over 200,000,000 cubic feet of wood annually, requiring over 225,000,000 gallons of creosote.) The use of oil in Germany for 1938 was about 25,000,000 gallons (100,000 tons) of coal-tar creosote.

Specifications for Creosote

The majority of the creosote that is produced, by distillation or blending, meets the German State Railroad specifications which are as follows:

Specific gravity	- 1.04 to 1.15 at 20°C.
Distillation	- up to 150°C., max. 3% - up to 200°C., max. 10% - up to 235°C., max. 20%
Water	- not over 1%
Tar acids	- not less than 3%
Crystal free	- at 30°C.

These and other specifications (for export, etc.) were unchanged throughout the war period; no emergency standards for creosote were permitted and no treatments with pure coal-tar for wood preservation purposes were reported.

The specification for exports to the United States during the years 1937 through 1939 was as follows:

Specific gravity	- 1.05 to 1.10 at 20°C.
Distillation	- up to 210°C., max. 5% - up to 235°C., max. 25% - above 355°C., not over 20%

Water - not over 1%

Crystal free - at 15°C

Wartime Substitutes for Creosote

The elimination of creosote for wood impregnation purposes after 1940 brought about a wide-spread use of the salt-type of preservative. The German State Railway, the largest consumer of treated wood, prepared standards for zinc chloride, sodium fluoride, or Flunax. Flunax is the trade name for a chemical compound that is manufactured and sold by I.G. Farbenindustrie A.G. and Rutgerswerke A.G. It is composed of 84 per cent sodium fluoride, 8 per cent xylenol, and 8 per cent caustic soda, and was the principal wartime substitute for creosote. The formula was selected by the German State Railway as an emergency measure on the basis of tests that were started in 1923 in which several hundred thousand pine cross-ties eventually gave an average life of about 16 years.

Use of zinc chloride, Basilit, and Wolman salts during the war period for pressure treating cross-ties was also reported. In addition to the German requirements, there was a large amount of the salt preservatives exported to the other countries of Europe that were controlled by Germany.

Recent Development with Creosote

There appears to have been no significant research in Germany during the past six years which directly concerned the improvement of coal-tar creosote. Only two studies were reported. Early in the war the Technical High School at Eberswalde conducted experiments in the field of creosote conservation. None of the results were known to have been published. The general procedure was to study the treating schedules and absorption results for railroad cross-ties when first pressure-impregnated by a full-cell process with a toxic-salt preservative in water solution. A second impregnation with creosote immediately followed; this left a thin shell or zone of creosote on the outer surface of the wood and was aimed at conserving the already limited supplies of creosote. It was claimed that the oil on the surface resulted in better seasoning properties and provided extra preservative where the decay hazard was the greatest. No actual tests or production at plants was known to have been made.

In Vienna, Dr. A. Nowak was reported to be making laboratory experiments with coal-tar pitch impregnations. His process, apparently, uses a solvent which is extracted for re-use after the treatment. This or a similar impregnating process for use of certain parts of glued-up railroad cross-ties is briefly mentioned in a FIAT report "Production

and Fabrication of Glued Wood Products in Western Germany" by H. O. Fleischer and R. A. Seborg, October 2, 1945.

A new development, indirectly related to creosote for wood preservation is a continuous distillation plant for coal-tar that was erected and put into operation in 1943 at Meiderich by Gesellschaft für Teerverwertung m.b.H. The plant was a result of eight years of work in the laboratory and pilot plant. Until bombed-out, it operated on a monthly distillation capacity of 8,000 tons of crude coal-tar. Once in operation, the distillation was continuous.

Although continuous distillation is not new, several techniques appear to be of special interest. The general principle is to pre-heat the crude coal-tar and carry out the fractionation in four columns, operating under vacuum. The initial heating is at a temperature of approximately 300° to 320°C. The promoters claim better yields and economy of operation.

Briefly, the details of the operation are first to remove water and oil fractions of very low boiling points. The crude coal-tar passes through a pump to be preheated in a gas fired heat exchanger (over) to a temperature of slightly above 300°C. By holding the tar under pressure (reported to be at 45 lbs. per square inch) in the oven, vaporization is retarded. The oven is so constructed that the tubes can be readily cleaned, and the heating apparatus and piping is well insulated. The hot tar, under pressure, is piped to the distillation column in the upper floor of a 5-story building. The rate for discharge is controlled into the first of the four distillation columns; this is at a flow of about 44 gallons per minute. The first column, teerkolonne, is about 10 feet in diameter and 35 feet high; it operates at a vacuum of approximately 26 inches of mercury. The temperature of the vapors at the top of the column are about 280°C. Leaving the top of this column, these vapors enter bottom of the No. 1 oil column (280°C) and discharge from the top at approximately 115°C; the column, 30 feet high and 10 feet in diameter, fractions the anthrazenol. The No. 2 and No. 3 columns are somewhat smaller and evaporation reduces vapor temperatures at the top to 115° and 90° respectively; the vacuum in the last is maintained at about 27½ to 29 inches of mercury. Solvaywaschol and naphthalinol are removed in this phase. A final cooling condenser is for the karbolol.

