Es bleiben also nur zwei Möglichkeiten:

1. Man akzeptiert die angegebene (oder eine ähnliche) Zerlegung. Dann folgt für die Primärreaktion ein asymmetrischer S-förmiger Druckanstieg, entsprechend einem seitlich asymmetrischen Geschwindigkeitsverlauf, wie er nach v. Müffling [1]) bei Kettenabbruch nach der II. Ordnung zu erwarten ist. An diese primäre Kettenreaktion schlösse sich, sie teilweise überlagernd, eine Sekundärreaktion an, für welche der Mechanismus einer Wärmeexplosion nicht von vornherein auszuschliessen, aber auch nicht zu beweisen ist. Der so konstruierte Verlauf der Primärreaktion hätte für eine Kettenexplosion viel innere Wahrscheinlichkeit für sich.

2. Der Druckanstieg mit einem Wendepunkt entspricht formal einer Reaktionsgeschwindigkeit mit negativem Temperaturkoeffizienten, mit Temperaturkoeffizient 0 im Wendepunkt. Diese Reaktion müsste unmittelbar nach dem Geschwindigkeitsmaximum (erster Wendepunkt in der Druckanstiegskurve) sich an die Primärreaktion anschliessen. Dieser Verlauf ist natürlich auch nicht auszuschliessen, aber eine Reaktion mit echtem negativen Temperaturkoeffizienten ist relativ unwahrscheinlich. Es wurde nach den Diagrammen die Temperatur des zweiten Wendepunktes bestimmt, was nur recht ungenau möglich ist, Tab. 6:

Tabelle 6

Temperatur des zweiten Wendepunktes T_w 0 abs.

Versuch	A_1	A_2	B_1	B_2	C_1	C_2	D	E
T_w	995	977	987	962	939	954	954	1040

Die Unsicherheiten in der Ablesung sind zu gross, als dass man daraus sichere Folgerungen ziehen könnte.

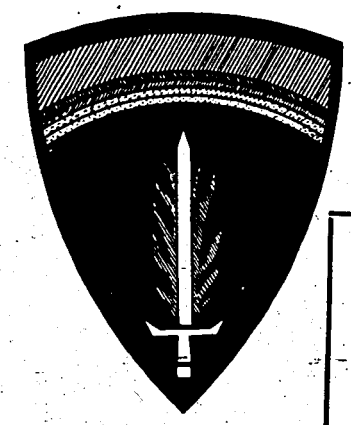
[1]) L. v. Müffling, Z. Physik 122 (1944) 787 ff.

Copy 1

FIAT FINAL REPORT 870

THE PRODUCTION OF STYROFLEX FILM

Klein, Walter A., and Lunn, John A.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 870

31 July 1946

THE PRODUCTION OF STYROFLEX FILM

BY

WALTER A. KLEIN
JOHN A. LUNN

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U. S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

This report covers the production of oriented polystyrene film called "Styroflex" starting with styrene polymer. It includes a description of the process, drawings and description of the equipment and a discussion of the properties and applications of Styroflex film.

TABLE OF CONTENTS.

I N T R O D U C T I O N

Objective:

The purpose of this investigation was to obtain complete operating data for the production of Styroflex film from Polystyrol.

Evaluation:

Norddeutsche See-Kabelwerke, Nordenham developed and during the war regularly produced film for cable insulation. The method of orientation is novel and in all probability is applicable to other types of plastics. The research group stated that other plastics, including polyethylene, polyamid, methyl methacrylate and polyvinyl chloride have been run experimentally on this equipment with promising results.

For cable insulation and for the manufacture of condensers, the maintenance of film thickness is of primary importance. Special precautions were taken thruout the operation to hold thickness tolerances to minimum limits and in the samples we saw produced, the results obtained were excellent.

No reliable information was obtained regarding the amount of rejects and scrap. We have reason to believe, however, that this percentage might average as high as 25 or 30%, and in very thin films might reach 50%. Much of this rejected material was used as a lining for aluminum foil for collapsible tubes which had a ready sale in Germany during the war but are of little interest for the United States market.

General:

For making Styroflex film there were originally seven complete extrusion and orientation units in operation at Nordenham. These were housed in seperate glass enclosures (1) to maintain constant temperatures and eliminate drafts, and (2) to avoid the toxicity of the volatiles (principally monomer) from the polystyrene. Two machines have already been evacuated for reparations.

Dr. H. Horn, who fathered the process and carried it thru the developmental and production stages was relieved of his post but joined an affiliated company, Felten and Guillaume of Cologne. Dr. Horn probably knows the process more intimately than anyone else in Germany. His article published in "Kunststoffe" BD 30 Heft 3, 1940 gives valuable supplemental information regarding the operation of the process.

RAW MATERIAL SPECIFICATION

Polystyrene was chosen for cable insulation because of the following characteristics:

1. When pure it shows excellent ageing characteristics.
2. Its plastic range makes it suitable for extrusion and orientation.
3. It has excellent resistance to moisture.
4. Its electrical characteristics are highly suitable for cable insulation or condenser insulation.

The material used was Polystyrol 111 manufactured by I. G. Farben, Ludwigshafen. No control test is employed for physical or chemical properties. The only specification for the polymer is the following.

It is to be manufactured by the continuous polymerization process to obtain greater uniformity.

Iron Content	0.00
Total Impurities	0.1% max.
Monomer Content	0.5% max. (only because of toxicity for operators)
K. value	60-62 (as determined by the Fikentscher equation)

No other materials of any type are used in the process. No plasticizer, lubricant, anti-oxidant, or stablizer is employed.

DESCRIPTION OF EQUIPMENT

A. Grinding.

An ordinary disc grinder is used, since real fineness is not required and particle size distribution is of no importance.

B. Extruder.

For extruding the Polystyrol 111 a standard, screw

type, rubber extruder built by Berstorff: Hannover is used having a 200 mm (8") screw. (See drawings 187 - Appendix 5). A novel feature is a transverse auxiliary screw for feeding the powder. This screw is in the bottom of the feed hopper, has an independent variable speed drive, having a range of 20, 40 and 80 RPM and is driven by a ½ HP motor.

A special clamp-on electrical heating element was added to the side of the hopper opposite to the discharge of the transverse feed screw because in operation this proved to be a cold point. The main screw of the extruder is driven at 5 RPM thru a gear reduction and a 5 HP, 720 RPM motor. The cylinder, head and die are of special design to meet the specific requirements of the operation. However, no special alloys or steels are used in these machines. The screw has a progressive pitch, wide at the feed end and narrow at the discharge end (See Drawing 187 - C Appendix 5).

The clearance between the screw and the cylinder is 0.1 inches. The design of the cylinder is entirely standard. The inside of the head is streamlined and the core is designed so that it can be adjusted for coaxial alignment. Between the end of the screw and the die a strainer is built in, consisting of a backing plate with a large number of drilled and surface countersunk holes (See drawing No. 187 - D Appendix 5). Various wire mesh screens can be assembled in this unit according to the film thickness required. The orifice or die opening is shaped to form an annular opening 6 cm (2.3") in diameter and 1 to 2 mm (0.04" to 0.08") wide.

The heating of the cylinder is accomplished by electrical heating elements extending to the feed end of the screw. Temperatures of the head and cylinder were measured by mercury thermometers. Both the head and die are heated with electrical band heating units, two on the head and one on the orifice. The temperatures of the cylinder, head and die are regulated manually with rheostats.

C. Spreader.

This is shaped like a parabola with the closed end rigidly attached to the core of the die. The extruded plastic tube is pulled over this unit as it comes out of the orifice so that the horseshoe spreader is entirely inside the tube.

Mounted on the periphery of the unit are small ball bearing rollers which reduce the friction of the stretched tube as it passes over the spreader. (See drawing 187 - E. Appendix 5).

The air jets on each side of the spreader and their function will be discussed under "Description of Process".

D. Trimmer, Takeoff and Windup.

Upon leaving the spreader, the doubled film is trimmed on each side by two sets of razor blades mounted on a stand in a fixed position. The trimmed sheets of film are separated at this point by carrier rolls (See drawing No. 187-A Appendix 5), and are wound up individually. The takeoff and windup mechanism present no new features. The individual sheets of film first pass over 2" highly crowned rolls to give a slight stretch in the center to compensate for intermediate shrink. The pull rolls are rubber covered and are positively driven. The windup rolls, driven by friction disc clutches, are entirely conventional.

E. Larger Orientation Units.

The question was asked as to whether this method of orientation was applicable to larger units. The management stated that a spreader 30 inches wide had been designed. This required a 14" screw and a special extruder. However, in the stress of war time it was never built. The important question is whether and accurate thickness control could be maintained in such a wide film, but the research group was optimistic about accomplishing this. It would have the obvious advantages of:

1. Higher output per machine.
2. Lower labor costs.
3. Production of wider films (which might find application for large condensers and in other fields).

DESCRIPTION OF PROCESS

The Polystyrol 111 from Ludwigshafen is reground, if the particle size is too large, to an estimated mesh size of 20 to 30.

The operation of the extrusion units is usually a continuous one, 24 hours per day, seven days per week, because of the time required to reach uniform conditions in the machine. Estimates of the period required to obtain such conditions varied from 6 hours to 20 hours.

Powder is manually dumped into the hopper and is fed to the main screw by an auxiliary, independently driven,

transverse screw. The main screw is driven at 5 RPM and the thruput of the machine is only 2 to 5 Kg. per hour depending on the thickness of the film being produced. The pressures developed in the head just behind the screen filters have been measured and vary from 200 to 250 atmospheres. The amount of stock in the hot barrel is approximately 7 Kg. so that travel thru the extruder takes from 1½ to 3 hours. Dr. Boos stated that there was absolutely no decomposition or discoloration of polymer due to this period of dwell.

The extruded tube as it is discharged from the round die is immediately stretched over the orientation unit by two men with four pairs of pliers. The film is thus stretched both laterally and longitudinally as soon as the machine is completely threaded and the tension is maintained. The doubled film then goes to take-off rolls. On the way, both edges of the flattened tube of film are trimmed with razor blades so that two separate sheets are pulled thru the takeoff unit by rubber covered pull rolls and the speed of these determines the thickness of the film. The trimmed scrap is led thru knurled rolls to waste boxes on each side. The stretch obtained in the finished film is about three to one in both directions as checked by heat shrinkage.

Perhaps the most vital section of the film path is that between the discharge side of the die and the orientation unit. As orientation starts on the stretching unit, the top and bottom segments of film are shaped in cross section like lenses. They are thin at the double edges and thick in the middle. Therefore, it is important to freeze the thin edge sections immediately, so that material will be borrowed from the plastic center portion of the lens-like sections in order to stretch the entire perimeter uniformly. This is accomplished by two air jets, one on each side, which are accurately spaced. The air opening is about 1/8" dia. and the air pressure is 2 inches of water. The proper placing of these jets and the control of the cooling which results is probably the <u>most</u> important single part of the operation.

The takeoff and windup mechanism is entirely conventional. The rolls of film are then slit to whatever width is required for cable insulation or collapsible tubes. A very nice slitting job was done for widths down to 1 mm.

Another highly important control point is the regulation of temperature in the cylinder, at the head and at the die. It has been found, also, that the mesh and number of screens used in the strainer back of the die is critical for various thicknesses of film. The three sizes of screen used are 100 mesh (bronze), 60 mesh (steel) and 20 mesh (steel).

Data covering these relationships have been collected and correlated over a period of years and is expressed graphically in Fig. 1. This is the operational "Bible" of Styroflex film extrusion machines.

For example (See Fig. 1, Appendix 5) for film 0.1 mm thick the head temperature is 160°C, the barrel temperature 145°C, two coarse mesh screens (with the axes of the wire mesh crossed) are used, the output in Kg. per hour is 4.9 and the speed in meters per hour is 89.

PROPERTIES OF STYROFLEX FILM

The physical and chemical properties of Styroflex film are summarized as follows:

Tensile Strength	approx.	700 Kg/sq. cm.
Per Cent Elongation		3-4
Compressive strength	approx.	950 Kg/sq. cm.
Sp. Gravity		1.05
Heat resistance (Martens)		60° - 70°C.
Inflammability (VDE)		High
Glow safety (VDE)		1
Water absorption 7 days		Nil
Taste and Odor		None
Resistant to:		Acids, alkalis, alcohol, mineral, animal and vegetable oils
Not resistant to:		gasoline, benzene, ether, turpentine, chlorinated hydrocarbons, esters, ketones.
DC Surface resistance		Over 3 million megohms
After 4 days at 80% Rel.Hum.		" "
After 24 hr. water immersion		" "
Volume Resistance		" "
Phase loss angle (tan δ) 1000 cycles		Less than 0.0002
Dielectric constant		2.5
Breakdown voltage	approx.	100KV/mm
Water Permeability gm/cm/hr/mm HG		0.00000003-4

Standard Sizes:

Films:

Thickness 0.01 to 0.15 mm 10% average, 15% max.
Width 1 to 250 mm.

During examination of Styroflex film it was noted that it is more brittle in a longitudinal direction than in the transverse as tested by doubling the film. This is in spite of the fact that the tensile strength in both directions is reasonably uniform. It must be recognized that an orientation method of this type is not ideal and absolute uniformity cannot be obtained by it. The directional characteristics can be changed by modifying the relationship between die size, spreader size and shape, and speed of extrusion.

An ingenious electrical device for measuring thickness has also been devised. In addition to the usual double roll micrometer which measures, indicates and records thickness they used an apparatus for electrical measurement which indicates, as the film passes between two electrodes of an air condenser the change in capacitance resulting from the change in film thickness. With this device variations of .0001 mm can be measured.

It has already been pointed out that no control test was set up for the raw material used, primarily because no competitive products were available. It was therefore a question of using the I.G.Farben material or shutting down the process. However, a very interesting control test was developed for the finished product. Originally X-ray patterns were studied but these did not show sufficient variation between good and poor products to be useful.

A very elaborate optical inspection test was worked out using polarized light to check the degree and quality of orientation. The polar angle between the longitudinal and transverse molecular axes is used as an index of the degree of stretch. A complete discussion of this test is available in an article by F. Horst Müller of Siemens and Halske A.G. under the title "Zur Physik des Styroflexes" published in 1940. Copies of this article in the original German are available under number M.C. 339, Microfilm Reel No. 100-AA Frames Nos. 111 to 135 incl. upon application to:

Office of Publication Board,
U.S.Department of Commerce,
Washington, 25, D.C.

The article is of a highly technical nature and it is hoped that interested readers will make careful translations so that none of the subject matter will be lost or modified. There is a brief outline abstract of the article in English. (Appendix 4).

COST OF POLYMER CONVERSION TO STYROFLEX

Oriented polystyrene films, made in the manner described in this report, will always be expensive because:

A. The output per machine is small.

B. The rejects, particularly in thin films, are high.

Apparently, however, the importance of the film to the cable industry is such that these high costs can be absorbed.

The cost of polymer in German marks is, of course, no criterion for polystyrol costs in the U.S. Likewise overheads, social security, workmen's compensation insurance, amortization, interest charges etc. under German accounting practice are not analagous to our own. Conversion costs, therefore, are expressed only in terms of man hours and power.

Output per machine per 24 hrs. average	= 200 lbs.
Man Hours (semi-skilled)	= 24
Foreman-Hours	3
Power consumed (Power & Heat)	192 K.W.H.
Steam consumed	0
Water consumption	negligible
Compressed air	

APPLICATIONS OF STYROFLEX FILM.

The development of Styroflex film started in 1934 and during this period many technical and mechanical obstacles have been overcome.

The following uses have been developed for the film:

1. Cable and Wire
2. Electrical Condensers
3. Collapsible Tubes

1-A Cables.

By far the largest and most important use of Styroflex was for the manufacture of high frequency cables. Coaxial cables having a solid center conductor are wrapped

helically with a transparent, thin, Styroflex tape leaving about 80% air space. Four flat styroflex wraps are then applied and the outer conductor consisting of copper tape is wound on. This in turn is covered with more insulating tapes of Styroflex and finally the outer lead sheath is extruded on.

Siemens offers a different construction using alternate layers of round cord and film for insulation and an outer conductor consisting of two half-bands with ring-like indentations for flexibility. Cables of the above types were said to be good for 4 megacycles.

For solid cables of the single conductor type the insulation was built up of many layers of Styroflex tape and covered with lead. This cable was very successful where high pressures were encountered. It is our understanding that the use of Styroflex in cable is being made the subject of a special report by the Communications Branch of FIAT.

1 - B Wire Insulation.

Styroflex tape has also been used for wire insulation with very successful results. However, unless the service is unusually difficult or the requirements abnormally rigid its cost is prohibitively high.

2 Condensers.

Over fifty tons of thin Styroflex films (0.01 to 0.02 mm) were sold annually for the manufacture of condensers particularly in the radio receiving field. Good mica sheet was almost impossible to obtain in Germany during the war and for condensers, Styroflex proved an admirable substitute. As in the case of cable, uniformity of film thickness is important. The film proved very useful in this application because of its excellent insulating qualities and because its dielectric constants are not affected by moisture. Condensers were baked after winding and the end shrinkage, where the film was unsupported, produced a waterproof barrier.

3 Collapsible Tubes.

This is an interesting war time use but has no peace time applications in the U.S. It is completely described in "German Plastics Industry" by Debell, Gloor and Goggin, Nov. 1945. It served as a method of using scrap which did not meet the specifications for electrical purposes.

General.

The principal novelty in this process lies in:

A. The orientation of polystyrene film.

B. The mechanical method of accomplishing it.

The oriented film is much more flexible than usual films from polystyrene. Its applications in the electrical field are important.

The orientation method is ingenious and if it can be applied successfully to other film forming materials it should prove to be of definite interest to manufacturers of films from plastic materials.

APPENDIX 1

LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Company	Location
Dr. Boos	Managing Director	Norddeutsche See Kabelwerke	Nordenham
Mr. Führ	Sales Manager	"	"
Dr. Menneman	Chief Engineer	"	"
Mr. Engler	Senior Director	"	"
Dir. Horn	Formerly Technical Director	" (Now unattached)	"
Mr. Kaufholz	Sales Manager	Berstorff	Hannover
Mr. Böhmer	Chief Engineer	"	"
Mr. Dünneweller	Sales Manager	Kampf	Bielstein

APPENDIX 2

LIST OF TARGETS VISITED

Name.	Location
Norddeutsche-See Kabelwerke	Nordenham
Mr. Julius Engler Dir. Heinz Horn	Nordenham
Berstorff	Hannover
Erwin Kampf	Bielstein

APPENDIX 9

BIBLIOGRAPHY

Copies of the reports, documents and microfilm listed below were transmitted to Washington D.C. Inquiries should be addressed to:

Office of Publication Board
U.S. Department of Commerce
Washington, 25, D.C.

1. Related reports published by Allied Intelligence Agencies:

CIOS Report, File No. XXIX-62, Items 9, 22
Investigation of German Plastics Plants.
FIAT Records Branch File No. TP896/P39

The German Plastics Industry. Q.M. Technical Intelligence Report by J.M. Debell, W.C. Goggin and W.E. Gloor. FIAT Records Branch File No. TP896/P26

FIAT FINAL REPORT NO. 724
Miscellaneous Chemical Processes and Plastics Machinery by Ernest W. Halbach. FIAT Records Branch File No. TP200/P1618

CIOS Report, File No. XXX-63, Item 22
Styroflex, a Plastic Produced by Norddeutsche Seekabelwerke. FIAT Records Branch File No. TP896/P48

BIOS Final Report No. 179, Items 21, 22, 31
German Cable Industry. FIAT Records Branch File No. TK5101/P534

A P P E N D I X 4

ABSTRACT OF ARTICLE "ZUR PHYSIK DES STYROFLEX"

BY

E. HORST MÜLLER

Copies of this article in the original German are available under Number MC - 339, microfilm Reel No. 100-AA Frames Nos. 111 to 135 inclusive upon application to:

Office of Publication Board
U.S. Department of Commerce
Washington, 25, D.C.

(Reprinted from Wissenschaftliche Veröffentlichungen aus den Siemens-Werken. XIX Band, 1. Heft 1940)

The report deals with "Styroflex", an oriented film of Polystyrene, and its physical, electrical and chemical properties.

In Sections 1, 2 and 3 the change of properties accomplished by orientation is related to the change in molecular structure. Lengthwise stretching, as well as double stretching, produces film having different characteristics. A correlation between degree of stretch or orientation and the optical properties of the film was determined, which showed that the refraction index can be used for determining the degree of orientation. This cannot be checked with accuracy by any other method.

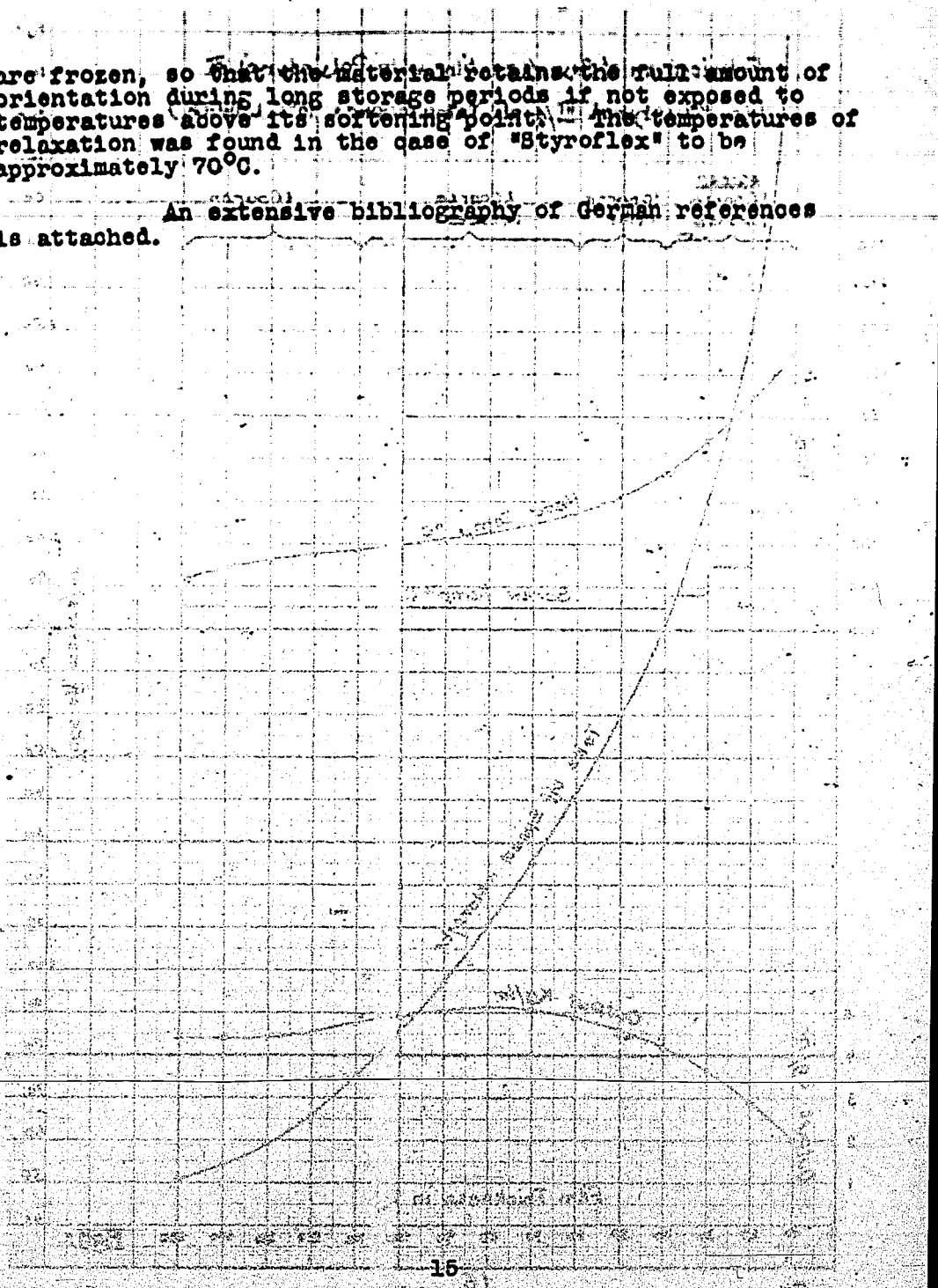
Sections 4 and 5 cover in detail the theory of molecular structure of oriented films and the best conditions for accomplishing the optimum stretch.

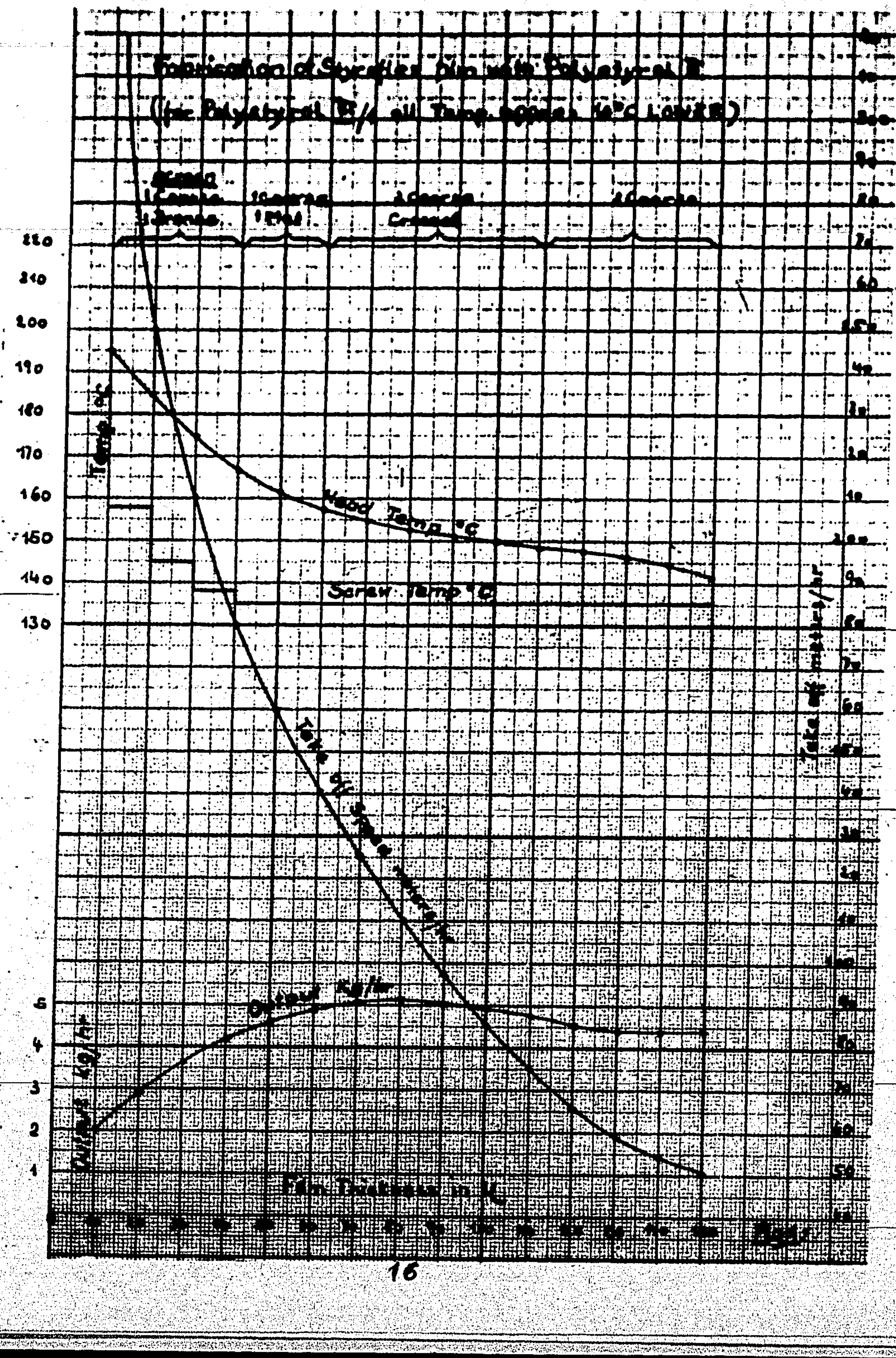
The apparatus described comprises a simple production control test. It consists of a polar microscope by means of which the degree of double refraction of a film or thread specimen can be measured.

The relation of dimensional stability to temperature and time of relaxation is discussed in detail. It is shown that in a properly oriented film, the internal forces

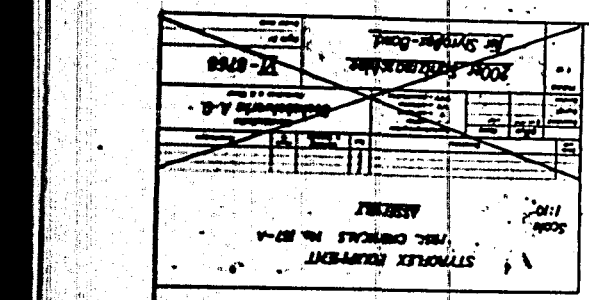
are frozen, so that the material retains the full amount of orientation during long storage periods if not exposed to temperatures above its softening point. The temperatures of relaxation was found in the case of "Styroflex" to be approximately 70°C.

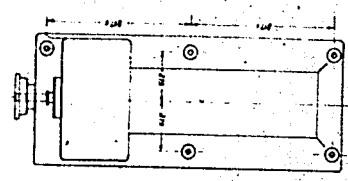
An extensive bibliography of German references is attached.