The pitch that is not distilled from the teerkolonne is usually about 50 per cent of the total crude tar. This, however, was reported to vary from 50 to 55 per cent depending upon the type of tar and the method of operation.

It was claimed that the percentage of pitch is less by this process than the regular batch stills. Considerable automatic control apparatus and recording devices are used.

An English translation from a technical paper, Stetige Distillation des Vielstoffgemische Steinkohlen- teer, published in 1944, is on file at The Official Depository of the Forest Products Subcommittee, Forest Products Laboratory, Madison 5, Wisconsin. A flow sheet, Drawing 1-6077, and a list of a number of German patents and recent patent applications are also on file at The Official Depository, Madison, Wisconsin.

APPENDIX A

Coal-Tar Distillation Plants Inspected in the Course of the Investigation Together with Details Regarding Each Target

and

Related Reports

Prepared by

Field Information Agency, Technical (U. S.)

APPENDIX A

Name: Aktiengesellschaft der Kohlenwertstoff-Verbande

Nature: Firm selling coal-tar products

Location: Waldring Strasse 71, Bochum (near Essen)

Date of Investigation: July 2, 1945

Personnel: Herr Kurt Haver, Syndikatsdirektor
Herr L.R.E. Schmidt, Engineer

Production: This is a selling and marketing firm which was organized by the Reich government during the war to control the distribution of all coal-tar distilling plants in Germany. Herr Haver was formerly with Verkaufsvereinigung für Teererzeugnisse, G.m.b.H., at Essen which was a private sales firm for the largest producers of coal-tar products.

APPENDIX A

Name: Gesellschaft fur Teerverwertung m.b.H.

Nature: A firm distilling coal-tar and producing by-products

Location: Varziner Strasse, Meiderich (near Duisburg)

Date of Investigation: June 29, 1945

Personnel: Dr. Edward Moehrle, General Director
Dr. W. Fischer, Chief Engineer

Production: This is the largest coal-tar distillation and by-products plant in Germany. The crude coal-tar is received from coking plants in the Ruhr, such as August Thyssen-Hutte, A.G.. The works is slightly damaged by bombing, however, shortages of coal-tar, power and gas seem to be a greater problem. The firm operates several other distilleries in Germany.

APPENDIX A

Name: Rutgerswerke A.G.

Nature: A firm distilling coal-tar and producing by-products

Location: Rauxel-Castrop (near Dortmund)

Date of Investigation: July 3, 1945

Personnel: Herr Fehr, Managing Director

Production: This concern distills and remanufactures crude coal-tar which it receives from coking plants in the Ruhr, such as Gutschoffsangshutte. This distillery is the second largest in Germany and is one of several operated by the firm. At the present time, although badly bombed, it is operating about 30 per cent of capacity to produce road tars. The personnel advised that no new distillation methods have been developed and the only investigation for coal-tar creosote was work over 20 years ago in the field of colored creosote fractions for painting exterior woodwork.

APPENDIX A

Related Reports Prepared by Field Information Agency,
Technical (U. S.)

- (1) German Wood Preservatives, other than Coal-Tar
Creosote for the War Period, by F. W. Gottschalk
- (2) Wartime Operation of Pressure Wood Preserving
Plants in Germany, by F. W. Gottschalk

APPENDIX B

Additional Information on the General Subject of

Coal-Tar Creosote

on file at

The Official Depository

for

Forest Products Subcommittee

Forest Products Laboratory, Madison 5, Wisconsin

APPENDIX B

Additional information on the general subject of coal-tar creosote on file at The Official Depository for the Forest Products Subcommittee, Forest Products Laboratory, Madison 5, Wisconsin, is as follows:

- (1) Die Auswertung des Kokereiteers bei der Gesellschaft fur Teerverwertung m.b.H. (The Evaluation of Coal-Tars), 11 pages, September, 1934.
- (2) Auf dem Werk Meiderich erzeugte Produkte (Products Manufactured by the Meiderich Works of Gesellschaft fur Teerverwertung m.b.H.), 4 pages, 1945
- (3) Lieferungen von Impragnieröl nach Amerika (Deliveries of Impregnating Oil to America (1924-1939) 1 page, 1945
- (4) Rohbeer-Verarbeitung (Report on German Coal-Tar Distillation for 1938-1943) 1 page, 1945
- (5) Beschaffungsbedingungen für Imprägnieröle (Specifications of Eighteen Countries for Creosote 4 pages, 1945
- (6) The Continuous Process of Refining the Various Components of Crude Coal-Tar, by W. Fischer, Chief Engineer, Duisburg-Meiderich, English Translation of German paper reported in Appendix