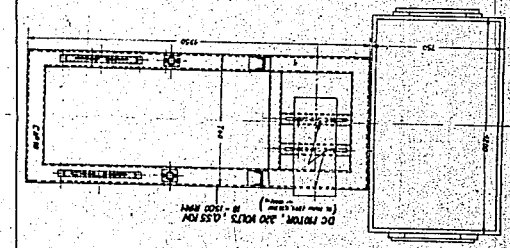


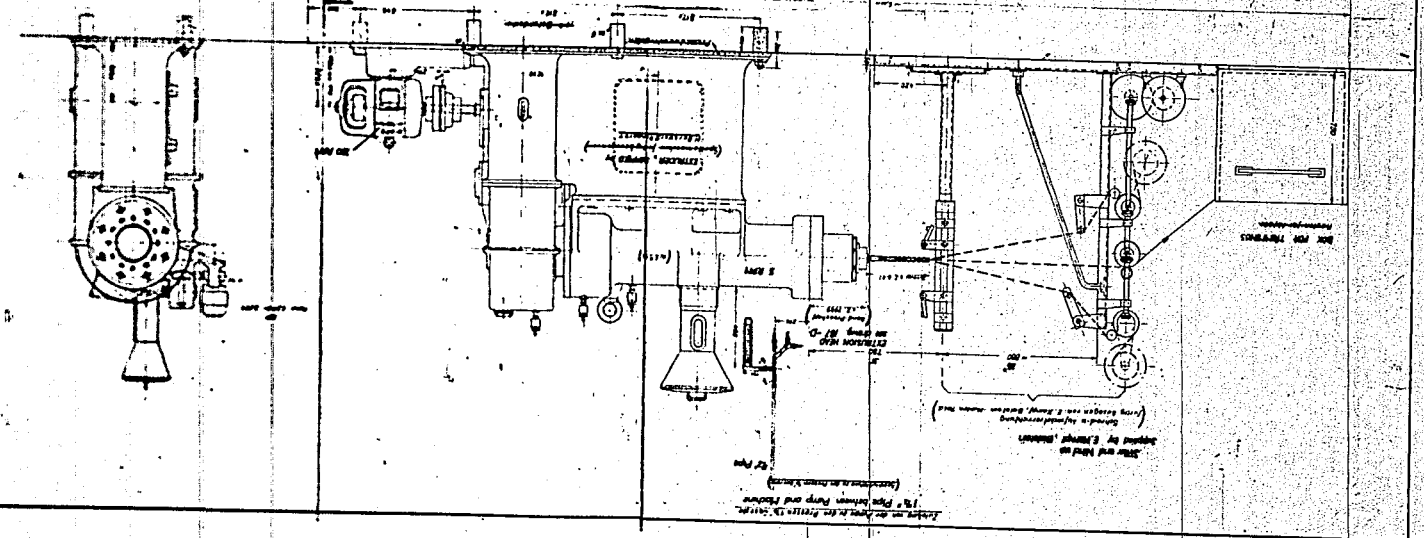


Temp °C
220
210
200
190
180
170
160
150
140
130
Head Temp °C
Screw Temp °C
Output kg/hr
6
5
4
3
2
1

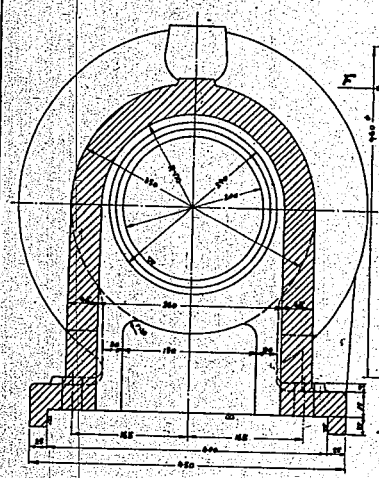


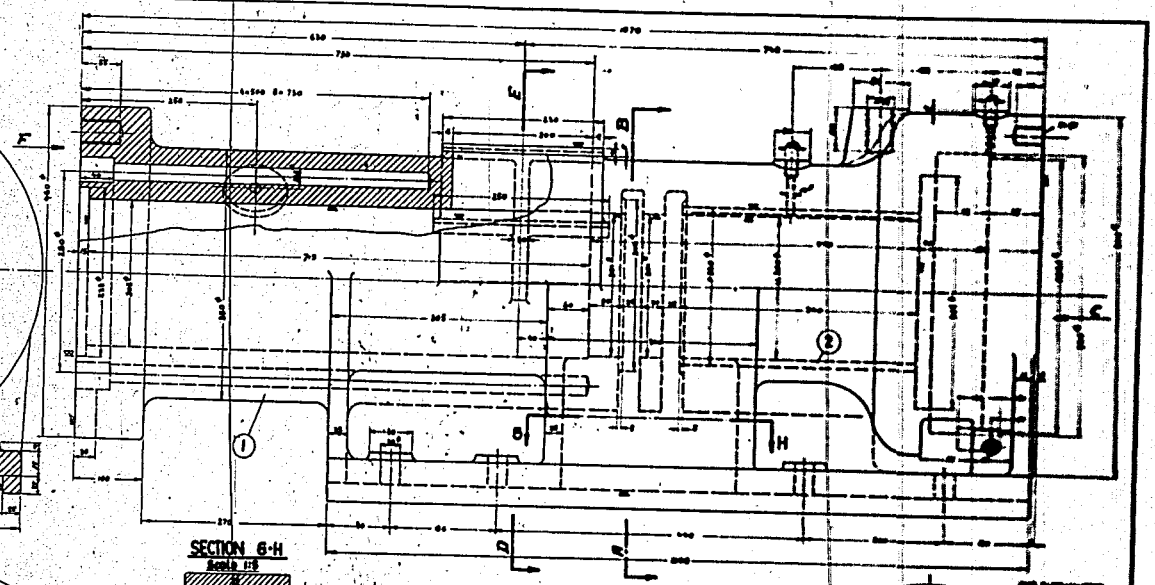




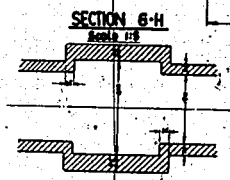


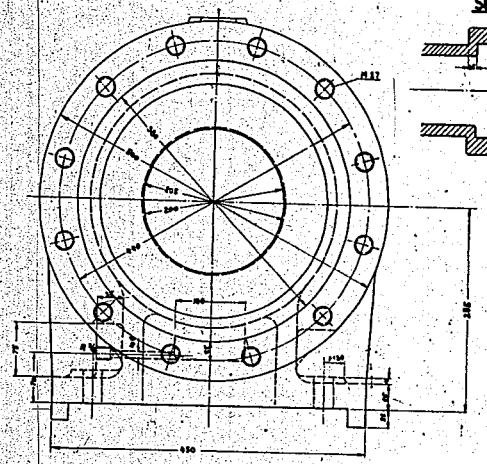
SECTION A-B



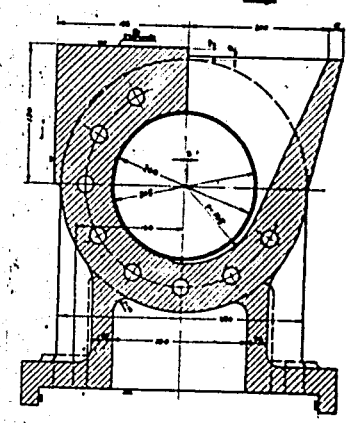


SECTION G-H

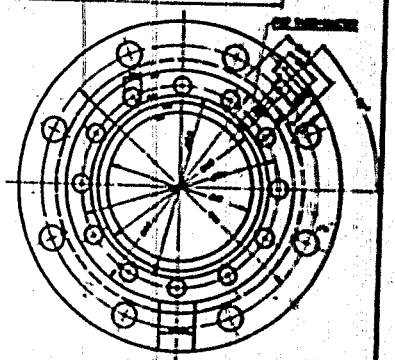




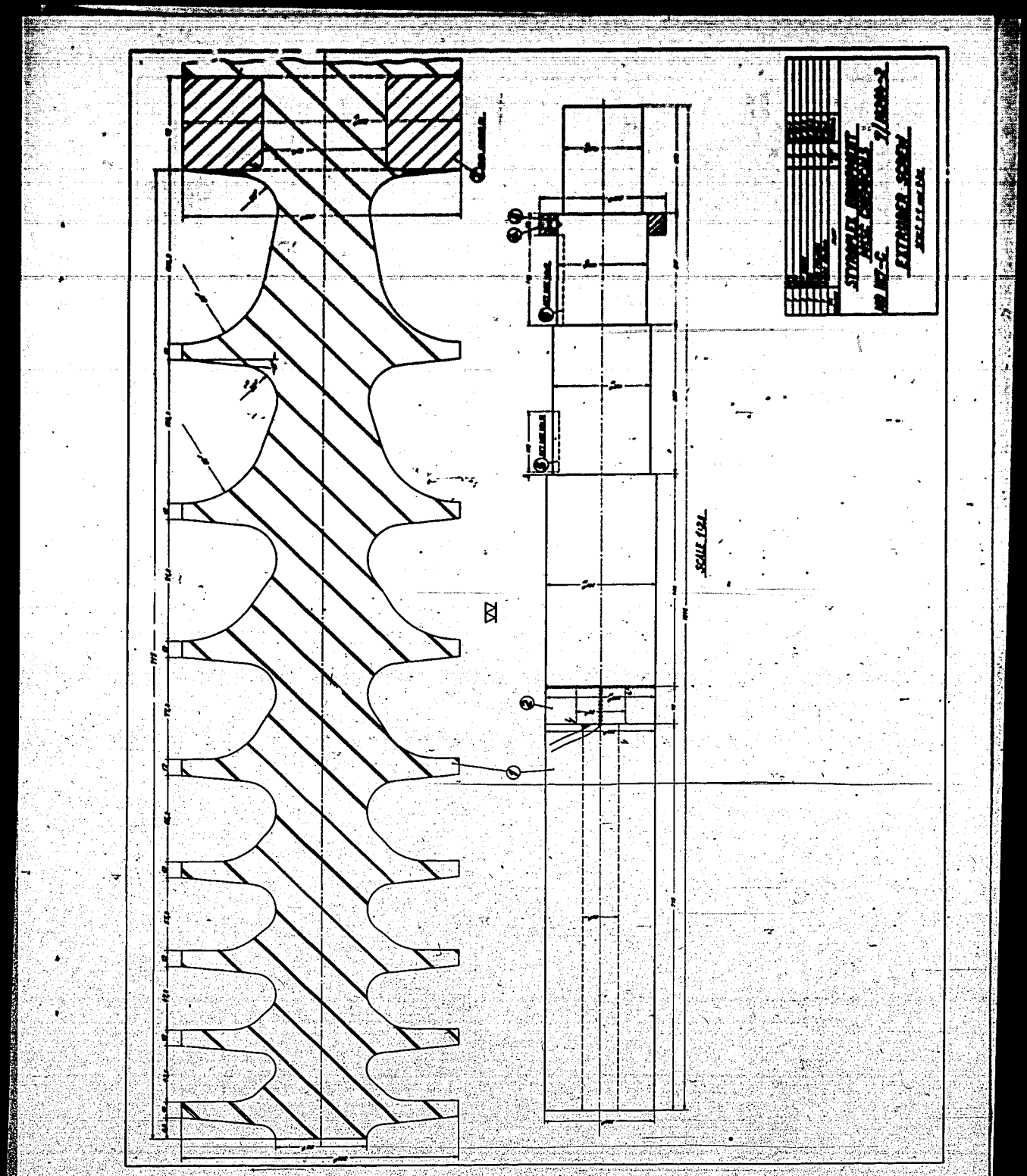
VIEW FROM 'C'

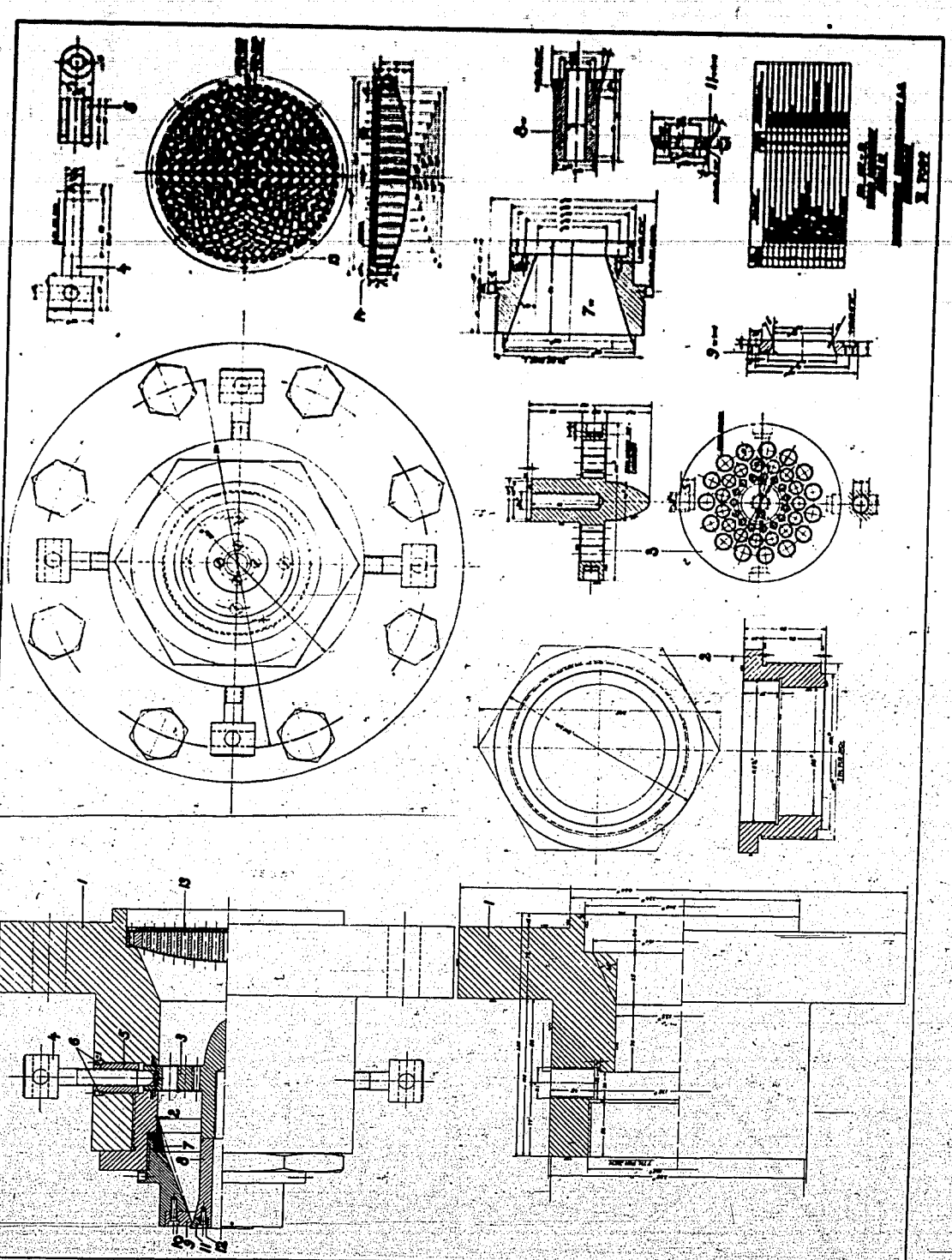


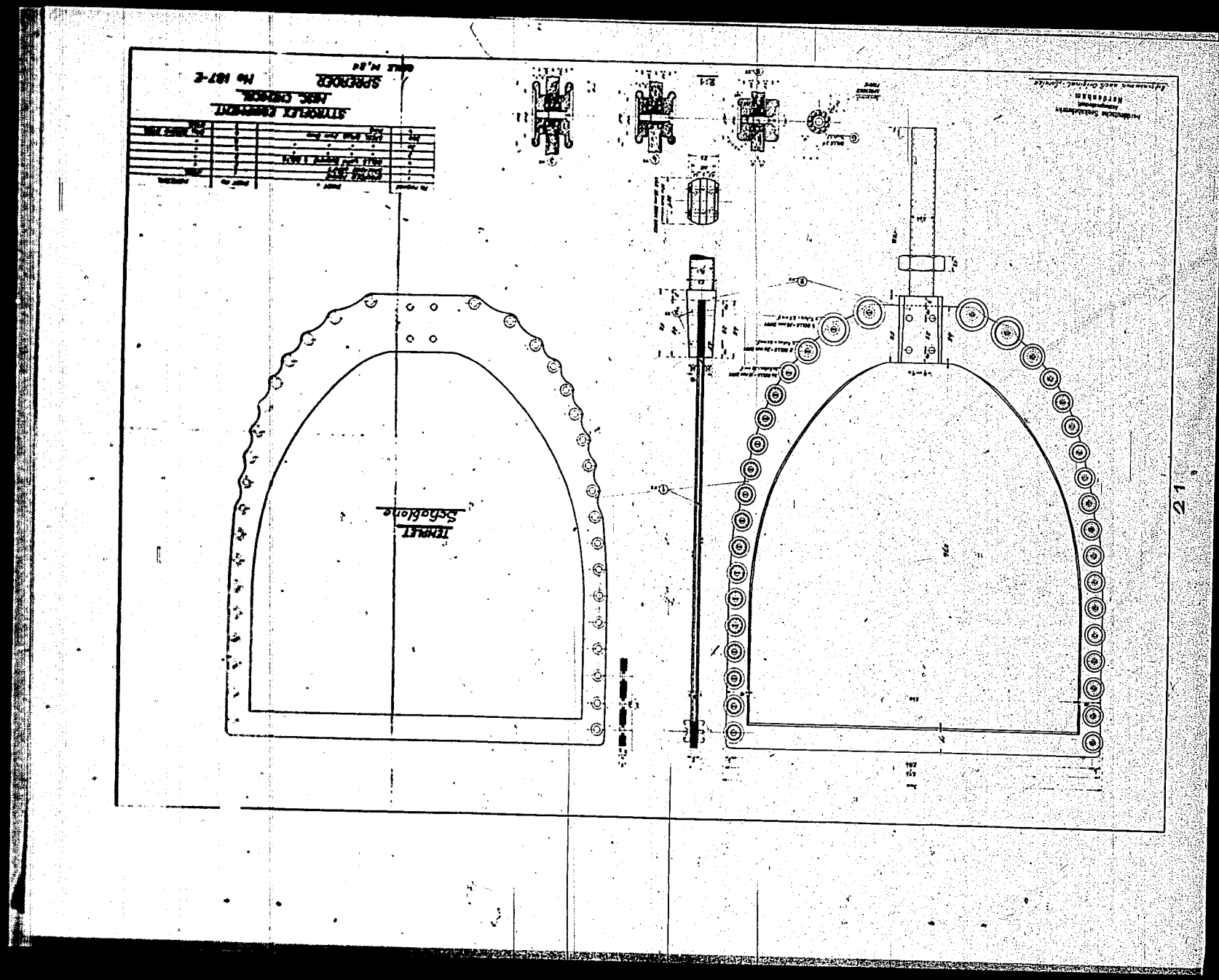
SECTION D-E



SCROLL COMPRESSOR
ASS. DRAWING NO. 117-A
EXTRUDER CYLINDER


SCALE 1:24



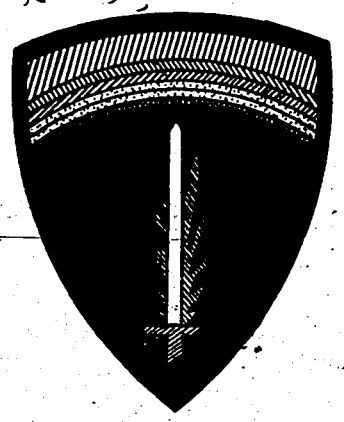


Copy 1

FIAT FINAL REPORT No. 849

ENGLISH TRANSLATION
OF
DEVELOPING USES FOR THE DISTILLATION RESIDUES FROM BUTADIENE OBTAINED BY THE REPPE SYNTHESIS

(Krzikalla (Dr.); Dürrheim ; Flickinger)



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 849 15 July 1946

ENGLISH TRANSLATION

OF

DEVELOPING USES FOR THE DISTILLATION RESIDUES FROM BUTADIENE OBTAINED BY THE REPPE SYNTHESIS

BY

GERMAN STAFF MEMBERS

I. G. FARBENINDUSTRIE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Processes of treatment of butadiene resin with sulphuric acid, its properties and uses are briefly described. The Reppe synthesis is used. The unpleasant odor due to olefinic substances can be removed by hydrogenation, also described. The most practical use of the residues (in war time), is for insulation medium T.R. In peace time use for Carboresin P. (Buna S-softener) is recommended. The work was done at I.G. Farbenindustrie, Ludwigshafen.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N.M. Elias. The abstract was prepared in the office of the Miscellaneous Chemicals Subcommittee, Industry Branch, Field Information Agency, Technical.

AUTHORS

Dr. Krzikalla
Mr. Dornheim
Mr. Flickinger
Staff members of I.G. Farbenindustrie, Ludwigshafen.

TABLE OF CONTENTS

Dr. Krs/Bm. 14th September, 1944.

DEVELOPING USES FOR THE DISTILLATION RESIDUES FROM BUTADIENE OBTAINED BY THE "REPPE" SYNTHESIS.

During the distillation of butadiene made by the Reppe synthesis about 3-4% higher boiling point, water insoluble, dark colored substance of Kp 19.25°C are left, which are not completely soluble in methanol and which have an unpleasant olefinic smell. The C-content is about 11-12%. With increasing boiling point the oxygen content is reduced. This butadiene oil most probably consists of a mixture of polymerisation products of the butadiene and of the condensation products of butyraldehyde. The hydrogepation figure is about 240, the molecular weight about 150, the S-content about 0.008%, the P-content below 0.005%, the viscosity about 12 sec/25°C. Ford beaker I". Residues to the extent of 70-80 tons a month are collected in Ludwigshafen if the B.III installation is run at full strength. +to about 20.0°(

The following is reported regarding the possibilities of its use:-

Already in 1939 Dr. Daumiller ascertained that the butadiene residue oils had a certain drying property and that furthermore the quality could be improved by treatment with a little sulfuric acid, due to the fact of the well-known resinous effect with olefines. For all that, the coloristic department would not show any interest in the products.

Owing to the fact that the collection of residue oils was increased in 1941 and the question regarding the use of it became urgent, this matter was once more taken up.

Butadiene Resin.

If one distils the residue in vacuum until nothing further comes over, there remains, always according to the age of the butadiene oil, a resinous brown residue amounting to 10-30%, which is easily soluble in benzine and which has a molecular weight of about 700 and an O-content of about 5.6%. The softening point is about 87°C (Krämer-Sarnow).

If the residue oil is boiled for 12 hours with a 2-3% concentrated sulfuric acid under reflex (oil bath about 130-140°C) and thoroughly distilled in vacuum, the resinous residue is increased to 60-70%. With this process a further resin formation due to the double bonds and the condensation of the aldehyde groups occurs, as also a separation of the water. The resin has nearly the same properties as that which is being produced without sulfuric acid. The small quantity of sulfuric acid gives the resin only a small acid figure of about 7-10, which has no disturbing influence on its use, in some cases it is also reduced to SO_2 and is driven off during the distillation. Details regarding the use of the volatile substances (about 20-30%) are given below.

The resin - called butadiene resin - has been tested by the Coloristic Department. It was proved that it was quite useful for the manufacture of exchange print varnishes for the low case-book and news print (works printing colors). It has approximately the same properties as coumarone resin. The butadiene resin was judged as useful after practical trials, but the requirements of the printing color industry, which uses solution mediums, was greatly reduced during the war and the price to be obtained did not give any special inducement. The resin was also suitable as a plasticizer for certain Buna articles and it has about the same properties as the naphtol softener. It could also be used as bonding medium for the manufacture of wood fiber plates.

Insulation Medium T.R.

In the meantime we got in touch with Dr. Graf (Oppau) regarding the use of the butadiene residue in the Chemical Engineering section and we explained its properties to him. Dr.Graf then developed an insulation medium T.R. by heating and blowing air through it. (J.71989 = O.Z. 13391) which is being used as binding medium for camouflage purposes. Owing to the fact that a great demand for camouflage colors exists during the war and that the price of Mk.45.-. per 100 kg. can be obtained for the crude residue oil without further treatment, this seemed to be the ideal solution for the possibility of using the total output of butadiene residue and so far Oppau has taken it all continuously.

Carboresin C.

Apart from this, the development of a drying oil was taken up again and it was made by Höchst, Hüls, and Schkopau from our rather variable butadiene distillation residues of the 1.3 process. It was shown that a drying oil could be obtained from the butadiene residues of the B.III installation after 6 hours of heating under reflux (about 110-130°C) with only about 1% concentrated sulfuric acid and pre-distillation up to a viscosity of about 21 sec/25°C in the Ford beaker IV of about 50-55% yield. This oil could be used very well as a binding medium, after the addition of dry materials, for inside painting and proved to be a substitute for linseed oil. This oil was reported to the Lacquer Commission under the description of Olefinic oil 14H. and received later the name of Carboresin C.. As a trial, we produced in the Alizarin Department 4 tons of Carboresin C together with 3 tons of distillate and these have proved themselves in practice and were found to be satisfactory. It was also tested for paper tube impregnation and here also it was found to be suitable.

Apart from the fact that the Carboresin is only an inferior linseed oil substitue, which in peace time could only be sold at a very low price, it has the disadvantage of an enforced by-product of about 30 tons per month of distillate of a boiling point of 130-210°C, which, owing to its content of olefinic substances, has an unpleasant smell, which makes it unsuitable for direct selling. This smell can be removed by hydrogenation, but this entails certain difficulties

Dr. Krz/Bm. 14th September, 1944.

DEVELOPING USES FOR THE DISTILLATION RESIDUES FROM BUTADIENE OBTAINED BY THE "REPPE" SYNTHESIS.

During the distillation of butadiene made by the Reppe synthesis about 3-4% higher boiling point, water insoluble, dark colored substance of Kp 19.25°C are left, which are not completely soluble in methanol and which have an unpleasant olefinic smell. The C-content is about 11-12%. With increasing boiling point the oxygen content is reduced. This butadiene oil most probably consists of a mixture of polymerization products of the butadiene and of the condensation products of butyraldehyde. The hydrogenation figure is about 240, the molecular weight about 150, the S-content about 0.008%, the P-content below 0.005%, the viscosity about 12 sec/25°C. Ford beaker IV. Residues to the extent of 70-80 tons a month are collected in Ludwigshafen if the B.III installation is run at full strength. +to about 20.0°

The following is reported regarding the possibilities of its use:-

Already in 1939 Dr. Daumiller ascertained that the butadiene residue oils had a certain drying property and that furthermore the quality could be improved by treatment with a little sulfuric acid, due to the fact of the well-known resinous effect with olefines. For all that, the coloristic department would not show any interest in the products.

Owing to the fact that the collection of residue oils was increased in 1941 and the question regarding the use of it became urgent, this matter was once more taken up.

Butadiene Resin.

If one distils the residue in vacuum until nothing further comes over, there remains, always according to the age of the butadiene oil, a resinous brown residue amounting to 10-30%, which is easily soluble in benzine and which has a molecular weight of about 700 and an O-content of about 5.6%. The softening point is about 87°C (Krämer-Sarnow).

If the residue oil is boiled for 12 hours with a 2-3% concentrated sulfuric acid under reflex (oil bath about 130-140°C) and thoroughly distilled in vacuum, the resinous residue is increased to 60-70%. With this process a further resin formation due to the double bonds and the condensation of the aldehyde groups occurs, as also a separation of the water. The resin has nearly the same properties as that which is being produced without sulfuric acid. The small quantity of sulfuric acid gives the resin only a small acid figure of about 7-10, which has no disturbing influence on its use, in some cases it is also reduced to SO_2 and is driven off during the distillation. Details regarding the use of the volatile substances (about 20-30%) are given below.

The resin - called butadiene resin - has been tested by the Coloristic Department. It was proved that it was quite useful for the manufacture of exchange print varnishes for the low case-book and news print (works printing colors). It has approximately the same properties as coumarone resin. The butadiene resin was judged as useful after practical trials, but the requirements of the printing color industry, which uses solution mediums, was greatly reduced during the war and the price to be obtained did not give any special inducement. The resin was also suitable as a plasticizer for certain Buna articles and it has about the same properties as the naphtol softener. It could also be used as bonding medium for the manufacture of wood fiber plates.

Insulation Medium T.R.

In the meantime we got in touch with Dr. Graf (Oppau) regarding the use of the butadiene residue in the Chemical Engineering section and we explained its properties to him. Dr.Graf then developed an insulation medium T.R. by heating and blowing air through it. (J.71989 = O.Z. 13391) which is being used as binding medium for camouflage purposes. Owing to the fact that a great demand for camouflage colors exists during the war and that the price of Mk.45.-. per 100 kg. can be obtained for the crude residue oil without further treatment, this seemed to be the ideal solution for the possibility of using the total output of butadiene residue and so far Oppau has taken it all continuously.

Carboresin C.

Apart from this, the development of a drying oil was taken up again and it was made by Höchst, Hüls, and Schkopau from our rather variable butadiene distillation residues of the 1.3 process. It was shown that a drying oil could be obtained from the butadiene residues of the B.III installation after 6 hours of heating under reflux (about 110-130°C) with only about 1% concentrated sulfuric acid and pre-distillation up to a viscosity of about 21 sec/25°C in the Ford beaker IV of about 50-55% yield. This oil could be used very well as a binding medium, after the addition of dry materials, for inside painting and proved to be a substitute for linseed oil. This oil was reported to the Lacquer Commission under the description of Olefinic oil 14H. and received later the name of Carboresin C. As a trial, we produced in the Alizarin Department 4 tons of Carboresin C together with 3 tons of distillate and these have proved themselves in practice and were found to be satisfactory. It was also tested for paper tube impregnation and here also it was found to be suitable.

Apart from the fact that the Carboresin is only an inferior linseed oil substitue, which in peace time could only be sold at a very low price, it has the disadvantage of an enforced by-product of about 30 tons per month of distillate of a boiling point of 130-210°C, which, owing to its content of olefinic substances, has an unpleasant smell, which makes it unsuitable for direct selling. This smell can be removed by hydrogenation, but this entails certain difficulties

and also affects the life of the contacts. It furthermore requires additional apparatus, storage, etc. The manufacture of Carboresin C. was not taken up, owing to the fact that the price did not offer much inducement and furthermore on account of its easy sale for the manufacture of insulation medium I.G. Carboresin P.