APPENDIX C

Additional Information directly related to
The Continuous Distillation Process for Coal-Tar

on file at

The Official Depository

for

The Forest Products Subcommittee

Forest Products Laboratory, Madison 5, Wisconsin

APPENDIX C

Additional information, directly related to the continuous distillation process for coal-tar, on file at The Official Depository for the Forest Products Subcommittee, Forest Products Laboratory, Madison 5, Wisconsin, is as follows:

- (1) German Patent No. 698370, Class 12r, Group 102, November 8, 1940. Gesellschaft fur Teerverwertung m.b.H. in Duisburg-Meiderich. Verfahren zur ununterbrochenen Fraktionierung von Teer. Rudolf Kertscher and Walter Fischer.
- (2) German Patent No. 706825, Class 12a, Group 5, June 6, 1941. Gesellschaft fur Teerverwertung m.b.H. in Duisburg-Meiderich. Verfahren zur ununterbrochenen Destillation von Stoffgemischen. Rudolf Kertscher and Walter Fischer.
- (3) German Patent No. 729670, Class 12a, Group 5, December 21, 1942. Gesellschaft fur Teerverwertung m.b.H. in Duisburg-Meiderich. Verfahren zur ununterbrochenen Destillation von Stoffgemischen. Walter Fischer.
- (4) German Patent Application No. G 101012, Class 12r Entered November 28, 1939. Gesellschaft fur Teerverwertung, m.b.H. in Duisburg-Meiderich. Verfahren zur stetigen Vakuum-destillation von Teeren. Walter Fischer.
- (5) German Patent Application No. G-104798, Class 12r Entered February 3, 1942. Gesellschaft fur Teerverwertung, m.b.H. in Duisburg-Meiderich. Verfahren zur stetigen Trennung von Teeren durch fraktionierte Destillation.
- (6) Stetige Destillation des Vielstoffgemisches Steinkohlenteer (The Continuous Process of Refining The Various Components of Crude Coal Tar) Original Copy in German. 8 pages, 1944.
- (7) Lageplan (Plant Layout of Gesellschaft fur Teerver-

APPENDIX C

wertung, m.b.H., Meiderich) Original photostat.
1 sheet, 1938.

- (8) Schema des Betriebsganges (Diagram of the Operation Flow-sheet for the Continuous Distillation Plant of Gesellschaft für Teerverwertung m.b.H., Meiderich). Original photostat, 1 sheet, 1940.

C. 1

FIAT FINAL REPORT NO. 480

GERMAN WOOD PRESERVATIVES OTHER
THAN COAL TAR CREOSOTE FOR
THE WAR PERIOD

MAY 1946
REC'D.
FIC I. P. & L. S-C.

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 480

7 NOVEMBER 1945

GERMAN WOOD PRESERVATIVES,
OTHER THAN COAL-TAR CREOSOTE,
FOR THE WAR PERIOD.

BY

F. W. GOTTSCHALK

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

41 p.

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GERMAN WOOD PRESERVATIVES,
OTHER THAN COAL-TAR CREOSOTE,
FOR THE WAR PERIOD

Introduction

Object

The toxic-salt wood preservatives, including the carbolineums and fire-retardants in use in Germany during the war, were investigated to learn of their composition and application. Prior to the war, several wood preservatives (used in water solution) and the creosote carbolineums were known to have reached a fairly developed state in Germany. In addition, laboratory work had been reported for the flame-proofing of wood.

Although coal-tar creosote was by far the most common wood preservative prior to 1940, accounting for over 90% of the German wood preservative needs, the use of creosote for wood-treating purposes was absolutely restricted during the war. The information obtained by this investigation relates to several new trends for the industry in Germany. This report is one of a number that have been prepared on forest products; other phases, which have certain relationships to this report, will be found in the following:

Coal-Tar Creosote for Wood Preservation in Germany
During the War Period, by F. W. Gottschalk (1)

The Wartime Operation of Pressure Wood-Preserving
Plants in Germany, by F. W. Gottschalk (2)

Manufacturing Firms Investigated

An investigation was made of the wood-preserving products offered by the following:

<u>Firm and Location</u>	<u>Preservative</u>
R. Avenarius and Co. GauAlgesheim and Stuttgart	Carbolineum Carbol Raco FeuFau* FM-I and FM-II*
Allgemeine Holzimpragnierung G.m.b.H. Bad Kissingen and Berlin	Tanalith-U Triolith-U Bandages
Chemische Fabrik Florsheim A.G. Florsheim/Main	Barol Holzka Autogen
I.G.Farbenindustrie A.G. Uerdingen	Basilit-UA Basilit-UALL Basilit-U Basilit-N Flunax
I.G.Farbenindustrie A.G. Frankfurt/Main (Hochst)	Intravan*
Rutgerswerke A.G. Berlin	Flunax

*Fire-retardant

In addition to the foregoing, this report includes information on the Staatlichen Materialprufungsa mt, Berlin.

Investigation of these targets was made at various occasions during the period June 12 through October 5, 1945, by F. W. Gottschalk, U.S.

Summary

Although there are a great number of wood preservatives other than coal-tar creosote on the market in Germany, they constituted only a small part of preservative chemical requirements prior to hostilities. Restrictions by the Reich government for creosote during the war resulted in a widespread need for the toxic-salt preservatives. Accordingly, Flunax, Basilit,

Wolman, and zinc chloride salts were the preservatives most commonly used at the pressure treating plants. The first three of these preservatives are essentially based upon sodium fluoride. Flunax, which was prepared especially for the war conditions, probably accounted for well over 60% of the preservative required to replace creosote during the last several years; Basilit and Wolman Salts together accounted for 20%, zinc chloride accounted for 15%, and miscellaneous preservatives accounted for 5%.

The numerous other preservatives, such as carbolineum, Raco, and Antogen, were sold in small lots for brush, spray, and dip applications, as were the fire-retardants which were never extensively used. In addition, mercuric chloride has been an acceptable chemical for the steeping treatments of poles; however, the shortage of quick silver limited the availability of the mercury preservative.

Of the 700,000,000 cubic feet of industrial timber sawn annually in Germany, only a small amount is preservative treated. Various estimates place the treated volume at approximately 35,000,000 cubic feet for an average war year; this is mostly railroad cross-ties, with some poles and timbers. There is no association nor company in Germany that compiles wood preservation statistics; therefore, accurate figures on production are impossible. For the wartime years of 1942, 1943 and 1944, the volume of treated wood was apparently at slightly less than prewar rates; shortages of labor and transportation did not contribute to an increased production.

Preservatives on the Market

Besides the coal-tar creosote, Flunax, Basilit, Wolman and zinc chloride preservatives, there are a great number of similar and competitive products on the market. All these are sold in small containers for brush and spray applications, the total quantity produced annually for any one of the following preservatives probably does not exceed a few thousand pounds or gallons. Some of the products of this secondary classification which were not investigated are listed below:

<u>Firm and Location</u>	<u>Preservative</u>
Adolf Boving Mainz	Imprex
Albert Chemische Werke Wiesbaden	Holzschutz
Beer Sohne Köln	Beersol-Salz
Beratungsstelle des Arbeitskreises Berlin	Osmol
Buscher and Hoffmann Eberswalde	Carbolineum
Chemische Baustoffe G.m.b.H. Hamburg	Nefotol
Deutsche Solvay-Werke A.G. Westergeln	Xylamon
E. Merk Fabrik Darmstadt	Merk-Salz
F. Schacht K.G. Braunschweig	Holzfluid
Guano-Werke A.G. Hamburg	Sikkuid
Gustav A. Braun Cologne	Itex
H. Allendorff und Co. Leipzig	FM II*
Hans Hauenschild-Fabrik K.G. Hamburg	Lithurin
Hans Vollmer Hamburg	HV3
Hardtmann and Schwerdter Dresden	Kulba

<u>Firm and Location</u>	<u>Preservative</u>
I. G. Gipperich and Co. Hamburg	Merutox
Isolin-Werk Schwarz and Hintze Hamburg	Isolin
Joh. Ditter Frankfurt	Johedi
Rember Chemische Fabrik Hamburg	Rembertol
Stolle and Kopke Rumburg	FM III*

*Fire retardant

There is no evidence to indicate that any of the foregoing concerns, and there are many others, offered any phenomenal preservative nor is there any information as to the compositions of these preservatives. These are usually sold in the immediate area or region of manufacture. Because of the lack of oils in Europe it appears that the majority of the preservatives are water soluble.

Composition of Investigated Preservatives

In addition to the following information, considerable other data are listed in the Addendum.

Carbolineum (Avenarius):

The manufacturing firm, R. Avenarius and Co., reported the preservative to be the same as they had produced for the past 60 years; except that for the war period, the supplies of 2,000 tons per year of crude coal-tar were not available. As a substitute, a carbolineum made from brown coal-tar was sold under the trade name, Tarbil; the product was known to be inferior to the prewar carbolineum. This company, in addition to making wood preservatives, engages in a great number of small-scale but related processes, such as the

manufacture of special lubricating oils, the preparation of fruit-tree sprays, etc.