A third variation for the use of the butadiene residues was worked out in co-operation with the "Kuro" for a war purpose, which was especially urgent and important. This product which was called Carboresin P. was produced by heating for 6 hours (oil bath temperature up to 200-210°C) with about 3% concentrate H_2SO_4 under reflux and distilling up to a viscosity of about 6 min/25°C in the Ford beaker IV giving a yield of about 70-75%. It shows, apart from about 6% water, a distillate of about 20-25%, which was hydrogenated as described below. The practical tests for this product have not yet been concluded. It has, however, been ascertained that this Carboresin P. is also suitable as a plasticizer for the manufacture of Buna S-vulcanisates which would, of course, also be in great demand in peace time. The tests are being continued. It should be reported to the "Kauteko".

Hydrogenation.

Volatile substances (boiling point 65-250°C), apart from condensation water, are obtained during the distillation in the manufacture of the above-mentioned products with sulfuric acid as a condensation medium and in case of a monthly production of 80 tons of butadiene oil it would give a monthly output of about 15-20 tons of butadiene resin, about 50 tons of Carboresin C and about 16 tons of Carboresin P.

They have an unpleasant smell, owing to their very unsaturated character and can, therefore, not easily be sold for many purposes, even though they have a very good solubility. They have hydrogenation figures up to about 350, Carbonyl figures up to about 150, as also low OH-figures up to about 150 and an oxygen content of about 10-12%.

All distillates can be hydrogenated and thereby be made to lose their unpleasant smell, viz. by hydrogenation in the presence of about 1.5% Raney-nickel at 200 Atm. and 140-160°C in 75% methanol solution in the autoclave. Products having high dissolving power for fatty oils, benzene and benzol soluble resins, nitrocellulose, plastipals and Luphenes is thereby obtained.

We have made a closer study of the distillate, which is discharged in the greatest quantity during the manufacture of the Carboresin C., because we have produced 3 tons of it, as mentioned above. The colorless hydrogenation product boils at about 65-195°C at normal pressure and has an OH-figure of about 280. The Carbonyl figure was 0 and the iodine figure 4.4, however, only after at least two hydrogenations. Under an agreement with the "Laro" we have split the hydrogenation into fractions according to its dissolving power

for nitrocellulose. The first fraction up to about 125°C (about 60% of the total charge) with a flash-point below 21°C gave a good nitrocellulose solution and could be used as a general solution medium. The second fraction up to 175°C with a flash-point above 21°C (about 25% of the total charge) did not give a nitro-cellulose solution, but could still be used as a solution medium for other purposes, such as resin-lacquer and alkydal-lacquer. The substance, which boils above 175°C (about 15%) is at present unusable as a solution medium, owing to its low volatility, but could be added to the Carboresin C.

We gave instructions to the Zw-Department (Dr. Walter Schmidt) to make a closer examination of the continued hydrogenation of the largest quantity of the distillate, especially with respect to the possibility of manufacturing and the life of the catalyst. The tests were made in a 20 litre pressure gas circulating apparatus at an oven-temperature from 70-150°C and in the presence of nickel catalysts as well as copper catalysts at 160-190°C. When these temperatures were exceeded at a through-put of not more than 1 kg. per kg. contact per day, the nickel catalyst showed an immediate sudden increase of the iodine figure and the copper catalyst a great decrease of the OH-figure. The oven-temperatures had to be continuously increased at intervals of 1-5 days in order to obtain products with a J.Z. $\leq$ 5 and a OH.Z. $\geq$ 230. Fibrous silicous materials and some made alkaline with 10% MgO. were used as carriers. The life of the contacts could never be prolonged to more than 14 days. Efforts to hydrogenate in the gas phase were without success, because a complete evaporation of the material could not be obtained. There was always a residue of 15-20% in the evaporator and the hydrogenated product did not contain the C_{10}-alcohol, as described below.

We have furthermore studied the hydrogenation of the whole butadiene residue. It was executed in the autoclave with Raney-nickel in about 75% methanol solution at 200 atm. and at about 140-160°C, whereby, at the same time, a condensation takes place in addition to the hydrogenation. After the methanol has been distilled off, the hydrogenation product still has a boiling point of about 35-115°C apart from 10% distillation residue. The OH-figure of all the distilled hydrogenation mixture was about 220. The fractional distillation (1.5 kg) in the Jensen column produced approximately the following fractions:-

(1)	Boiling point	14	up to	37°C	15%	OH-figure	94.
(2)	"	"	37	" 65°C	13%	"	123.
(3)	"	"	65	" 80°C	13%	"	309.
(4)	"	"	80	" 82°C	25%	"	337.
(5)	"	"	82	" 87°C	25%	"	367.
(6)	"	"	82	" 115°C	13%	"	266.

An uniformly boiling alcohol with a boiling point at 13 mm. of 80-82°C can be distilled off in fractions 3 to 5 with a yield of about 40-45% of these total distillate. This gives the following analysis:-

	Found.	Calculated for $C_{10}H_{22}O$.
C.	76.2%	76%
H.	13.7	13.9
O.	10.2	10.08
Mol.	156	158
OH-figure	356	358

The same alcohol can also be distilled from the distillate of the Carboresin C. giving a yield of about 10-12%. The analysis proves that a C_{10}-alcohol exists, which is still unknown in the literature. As the wellknown straight-chained C_{10}-alcohols have a considerably higher boiling-point, it can be assumed that a strongly branched alcohol exists. A number of derivates habe been produced from this alcohol.

Diacetate boiling-point 13 83-84°C Saponification No. 284 (calculated 280)

Vinyl ether " " 18 81°C

Neutral Phthalic acid ester. boiling-point 2. 225-227°C. Saponification No. 250 (calculated 244)

Neutral Adipic Acid ester. boiling-point 4. 205-208°C. Saponification No. 268 (calculated 264)

Low fatty acid ester. boiling-point 2. 185-240°C. Saponification No. 277 (calculated 260)

By heating for 12 hours in the presence of alkali one obtains a C_{10} acid, boiling-point at 2 mm. 92°C SZ.330 (to 325) which is also not known in the literature. The above-named esters were tested in the coloristic department for their use as plasticizers and were found to be suitable. The value of the cold resistance, especially of the phthalic acid ester in the film, equals that produced with a good proportion of Palatinol F.

If one assumes a yield of butadiene oil residue of about 80 tons per month, a monthly production of about 30 tons of C_{10}-alcohol can be estimated; the first runnings to be used as solvents. One has, however, to reckon with difficulties regarding the life-time of the contacts during continuous hydrogenation. A further study of the manufacturing process would, therefore, be necessary. The delivery of the butadiene residue to Oppen for insulating medium T.R., which does not mean any burden for the factory, is a present the simplest solution, especially so as at present the hydrogenation capacity is very restricted.

Summary.

According to the "Reppe" process the following can be manufactured from the distillation residues of the butadiene:-

(a) By condensation with a little sulfuric acid:-

(1) Butadiene resin (Benzine-soluble resin)
(2) Carboresin C. (drying oil)
(3) Carboresin P. (Buna S-softener)

(b) By blowing through air (Oppau).

(4) Insulation medium T.R. (Binding medium for camouflage colors).

(c) By hydrogenation of the distillates which are discharged during the manufacture of items 1 to 3 or of the butadiene residues:-

(5) Solution medium.
(6) C_{10}-alcohol, which is suitable for the manufacture of softeners.

The most simple and practicable utilization for the factory at present is the use of the residues for the manufacture of the insulation medium T.R., in peace-time perhaps for Carboresin P.

Signed: Dornheim.
Flickinger.
Krzikalla.

Copy 1

FIAT FINAL REPORT NO. 489

SURVEY OF FANS AND TURBO BLOWERS

Madison, R. D.

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. 489 13 November 1945

SURVEY
OF
FANS AND TURBO BLOWERS

BY

R. D. MADISON

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

TABLE OF CONTENTS

OBJECT

The purpose of this paper is to report the investigations in Germany of those companies making fans and turbo blowers and others designing and testing same and to compare their design and construction with those in the United States.

CONCLUSIONS

(1) Prior to the war the axial flow fan had received more attention than in the United States, especially for multistage work. During the war it had received less.

(2) Except in a few instances the centrifugal fan showed no more improvement than in the U. S.

(3) Fans generally contained more blades.

(4) More use was seen made of mixed flow inlets.

(5) Backward curved blades found in more general use.

(6) More use has been made of higher speeds and steam turbine drives.

(7) Not as much interest evidenced about noise.

COMMENTS

(1) The theory of the airfoil shape for axial flow fans was first applied in Europe. Much of the work on single blades and blades in cascade was done in Germany. During the war very little testing was carried on for any fan work except for turbo-supercharges for aircraft and diesels and compressors for jet propulsion. More attention is probably paid to pivoted bladesand automatic adjustment while running.

(2) The design and proportions of centrifugal fans have become pretty well standardized. No general improvement has been noticed. Some use of stepped blades was seen. Trends, as compared with our practice are discussed below.

(3) Except in the case of the forward curved blade fan there seemed to be a larger percentage of fans with more blades than we are accustomed to use. This is particularly true of those with mixed flow inlets.

(4) More use seemed to be made of mixed flow inlets whether of the forward, radial or backward curved blade types. Since the mixed flow inlet comes under the higher specific speed types, its value with forward curved blades is questionable.

(5) While backward curved blades are much used in the United States they seem to be more prevalent in Germany especially in compressor design. This is probably due to the use of higher speeds as noted below.

(6) Since Germany has 50 cycle current and the maximum motor speed is 3000 Rpm. as compared with our 3600 Rpm. it is not fast enough for many cases requiring moderate pressures. As a result, they use step-up drives or steam turbines. It is not uncommon for speeds of 8000 or 9000 Rpm. to be used. This lends itself to backward curved blades and a smaller, better proportioned impeller in centrifugal fans and thinner, flatter blades in the axial design. In lower pressure work where we would use 1800 speed they are likely to use 3000, and the same applies. Moreover, they are more accustomed to the use of steam turbines in industry.

(7) Testing of fans for noise seems to be less prevalent than in the United States. Some work has been done during the war in the way of testing for noise on war products. Perhaps the reason for less concern is the use of a less pronounced cut-off and more blades in the impeller.

INTRODUCTION

At the outset it is hoped that those reading this report are familiar with American practice in general. The time required to survey the field and compile the findings is limited. However it is felt that by covering German practice in general the reader can make his own appraisal.

The basis of the list of plants to visit originated with a list furnished by Secretary Monroe of the

National Association of Fan Manufacturers. This list contained the names of those companies of which we had knowledge prior to 1938 but did not contain some of the largest companies. Other data from FIAT files and later German registers helped to add to this list. The fact that the German term "Kompressoren" may refer to piston, rotary or centrifugal or axial flow compressors made some visits of no value. Discussion with the personnel at fan and compressor companies helped to clarify this matter as the investigation proceeded.

No attempt was made to cover all companies making fans and blowers. However, it is hoped that a representative group, both large and small, has been contacted. Approximately 40 plants or individuals have been visited. These were scattered throughout central Germany and the western and southern parts. The northern part including Lübeck and Kiel was not visited for lack of time and the distance to cover. Nor was the eastern part, occupied by Russia, possible to visit.

The terms fans and turbo-blowers are referred to in German as "ventilatoren" and "turbo-gebläse," respectively. The latter are generally one stage with spiral housing and no diffuser. They may in some cases be 2 or 3 stage but without water cooling. Compressors are referred to as "Kompressoren" and are multistage in design and almost always water cooled. While it was not the purpose of this survey to include compressors which work has been undertaken by others (see report on Pumps and Compressors by L. P. Jehle) the fundamental principles are the same and consequently it may be beneficial if a few of the principal details are herewith included.

Also allied subjects will be touched upon as they came under the observation of the writer. This data was not sought but the products were made at the same factories that made fans and generally used in conjunction with fans.

CENTRIFUGAL FANS

Fan Blades

Forward curved blades were seen in many instances but their prevalence is less than in the United States. The wide, shallow blade type was rare (Fig. 37).

Generally the forward curved blade is deep radially and bent forward at the heel and tapered to the backplate to give stiffness (Fig. 9). In this way no tie rods are necessary. Frequently every other blade was a shorter blade and in some cases two intermediate blades of differing depths are used (Fig. 1).

Several of the forward curved blades were relatively narrow at tip. Noticeable in this respect were some mine fans with equally narrow housings and very long diffuser outlets (Fig. 14).

Straight, radial blade fans are not common. Where the performance of the straight blade type is desired the heel is usually bent forward to meet the air flow with lowered shock loss. Here again it is frequent to have every second or third blade extend downward at the hub to give stiffness. In one case of radial blade construction each blade extended to the hub and was curved to give mixed flow entrance at inlet (Fig. 2).

Backward curved blades seem to predominate both for low and high pressures. For ventilation work the blades are frequently shallow with 8 to 20 deep blades extending clear to the hub. In such cases these blades are curved forward to give disc action at inlet edge. The total number of blades vary from 48 to 64 in the larger sizes. These are often operated as exhausters without housings since the velocity pressure at discharge is low (Fig. 3). For moderate pressures as in power plant fans every other blade is sometimes continued down tangent to the hub (Fig. 4). Stiffening rings are added to backward curved blades when they are wide. For the higher pressure fans and compressors long backward curved blades predominate, with 16 to 32 in number depending on size and width at tip. In the latter case the intermediate blades may extend downward about half way from the tip (Fig. 5). A Z section is generally used on the narrower types.

No particular improvement was noted on centrifugal super-charger fans. Impellers are smaller than formerly which indicates higher speeds. Open type straight blade impeller used and carefully machined in successive stages. Back plate scalloped out between blades and blade entrance bent over hot after machine operations. Two stage fan had variable inlet vanes

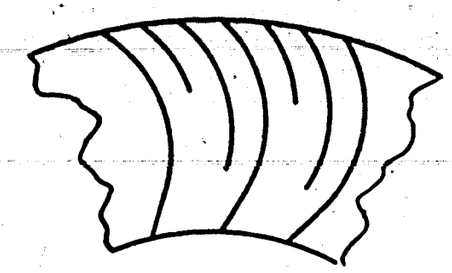


Fig. 1
Deep Forward Curved Blades

Fig. 2
Pelzer Mixed Flow Inlet
Radial Blades

Fig. 3
Meierling Backward Curved Blade Fan
For Use Without Housing

actuated by ring gear and pinions. Large underground factory at Wiesensteig machined superchargers.

Aside from tie rods, which are rarely used, two methods of stiffening blades were observed. One was twisting the blades alternately so that stresses in the flange and backplate were set up upon change in fan speed (Fig. 6). Another type used double thickness vanes with spacer and rivet at the thickened part (Fig. 7). Another variation of this is a half round riveted to the leading edge of the blade heel. This design probaoly served the purpose of taking part of the wear due to dirt in the gas.

Wearing Plates were added to fans handling dirty air but always placed on the under side of the blade instead of on the top side where the wear occurs. Localization of wear along the edge does not take place by this means but a complete reblading job is usually necessary. In one case wear was taken care of by a deposit of welding rod, called Remanit, over the greater part of the face. This is a very hard material after laid. The fan was a hot gas fan with very thick blades, flange and backplate, all about 3/4 to 1 inch.

Stepped blades were seen in several cases and for different purposes. In one case the blades were stepped back in 3 stages. Water spray in the fan inlet separated out on the blades and jumped from blade to blade causing the air to go through this mist. The blades had backward slope with very little overlap (Fig. 8). Another form was just the opposite type with blades stepped forward. This is apparently a high lift device to cause the air to better follow the general blade curvature. In a large fan of about 4 feet diam. the stagger was about 1½ inches and the overlap the same (Fig. 9). This type of stagger was seen on both forward and backward curved blades of relatively deep type, never more than one stagger or offset. The forward curved type was for mine ventilation. This fan also had a compound flange plate with the break in the slope at the same point as the blade offset.

In most cases the blades are welded to flange and backplate in the low pressure types. Only occasionally was round or flat head riveted construction used. On the higher pressure fans and invariably on compressors, countersunk riveting was employed using a large number of small rivets. These are driven cold in reamed holes.

Fig. 4
B.8 W. Backward Curved Blade Fan, Reinforced

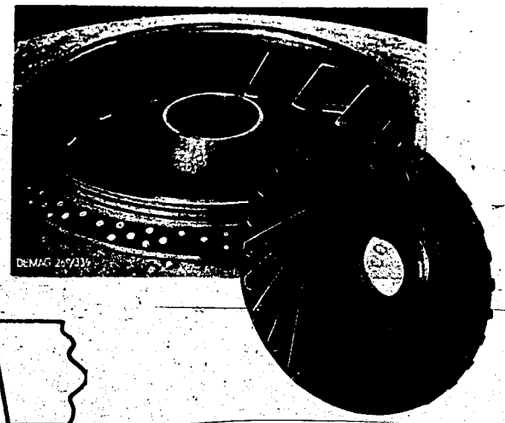


Fig. 5
Demag Turbo Compressor Blades

Fig. 6
Schiele Angled Blades

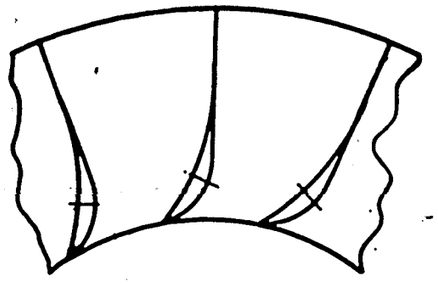


Fig. 7
Schiele Thickened Blade

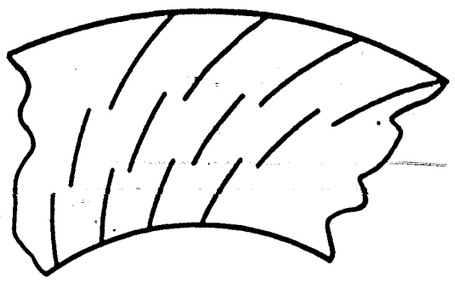


Fig. 8
Schiele Dust Washing Fan

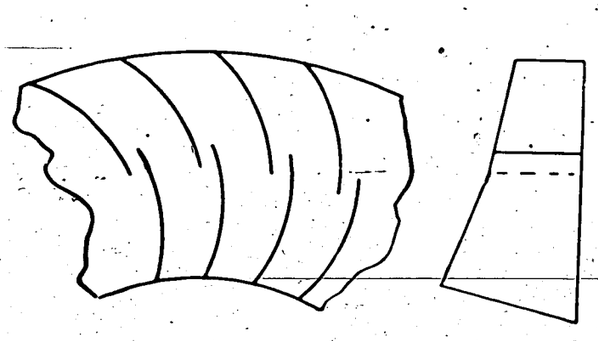


Fig. 9
W.D.G. Mine Fan

Fig. 10
BBC Compressor Blade

In these high pressure fans the blade cross-section was of Z shape to facilitate riveting. (Fig. 5) In one case the rivets were machined from the sides of the blades and cold riveted over in countersunk holes. This arrangement was for very high speeds on compressors. (Fig. 10)

Flanges

Almost invariably all fan flanges were of sloping construction. With backward curved blades and sloping flanges the air path is more likely to be completely filled. Low pressure work involving shallow flanges permits the flanges to be made of uniform thickness. High pressure work causes them to thicken the flange near the inlet to produce a light weight uniformly strong section. These are hot forged and generally so purchased. The inlet proper is another forging of thickened section, turned to form a smooth approach and riveted to the flange plate (Fig. 5). For moderate pressures some have resorted to a compound flange formed of two plates of different thickness, riveted or welded together (Fig. 11). In a few cases these elements had different slopes, giving in effect a curved path to the air. Two and sometimes three such plates were used to make a flange. Intermediate flanges or stiffening rings, were found on the wider, backward curved blade fans.

Backplates

In the lower pressure work, backplates follow the usual lines of construction, - flat plate riveted to cast iron or steel hub. Compressors have forged backplates of tapering section terminating in a thickened hub. These hubs are fastened to shaft by the conventional key. In one instance a large turbo-blower fan was fastened to the shaft by tangent keys, as indicated. (Fig. 12) Also, in one instance, small strips were placed down the outside of the backplate to act as a fan and prevent leakage. In some cases the last stage or two of a very high pressure compressor has small enough diameter impeller so that single thickness backplates are possible.

Hubs

These followed the conventional design except in two cases where the hub was of double cone steel construction with the blades welded to it. (Fig. 13) This was on a double inlet volume type fan.

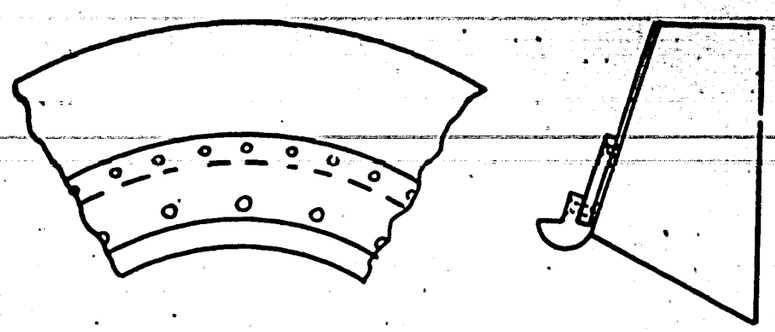


Fig. 11
Compound Flange

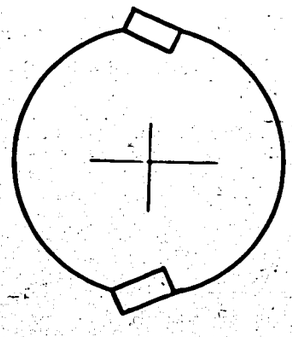


Fig. 12
Tangent Keys

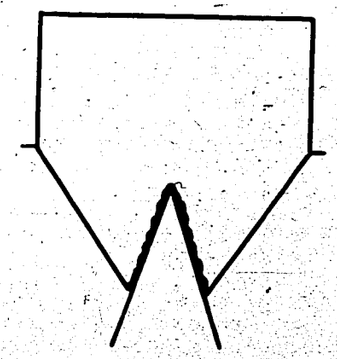


Fig. 13
Conical Hub

Housings

Housings differed very little from our own standards. Both welded and riveted constructions were seen, the latter being more prevalent in the larger sizes. Only one rolled scroll design seen. Cast iron is generally used on turbo blowers and compressors. An occasional large turbo blower was seen made of heavy steel plate, welded, but this was often due to shipping difficulties in late stages of the war.

Most low pressure fans had the usual cut-off but it was well rounded. No sharp cut-offs seen. In a few cases the cut-off was entirely absent, the scroll leading directly to the fan outlet.

Cleanout doors were provided on forced and induced draft fans where needed. Also, provision was made for removing fan wheel through a quarter section of housing. Inlet boxes are not as flat as is our custom.

Mine fans were of steel plate, riveted and reinforced (Fog. 14). The volute was an expanding spiral in width as well as depth. Reversing fans are made with the usual dampers. The exhaust damper, however, is double hinged so that the flow is favorable in both positions.

Removable scroll liners were found in some housings of fans handling dirty air. These were fitted to fans of both round and rectangular cross-section.

Dampers

Sliding blast gate dampers were found in some cases on inlet or discharge sides of fans. Multiblade dampers do not seem to be common. In some cases opposed leaf dampers (2 leaves) pivoted on one edge and operating together were found. Either hand or automatic control was possible. The accompanying cut (Fig. 15) shows a double width, double fan, with such dampers, set up for direct connection to the base of a long diverging vertical stack.

Only one type of variable inlet vane control was found on centrifugal fans. (Fig. 16) This was of conventional type, flat radially pivoted vanes, operating from outside mechanism. No fixed inlet vanes were seen.

Compressors

Several features of compressor design have been

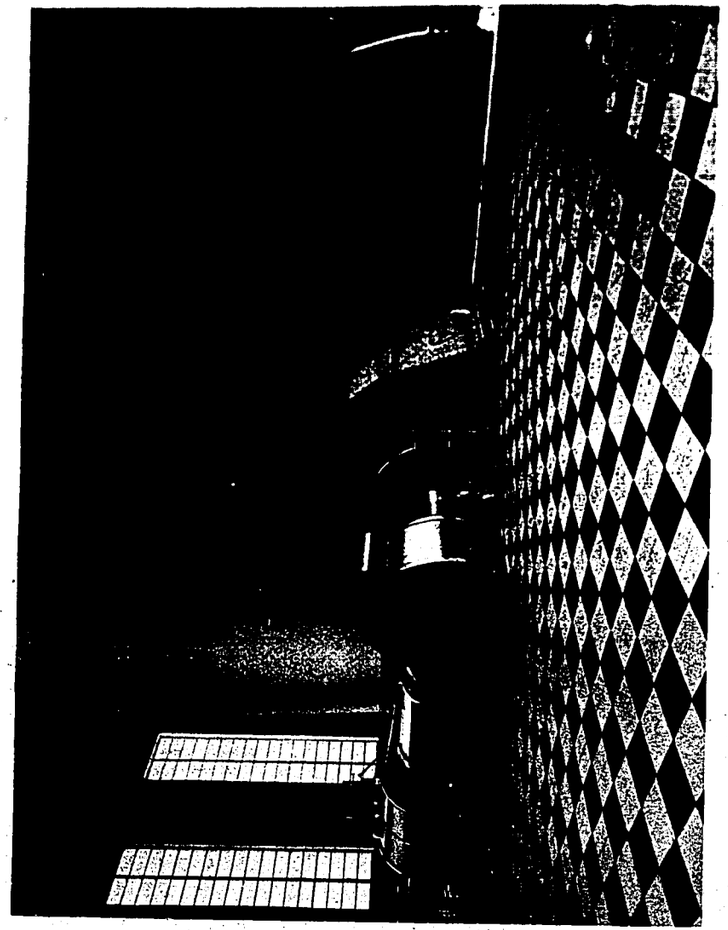


Fig. 14
WDG Mine Fan with Diverging Stack

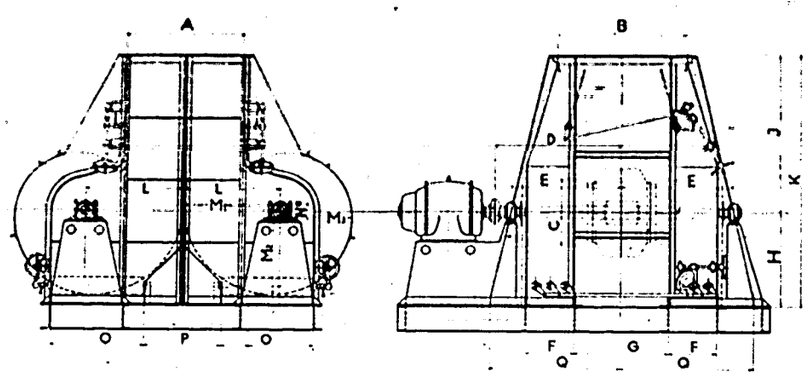


Fig. 15
B & W Double Inlet, Double Induced Draft Fan

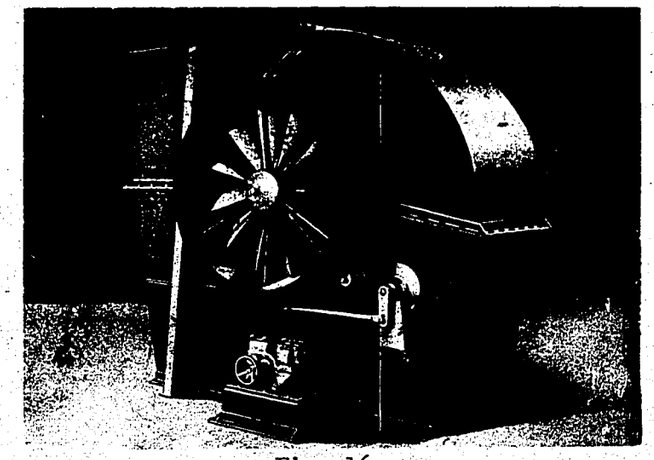


Fig. 16
B & W Variable Inlet Vane Control

treated previously. Under this heading some of the features peculiar to compressor design will be discussed.

While some German centrigugal compressors depend upon annular diffusers to transfer velocity pressure leaving the impeller to static, the majority use diffuser vanes to accomplish this purpose. In either event the width of the diffuser closely fits that of the impeller at the tip. These diffuser vanes are generally cast integral with the partition plates. In some cases the vanes are made movable and can be operated while running (Fig. 17, 18). As this greatly complicates the structure, it is used only in those instances requiring a wide range of air delivery at good efficiency. Even in such cases the vanes are not made variable for all stages but only every other one or every third one is so fitted.

In a few cases the return vanes are cast integral with the outer shell or casing (Fig. 18). In most cases, however, the diffuser and return vanes are cast in a single diaphragm and this is turned to fit into a machined groove in the casing (Fig. 19). Another variation found on large number of stages is to fit the diffuser ring to the diaphragm plate which has the return passage cast therein and this is, in turn, fitted to the casing (Fig. 20).