Carbol:

Sodium fluoride - 40%
Potassium dichromate - 50%
Dinitrophenol - 10%

During the war when it was not possible to obtain chromate, the preservative was made with zinc sulphate, and later the formula was revised to 90% sodium fluoride and 10% dinitrophenol. Another early war substitute was Carbol-HZ, consisting of 85% zinc sulphate and 15% mercuric chloride. The composition of the preservative, apparently, was entirely dependent upon the chemicals that were available at the time. Carbol was offered as a competitive preservative to the Wolman and Basilit salts; however, the manufacturer advised that Carbol had never been used in pressure treatments.

Raco:

Dinitrophenol - 100%

Raco was advertised for brush applications around windows and doors and for house interiors. The total sales were very small. Another preservative promoted by this manufacturer was Ravenar; it had practically no market.

Feu Fau:

Ammonium phosphate - 48%
Ammonium sulphate - 48%
Sodium fluoride - 4%

The proportion of phosphate and sulphate was about equal when chemicals were available; the recommended method for the application of Feu Fau was by brushing or spraying two or three coats. The material was only for well protected interior service. There are no records for fire tests or effectiveness in service; the product was on the market in 1938,

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but no significant sales were reported. About 1942, Feu Fau was replaced by the Reich government formula FM-I which was of about the same composition. FM-I is discussed in a later section of this report covering fire retardant treatments. The company also promoted at this time the FM-II formula; this also was known under the trade name of Antignol. Another flame proofing, Acola, was similar to FM-III. The manufacturer of these fire retardants reported that practically no sales were made and none of the flameproofing agents were used in pressure treatments.

Tanalith-U (Unsoluble):

Sodium fluoride - 26%
Sodium arsenate - 25%
Potassium dichromate - 37%
Dinitrophenol - 12%

This is the principal Wolman salt used in Germany. The preservative is prepared at one of three plants, Uerdingen, Bad Kissingen, or Dresden, as a well-mixed, dry chemical, usually in 220 pound drums. The majority of the preservative has been packaged at the Uerdingen plant of I.G. Farbenindustrie A.G., who has an agreement whereby they can manufacture and sell salt of the same composition under their trade name, Basilit. Tanalith is one of the common preservative salts used for pressure treating, for steeping, and for painting in Germany.

Triolith-U (Unsoluble):

Sodium fluoride - 55%
Potassium dichromate - 35%
Dinitrophenol - 10%

The "U", in this and other designations, refers to "unsoluble"; differentiating between an early formulation which did not contain the dichromate. German coal mines have treated almost exclusively with some form of Wolman salts in their small pressure treating plants for the past 30 years. During the war the shortages of chemicals, especially dichromate and arsenate, brought about a variety of emergency formulas. These included Triolith K, consisting of 85% NaF, 3% $K_2Cr_2O_7$, and 12% dinitrophenol. Tanalith K had a

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proportion of 50% $\text{Na}_2\text{H AsO}_4$, 30% NaF , 15% dinitrophenol, and 5% hexamethylene tetramine. Various reports indicate several lots of salt were prepared during the past few years of still other ratios of chemicals. It was claimed that the total Wolman salts sales in 1938 amounted to 1,000,000 pounds for Germany and 4,400,000 pounds for exportation. During the war, the lack of creosote increased the Wolman salts volume to about 1,815,000 pounds for Germany and 11,000,000 pounds for exportation. The report was not clear as to whether the foregoing production was Wolman salts alone or whether it included Basilit salts.

Bandages:

Several concerns in Germany furnish the bandage type of preservative. The firm of Allgemeine Holzimpragnierung G.m.b.H. claims to make 300,000 of their Wickel bandages and Zopfschutz each year for German and export requirements. The Wickel bandage consists of a strip of several layers of quilted cloth into which a quantity of dry preservative has been sewn. The bandage, usually attached to a tar-paper backing, is most commonly applied by wrapping around the base of poles in service. The Zopfschutz is the same device except that the shape is varied so that the cloth can be nailed to the top of poles or posts. The salt preservative used for this diffusion method of treatment is either Tanalith or Triolith. There have been no improvements or changes in these bandages since 1938.

Barol:

This is a coal-tar carbolineum that is similar and competitive to the R. Avenarius product. During the war, very little was manufactured due to the limitation on coal-tar.

Holzka:

Holzka is an oil plant made with a high percentage of coal-tar oils that contain considerable phenols. The colors are produced by stains; the paint has practically no colored pigment.

Antorgan:

A preservative paint made of zinc chloride, ammonium fluoride, and sodium hydroxide. It is claimed that the secret is the method of adding the zinc chloride to the solution so as finally to form zinc fluoride which is only soluble in the NaOH solution. Antorgan is made in many colors; most of the color is stain or dye obtained from Siegle und Co., Stuttgart. About 1% of the colored preservative is dye; very little pigment is added. All the Chemische Fabrik Florsheim preservatives are of very minor sales volume, probably not over 1,000 pounds annually during the war for each preservative. The major products of the firm are lubricating and other special oils.

Basilit-UA (Unsoluble, arsenate added):

Sodium fluoride - 26%
Sodium arsenate - 25%
Potassium dichromate - 37%
Dinitrophenol - 12%

This is exactly the same formula as Tanalith-U. By agreement with Allgemeine Holzimpragnierung G.m.b.H., the I. G. Farbenindustrie A.G. manufacturers preservatives for Allgemeine and can sell the same products under the I.G.F. trade name of Basilit. It appears that Wolman salts has the exclusive right to sales in the mining field, but that Wolman and Basilit salts are competitive in the field of poles, timber, and cross-ties. The UA formula is reported to have a pH of 5.0 to 6.5. During the war period the shortage of chemicals resulted in special formulations as Basilit A33, consisting of 57% NaF , 33% Na_2HAsO_4 , and 10% dinitrophenol. A large part of Basilit salts are used for pressure impregnations.

Basilit-UALL:

This is exactly the same formula as UA, but it was reported that material with this label took a different price.

Basilit-U (Unsoluble):

The formula is identical to Triolith-U; the I.G.F. company lists this U-salt as accounting for 10% of their

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Basilit sales.

Basilit-M. Extra (Wartime Special):

Sodium fluoride - 84%
Dinitrophenol - 11%
Potash or organic corrosion inhibitor - 5%

Due to the Reich government restrictions on chromate and arsenate salts, this was a special wartime preparation. This formula is essentially the same as that used for Triolith-K. At times a yellow or green dye was added to aid in determining the depth of penetration; one dye which reports indicated was not filtered by the outer wood fibers is palatinechtgrun, a standard color.

Flunax:

This preservative was largely developed by joint investigation between the German State Railway and Rutgerswerke A.G. who now manufacture the salts along with I.G. Farbenindustrie A.G.; full details are given in the Rutgerswerke A.G. section which follows.

Intravan:

Diammonium phosphate - 78%
Boric acid - 12%
Leonil S (wetting agent) - 10%

This was probably the most exploited fire-retardant in Germany; however, it suffered the fate of the other wood treating materials - that of lack of chemicals. During the war, the manufacturer, I.G. Farbenindustrie A.G., was forced to change to the Reich government formulated fire-retardants, FM-I, FM-II, and FM-III. Sales of all fire-retardants were entirely by small container lots for brushing and spraying. No significant installations were known to the Farbenindustrie officials and the only actual use that they could recall was a one coat job in the attic of a company house. This flameproofing agent was recommended as a three coat application. No test data were available, except several small "dog house" tests conducted for a local fire chief to show the comparative resistance of the flameproofed wood. It was reported that the "Locron" flameproofing manufactured by the Ludwigshafen plant of

I. G. Farbenindustrie A.G. was undoubtedly of similar composition to the Intravan and no more extensively used.

Flunax:

Sodium fluoride - 84%
Xylenol - 8%
Caustic soda (38% conc.) - 8%

This preservative was developed by the Rutgerswerke A.G. who are one of the largest distillers of creosote and who operate the largest number of wood preserving plants in Germany. Based upon a 1938 directive by the Reich government, which by 1940 entirely prevented any coal-tar creosote from being used for wood impregnating purposes, the field of acceptable salt preservatives was studied. The Wolman and Basilit salts were first considered; however, the shortage of chromate created additional complications. After comparing various earlier tests with available chemicals, the German State Railways and the German State Telephone and Telegraph authorities approved Flunax, sodium fluoride, zinc chloride, and the U-salts. The probable availability of the compounds required in Flunax and the service tests with several thousand pine cross-ties impregnated in 1923 were the main reasons for its selection; these early treated ties gave an average service life of 16 years. As a result, over 60% of the railroad cross-ties were pressure treated with Flunax instead of creosote during the war because the chemicals of the formulation were available.