Most multistage centrifugal compressors under 3 stages (and some up to 6 stages) work on adiabatic compression and are not cooled. Larger numbers are water cooled and two methods are in use, internal and external. The former method (Fig. 21) is not much used and is rapidly giving way to external cooling. Internal cooling means large dismeter diaphragms with thin water channels. The air cooling is done by a great number of fins on the return air side. Since large diameters are used the diffuser is of the annular type. Moreover, the diaphragm is cast as part of the shell to facilitate water connections. This means the compressor is split horizontally as well as ~~vertically~~ between stages, the latter being held together by long bolts through the end bells. Numerous clean out doors must be provided in each stage but some cleaning can be accomplished by reversal of the water flow. Most centrifugal compressors are cooled by external water tubes of the finned type, usually one cooler for 3 stages (Fig. 22). The tubes are frequently grouped 3 to a sub-header. The cooler assembly is generally mounted vertically or inclined, with only the top header above the floor and beside the compressor. External cooling

Fig. 17
BBC Variable Diffuser Vane and Assembly

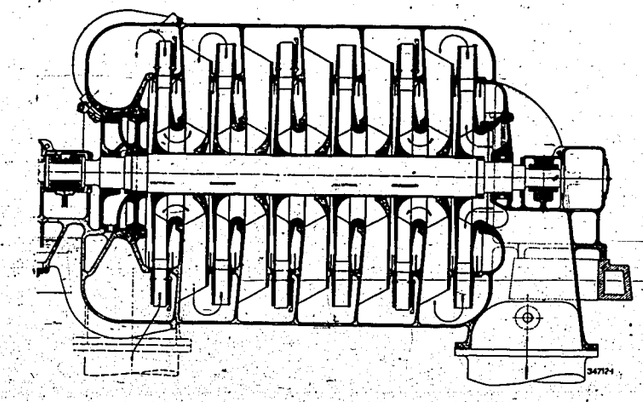


Fig. 18
BBC Compressor with Fixed and Variable Diffuser Vanes

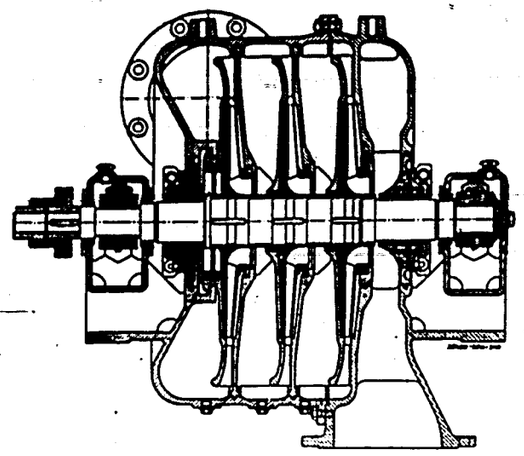


Fig. 19
Demag Three Stage Turbo Blower

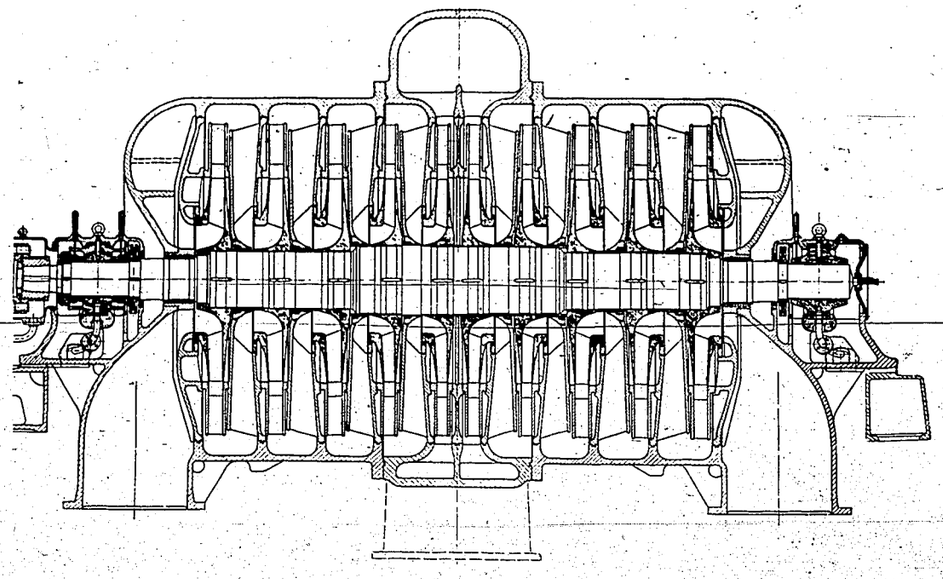


Fig. 20
G.H.H. Double Flow Compressor

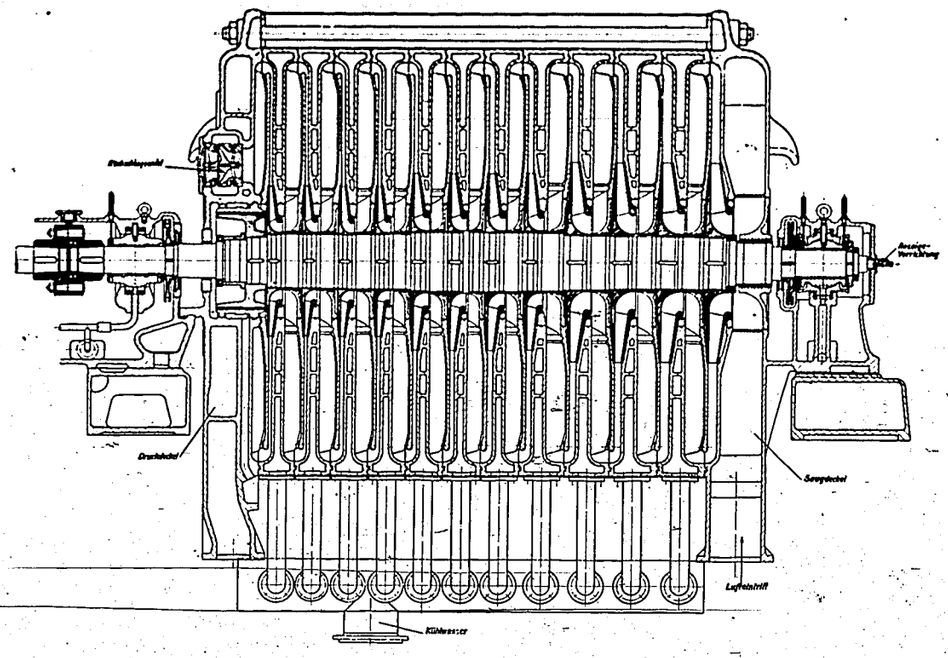


Fig. 21
G.H.H. Internal Water Cooled Compressor

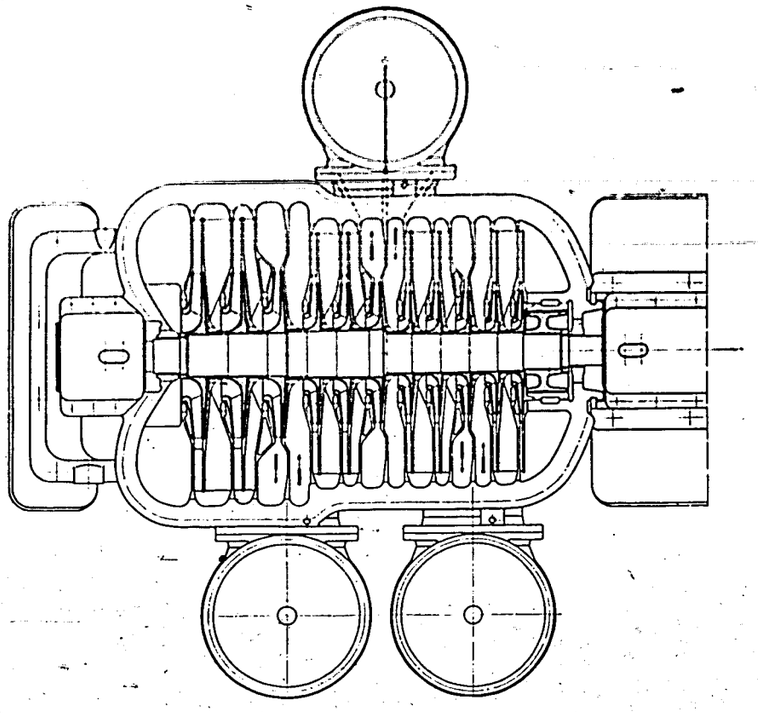


Fig. 22
G.H.H. External Water Cooled Compressor

has the advantage of shorter bearing centers for the compressor and smaller diameter shell as well as simplification in accessibility.

Short labyrinth seals (Fig. 23) are supplied on each side of each impeller and a more elaborate type of seal (Fig. 24) on the balancing piston. In one case, a further seal was supplied on the side of the balancing piston to aid in correcting for change in thrust under varying load. Slight end play is needed to accomplish this automatically.

Regulation

Regulation of flow through a compressor is accomplished in many ways, primarily to suit the needs of the application. It is invariably tied up in most cases with that portion of the pressure curve to the left of the crest, called the surging or pumping range. No attempt will be made to go into detail as to the automatic controls for this purpose. Much will be found in the catalogs and papers filed with the original of this report. However, a brief outline of the methods found in Germany may be of interest:

(1) Variable speed. The steam turbine is by far the most used means for variable speed. Slip ring motors are not much used in the larger sizes. D.C. motors are only used on board ship. There is a system called the Scherbius system (used by BBC) employing an induction motor as the main drive. A 3 phase commutator machine is connected to the rotar circuit of the induction motor. The slip energy in this system which would normally be lost in heat is taken up and converted to useful work on the shaft.

(2) Constant speed - Throttling. This is one of the simplest controls. Throttling is on the suction side of blowers and on the discharge side of exhausters.

(3) Constant speed - Cut-out. This is featured by Demag for very light loads to prevent surging. The discharge is cut off from the load and fan opened to atmospheric pressure. At the same time the suction is throttled. It comes on again when the load demands it. This reduces the no-load horsepower because of the lighter density of air in the machine.

(4) Constant speed - Blow off. This is a device to

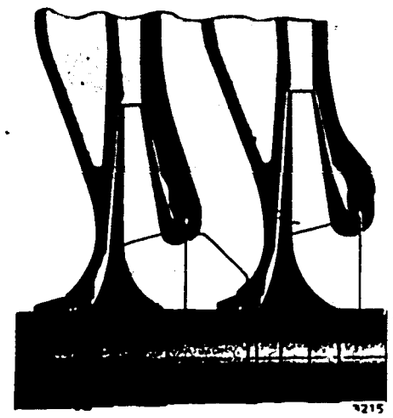


Fig. 23
Demag Fan Seals

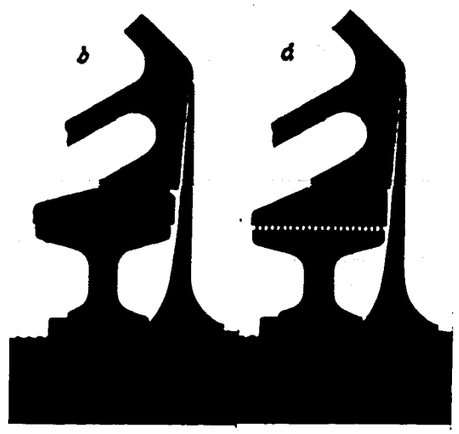


Fig. 24
Demag Balance Seals

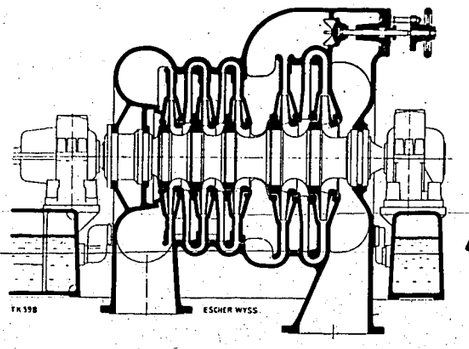


Fig. 25
Escher Wyss Compressor
with By-Pass

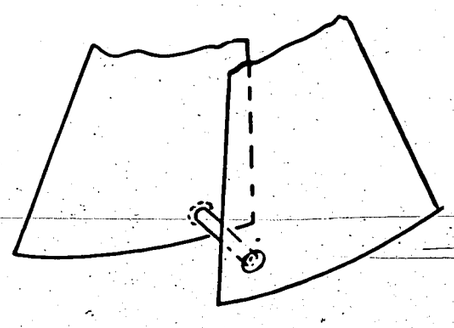


Fig. 26
Disc Fan with Tie Rivet

prevent surging for small capacities. A valve in the discharge allows excess volume of air to leak to atmosphere. The compressor always operates to the right of the surge point. The difference in volume between this amount and that required, leaking off.

(5) Constant speed - By pass. (Fig. 25) This is a means of regulation by externally by-passing some of the stages.

(6) Constant speed - Movable diffusers. This is another form of throttling much used by BBC and is primarily used to keep up good efficiency over a wide range of operation.

(7) Constant speed - Power Recovery. This is a device used by BBC on axial flow compressors. There is a sub-stage fan ahead of the regular first stage and this is normally throttled off. When the compressor capacity drops below the surging point, the excess air required to prevent this is by-passed to the inlet of the sub-stage fan. Part of the energy in the otherwise blow-off waste air is put back on the shaft through the sub-stage fan acting as a turbine.

AXIAL FLOW FANS

Aside from the common disc fans, axial flow fans divide themselves into two general classes (1) low pressure, single stage type and (2) high pressure, multistage type. The low pressure disc type favors flat blades. In the larger sizes the number of blades is sufficient to overlap and be stayed to each other at the tips by spacers (Fig. 26). In two cases a unique but crude looking arrangement was seen with each blade consisting of strip metal bent into a close V shape, twisted for variable pitch and fastened to the hub at the ends (Fig. 27).

Single Stage

Two or three types were seen. The single stage generally differs from multistage because it is convenient to use higher lift sections. Normally this would cause more short circuiting of the air over the tip of the blades but when built as a velocity type with long diffusers and discharge guide vanes, the clearance at blade tip is not so important.

One such fan for power plant use had 8 blades of

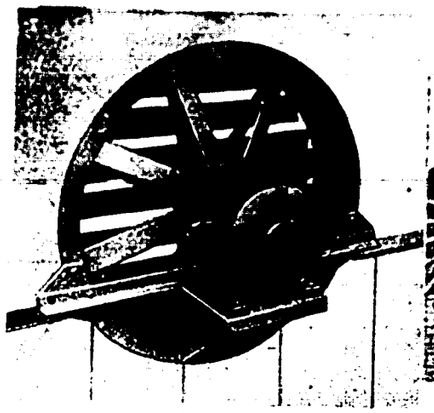


Fig. 27
Meierling Double Disc Blades

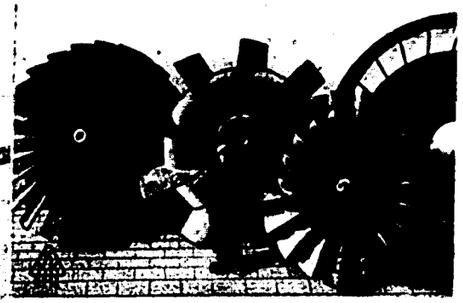


Fig. 28
K.K.K. Axial Flow Fans

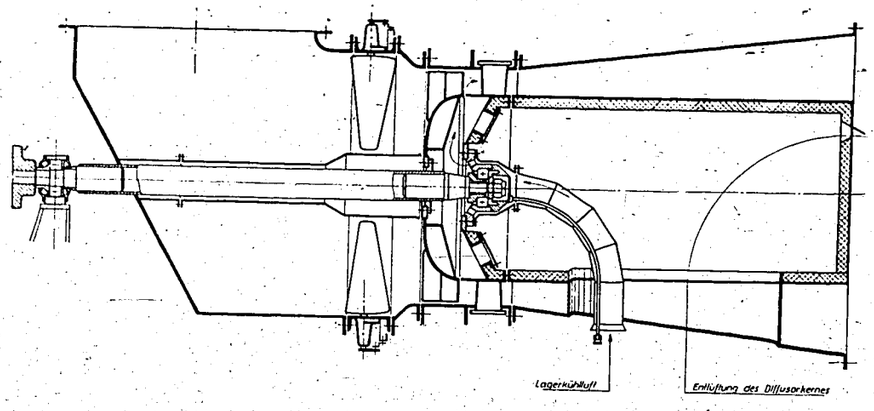


Fig. 29
K.K.K. Axial Flow Fan with Variable Inlet Vanes
and Air Cooled Bearing

thick airfoil section with considerable camber and about 40% hub. Housing had elbow entrance with long difuser outlet and diffuser vanes. The fan shaft extended through casing and was coupled to motor by floxible coupling.

Another type (Fig. 28) also used for power plants consisted of many single thickness blades (12 to 24) curved and welded to a rounded hub but extending well down toward the center. These were generally 60 to 70 percent hubs with long diffuser vanes of slight curvature. When used for hot gases, the enclosed bearing was ventilated by a fresh air duct and discharging into diffuser by natural fan draft (Fig. 29). The fan blades were hot forged to produce a thinner section on leading and trailing edges.

Another variety of this fan was to have stepped blades (Fig. 30) to give higher lift values than with one continuous curve. Generally the two blades were tied together at the tip for stiffness.

A variable inlet vane (Fig. 31) was used with these types of fans for regulation. The air rotation could be either with or against rotation depending on the blade setting. The vanes were radial, large in number and without central support, two bearings outside the air flow forming the pivot.

The fan blades and regulating vanes were made on Schicht Patents: Nr. 633155 May 6, 1933, Nr. 713617 March 12, 1937, Nr. 722424 April 16, 1942.

Two interesting wind tunnel fans were seen at the L.F.A. laboratories in Brunswick. The blades of these fans were of hollow steel construction reinforced longitudinally and transversely with welded in ribs. The single stage fan was about 30 percent hub with diffuser vanes. The two stage fans were about 40 percent hub with the diffuser vane for the first stage acting as contravane for the second. The single stage fan replaced one formerly of wood. Light gauge metal extensions had been added to the tips to reduce clearance. Both of these fans had blades pivoted and locked to their hubs but could be changed slightly if desired. A similar fan, but with lighter hub construction was seen at one of the manufactures plants (Fig. 32).

A single stage super-sonic model of axial flow design has been tested by Mr. Encke at the AVA laboratory in Göttingen. The wheel was destroyed and no further testing has been done. However, the blade shape is of interest because the leading edge was not rounded as an ordinary airfoil, but long and slender, tapering to a point. The space

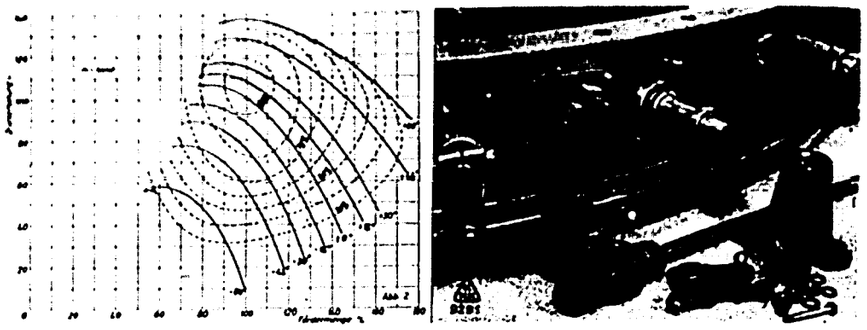


Fig. 31
K.K.K. Variable Vane Control

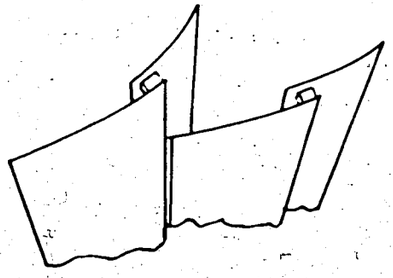


Fig. 30
K.K.K. Stepped Blades (Schicht)

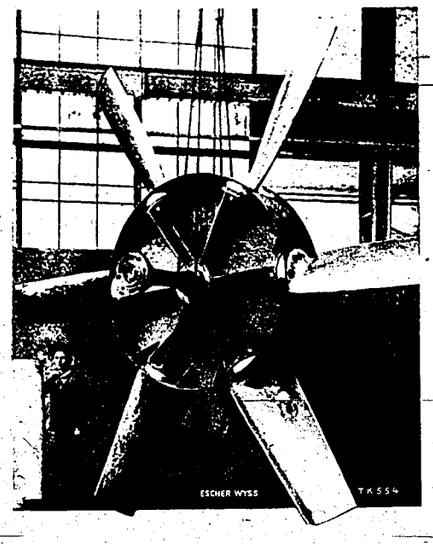


Fig. 32
Escher Wyss Axial Blades Pivoted

between adjacent blades forms a converging channel on the entering side, as in a supersonic wind tonel, and a diverging channel on the leaving side. Flow in the throat of this passage way should have a Mach number of 1. If this can be accomplished, compression will take place before and after the throat between blades. While this would enter a new field for high pressure blowers a more critical flow condition exists and would suggest its use only for steady flow conditions.

Multistage Axials.

These are built only by the larger companies. They are built in any number of stages from 2 to 11 or 12. As the pressure increases with the number of stages, the percent hub usually increases also. Likewise, the number of blades may be from 12 to 24 depending on the hub size. Generally the height of blade is a little greater than the width.

Essentially, the airfoil shape is thin and without much camber. This is desirable on account of the very high air velocity between blades as well as to reduce rotating weight. It is not uncommon to pivot the blades (Fig. 32) so that slight adjustment can be made in their angle. Up to 4 stages axial compressors can be obtained with automatic adjustment of blade angle while running (Fig. 33). While the impellers are usually mounted (shrunk) on a common shaft, two stage fans may be equipped with contra-rotating impellers. Two such fans were seen, one in the manufacturer's assembly plant and one in a research laboratory. The speeds of both impellers should be the same, thus no curvature to the guide vanes is necessary. Another variation in the two stage (Fig. 34) design is to have vanes ahead of each impeller to direct air flow against rotation. This makes a compact unit and identical impeller shapes.

Special attention is given to the axial alignment of fans in their housings and the clearance at blade tips. This clearance is generally held to one tenth of one percent of the wheel diameter. Thus a 32 inch diameter would normally have a clearance of 1/32 inch. In one case the edge of the blade at tip was ground off on the back side to leave a sharp leading edge.

Housings are cast iron or steel in the larger sizes and split horizontally. Where elbow type of end bells are used, these are also split and bearing cast integral with the lower half (Fig. 35). Where few stages are used, welded steel

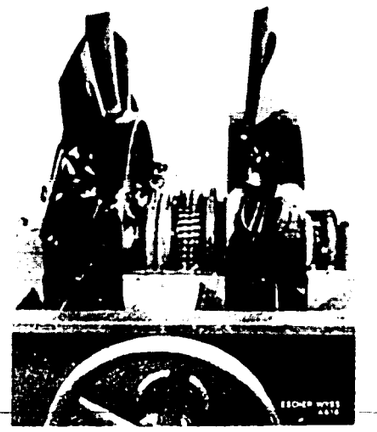


Fig. 33
Escher Wyss Axial Flow

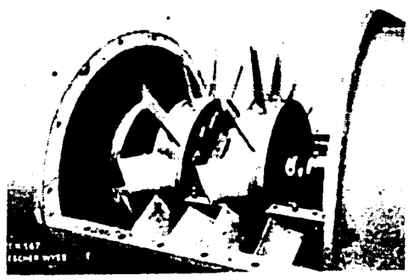


Fig. 34
Fans with Variable Pitch Blades

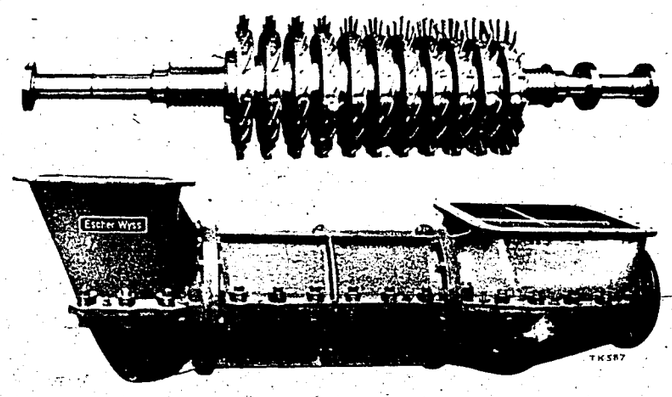


Fig. 35
Escher Wyss Axial Flow Compressor

plate is more common, even to the construction of the end connections. These types are not horizontally split unless great accessibility is required, as for example those blades having stationary or running adjustment of blade angle.

The motive power is about the same as for centrifugal types. Motors are generally used up to 3000 Rpm and turbine drives to 9000 Rpm. In some cases the shafts are operated at about twice the fundamental critical speed. In other cases, the impeller hubs are shrunk one to the other to form the equivalent of a large diameter hollow shaft. Two forms of connection are used (1) shrink rings and (2) stepped and turned grooves (Fig. 36). In this case operation below the first critical speed is possible.

Materials

Aside from the common materials, cast iron and steel plate, the chrome alloys were much used for high speed. Chrome vanadium, chrome manganese and chrome molybdenum were some of these. Chrome-nickel seemed to be used primarily where stainless properties were necessary.

Aluminum and silalumin (an alloy of silicon and aluminum) were used some for impellers.

Babbitt with about 10 percent tin was the common bearing material. In some cases during the war plain cast iron bearings were used on slow speed as substitute material.

Wood was largely used for some chemical fans, lead for others. No rubber was seen. The plastics, Wiedenur and Igelit were also observed. These were drillable but brittle.

Some experimental work was done on porcelain for gas turbine blades. The outcome is doubtful but, for temperatures above that for which alloys may be used, this will prove a fertile field for research.

Bearings

Ball, cylindrical and tapered roller bearings are used for speeds up to 3000 Rpm, that is, all motor speeds. Above this speed and for all heavy multistage work "weismetal" (babbitt) bearings are used entirely. These are sometimes ring oiled and sometimes pressure lubricated, in which cases the oil is internally or externally cooled, respectively.

For the high speeds which are generally used throughout Germany the finish of bearing surface as well as the shaft surface is given great care.

Center bearings are rare. When used, they act only as steady bearings. Except for small or short fans where "en bloc" casting is feasible, self-aligning bearings is the general practice for both sleeve and ball and roller types. The length of sleeve bearings seems to range from 1 to 1½ shaft diameters. The use of temperature indicating devices seems to be prevalent.

Iron bearings were used on some slow speed work, but more as substitute material. In one case for a small low speed drier, the ball bearings were housed in a plastic housing and on the slower shaft a plastic sleeve was used, water lubricated.

Ball and tapered bearings may be called upon to take light thrust loads. Some single stage fans have balancing holes through the hub, communicating into a close fitting chamber on the back side to equalize the thrust load. Invariably, all uni-directional multistage fans are provided with balancing pistons on the high pressure end. Double flow, balanced, types are frequently found on very high pressure or large volume fans. Where the thrust load is not constant or where axial alignment is necessary a Mitchell thrust bearing is used.

Couplings

The bushed pin type coupling is the more frequently found type of flexible coupling. They are much the same as ours but leather is used for the bushings as well as rubber.

Then there is the claw type of coupling. The spaces between mating jaws is filled with rectangular laminated plates. It is for heavier duty than the above and also frequently found. Very few gear type couplings were noticed.

For high speed work the Bibby type coupling seems to predominate. The rim of each half is serrated and filled with a corrugated flat spring. This and the pin type have American counter parts.

Electric motors are frequently coupled to fans by step-up gears. These are usually separate gear housings

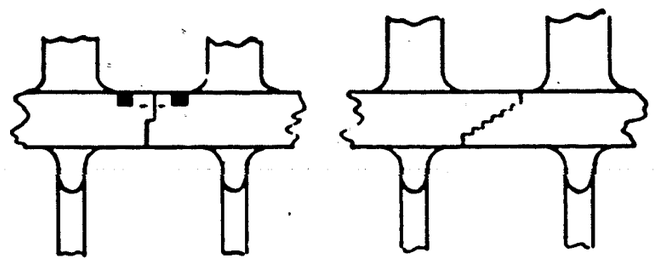


Fig. 36
BBC Fan Hubs Made Into Hollow Shaft

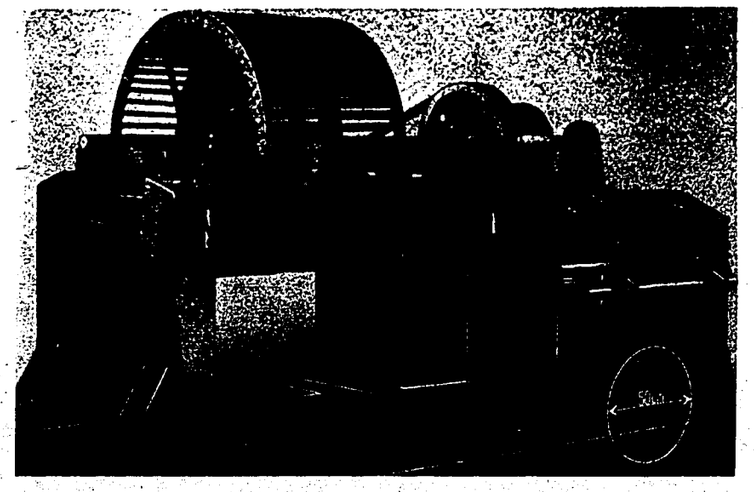


Fig. 37
Schenck Mechanical Balancing Machine

except in the case of Turbo-blowers. Here the teeth of the high speed pinion are usually cut directly on the fan shaft forging, making a self-contained unit.

The Voith-Sinclair variable speed hydraulic coupling is some used for fan drives (see Mr. C.S. Becker's report on this coupling). No variable electric transmissions seen.

Fan Balance

In view of the dependence of fans upon good balance the writer interviewed 3 balancing companies which furnished practically all of the machines used by that industry. Two of these companies were almost totally bombed out. The third, Carl Schenck of Darmstadt had the latest and most interesting equipment for this purpose. It is not the intent of this report to go into complete detail about these machines. Complete descriptions will be found filed with the original report. However, the basic principles of operation are worth treating here.

Roughly, two late types of dynamic balancing machines are available, the mechanical and the electrical. The mechanical system is similar to that found in the U.S. A heavy compensating bar is made to move in phase relation with the rotating impeller. The bar can be rigidly locked in any position throughout its length. When it is locked in one of the planes of correction, the fan shaft vibrates with zero displacement in this same plane. The reading of vibration at the opposite bearing is an indication of amount (when corrected) and phase of the unbalance in the other plane of correction.

Another variety of the mechanical system is to produce a vibrating image of the rotating system (Fig. 37). By locking the image first in one plane of correction and then in the other, components are obtained which may be resolved into the original forces.