Fire-retardants

Several flameproofing compounds which were offered by chemical manufacturers have already been covered in this report; these include Feu Fau and Intravan. In addition, the Reich's Labor Minister in 1937 specifically approved four fire retardant compositions as follows:

FM-I:

Diammonium phosphate - 40%
Ammonium sulphate - 55%
Leonil S (wetting agent) - 5%

FM-II:

Potash water glass (24°Bé) - 80%
Silicon dioxide - 20%

FM-III:

Sodium and potassium carbonate - 99%
Special soap (wetting agent) - 1%

FM-IV:

Milk of lime (30% conc. in suspension
in water) - 100%

These formulas were a result of earlier laboratory work by private firms, technical high schools, and governmental laboratories. Any manufacturer could sell any of the four fire-retardants providing he had approval of the Reich government and providing periodic tests confirmed the effectiveness of the product. The flameproofing agent was intended only for paint applications to wood; no consideration for treatment by pressure impregnation was given. FM-I, for example, was to be supplied as dry chemical, but mixed with water by the customer to form a 33 1/3% solution.

The required application of FM-I solution per coat was designated as 450 grams per square meter of wood surface; this is approximately one pound of solution per square yard (about 270 square feet per gallon). The regulations specifically caution against exposing the flameproofed wood to rain or dampness and inflammable oil paint. Three coats are recommended, with at least 24 hours between applications, and notations suggest renews at regular intervals and at least 20% extra chemical to account for loss during application. No data to show the comparative effectiveness of the four flameproofing formulas could be located because of bomb damage to records.

There was no record of such fire-retardants as Cellon, Gluckauf, or Minalith, which had been promoted in Germany many years ago. These apparently were not on the market before the war. The formula of Minalith was listed from several sources as approximately 84% diammonium phosphate, 10% sodium fluoride, 1% dinitrophenol, and 5% potassium dichromate; when used it was recommended that treatment was by the pressure method. Minalith was only reported to be used in the past at mines.

Cost of Preservatives

There is practically no reliable information as to the cost of the various preservatives. The cost of Wolman salts was reported to be about 1.85 marks per kilogram in 1926. Various sources of information indicated that Basilit sold from 1.00 to 2.00 marks per kilogram during the war; Wolman salts was listed at 1.75 to 3.75 marks per kilogram. No other worthwhile cost data were available.

Other Wood Preservatives

Preservatives that were reported in the German literature of many years ago, including Antinonium, Bellit, Fluoxith, Fluoran, Malenit, Malentivic's red oil, etc., have not been used or offered for at least ten years. Petroleum soluble preservatives are non-existent.

Service Records

No service data have been compiled for any wood preservative at any time during the war period. This may be partly due to the shortage of technical man-power, but it is also associated with a general lack of interest in such information. The majority of the claims for the newer, and even the older preservatives, is in the form of testimonial letters which have doubtful value.

Wood Preservation Laboratories

Only two active research laboratories were observed; one was the I.G.Farbenindustrie A.G., Uerdingen and the other was the Statlichen Materialprüfungsamt, Berlin. The first one was largely concerned with toxicity testing. The method favored by this company is as follows:

The nutrient is a disc of 1/8" thick white paper-board that has been impregnated with a 6% solution of malt extract. The board, being the same diameter as the inside of the Kollé flask, is cut into segments to permit placement, sterilized by moist heat, and then inoculated. After 14 days at a temperature of 77°F and relative humidity of at least 70% (in a humidity chamber), three test blocks are introduced. These are cut to an exact size (after oven drying at 212°F) of 1.5 by 2.5 by 5.0 cm.; one block is untreated, the second is preservative treated and

leached, and the third is treated and not leached. Duration of exposure is 4 to 6 months after which the untreated block loses about 30% of its weight. At the end of the test the exterior fungi growth is removed by scraping, the block dried at 212°F, and weighed. Data are prepared based on weights, appearance, and simple hardness tests. Pine sapwood is preferred; four fungi are used as follows: Coniophora cerebella, Lenzites trabea, Polyporus vaporius, and Merulius lacrymans.

The trend of the laboratory work of the Staatliches Materialpruefungsamt is shown by their list of publications for the Biology Department. A large number of papers concern the subject of the prevalent German beetle. In 1942 papers on termites appeared. Other subjects include corrosion of metals by preservation, the penetration of chemicals into wood, and toxicity tests. A complete list of these recent publications, including a few miscellaneous papers from other sources, appears in the Appendix.

Shipping and Mixing Salt Preservatives

The principal toxic-salt preservative, Flunax, is shipped in 110 pound multiple-layer paper bags. The chemical is mixed by adding the required weight of dry chemical to about 4 to 6 cubic meters of warm water. Agitation is usually by hand. Occasionally, there was evidence that the concentration was checked by hydrometer at the treating plants; essential specific gravity data as furnished by the German State Railroad for determinations at 20°C (68°F) is as follows:

	Flunax	NaF
1.5%	1.0114	1.0129
2.0%	1.0160	1.0183
2.5%	1.0206	1.0237
3.0%	1.0252	1.0292
3.5%	1.0298	1.0346

At no pressure treating plant inspected (60% of the major treating plants in Western Germany were investigated) was there a control or research laboratory. It was evident that technical control at the plants for creosote in the past, and the salt preservatives during recent years, was entirely lacking. As a result the plant operators and supervisors knew very little as to what they were to

accomplish and material of improper treatment was passed unnoticed. Easily determined controls such as penetration and retention of chemicals, were disregarded.