The electrical system (Fig. 38) employs moving coil pickups, amplifier and wattmeter indicator. The unbalance as well as the corrections are made at 2 predetermined points at right angles to each other and in each of two planes of correction. Complicated vector diagrams are thus eliminated. The neutral point is determined. With the aid of trials with

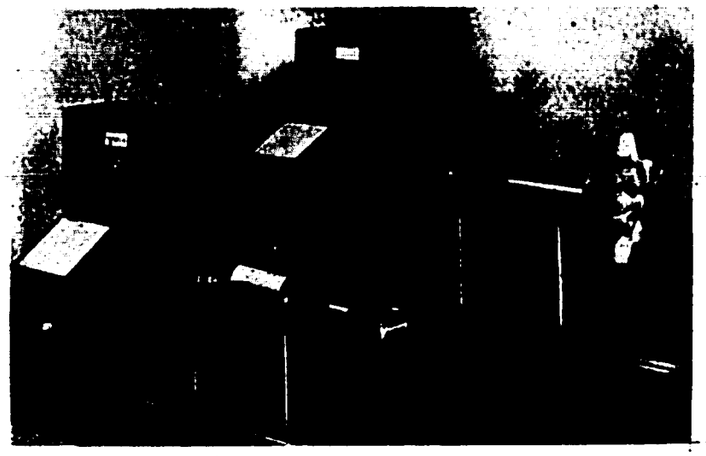


Fig. 38
Schenck Electric Balancing Machine

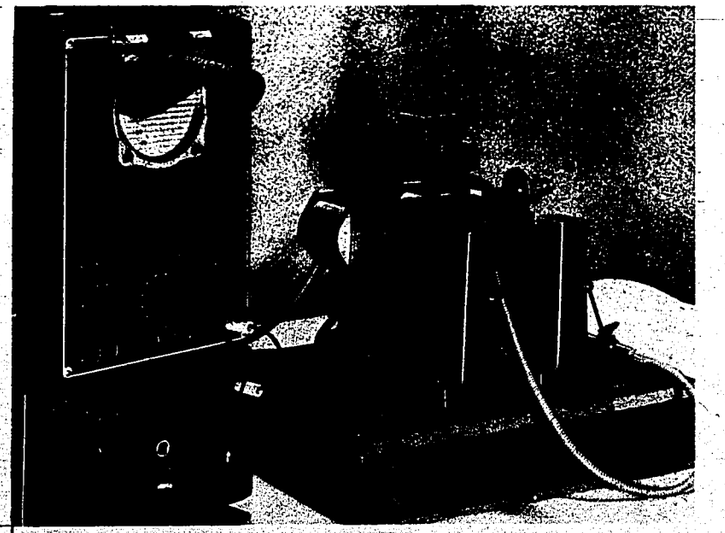


Fig. 39
Schenck Electronic Balancer

fixed masses in each plane the forces are determined and graphed. The system is very sensitive and free from external influences. It is quick and lends itself particularly well to cases where balance weights can be applied at fixed points. This would normally mean 4 balance weights to be applied. Where this is not feasible or desirable the 4 weights may be reduced to 2 weights, through a simple graph and only the two wights applied. Where weights are bolted or riveted to the fan in the outermost planes, the 4 weight method has the advantage that a simpler rebalancing job can be done in the field when this becomes necessary.

Another variation of this principle (Fig. 39) has been applied to very small parts to be rotated at high speeds. A sine wave of unbalance is thrown upon the screen of a cathode ray oscilloscope. With the aid of an electric eye (similar to that used for the movies) two spots at 90 degrees in each plane of correction are picked up and superimposed on the sine wave picture in the oscilloscope. The displacement of these spots gives a measure of unbalance. If the part to be balanced is a motor, it is driven under its own power in its own bearings. If it is an armature or fan, it is operated from a compressed air jet at right angles to the plane of vibration.

Patents covering these electrical methods are DRP 710,883 and 745,193. For fans, a number R63 machine to balance parts 2 meters diam. by 3 meters long and weighing 100 to 2000 kg. would require about 15 H.P. and cost about 15,000 marks (prewar value)

Testing

Testing procedure followed standard methods, Prandtl tube used for velocity pressure and static, some statics taken with flush taps. Straightening vanes much used, sometimes tube nests. Frequently found multiple manometers arranged for simultaneous photography.

Dr. Ernest Schmidt of LFA Laboratory has developed a unique system of photographing boundary layer separation. Parallel sheets of light are introduced into a rectangular system of mirrors. Between two mirrors and axial with the light beams is placed a longitudinal section

of nozzle forms to be tested. Streamline flow shows no distortion of beams but when boundary separation takes place the heat developed distorts the rays within the heated zone. Method is quick and easily photographed. Set-up used for stationary blades or nozzles with hot air flow of different velocities for gas turbine development. Schlieren mthod used for turbulent combustion. Air tests much used by Escher Wyss for development of flow through pumps and water turbines.

Sound meter testing developed by Prof. Lubcke taken at one meter distant from machine and at one meter spacing surrounding it. When shielding of michrophone in air flow is necessary recommends use of Fuhrmann Airfoil with air communication at zero points of pressure at re-establishment of flow. This is usually over half way back from leading edge. In propeller in free field, the fundamental sound predominates the harmonies below Mach number one and the system reverses above that speed.

Adiabatic efficiency tests on turbo-blowers reported up to 78.5 percent and with vane diffusers 83. On axial stage blowers efficiencies of 86 to 89 reported. Isothermal efficiency of cooled centrifugal compressors 65 to 70 percent. Temperature rise about 185°c first stage and about 160°c following stages.

Hot gas fans handle air to 350 to 500°c. One company reported tests on a fan for 500°c handling 450,000 cu. meters per hr., 320 mm water pressure with 75 percent adiabatic efficiency. Mine fans handle air normally at 200 to 250 mm water pressure, up to 400 mm max. and max. volume of air 1,500,000 cu. meters per hr.

Single uncooled centrifugal compressors go to .8 atmospheres. Low pressure turbo-blowers range from 3,000 to 200,000 cu. meters per hr. at 3.5 atmosphere while high pressure compressors range from 10,000 to 100,000 cu. meters per hr. with pressures up to 9 or 10 atmospheres.

Tests on an axial flow fan, showing the effect of guide vanes before and after the runner will be found in the Appendix.

ASSOCIATED SUBJECTS

A few paragraphs on materials seen in fan shops may be of timely interest. The usual cyclone collector

seen is made with a spiral top. The air, instead of entering a cylindrical surface through a long rectangular opening, enters at the top of a cylinder through round or square opening and is guided down into the cylinder through a spiral form. Also, a spiral angle, about 2 inches high, is fastened to the bottom cone on the inside to guide material to the bottom opening. In some cases vertical or spiral vanes were placed at entrance to the discharge stack to prevent whirl and recover some of this energy.

Some round duct connections were seen where the branch duct entered the main with very long slopes and change in shape to cause minimum disturbance.

Some rotating dust collectors seen particularly for sintering cement and bricketing plants. Consisted of several concentric cylinders with spiral plates to lead dust to hopper and screw conveyor discharge. They were mounted at small angle to horizontal and driven at moderate speeds (200 to 300 Rpm). (WDG folder filed with original report.)

Bag filters were also seen at WDG. These were of usual construction with long cylindrical bags and striking mechanism with dampers arranged to close off one section at a time prior to shaking.

Only one air washer seen. This had two banks of sprays, both opposed to the air flow. Followed general lines of construction as ours except spray nozzles were made of porcelain. Nozzle was customary spiral type, each piece, body and cap, molded completely finished. Cap was screwed and cemented in place.

Most of the unit heaters were extended surface, plate type. Each plate assembled with numerous tubes of about ½ diameter. Another variation was a patented construction (Pollrich) using smaller plates of equilateral triangular shape containing a group of three tubes only. These were so nested in the heater as to make practically a continuous surface. Some spiral fin heater surface on about 1 inch diameter tube was seen. This was constructed like Aerofin. Fin spacing of plates was about 1/10 inch, spiral construction somewhat greater.

Although some copper heaters were seen, most were made of steel plates and tubes, tubes are welded into headers and hot dipped galvanized. One company had fan operated gas furnace supplying heat to galvanizing bath, waste heat being used to dry heaters from cleaning tanks.

Gas unit heaters seen in a few cases, using plate construction for interchanger. Gas fired unit heaters and household hot water heaters favor combustion without premixing with air. Burners are very small pipes with small holes or oval tubes with narrow slots. Good soft flame is made with slight yellowish tip.

Dr. Klein reports no progress made during the war in air conditioning. Large underground factories had to be cooled but this was done chiefly through the use of cold water coils. One tunnel factory visited was favorably situated for natural ventilation. He reported axial flow fans gaining in use but must be carefully selected lest they get off-rating and make noise. He believes there is undue optimism with radiant heating and a good deal of it will be dispelled as systems are put into operation. Where ventilation is needed the air can also supply the heat.

----- APPENDIX -----

Books and Pamphlets

1. Ventilatoren, by Bruno Eck. Springer 1937 (out of print)
2. Ventilatoren Verlag Aulangen by Rode. De Gruyter
3. Axial Gebläse Vom Standpunkt Curt Keller Lehman and Co.
4. Schallabwehr (sound) in Bau and Machinenwesen E. Lubcke Springer 1940
5. Einführung in de Technische Thermodynamik by E. Schmidt English ed. 1936 German ed. 1936, 1944
6. Theoretische Einführung in die Gas dynamik by Dr. Robert Sauer Springer 1943
7. Hydro v Aeromechanik by Tietjens (vom Prandtl) Springer 1944
8. Aerodynamik der Luftschranbe by Weinig. Springer 1940
9. Report by Dr. Billing on sound distribution about rotating propellers AVA, UM, Nr. 3150
10. Report by Prof. Encke of AVA on axial flow fan work at Göttingen Laboratory
11. Staubbekämpfung (combating dust) in der Industrie by Bodenmüller in Der Bergbau. Sonderdruck ans Nr. 21 vom 14 October 1937
12. Axial Blowers, W. Gaehler Escher Wyss News Vol. 13, 1940
13. Compressors and Pumps (including heat pumps) Escher Wyss News Vol. 14, 1941
14. Aerodynamic turbine with closed circuit, Prof. Dr. J. Ackeret and Dr. C. Keller. Also a comparison with steam and gas turbines by Dr. C. Keller Escher Wyss News 1942/43.
15. Propeller Vibration by Max Schilhansl. Der Deutschen Akademie der Luftfahrtforschung. vorgelegt am 13 Mai 1942
16. Stresses in Rotating Discs (Keller) by Dr. F. Salzmann Escher Wyss News Vol. 11 No. 3 July, Sept. 1938
17. Der Einfluss Aerodynamischer Eigenshaften auf Shallfeld U Strahlungsleistung einer Luftschraube by Dr. Ernsthausen, Akustische Zeitschrift July 1941.
18. Regelung von Kreiselverdichtern by Dr. Ing. F. Kluge Zeitschrift des Vereines Deutscher Ingenieure Bd 84(1940) Nr. 44
19. Das Turbogebläse in Hochofen und Stahlwerkshetrieb by F. Kluge. Bericht Nr 98 des Machinen-ausschusses des Vereins Deutscher Eisenhüttenleute im NSBDT

INTERVIEWS

1. Atlas Werke A.G. Munich, Kuglmüllerstr.10 Dir Gramann and Dr. Zenneck. Acoustical work done at Bremen plant.

2. A.V.A. Aerodyramische Versuch Anstalt. Göttingen Research Laboratory - Mr. Encke on axial flow fans. Dr. Holstein.

3. BBC Brown Beveri Co. Office, Heidelberg, Robert Bunsen Schule Keplerstr. Mr. Köckritz, Sales Plant, Mannheim, Käffertal Kronprinzenstr. Dir. Meyer, Engineer Crämer, Cent. and Axial Compressors.

4. B.M.W. Bayerische Motoren Werke, Munich, Engr. Karl Fickert. Altitude chamber for jet engines.

5. B & W Babcock and Wilcox. Oberhausen. Dr. Ing. Jantscha. Forced and Induced Draft Fans.

6. Daimler Benz. Eislingen. Experimental Lab. Eng. Michalsky. Turbo Superchargers. Also Heiningen for Dr. Otto Schmidt. Also Tunnel Factory at Wiesensteig.

7. Demag. Duisberg Werthauerstr. 64 Eng. Moritz, Schierl and Dr. Engel. Turbo-blowers and compressors.

8. D.V.L. Deutche Versuchanstalt fur Luftfahrt. Dr. Ernsthansen reported in Helmholtz Inst. Brannenburg Innsbuch. Dr. Van der Null reported in Berlin.

9. Dr. Ernsthausen. Was unable to be seen Specialist on Sound.

10. Escher Wyss. Ravensburg. Mr. Schwab, Commercial Dept. Turbo-Blowers and Compressors.

11. Exhausterenwerke Nürnberg. Maximillianstr. 22 Fully damaged.

12. Frankfurter Machinenbau, formerly Pokorney & Wittekind Frankfurt am Main. Solmstr. 2/26 Piston compressors only.

13. Guttehoffnungshütte Aktiengesellschaft Oberhausen-Sterkrade Engr. Kurt Koch and Ernest Thomann. Turbo Blowers and Centrifugal Compressors.

14. Gebruder Hoffmann Darmstadt, Pallaswiesenstr. 72 Completely bombed out.

15. George Kiefer Machinenfabrik, Stuttgart Feuerbach Heilbronnerstr. 384-390. Mgr. Otto Kiefer. Fans and Air Conditioning Equipment.

16. Dr. Ing. Albert Klein. Lautenbacher Hof bei Bad Zeinach. Air Conditioning Engineer. Also had ships, Luftteocknische Gesellshaft at Stuttgart and Zuffenhausen.

17. K.K.K. Kühule-Kopp and Kausch Aktiengesellschaft. Frankenthal/Pfalz - Dr. Winkler and Dipl. Eng. W.C.H. Graef. Axial flow fans and turbo-blowers.

18. L.F.A. Luft Fahring Anstalt (Similar to Wright Field, Dayton) Brunswick. In woods near airfield. Prof. Ernest Schmidt. (Prof. Dr. Eckert evacuated) Wind Tunnels and Gas Turbine Research.

19. Prof. Ernest Lubcke, Berlin, Westend Allee 92 d. Formerly with Siemens Schuckert, Berlin. Sound.

20. Weingarten Machinenfabrick, Weingarten. Dr. Lutz. Make punches and shears comparable to clearing, Toledo. No fans.

21. Heinrich Meierling, Ventilatoren Fabrik Laufenburg/ Baden Willy Meierling. Low and High Pressure Fans.

22. Motorwerke Mannheim (formerly Benz) Mannheim, Carl Benzstr. 5. Medium speed Diesel engines. No fans.

23. Müller and Neumann, Specialfabrik Luftecknischer Anlangen, Wuppertal/Barmen, Rott 20. No one at plant.

24. Friedrich Pelzer Machinery Co. Dortmund, Kaiserstr. 176/a - Engr. W. Ocken. Small fan company.

25. Anton Piller K.G. Osterode/Harz, Abjunst 24 Mgr. Von Minden. Mostly small cast iron blowers.

26. Paul Pollrich and Co. Ventilatoren & Machinenfabrik, Düsseldorf Schliessfach 240. Fans and General Air Conditioning Equipment.

27. Pumpenfabrik Urach, Urach. Dir. Konrad Becker Hydraulic and air compressors, piston type. No fans.

28. R. Schafer v Urbach, Ratingen, Kaiserwethestr. 26 b. Piston compressors for air and water. No fans.

29. Carl Schenck Machinenfabrik, Darmstadt, Landwehrstr 55, Dir. Buschner, Dr. Federn. Dynamic Balancing Machines for Fans.

30. G. Schiele and Co. Eschborn. Ch. Engr. F.A. Hackmann. Most special fans and blowers.

31. Oscar Sichtig and Co., Karlsruke, Rheinhafen Südlich Uferst 3, Mr. Penz. Fans and air conditioning equipment.

32. Julius Springer, Berlin, Publisher. Books on fans and air flow.

33. Kaczmarek Stefan Ing. Neu Ulm, Wilhelmstr. 25. Heating Engr. central systems.

34. Trebel Co. Düsseldorf Munsterstr. 421-7 Balancing machines. Totally bombed.

35. Van der Null, DVL Berlin. Centrifugal fan design. Evacuated to England.

36. V.D.I. Verein Deutscher Ingenieur, Berlin. Fan and Compressor Codes.

37. J.M. Voith. Heidenheim/Brz. Wm. Kugel Ch. Designer Hydraulic Couplings. Axial flow fans.

38. Johann Weber, Nuremberg, Maiachstr. 105. Plant closed Exhaust systems and sheet metal work.

39. Wepuko Werkzeug-Pumpen. Wetzingen Ing. Fritz Tyumm Piston compressors only.

40. W.D.G. Westfalia-Dinnendahl-Gröppel. Gröppel plant at Bochum made mining equipment. Westphalia plant

made pitcages and structural steel. Dinnendahl plant at Essen made mine fans. Mr. Zettelmeyer at Essen. Mgr. Dissmann at Bochum.

41. Gebr. Winkelstrater formerly Winkelstrater and Sure Wuppertal/Wichlinghausen. Breslauerstr. 59 Fritz and Helmut Winkelstrater. Fans and Air Conditioning Equipment.

AXIAL FLOW FAN TESTS

Showing Various Arrangements of Blades and Vanes
J. M. Voith Co. - Heidenheim - April 13, 1944

Dr. Schilhouse, Chief Marcinowski, Editor

Herewith are shown some test curves on an axial flow fan that may be of interest. They show the relative effect of placing curved vanes before and after the runner and when before, the effect of curving the vanes with or against rotation. The values plotted are in dimensionless units as indicated below. A synopsis of the report follows:

Purpose: The problem was to operate an engine cooling fan for the VDL from point 1 (Vol. Q = 56 m^3/sec., press. 650 mm water) to point 2 (Vol. Q = 140 m^3/sec., press. 320 mm water) with a constant speed motor of 850 kw. The efficiency must therefore be at least 53 percent for point 1 and 65 percent for point 2. The basis of the design was a characteristic chart of an axial flow fan tested by B. Eckert and reported in the 1940 yearly edition of German Aeronautical Research Society, p. 270. (Data not available as yet)

The following symbols are used:

$C_m = \frac{Q}{F_{blower}} = \frac{Q}{\frac{\pi}{4} r_a^2 (1-\nu^2)}$ where ν = hub ratio

$\omega = \frac{\pi n}{30}$ = angular velocity

$\frac{\rho}{2} = \frac{\gamma}{2g}$ = half of the air density. γ = 1.25 kg/m^3 the spec. grav. of the air

Δp_{total} = total pressure drop (impeller & diffuser) in mm. water

Q = volume in m^3/sec.

M_d = torque driving the blower shaft in mkg.

S = axial thrust of the blower impeller in kg.

$\varphi = \frac{C_m}{r_a \omega}$ = coefficient of flow

made pitcages and structural steel. Dinnendahl plant at Essen made mine fans. Mr. Zettelmeyer at Essen. Mgr. Dissmann at Bochum.

41. Gebr. Winkelstrater formerly Winkelsträter and Sure Wuppertal/Wichlinghausen. Breslauerstr. 59 Fritz and Helmut Winkelsträter. Fans and Air Conditioning Equipment.

AXIAL FLOW FAN TESTS

Showing Various Arrangements of Blades and Vanes
J. M. Voith Co. - Heidenheim - April 13, 1944

Dr. Schilhouse, Chief Marcinowski, Editor

Herewith are shown some test curves on an axial flow fan that may be of interest. They show the relative effect of placing curved vanes before and after the runner and when before, the effect of curving the vanes with or against rotation. The values plotted are in dimensionless units as indicated below. A synopsis of the report follows:

Purpose: The problem was to operate an engine cooling fan for the VDL from point 1 (Vol. Q = 56 m^3/sec., press. 650 mm water) to point 2 (Vol. Q = 140 m^3/sec., press. 320 mm water) with a constant speed motor of 850 kw. The efficiency must therefore be at least 53 percent for point 1 and 65 percent for point 2. The basis of the design was a characteristic chart of an axial flow fan tested by B. Eckert and reported in the 1940 yearly edition of German Aeronautical Research Society, p. 270. (Data not available as yet)

The following symbols are used:

$C_m = \frac{Q}{F_{blower}} = \frac{Q}{\frac{\pi}{4} r_a^2 (1-\nu^2)}$ where ν = hub ratio

$\omega = \frac{\pi n}{30}$ = angular velocity

$\frac{\rho}{2} = \frac{\sigma}{2g}$ = half of the air density. σ = 1.25 kg/m^3 the spec. grav. of the air

Δp_{total} = total pressure drop (impeller & diffuser) in mm. water

Q = volume in m^3/sec.

M_d = torque driving the blower shaft in mkg.

S = axial thrust of the blower impeller in kg.

$\varphi = \frac{C_m}{r_a \omega}$ = coefficient of flow

$\Psi = \frac{\Delta p_{total}}{\frac{\rho}{2}(r_a \omega)^2}$ = coefficient of pressure

$\eta_g = \frac{Q \Delta p_{total}}{M_d \omega}$ = total efficiency of the blower

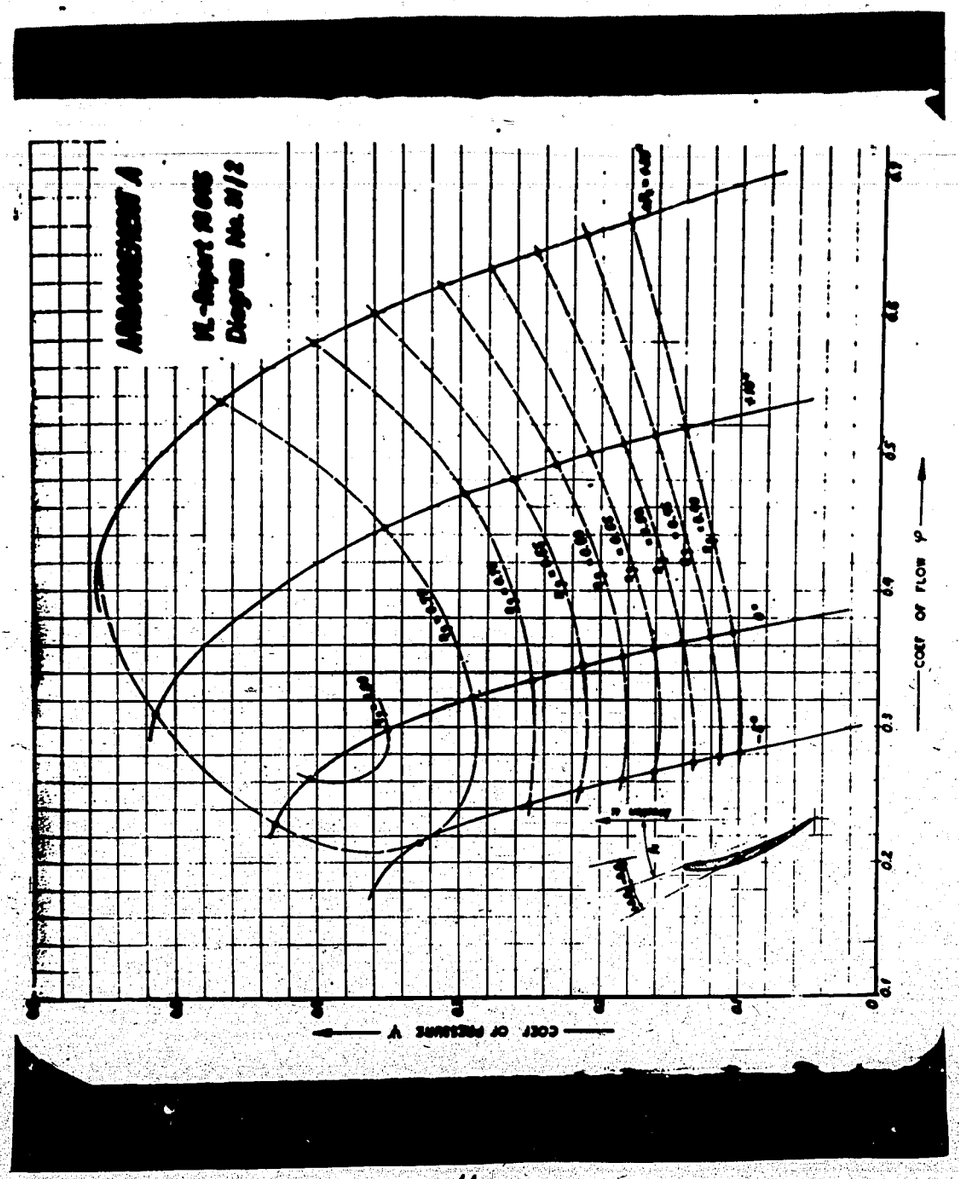
$k_s = \frac{S}{\frac{\rho}{2}(r_a \omega)^2 \pi r_a^2}$ = coefficient of thrust

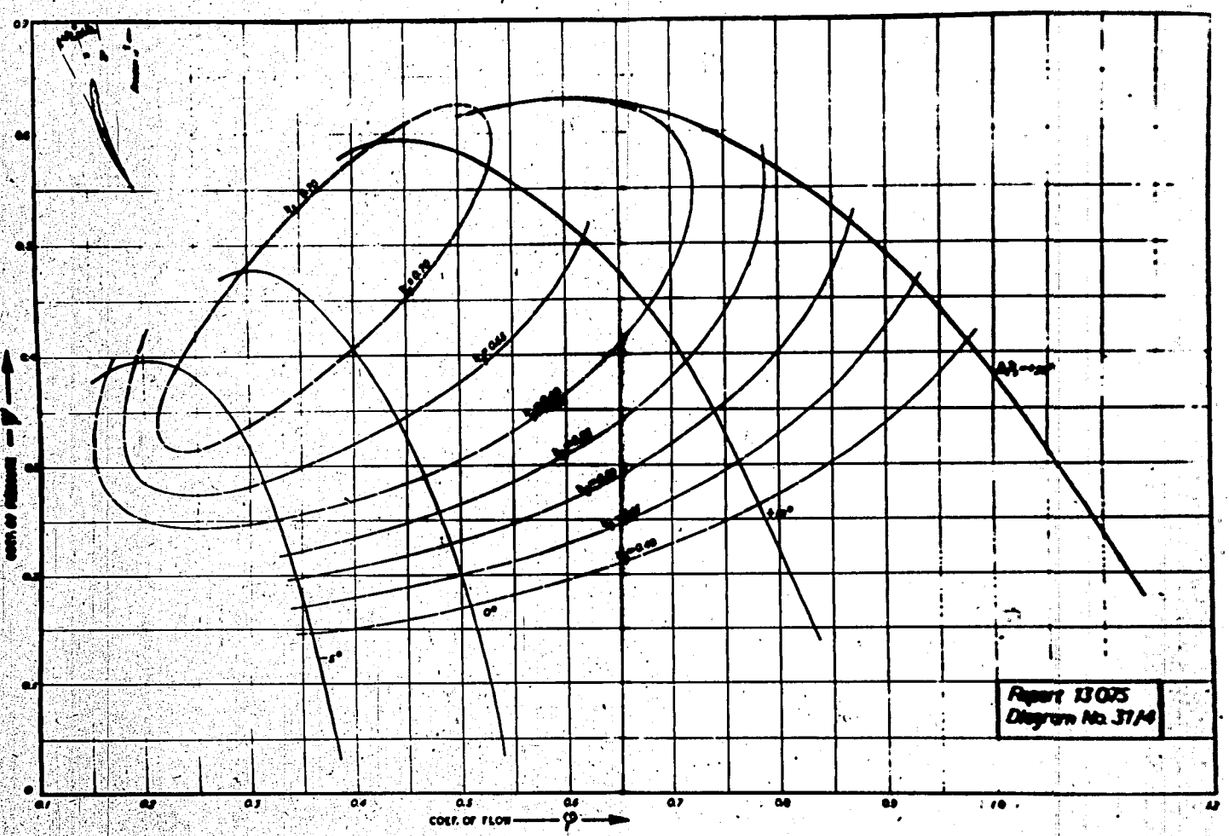
$k_d = \frac{M_d}{\frac{\rho}{2}(r_a \omega)^2 \pi r_a^3}$ = coefficient of thrust (respecting power factor)

Evaluation: Charts 31/2, 4, 6 show the results according to arrangements A, B and C respectively. Chart 31/5 shows the 3 throttling curves for the zero (standard) construction. Charts 31/9, 10 show the thrust k_s and torque k_d respectively.

Results: Curve satisfies point 1 but is too low for point 2 unless the impeller vanes are turned about +15°. In that event the efficiency is too low. Also, it would be hard to make variable pitched blades with such a high hub ratio. Chart 31/5 shows the influence of changing vane angle, both with standard blade angle and with +2°. Also, k_d (max) lines are given for these two blade settings based upon actual power available, where k_d (max) = .076.

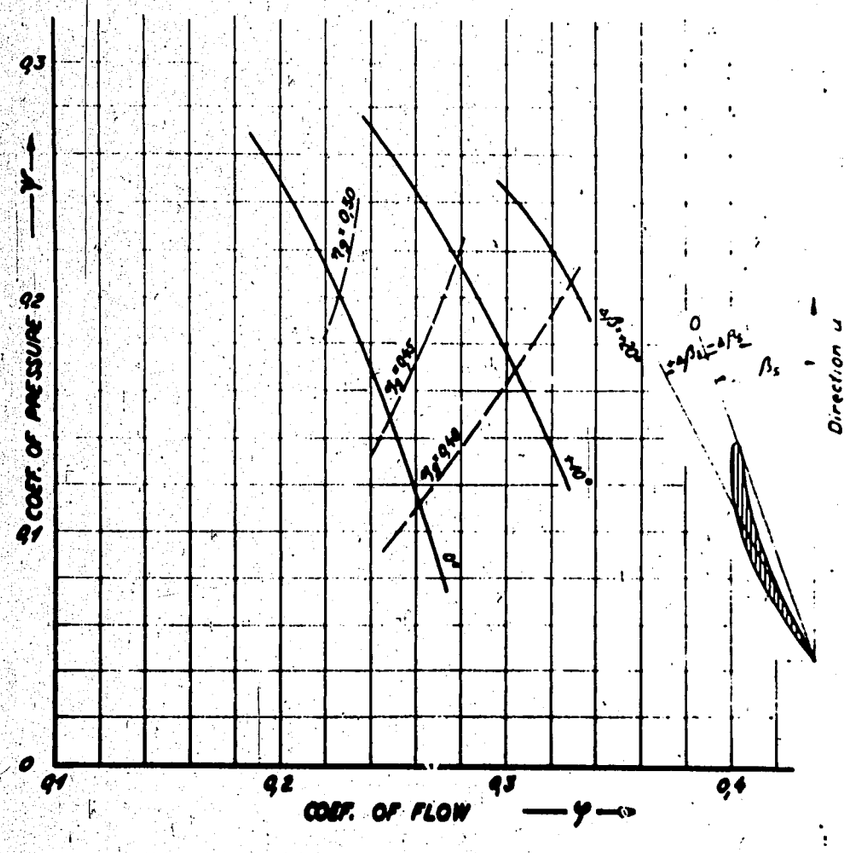
Suggestions: It is seen that the curve $\Psi - \varphi$ must be shifted to the right. One way is to use fewer blades but that would drop the pressure for point 1. Another way is to change diameter, hub ratio or even the speed. In view of the fact that smooth flow must be maintained all the way from point 1 to point 2 little is to be gained by these devices. In any event point 1 is likely to become unstable unless a by-pass is used for that portion of the curve, which by-pass is recommended. Also, it is suggested that the impeller angle be increased 2° and blades made so that further slight adjustment can be made if necessary. Also, it is recommended that the vanes ahead of the impeller be made adjustable and this will give a broad characteristic curve which seems to be what is required of the specifications.

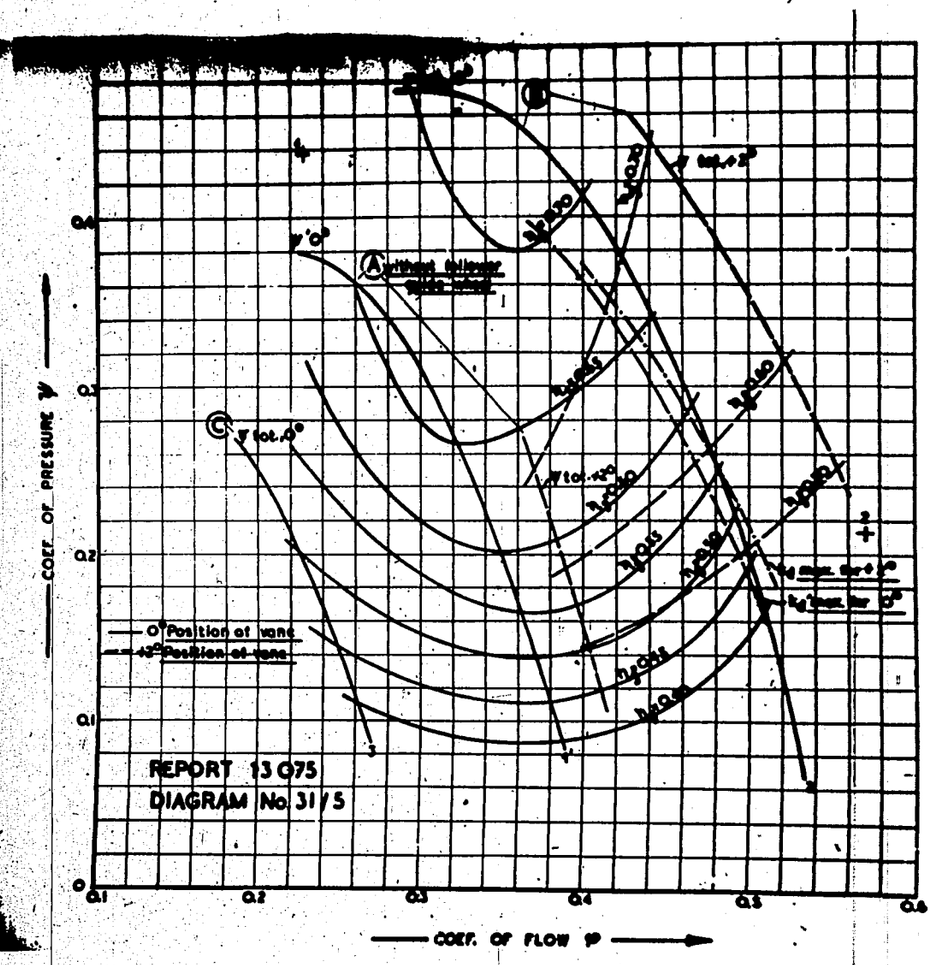


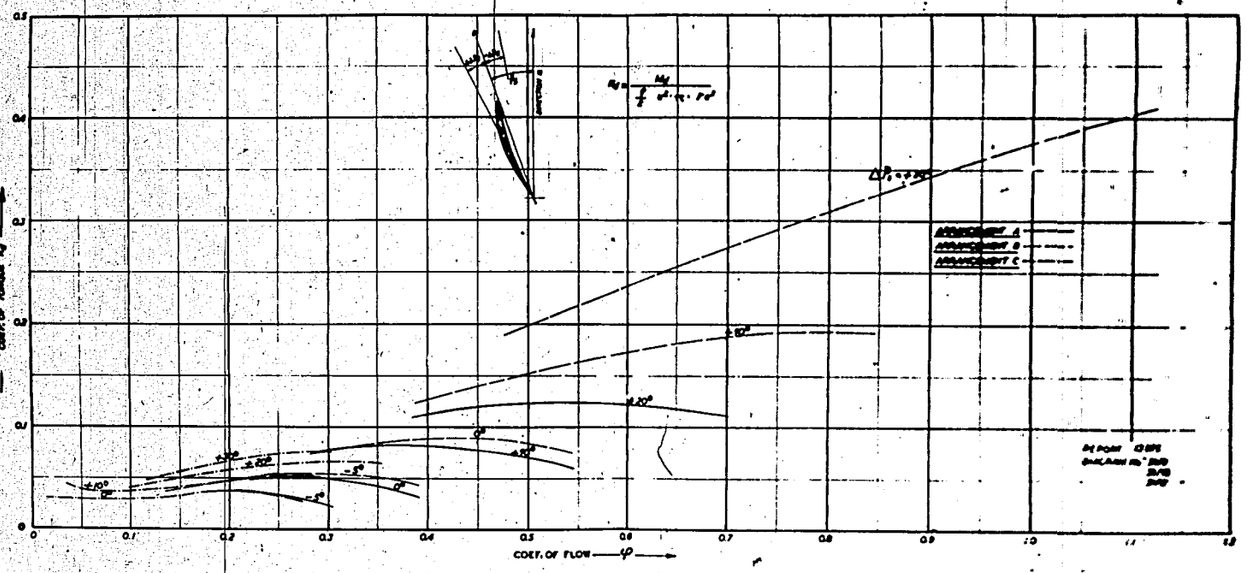


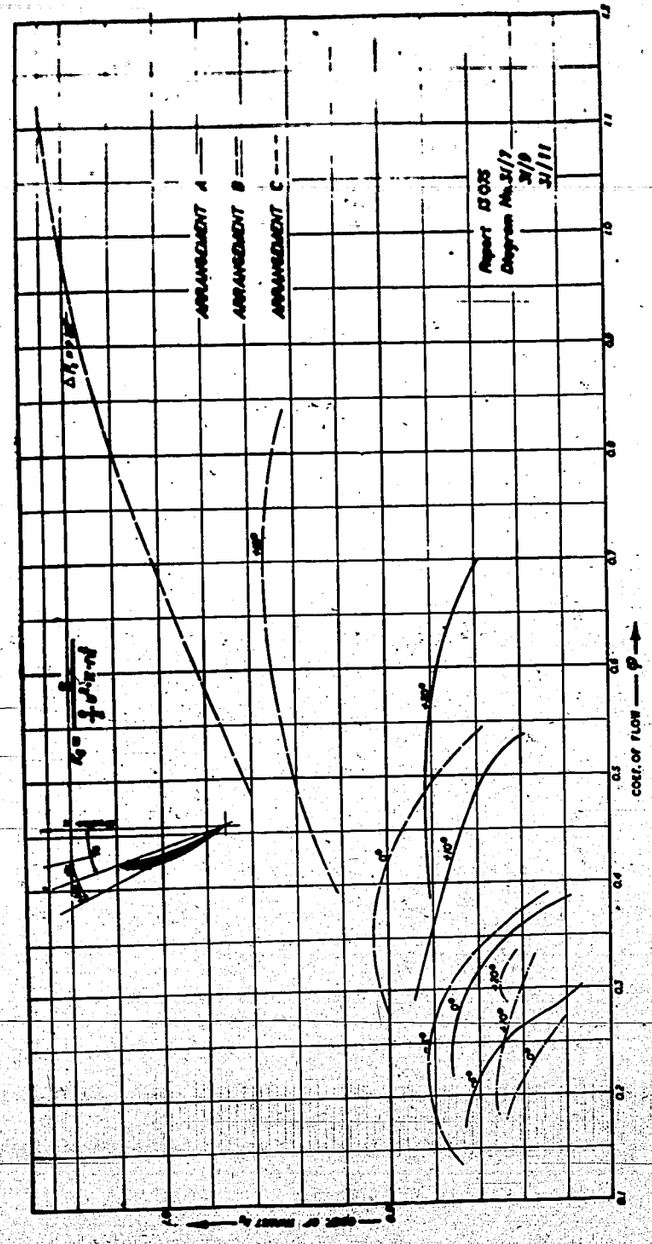
Arrangement C

Report 13075
Diagram Nr. 31/3



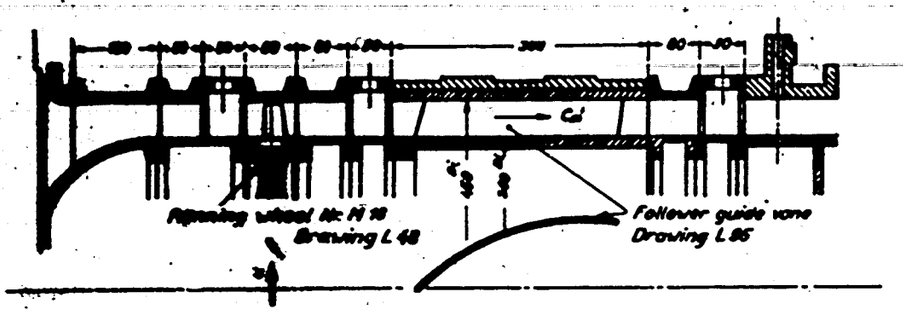

COEF. OF PRESSURE ψ
COEF. OF FLOW φ
0° Position of vane
+12° Position of vane
REPORT 13 G75
DIAGRAM No. 31/5


COEF. OF PRESSURE ψ
COEF. OF FLOW φ

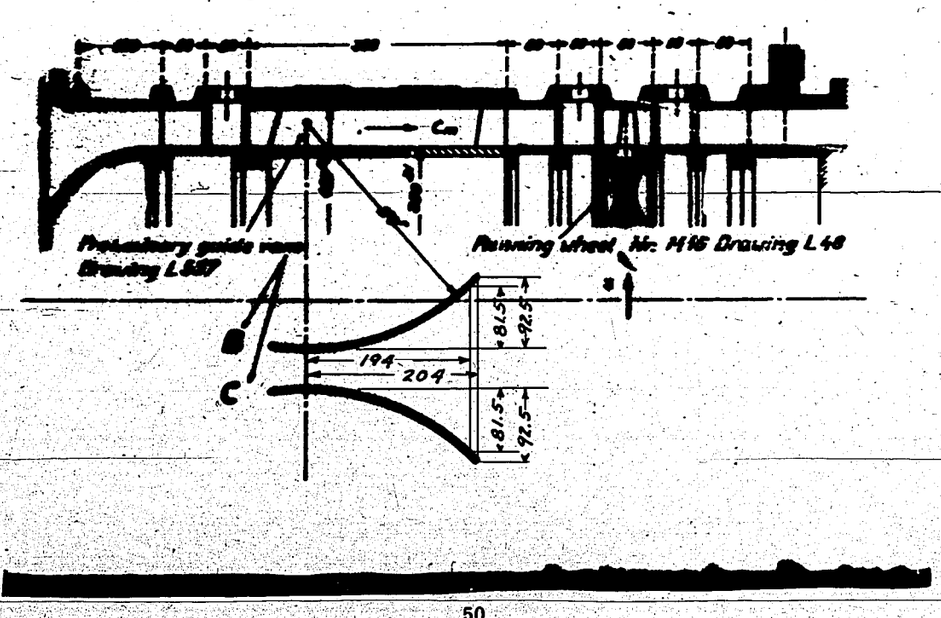


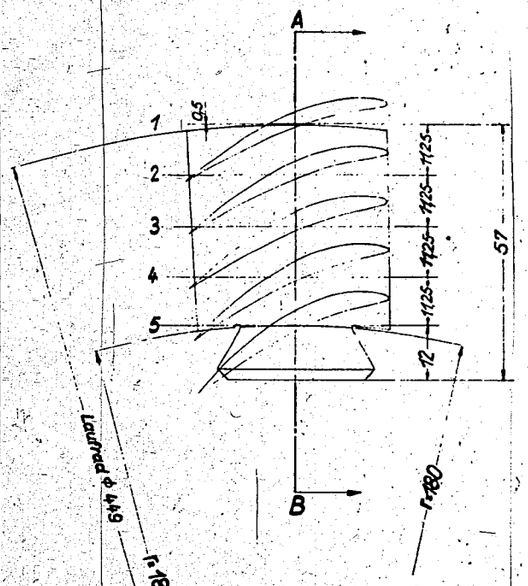
Arrangement A

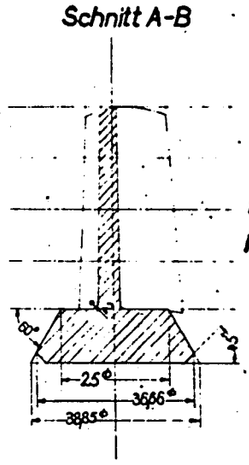
Report 13075



Arrangement B; C







Schaufelzahl z = 16;
rechtsgängig gezeichnet
rechtsgängig ausgeführt

Schablone für Schaufelfuß W21258/2
Gegen " " Nabe W21258/1
Schablone zur Bearbeitung der
Schaufeln W7491

	Datum	Name
Gezeichnet	5.4.73	Wallacher
Geprüft		
Genehmigt	7.5.73	Lugar
Norm-Ausgabe		

J. M. Voith
Heidenheim

Büro VL	Adlershof „4" Versuch	Änderungen: Datum / Name
Maßst. 1:5	Schaufel zum Laufrad M16 (für Nachleitrad)	L48
Werkstoff Elektron		Ersatzt durch / Ersetzt für

Y89

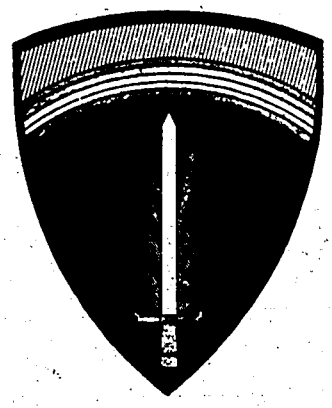
Copy 1

FIAT FINAL REPORT 594

HIGH PRESSURE CHEMICAL LIQUID PUMP
FORCE FEED LUBRICATORS
POSITIVE ROTARY SUPERCHARGER

(Manufactured by Robert Bosch G.m.b.H.- Stuttgart)

Mathewson, R. C.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)
FIELD INFORMATION AGENCY, TECHNICAL

FIAT FINAL REPORT NO. 594 — 21 March 1946

HIGH PRESSURE CHEMICAL LIQUID PUMP
FORCE FEED LUBRICATORS
POSITIVE ROTARY SUPERCHARGER
(Manufactured by Robert Bosch G.m.b.H. - Stuttgart)

BY

R. C. MATHEWSON

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

States the general lack of new development and describes with 8 illustrations the features of useful improvement in design of one high pressure chemical pump, six lubricator pumps and one rotary supercharger. 2 pages of text and 8 illustrations.

TABLE OF CONTENTS

PERSONNEL OF TEAM

Mr. O. D. Treiber
Mr. Arthur Pope, Jr.
Mr. R. C. Mathewson

Foreword - Pumps, lubricators and superchargers manufactured by Robert Bosch were investigated and in general it was found that their present designs follow well known standard practice. The following report describes some unusual features which appear to be improvements over previously known designs.

The illustrative drawings referred to are shown on Pages 4 through 10 and are identified by figure numbers corresponding with the numbered paragraphs of the report.

SECTION I

High Pressure Chemical Liquid Pump

1. Drawing PEZ5192/1, illustrates a special pump developed for I. G. Farben Industries to pump chemical liquids, which may be of corrosive nature, at pressures of 10,000 to 14,000 #/sq. in. The delivery valve assembly of a standard Bosch, individual type Diesel injection pump, is replaced by the apparatus shown on above drawing. The high pressure pump plunger is returned by a spring(4). The suction valve (15) is at the side and two discharge valves (12) and (12) at the top of the pump.

Using a suitable fuel or a lubricating oil in the standard type of pump, pressure is applied to the underside of the spring loaded plunger. This acts on the smaller plunger which does the actual pumping of the chemical liquid. The quantity of liquid delivered can be controlled by movement of the standard type pump control rod to by-pass more or less of the cylinder volume as may be desired. The design also ensures that when corrosive liquid is being pumped, none of it can come in contact with the working parts of the standard type pump.

SECTION II

Force Feed Lubricators

Robert Bosch have specialized in the manufacture of force feed lubricators and the following are developments of lubricators made since 1937 which embody some of the Bosch standard lubricator design and parts.

2. Drawing MGA-6/3, shows a small cylinder lubricator designed for the Hirth Aviation engine with six feeds, and without individual adjustment. Delivery per feed per stroke is around .006 cm^3.

3. Drawing MGE-6A1, shows a six-unit barrel type, cylinder lubricator for small 2 cycle M.A.N. Diesel engines suitable for working against 700 #/sq. in. pressure.

4. Drawing SP/BU3/1, illustrates a lubricator with an axial cam operating a single three diameter plunger. The largest diameter being formed by the drive member and the two parts secured together by a pin. This plunger, by its reciprocating and rotating motion, acts as a piston valve to control both inlet and outlet ports. Flat spots on the plungers provide the port controls. Each of the three diameters thus provides a pump, one at the outer end and the others between the smaller and larger diameters of the plunger.

5. Drawing OEZ3006A, shows a design of lubricator of the multiple plunger, "barrel" type for use on two cycle engines with a control to vary the lubricating oil supply with varying engine load.

6. Drawing OEZ2531/D shows an individual plunger, enbloc type lubricator designed for pressures of 6,000#/sq. in., used for pumping the oil for cooling and sealing of a high pressure compressor.

7. Drawing OEZ3057UC, shows an individual plunger, enbloc type lubricator made for German Navy steam engines to deliver 5 mm^3 per feed per stroke at 1400# per sq. in. and designed so that delivery could not be affected by counter pressure.

SECTION III

Positive Rotary Supercharger

8. Drawing PEZ9088/1, shows a positive, rotary vane type blower. A few experimental samples were made. It has two fixed vanes in each rotor and was designed for operation up to 4,000 RPM and to have a capacity of 3 liters per revolution at 4 to 4.5#/sq.in. discharge pressure. Volumetric efficiency was 80 to 85% and adiabatic efficiency 50 to 55%. It was stated that the unit was considered noisy at 4,000 RPM.

APPENDIX I

Full size prints of the drawings from which the eight figures were taken have been forwarded to the Joint Intelligence Objectives Agency, Room 2213, Munitions Building, Washington, D.C. to be available for more detailed reference.

Fig. 1 PEZ5192/1 - Indirect High Pressure Pump.

Fig. 2 MGA-6/3 - Small Cylinder Lubricator.

Fig. 3 MGE-6A1 - Six Unit Barrel Type Cylinder Lubricator.

Fig. 4 SP/BU3/1 - Three Pump Lubricator with One Rotating and Reciprocating Plunger.

Fig. 5 OEZ3006A - Multi Plunger, "Barrel" Type Lubricator.

Fig. 6 OEZ2531/D - Lubricator for Pressures of 6,000 pounds per Square Inch.

Fig. 7 OEZ3057UC - Lubricator for Steam Engines.

Fig. 8 PEZ9088/1 - Vane Type Supercharger.

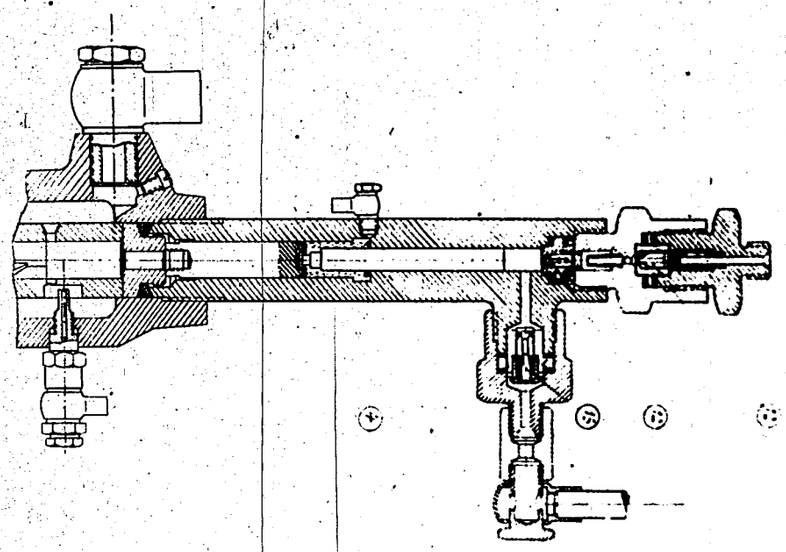


Fig 1
Drg. FEZ 5192/1
Indirect High Pressure Pump

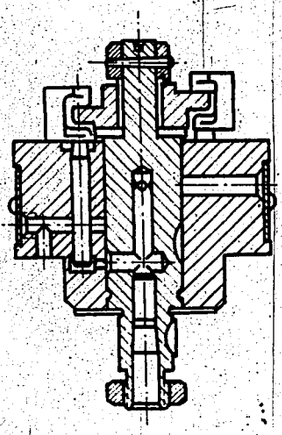


Fig 2
Drg MGA E/3 Lubricator

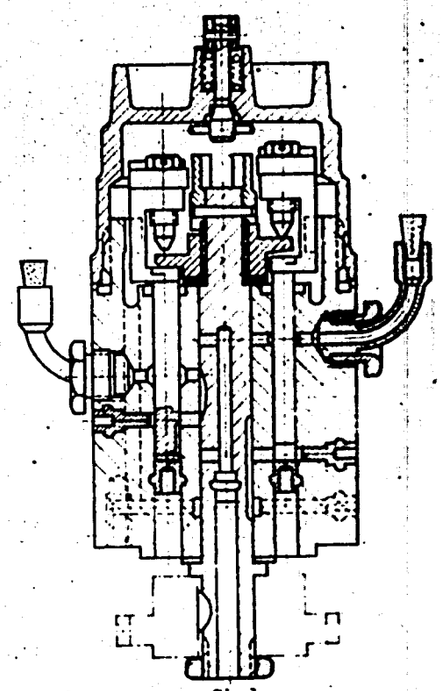
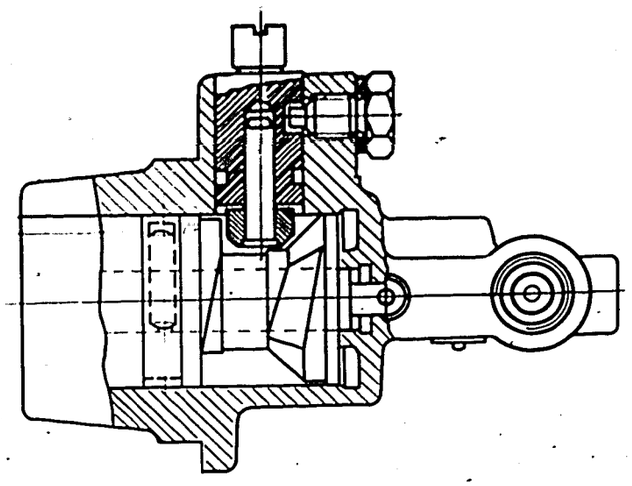


Fig 3
Drg. MGE 6A1 Lubricator



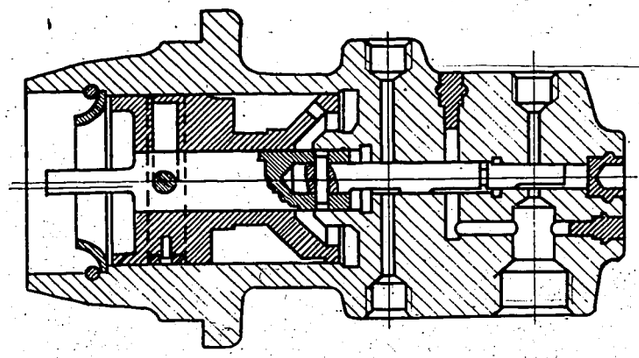


FIG. 4

Drg Sp/BU 3/1 Rotary Cam Lubricator

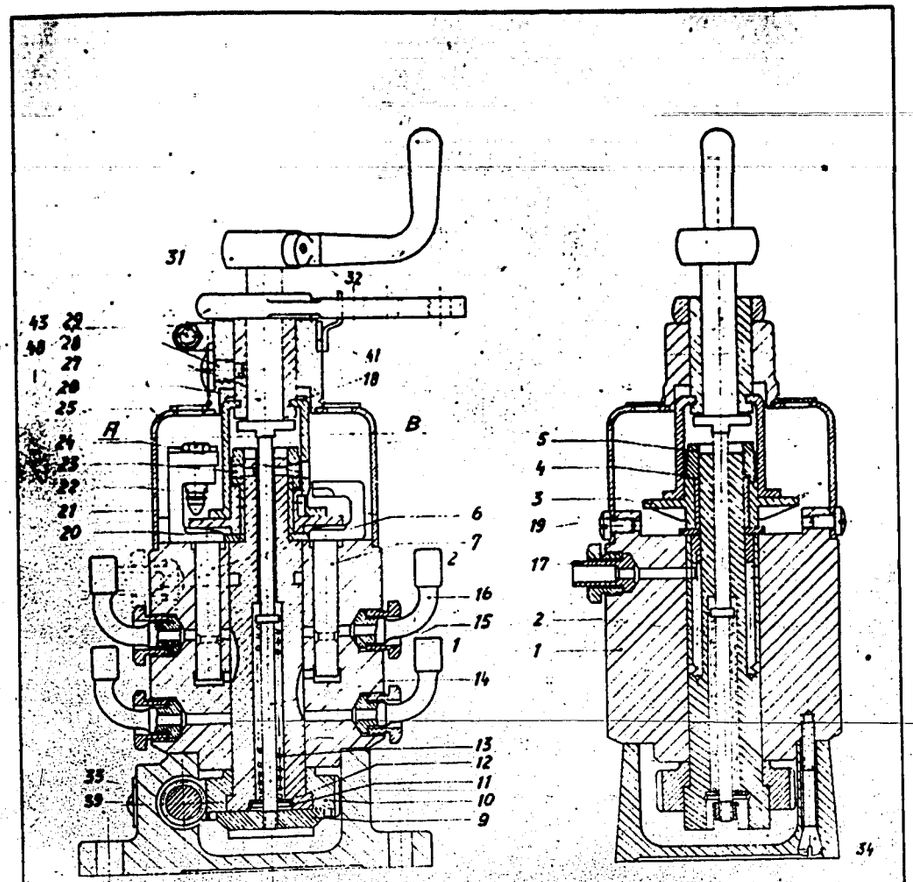


FIG. 5

Lubricator for 2-cycle engine, with control to vary quantity with load

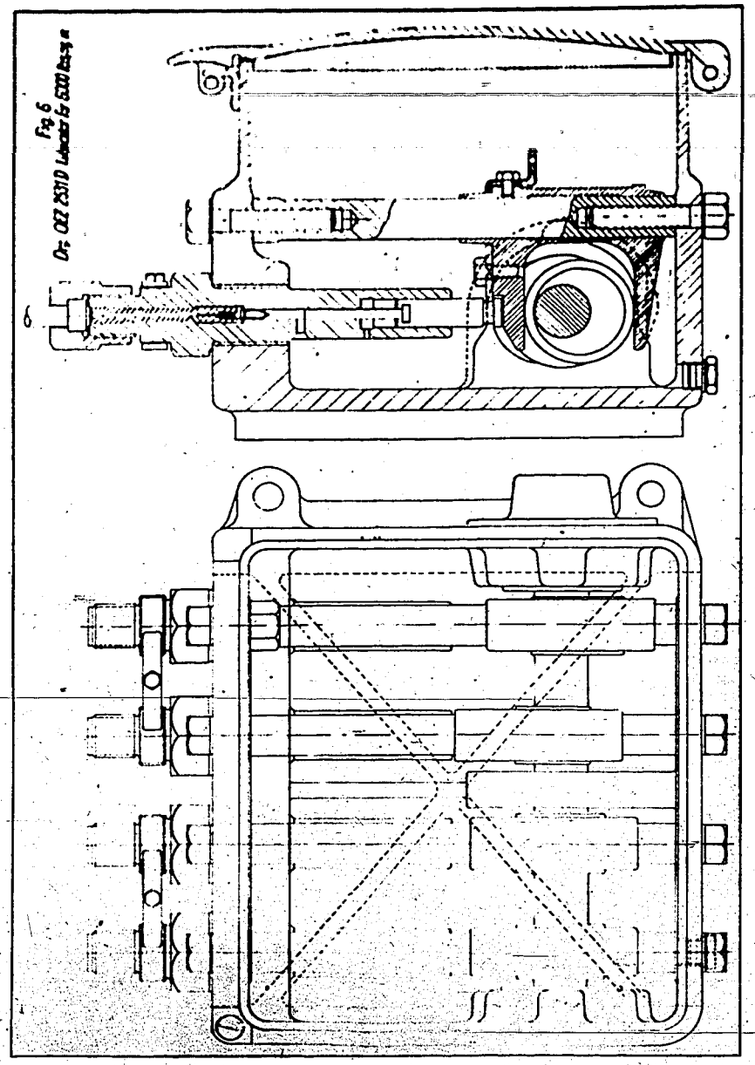


Fig 6
Dr. OEZ 3310 Lubricator for Navy Steam Engines

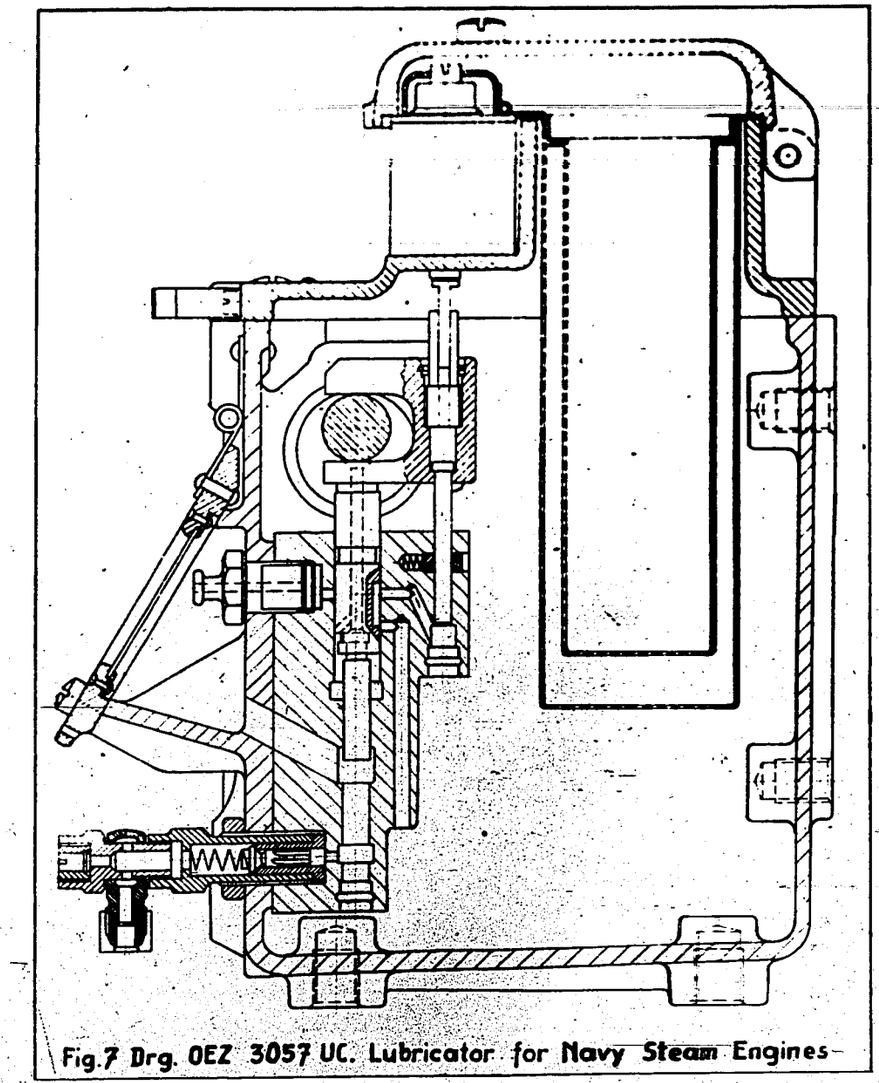
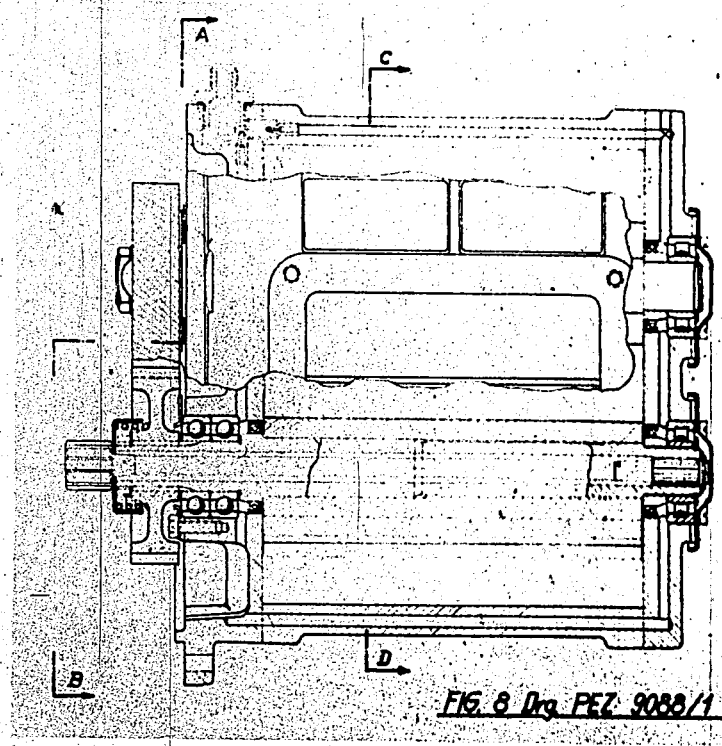