Method of Pressure Treating

Cross-ties are not acceptable for treatment by the German railroads until air-seasoned to weigh less than the following:

Pine:	37	pounds	per	cubic	foot
Beech:	46	"	"	"	"
Oak:	50	"	"	"	"

The specified method of pressure treatment for Flunax, sodium fluoride, zinc chloride, or the U-salts as outlined by the German State Railways, and which in turn was the most commonly used treating schedule during the war, was as follows:

Initial vacuum - not less than 24 inches of mercury for not less than 30 minutes. Fill retort with solution at 122° to 140°F without breaking the vacuum and maintain pressure of not under 105 pounds per square inch for 60 minutes for pine and not under 90 minutes for beech, oak, and larch.

The final vacuum should be at least 16 inches of mercury for 5 minutes. Approximate retentions to be accomplished by this schedule are:

Species	Pound per Cubic Foot		
	Flunax	NaF	ZnCl ₂
Beech	.37	.37	.75
Pine	.25	.25	.50
Oak-larch	.13	.13	.25

The above retentions of fluoride compounds are a reduction of about 33% as the result of an order by the Reichsbahn in November of 1943 as compared to the theoretical absorptions listed in specifications in 1939. On the same date of change, the zinc retentions were increased by about 20%.

CONCLUSIONS

When the German government issued directives in 1938 which prohibited use of coal-tar creosote for preservatives, the wood preserving industry re-encountered the problems of World War I. However, the knowledge gained for salt preservatives during the interim was almost valueless because the essential chemicals were not available. Having accomplished nothing in the field of seasoning, treating methods, or handling, the German wood preservation industry during World War II was about 30 years behind the American industry.

APPENDIX A

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APPENDIX B

der Abteilung Werkstoff-Biologie
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24.*Wicht	Die Prüfung von Holz- schutzmitteln auf ihre Verdunstbarkeit. (Testing Wood Protect- ive Agents as to their Volatility).	Wiss. Abh. d. D. Material- prüfungsanst. I. Folge, H.5, S.38-39, 1940.
25. Böhm	Ein Verfahren für die chemische Untersuchung von Holzschutzmitteln, die aus einem Gemisch von Fluoriden mit chrom- und arsensauren Salzen bestehen. (A Method for chemical- ly testing Wood Protect- ives, Consisting of a Compound of Arsenates and Chromates).	Wiss. Abh. d. D. Material- prüfungsanst. I. Folge, H.5 S. 40-43, 1940

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27. Schikorr	Über den chemischen Angriff von Holzschutzmitteln auf Eisen. (Chemical Influence (Corrosion) of Wood- Protectives on Iron).	Wiss. Abh. d. D. Materialprüfungs- anst., I. Folge, H.5, S. 58-68, 1940.
28. Schulze	Vergleichende Untersuchung von Leichtbauplatten und anderen Dämmstoffen auf Fäulnis-, Schimmel- und Insektenbeständigkeit 1. selbst. wandbildl. Leicht- bauplatten. (Comparative Tests on Wall-boards and other Insulating Material as their Resistance against Rot, Mold, and Insects, 1. self- supporting Wallboards).	Holz als Roh- und Werkstoff, 3, Nr. 11, S. 357-364, 1940.
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35. Becker	Untersuchungen über die Ernährungsphysiologie der Hausbockkäfer-Larven. (The Testing of the Nutrition of Wood-Beetle Larvae).	Z. vergl. Physiologie, 29, H. 3, S. 315-388, 1942.
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48. Becker	Beiträge zur Kenntnis des Hausbockkäfers. (More Information on the Hausbock beetle).	Zeitschr. f. hygienische Zoologie u. Schädlingsbekämpfung, 34, H. 6/7, S. 83-107, 1942.

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50.*Theden	Beitrag zum Verhalten der Bläuepilze: Die Feuchtigkeitsansprüche eines Bläuepilzes. Die Ursache, die ihn an Befall des Kernholzes hindert. (The Habits of Blue Fungi. Its Moisture Requirements, Reasons that Prevent it from Attacking the Heartwood).	Wiss.Abh.d.D. Materialprüfungsanstalt, II. Folge, H. 3, S.85-88, 1942.
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