Fig.7 Drg. OEZ 3057 UC. Lubricator for Navy Steam Engines



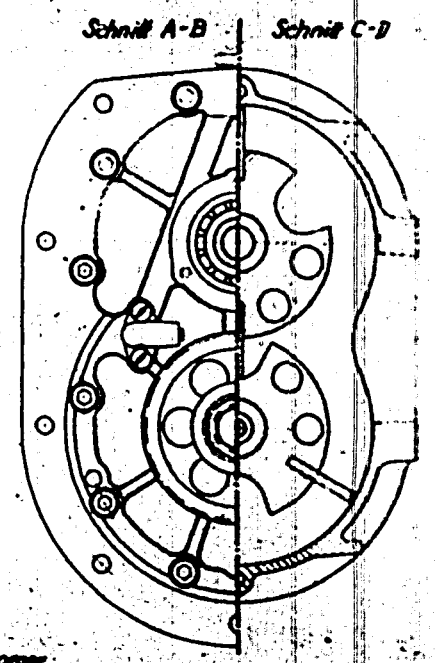


FIG. 8 Drg. PEZ 9088/1 Supercharger

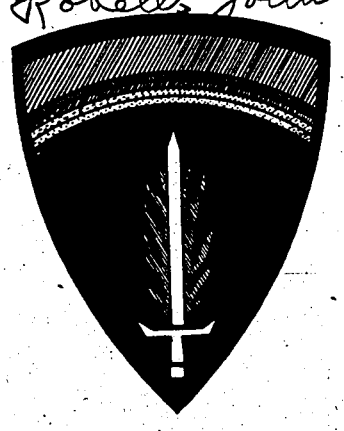
Copy 1

FIAT FINAL REPORT 840

GESELLSCHAFT FUR LINDE'S EISMASCHINEN

CALCULATION OF REGENERATORS FOR LINDE-FRANKL INSTALLATIONS AND OVERALL UTILITIES REQUIREMENTS FOR LINDE-FRANKL OXYGEN PRODUCING UNITS

Robell & John



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 840 1 July 1946

GESELLSCHAFT FUR LINDE'S EISMASCHINEN

CALCULATION OF REGENERATORS FOR LINDE-FRANKL INSTALLATIONS AND OVERALL UTILITIES REQUIREMENTS FOR LINDE-FRANKL OXYGEN PRODUCING UNITS

BY

JOHN ROBELL

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U.S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Information, description and methods of calculating the regenerators used in the Linde-Frankl installations are given, as well as overall utilities and space requirements for oxygen producing units.

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The Gesellschaft für Linde's Eismaschinen A.G. in Hollriegelskreuth near Munich was visited on June 6th, 1946. The purpose of the visit was to obtain information on the regenerators and centrifugal expanders used in the Linde-Frankl installations.

Evaluation:

Dr. Rudolph Linde, Dr. J. Wucherer and Dipl. Ing. C. Hochgesand were interviewed. According to Dr. Linde the centrifugal expanders for all their installations were manufactured by "Surth Machinen-Fabrik", near Köln, and no information on performance data was available at Linde. This subject will be covered in a subsequent report after a visit to Sürth.

Guide to the Reader:

The reader is referred to a report by H.M. Weir, U.S., CIOS No. 30 - XXVII - 55, which covers the subject of gas liquefaction and fractionation plants built by Linde.

REGENERATORS

1. General

Until the appearance of a patent by Matthias Fränkl (DRP.490878) heat exchangers were employed for cooling air before its liquefaction and separation. The exchangers heretofore employed consisted of well known tube bundles, in which the warm air was cooled by the cold separation products leaving the fractionation columns. For greater efficiency of these heat exchangers it is necessary to provide larger transfer surfaces, longer gas paths and/or higher gas velocities. Transfer surfaces of this type are expensive; furthermore, increased gas velocities cause an increase in the pressure drop of the gases, which in the final analysis increases the overall power consumption. As a result of the above, the efficiency of the heat exchangers was limited.

2. Description

The cold regenerators proposed by Fränkl are of the

same type as those frequently employed in the metallurgical industry. There, however, they reached a maximum efficiency of approximately 80%, while in the separation of air, cold regenerators with an efficiency of more than 99% have been constructed.

These regenerators are cylindrical vessels 4 to 5 meters high, of suitable diameter, filled with a packing having the greatest possible surface. The general arrangement is shown in Figure 1. The flow of gases is controlled by regulating equipment at the top of the vessel, which is actuated by means of compressed air, while automatic valves are provided at the lower end. Two cold regenerators always operate together. For this reason four regenerators must be provided for the separation of air: one pair for the heat exchange between the air and the oxygen produced, and one pair for the exchange between the air and the nitrogen.

The operation is as follows: the air flows downward through the first regenerator into the separating apparatus, warming this first regenerator and thereby cooling itself. The separation products leave the apparatus and flow upwards through the second regenerator, cooling it while they are warmed. After 1 to 4 minutes the valves are automatically reversed, the air is cooled in the second regenerator and the cold separation products are warmed in the first regenerator. From the fact that air and cold gases flow through the cold regenerators in opposite directions it is apparent that these vessels act as counter current exchangers. The reversal periods are set in such a way that the temperature fluctuations at the upper and lower ends of the regenerators do not become too great.

3. Construction

Figure 2 shows the packing material used by Linde, which was proposed by Frankl and proved to be the best. This material consists of a 25 mm. wide corrugated aluminium strip wound in a flat spiral of such a diameter as to fit closely the inside diameter of the vessel. These "pancakes" are held together by clamping wire and are piled one on top of the other into the vessel.

4. Design Data

Figure 3 gives pressure drop data of Linde-Frankl regenerators.

According to Dr. Wucherer the apparent specific weight of this packing material is one third of the specific weight of aluminium. For air pressure at 4.5 atmosphere pressure they use 0.3 kg. of packing / 1 cu.m. of air / hour. For air at 1 atmosphere they use 0.38 to 0.4 kg. of packing / 1 cu.m. of air / hour. 1 cubic meter of assembled packing of this type gives approximately 1000 square meters of heat exchange surface.

For more details on calculating regenerators the reader is referred to an article by H. Hausen entitled "Approximation process for calculating Heat Exchange in Regenerators" Z.Angew. Math. Mech. Vol.II (1931) No. 2.

5. Advantages

The high efficiency of these regenerators has already been mentioned. Also, it can readily be seen that their cost is very much lower as compared with tubular units.

To the above must still be added an important advantage of the cold regenerators. In the old processes all moisture and carbon dioxide contained in the air had to be carefully removed prior to the introduction into cold heat exchangers. If not - ice and solid carbon dioxide obstruct the exchangers very rapidly. With the cold regenerators, the ice and solid carbon dioxide are deposited on the packing, and following a reversal of the flow, are sublimed and thereby removed from the regenerator during its operation.

6. Disadvantages

As explained above, the air and the separation products flow consecutively through the same vessels. Therefore it is not possible to produce absolutely pure fractions; at each reversal the volume of the air trapped in a regenerator is mixed with the fractions. Furthermore, the products are also polluted with the water vapor and carbon dioxide picked up from the accumulator.

As a consequence of the above when using regenerators, it is not possible to produce oxygen at 99.7% which can be made by standard methods, nor nitrogen at 99.98% purity required for the synthesis of ammonia. The real field of application of regenerators is the production of oxygen of 40 to 98% purity.

UTILITIES REQUIREMENTS OF LINDE-FRANKL OXYGEN PRODUCING UNITS

Figure 4 gives the power consumption and costs of Linde-Frankl installations.

Figure 5 gives power consumption and cooling water requirements for different types and sizes of oxygen and nitrogen producing units.

Figure 6 gives space requirements and weights of different oxygen and nitrogen producing units.

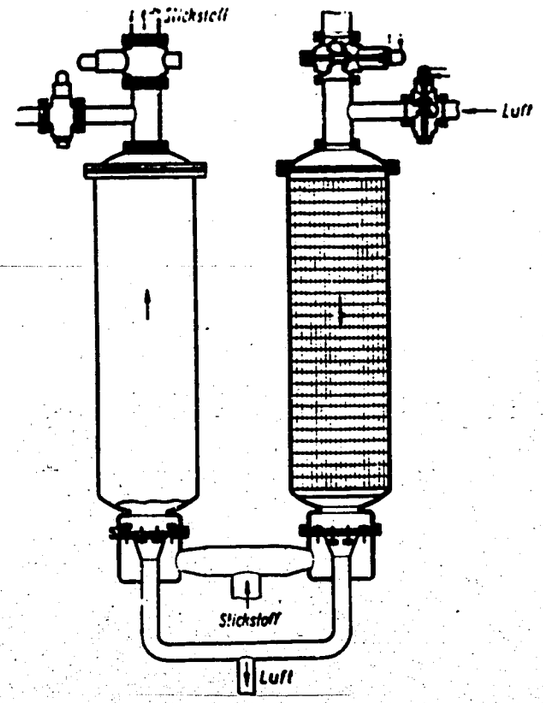
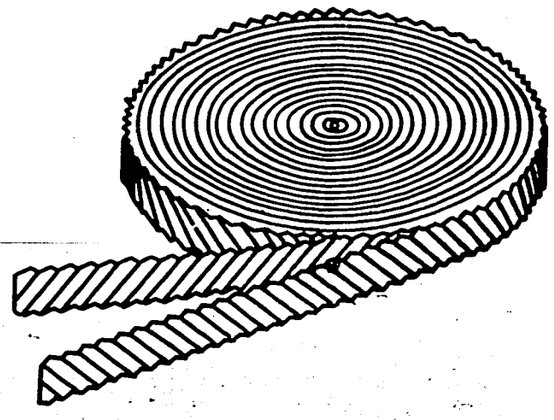
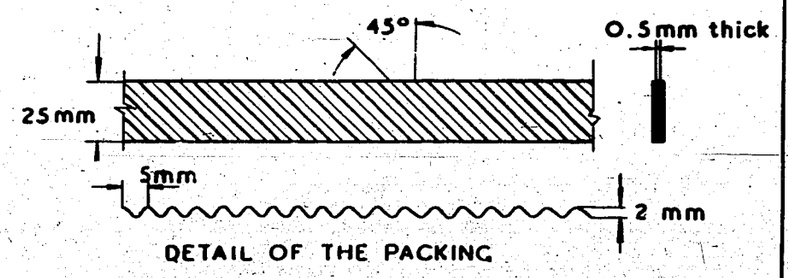


Fig. 1
Couple of cold accumulators.
(Luft = air, Stickstoff Nitrogen)



PACKING FOR COLD REGENERATOR



DETAIL OF THE PACKING

FIGURE 2

PRESSURE DROP OF AIR FLOWING THROUGH LINDE REGENERATORS BY LINDE.

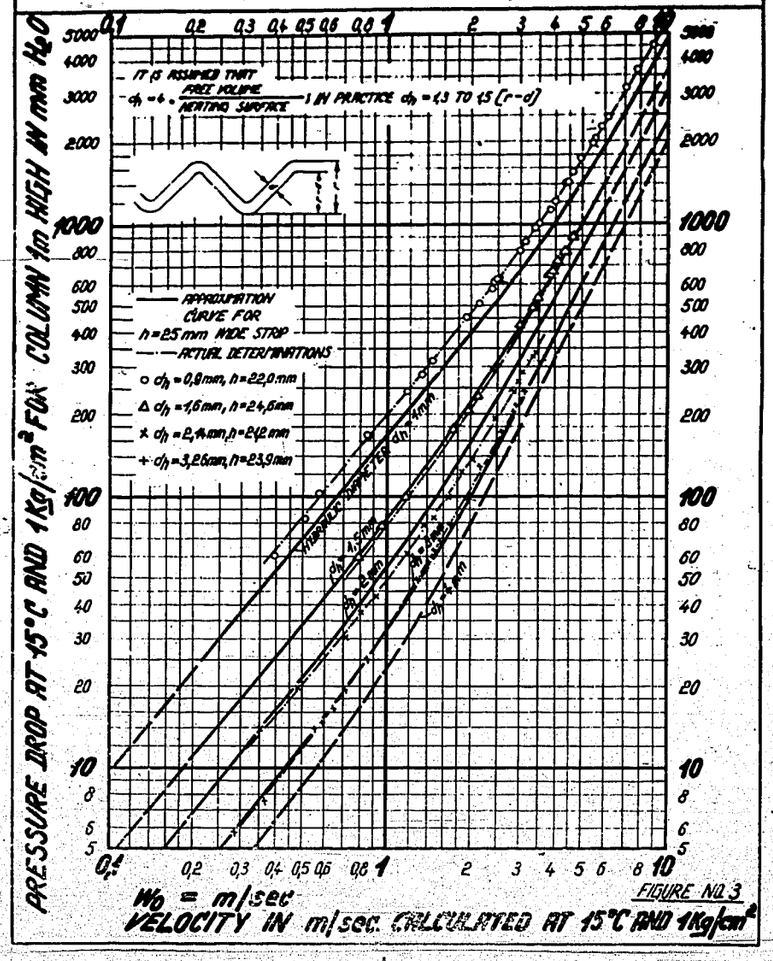


FIGURE NO 3

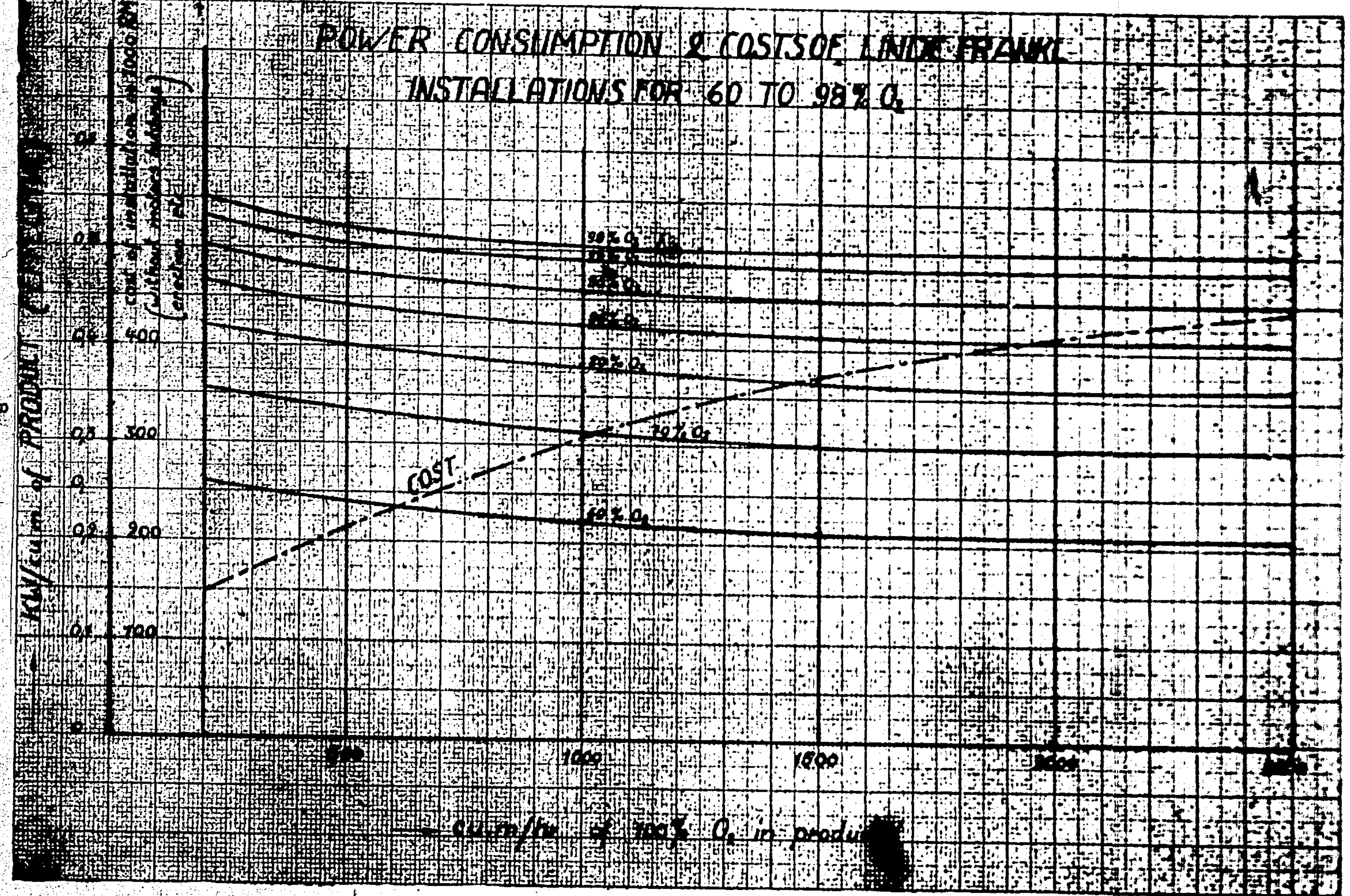


FIGURE NO. 4

POWER CONSUMPTIONS AND COOLING WATER REQUIREMENTS FOR DIFFERENT TYPES OF OXYGEN AND NITROGEN PRODUCING UNITS.

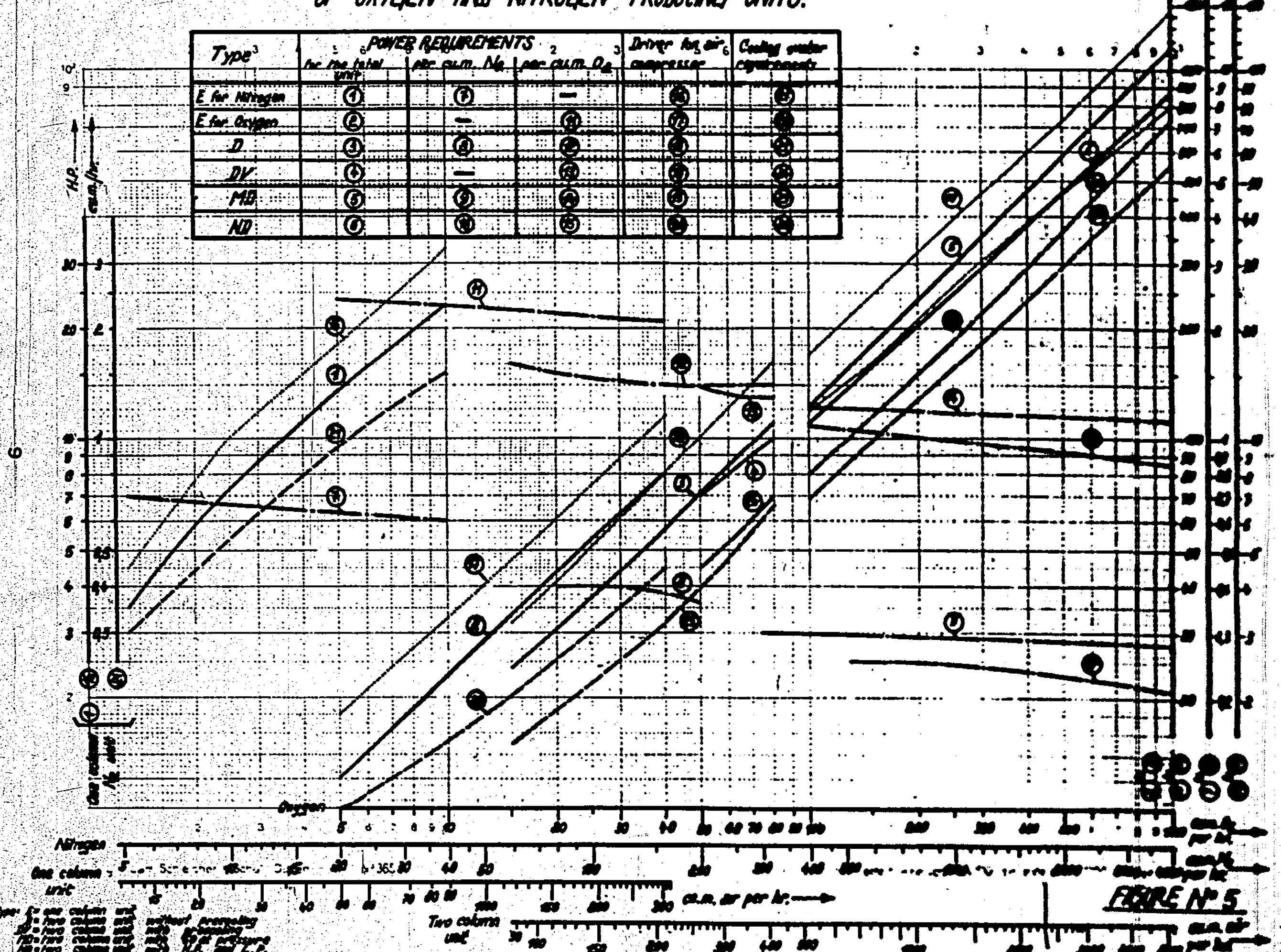
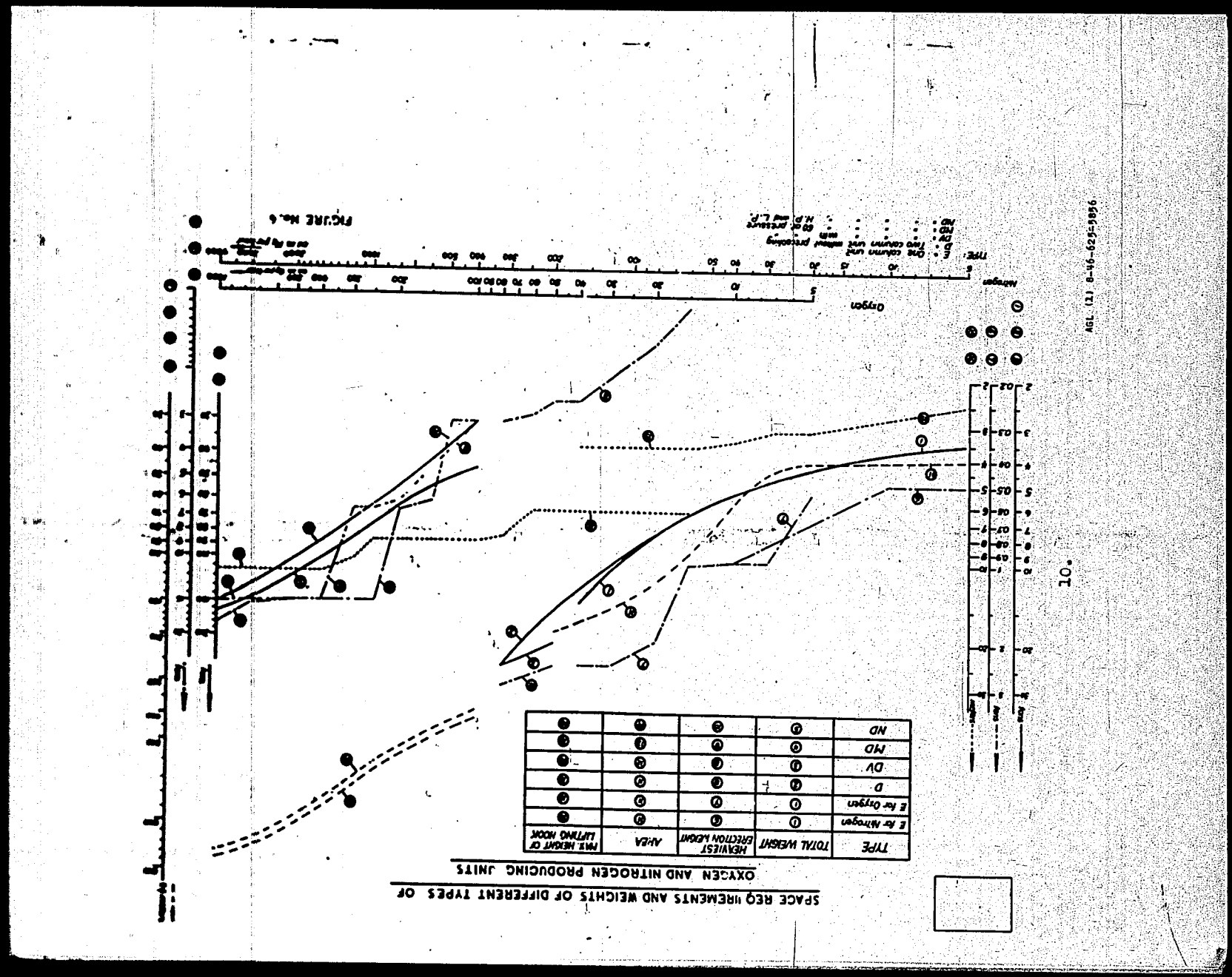


FIGURE No 5



SPACE REQUIREMENTS AND WEIGHTS OF DIFFERENT TYPES OF OXYGEN AND NITROGEN PRODUCING UNITS

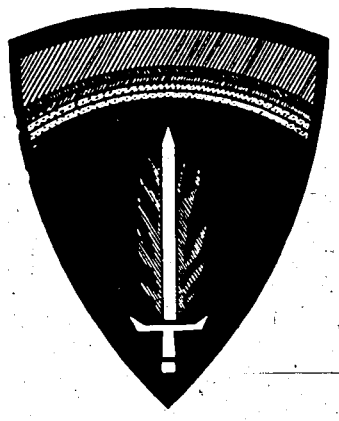
TYPE	TOTAL WEIGHT	HEAVIEST DIRECTION WEIGHT	AREA	MAX. HEIGHT OF LIFTING HOOK
E for Nitrogen	①	⑧	⑮	㉒
E for Oxygen	⑦	⑭	㉑	㉘
D	⑬	⑳	㉗	㉞
DV	⑲	㉖	㉝	㉟
MD	㉕	㉜	㉟	㉟
ND	㉛	㉟	㉟	㉟

Copy 1

FIAT FINAL REPORT 917

MANUFACTURE OF 2-ETHYL-ANTHRAQUINONE AT THE I.G. FARBENINDUSTRIE PLANT IN LUDWIGSHAFEN.

Robell, John



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 917

29 August 1946

MANUFACTURE OF 2-ETHYL-ANTHRAQUINONE AT THE I.G. FARBENINDUSTRIE PLANT IN LUDWIGSHAFEN.

BY

JOHN ROBELL

TECHNICAL INDUSTRIAL INTELLIGENCE DIVISION

U.S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Briefly describes process and equipment used at I.G. Farbenindustrie Plant at Ludwigshafen for the production of 2-ethylanthraquinone.

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

At the request of the Department of Commerce, a brief study of the production of 2-ethyl-anthraquinone was made. The Ludwigshafen Plant of I.G. Farbenindustrie was visited on July 9, 1946. All information was obtained from Dr. F. Teller who is in charge of the production of this chemical.

Evaluation:

The plant was built during the war and production started in 1942. The highest daily capacity attained was 3000 kg/day, however the maximum monthly production did not exceed 40 to 50 tons. The plant was damaged by bombing and the total production of this material until the end of the war amounted to approximately 120 tons.

Guide to the Reader:

According to Dr. Teller, all drawings, records and operating data were burned during bombing attacks. The flow sheets accompanying this report were rapidly sketched during the visit and may not be complete in all details.

CHEMICAL BASIS OF THE PROCESS AND YIELDS

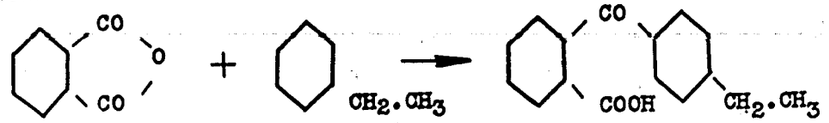
General

In the first step of the process, p-ethyl-benzoyl-o-benzoic acid is produced by adding at 35 - 40°C., phthalic anhydride to ethylbenzene in presence of aluminum chloride, using an excess of monochlorbenzene as solvent, It is a Friedel-Crafts condensation reaction.

In the second step of the process the p-ethyl-benzoyl-o-benzoic acid is reacted at 85 - 87°C. with concentrated sulfuric acid to effect ring closure, with the production of 2-ethyl-anthraquinone.

1) p-ethyl-benzoyl-o-benzoic acid

The formation of this chemical can be represented as follows:



phthalic anhydride	ethyl benzene	ethyl-b-acid
$C_8 H_4 O_3$	$C_8 H_{10}$	$C_{16} H_{14} O_3$
M = 148	M = 106	M = 254

Theoretically the following weights of materials are involved:

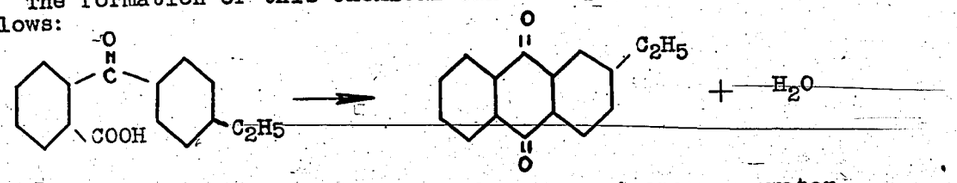
570 kg. + 408 kg. = 978 kg.

Practically a yield of 90.3% of the theoretical is obtained and 0.903 x 978 = 883.5 kg. of product are recovered from the above quantities.

In this report this product will be referred to as "ethyl-b-acid".

2) 2-ethyl-anthraquinone

The formation of this chemical can be represented as follows:



ethyl-b-acid	2-ethyl-anthraquinone	water
$C_{16} H_{14} O_3$	$C_{16} H_{12} O_2$	H_2O
M = 254	M = 236	M = 18

Theoretically the following weight of product should result:

100 kg. 92.9 kg. 7.1 kg.

Practically a yield of 75.33% of the theoretical is obtained, and 70 kg. of crude ethyl anthracuinone are obtained from 100 kg. of ethyl-b-acid.

FIRST STEP - PRODUCTION OF ETHYL-B-ACID (See Flow Sheet Fig. 1)

1. Process Description

3400 kg. of anhydrous chlorobenzene and 430 kg. of ethylbenzene are pumped from storage tanks 1 and 2 into condensing vessel 3. The agitator is set in motion and 570 kg. of dry phthalic anhydride are slowly introduced into this vessel.

1055 kg. of pure aluminum chloride, free of iron and passed through a crusher are introduced into the condensing vessel 3 over a period of 5 to 6 hours. With the first addition of $AlCl_3$, ceramic fan 26 is started: gases driven off during the reaction, consisting mainly of HCl traces of carbonyl chloride and some ethylbenzene and chlorobenzene are conducted through a porcelain pipe to porcelain wash tower 25, through ceramic tower 27 and discharged into the atmosphere. Both towers 25 and 26 are provided with spray nozzles and water is used to wash the gas. The wash water is collected in tank 6 and discarded. In order to prevent losses of $AlCl_3$ the chlorobenzene and the ethylbenzene must be very pure.

The condensation operation is started at room temperature. After the raw materials are all introduced, the charge is agitated for another hour at 35 to 40°C. maximum. It takes about 10 hours to perform the whole operation including charging of raw materials. This operation is performed in a batchwise manner and two condensing vessels are used.

From the condensing vessel, the melt is conducted to proportioning pump 4 which discharges it to decomposer 5. The melt enters the middle of the decomposer and flows over a porcelain distributing tray. To this place is also introduced 10% sulfuric acid from storage tank 28 in a volume ratio of 1 part of acid to 1 part of melt. The decomposer is filled with clay balls below the distributing tray. This operation takes about 6 to 7 hours.

The melt at 85° to 90°C. flows slowly from the decomposer to decomposer separator 7, in which decantation takes place. The melt should run uniformly and should be hot. If it cools down there is danger of crystalline obstructions forming in the pipe lines which are difficult to remove. $AlCl_3$ solution is withdrawn from the bottom and the ethyl-b-acid from the top of the separator 7. The $AlCl_3$ solution flows to separator 30 where a second decantation is performed; any entrained chlorobenzene is withdrawn from the top and sent to crude chlorobenzene storage tank 12 and thence to chlorobenzene distillation system described below. $AlCl_3$ solution is withdrawn from the bottom and sent to the sewer. It was planned to install an aluminum

recovery system at a later date.

The ethyl-b-acid coming from separator 7 enters the bottom of washer 8 where all aluminum salts are removed, by agitating the melt with 1 cu.m. of hot water at 80 to 90°C., per batch. The melt leaves the washer from the top and enters washer separator 9 in which another decantation takes place. The washed melt is withdrawn from the top and the separated wash-water from the bottom.

The washed melt is then introduced into the bottom of extractor 10. Also 2.7% NaOH coming from storage tank 29 is introduced into the extractor. The caustic soda must not be stronger than 2.7%, otherwise the separation in the next step is not satisfactory. The temperature should be about 80°C. and 160 kg. of 100% NaOH are required per batch.

The effluent from the extractor leaves it from the top and flows to pure separator 11, where decantation takes place. The chlorobenzene is withdrawn from the bottom and flows to crude chlorobenzene tank 12. Centrifugal pump 13 takes suction from this tank and discharges the crude chlorobenzene into continuously operated evaporator 14, where a temperature of 130 to 140°C. is maintained. The distillate is condensed in evaporator condenser 15 and enters evaporator separator 16 where decantation takes place. Water is withdrawn from the top. The chlorobenzene withdrawn from the bottom is dried by passing through two towers 17, connected in series and packed with solid caustic soda, and is returned to chlorobenzene storage tank 2.

From the top of the pure separator 11, the sodium salt of ethyl-benzoyl-benzoic acid flows to two buffer vessels 18, provided with agitators. The solution is withdrawn from the bottom and conducted to buffer separator 19 where decantation takes place. The last traces of chlorobenzene are withdrawn from the bottom and reciprocating pump 20 taking suction from the top discharging the liquid into precipitator 21. In this vessel the ethyl-b-acid is precipitated at 25 to 30°C. by 10% sulfuric acid. The liquid and the acid are introduced from the bottom and the effluent leaves from the top of vessel 21. Only enough acid should be fed, to barely turn congo red indicator yellow. If too much or too little acid is fed, troubles are experienced in the next operation. The precipitated ethyl-b-acid coming from the top of precipitator 21 goes to rotary filter 22. The ethyl-b-acid cake is washed neutral by water fed through spray nozzles and by diluting the product with water in the filter tray. If any chlorobenzene gets into the precipitator it may damage the filter cloth of the rotary filter.

The filter cake drops on a belt and is conducted to shelf dryer 23. This cake should be neutral and the amount of wash-water is adjusted accordingly. From there the final dried product is filled into barrels.

As already mentioned above, a yield of 90.3% is obtained and 155 kg. of ethyl-b-acid are obtained from 100 kg. of phthalic anhydride.

2. Plant Capacity and Utilities

When operating with two condensing vessels it is possible to make 4 batches per day and the plant capacity under those conditions is about 3534 kg. per day. Here is the time required for each operation:

Condensation (including charging)	about 10 hrs.
Decomposition	" 6 "
Extraction	" 6 "
Precipitation	" 12 "
Drying	" 12 "

For producing 100 kg. of ethyl-b-acid, the following utilities are required:

Electricity	42 kwh.
Steam	2.7 tons.
Cooling water at 20°C.	240 cu.m.
Operating labor	11 man hours.

3. Chemical Control

The following chemical tests are regularly made:

The raw materials, ethylbenzene, chlorobenzene and phthalic anhydride must be 100% pure and dry. Phthalic anhydride is hygroscopic especially when in fine powdered form, and special precautions should be taken to keep this material dry. Regular tests are made to check on the purity of these materials.

At the outlet of condensing vessel 3 the product is tested for the quantity of unreacted phthalic anhydride.

A sample of chlorobenzene liquor leaving the pure separator 11 is shaken with 2% NaOH and the aqueous layer is then precipitated with dilute H_2SO_4 to make sure that the crude chlorobenzene does not contain any ethyl-b-acid.

The liquor flowing to the filter has to be continuously checked with Congo red indicator to prevent an excess or

deficiency of acid.

The final product is given the following tests:

a) Moisture test - 10 grams of ethyl-b-acid are dried for 3 hours at 100°C. The loss of weight must not exceed 2%.

b) Ash test - The ash content must not exceed 1%.

c) Chlorine test - The chlorine content should be under 0.2%.

d) Melting point test - The melting point should be between 118 and 123°C.

SECOND STEP - PRODUCTION OF 2-ETHYL-ANTHRAQUINONE (See Flow Sheet Fig.2)

1. Process Description

1868 kg. of 96% sulfuric acid as well as 3012 kg. of 24% oleum, giving together 4880 kg. of 8% oleum, are introduced into pressure vessel 31 and heated to 85°C. When this temperature is reached, 600 kg. of pure ethyl-b-acid are rapidly added. The mixture is stirred for 4 hours while the temperature is maintained at 85° to 87°C. A sample is taken and if no presence of ethyl-b-acid is found, the charge is cooled to about 25°C. Compressed air is let into the vessel 31 and the charge is transferred to washing vessel 32, previously filled with 16 cu.m. of cold water. The mixture is stirred for about 30 minutes and forced by compressed air into filter press 33. During the filtration, the filter cake is washed with warm water until it is neutral. The filter cake is then introduced into dehydration vessel 34, which has been previously heated to 50°C. The product is stirred and the temperature increased to 125 - 130°C. during which time the 2-ethyl-anthraquinone is dehydrated and fused. Compressed air is used to force the fused product on iron trays 35 and it is ready for the final purification which is done by sublimation.

The tray assembly mounted on a carriage is introduced into electrically heated sublimation furnace 36. A vacuum of 3 mm. Hg. absolute is applied and the temperature is maintained at approximately 300°C. According to Dr. Teller this final purification can also be done by distillation.

2. Plant Capacity and Utilities

With the equipment as installed, 420 kg. of 2-ethyl-anthraquinone per 24 hours can be produced from 600 kg. of ethyl-b-acid.

The final purification of the product is done by sublimation in a furnace which is rather antiquated and designed for other production. Therefore the utilities are divided between the production of the raw 2-ethyl-anthraquinone and the final pure product.

For the production of raw 2-ethyl-anthraquinone from ethyl-b-acid, the following utilities are required:

Electricity	76 kwh.
Steam	0.5 tons.
Cooling water at 20°C	200 cu.m.
Operating labor	11 man hours.

For the production of pure 2-ethyl-anthraquinone by sublimation of the raw product, the following utilities are required:

Electricity	450 kwh.
Steam	1.7 tons.
Cooling water at 20°C	150 cu.m.
Operating labor	10 man hours.

3. Chemical Control

A sample of the melt from vessel 31 is poured into water, the precipitate collected and washed neutral. This precipitate is then boiled with a 10% caustic soda solution and refiltered off. The filtrate after acidification should not show any coagulated flakes which would indicate the presence of ethyl-b-acid.

The crude 2-ethyl-anthraquinone should be about 94 - 96% pure.

The pure 2-ethyl-anthraquinone should be over 99% pure.

PLANT EQUIPMENT

(Item numbers refer to flow sheets)

Here are described the main pieces of apparatus:

Item No:

1 : 1 ethylbenzene storage tank, 19 cu.m. capacity, steel construction.

2 : 1 chlorobenzene storage tank, 19 cu.m. capacity, steel construction.

3 : 2 condensing vessels, 5 cu.m. capacity each, with propellor agitator at 40 R.P.M.; cast iron

construction.

4 : 1 proportioning pump.

5 : 1 decomposer; tower 1 m.dia. x 6.5 m. high; porcelain construction.

6 : 1 wash water receiver; 700 liters capacity; porcelain construction.

7 : 1 decomposer separator; 700 liters capacity; porcelain construction.

8 : 1 washer provided with agitator at 450 R.P.M., 465 liter capacity; porcelain construction.

9 : 1 washer separator; 700 liters capacity; porcelain construction.

10 : 1 extractor provided with a 5 beam agitator at 120 to 180 R.P.M., and with temperature and pH measuring instruments; steel construction.

11 : 1 pure separator; capacity 700 liters, iron construction.

12 : 2 crude chlorobenzene tanks; capacity 6 cu.m.; steel construction.

13 : 1 centrifugal pump; steel construction.

14 : 1 "Wiegand" evaporator with tube bundle; 500 kg/hour capacity; steel construction.

15 : 1 evaporator condenser, steel construction.

16 : 1 evaporator separator; 250 liters capacity; steel construction.

17 : 2 drying towers; 750 liters capacity each; filled with solid NaOH.

18 : 2 buffer vessels, provided with agitators rotating at 36 R.P.M.; 9900 liters capacity each.

19 : 1 buffer separator; 700 liters capacity; iron construction.

20 : 1 reciprocating pump; 1200 liters/hour capacity; steel construction.

21 : 1 precipitator, provided with porcelain agitator; 50 liters capacity; all porcelain construction.

22 : 1 "Imperial" rotary vacuum filter; 1.5 sq.m. actual filtering surface; polyvinylchloride filtering cloth; rubber lined construction.

23 : 1 "Buttner" shelf dryer; about 5 m. diameter, with 18 shelves; revolving paddles; steam heated coils around shelves; 300 kg. per hour capacity.

28 : 2 sulfuric acid storage tanks; 18 cu.m. capacity each; steel construction brick lined.

29 : 1 caustic soda storage tank 19 cu.m. capacity; external bottom heating coil; steel construction, rubber lined.

31 : 1 cast iron steam jacketed pressure vessel, provided with an agitator; capacity 4 cu.m.

32 : 1 acid brick lined steel pressure vessel, provided with an agitator; capacity 22 cu.m.

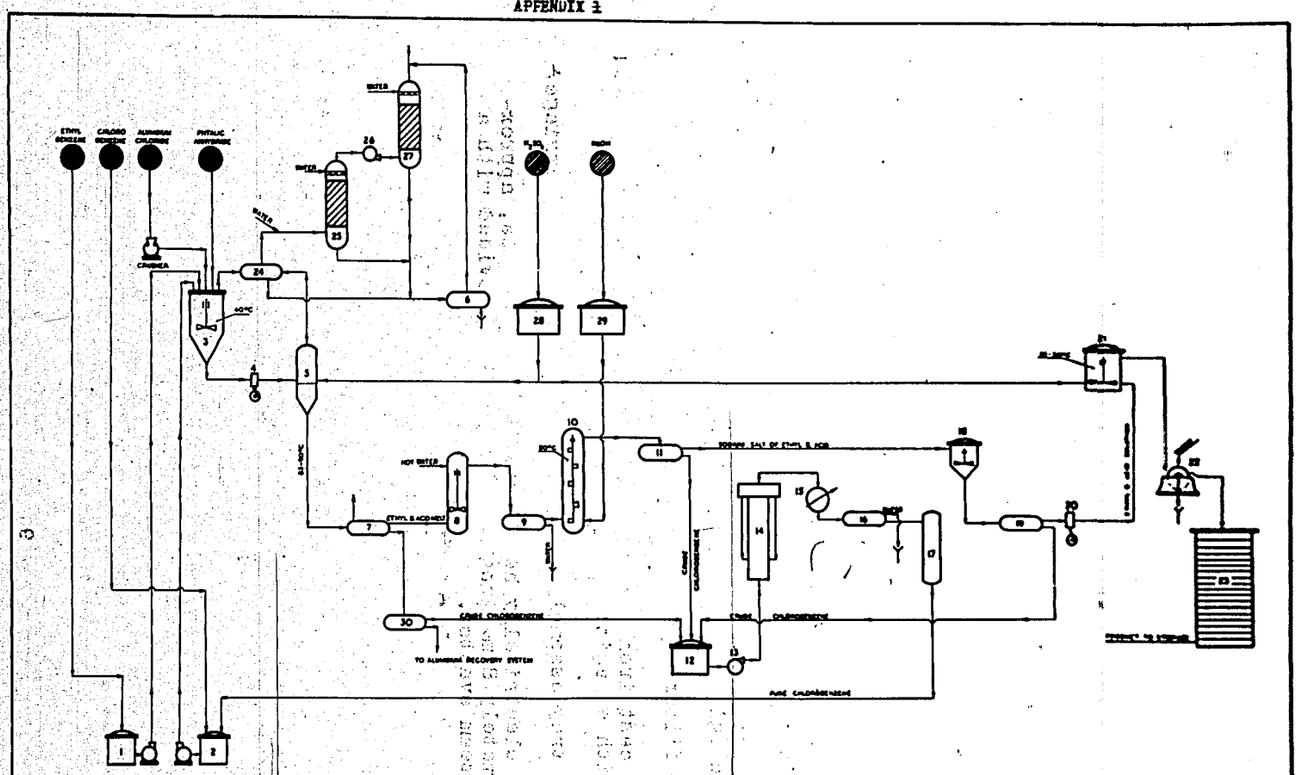
33 : 1 filter press with 20 frames type "Monstre".

34 : 1 cast iron, steam jacketed pressure vessel, provided with an agitator; capacity 1.5 cu.m.

35 : 1 tray assembly consisting of 8 trays on a carriage.

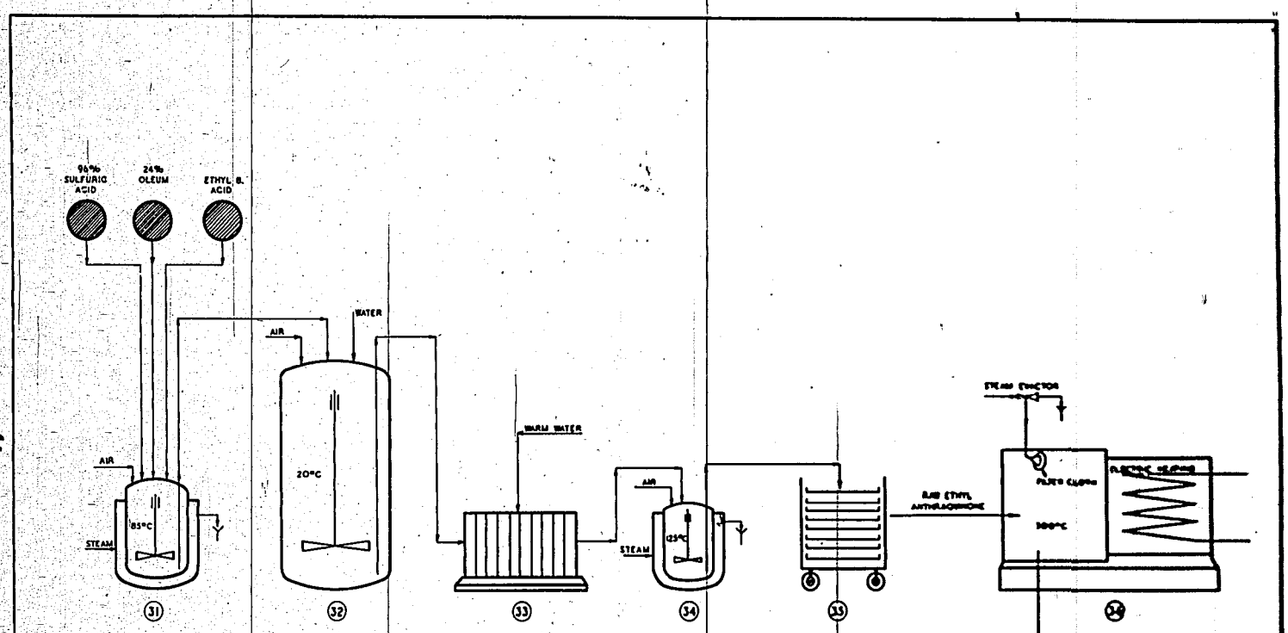
36 : 1 electrically heated sublimation furnace, approximately 8 m. long x 3 m. diameter provided with a steam evactor.

APPENDIX 3



1	ETHYL BENZENE STORAGE TANK	8	WASHER SEPARATOR	17	DRYING TOWER	25	WASH TOWER
2	CHLORO BENZENE STORAGE TANK	10	EXTRACTOR	18	BUFFER VESSEL	26	FAN
3	CONDENSING VESSEL	11	PURE SEPARATOR	19	BUFFER SEPARATOR	27	WASH TOWER
4	PROPORTIONING PUMP	12	CRUDE CHLORO BENZENE STORAGE TANK	20	RECIPROCATING PUMP	28	SULFURIC ACID STORAGE TANK
5	DECOMPOSER	13	CENTRIFUGAL PUMP	21	PRECIPITATOR	29	CAUSTIC SODA STORAGE TANK
6	WASH WATER RECEIVER	14	EVAPORATOR	22	ROTARY VACUUM FILTER	30	CHLORO BENZENE SEPARATOR
7	CHLORO BENZ. SEPARATOR	15	EVAPORATOR CONDENSER	23	SHELF DRYER		
9	WASHER	16	EVAPORATOR SEPARATOR	24	GAS SEPARATOR		

MANUFACTURE OF 2-ETHYL ANTHRAQUINONE
FIAT FINAL REPORT No. 917
I FLOW SHEET OF THE FIRST STEP
DATE AUG 8, 1945
FIG.1



31	ACID REACTION VESSEL
32	WASHING VESSEL
33	FILTER PRESS
34	DEHYDRATION VESSEL
35	TRAY ASSEMBLY
36	SUBLIMATION FURNACE

MANUFACTURE OF 2-ETHYL-ANTHRAQUINONE
FIAT FINAL REPORT No. 917
FLOW SHEET OF THE FINAL STEP
DATE AUG 15, 1945
FIG.2

AGL (1) 9-96-625-6199

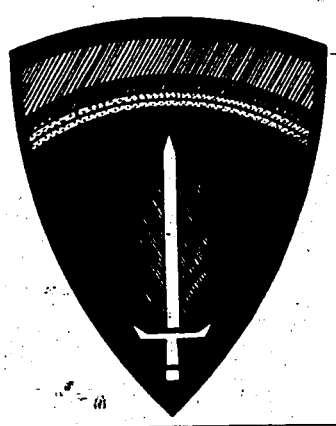
Copy 1

FIAT FINAL REPORT 888

METHANOL SYNTHESIS AT

I.G. FARBENINDUSTRIE PLANT AT OPPAU

Robell, John and Dowling, Wm. L. E.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 888 — 1 August 1946

METHANOL SYNTHESIS AT I.G. FARBENINDUSTRIE PLANT AT OPPAU

BY

JOHN ROBELL
WILLIAM L.E. DEWLING

TECHNICAL INDUSTRIAL INTELLIGENCE DIVISION

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

Presents information on process and equipment design of the methanol synthesis plant at Oppau, and reviews the latest developments achieved by I.G. Farbenindustrie in the art of methanol synthesis.

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The I.G. Farbenindustrie plant at Oppau was visited on several occasions between July 15 and July 27, 1946, to study the methanol plant and obtain all necessary information.

Evaluation:

In general, the process employed at Oppau for the synthesis of methanol is similar to that used in the United States. However, certain process and design features incorporated in this plant, and improvements made in newer plants built elsewhere in Germany by I.G. Farbenindustrie, are considered to be of particular interest.

Guide to the Reader:

Synthetic methanol production has been investigated at Oppau only. Information on other, more recently built methanol plants, was obtained from interrogated personnel who have been connected with other installations. The reader is referred to Appendix 2 for a list of previous reports on this subject.

PART I - METHANOL SYNTHESIS SYSTEM

General:

The methanol production technique at Oppau is based on experience gained in the manufacture of ammonia and isobutyl alcohol. The first isobutyl unit at Oppau was attached to the ammonia plant, use being made of certain ammonia plant equipment and building facilities.

Methanol, which is used at Oppau for the production of formaldehyde, was formerly received from the I.G. Plant at Leuna. Later, as the demand for formaldehyde increased, a new isobutyl plant was constructed at Oppau and the isobutyl plant, connected with the ammonia plant, was converted to methanol production.

At present there are two complete methanol synthesis loops in operation at the ammonia plant, each having a capacity of 90 to 100 tons per day, and the new isobutyl plant is shut down because of an insufficient supply of gas.

According to the interrogated personnel the modern methanol plants built elsewhere in Germany by I.G. Farbenindustrie are very similar in construction and layout to the new isobutyl plant at Oppau. However, a different catalyst is used and the space velocity for methanol synthesis is about 3 times that for isobutyl synthesis.

Methanol is produced from hydrogen and carbon monoxide, in the presence of a suitable catalyst according to the following reaction:

$$2\,H_2 + CO \rightarrow CH_3OH$$

The following undesirable side reaction, giving small amounts of dimethyl ether also takes place:

$$2\,CH_3OH \longrightarrow (CH_3)_2O + H_2O$$

If the temperature of the catalyst is allowed to rise above about 400°C. the following highly exothermic reaction takes place with further increase in temperature:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

The raw material used for methanol synthesis at Oppau is a water gas of approximately the following composition:

52.5% H_2, 41% CO, 5% CO_2, and 1.5% N_2

Sulfur is removed from this gas by passing it through activated carbon at low pressure. A portion of the gas is sent through a low pressure CO conversion system to adjust the ratio of H_2 to CO to the proper proportion and the combined gas is then compressed to 25 to 27 atm., and scrubbed with water for the removal of CO_2. This is followed by a final compression to about 260 atm. after which it is sent to the synthesis system as fresh make-up gas.

Process Description

Fig. 1 gives the flow diagram of a methanol synthesis loop. Although the equipment is generally designed for a maximum pressure of 325 atm., the usual operating pressure at Oppau is 250 to 260 atm.

The fresh make up gas has the following approximate composition:

68.0% H_2
29.0% CO Ratio $\frac{H_2}{CO}$ = 2.2 to 2.4
0.5% CO_2 Maximum sulfur content, 1 to 2 mg/cu.m. of gas
2.1% N_2
0.2% CH_4

This gas is passed through a vessel containing activated carbon which removes catalyst poisons such as carbon oxysulfide and iron carbonyl. The removal of these impurities takes place at room temperature, and it is necessary to inject into the gas stream about 0.5 gm. of ammonia per 1 cu.m. of gas, as well as oxygen in slightly over the stoichiometric amount for oxidizing the sulfur contained in the gas. The purified gas is introduced into the synthesis loop at the suction side of the circulator.

Starting at this point the flow of gas is as follows: The gas leaving the circulator passes through an oil trap, where lubricating oil is removed, and is then conducted to the interchanger. In this vessel the gas is heated by the gas leaving the converter and, after passing through the starting heater, enters the converter. A portion of the cold gas by-passes the interchanger and is injected between the catalyst beds in the converter for temperature control. The gas leaving the converter passes through the interchanger where it is cooled by the incoming gas and then goes to a double pipe water cooler in which the product is condensed. The product is removed from the gas stream in the product separator following the water cooler and the non-condensed gases are returned to the suction of the circulator. A constant bleed is maintained after the product separator to control inert gas concentration in the loop.

Condensate removed from the product separator containing methanol, water, dimethylether, higher alcohols and impurities is known as "raw methanol" and is sent to the distillation system.

Description of Equipment.

One complete synthesis loop consists of the following equipment:

2 Activated carbon vessels - suitable for either 2 or 3 synthesis loops. One is operated and one is spare. These vessels are vertical towers 500 mm. I.D. x 8 m. high and each contains 4 meters of activated carbon (M Khole) packing. The packing is 7 to 10 mm. in size. See section on catalyst for preparation of activated carbon.

1 Circulator - At Oppau several of the old vertical-type steam driven circulators, originally installed for ammonia production, are used. The new plants are equipped with more modern machines. For instance, at the Waldenburg plant where 3 methanol loops were erected for a total production of 300 tons per day, 3 electrically driven circulators each having a capacity of 100,000 to 110,000 cu. m. per hr. NTP, were installed. They are constant speed units and operate at 122 R.P.M.

1 Oil Trap - Oppau uses standard vertical cylindrical vessels. The newer methanol plants are using cylindrical vessels 600 mm. I.D. x 6 m. long, installed at a small angle from the horizontal in order to provide a large disengaging surface.

1 Product separator - Oppau uses standard vertical cylindrical vessels. Newer plants have inclined vessels, similar to the oil traps, and are 800 mm. I.D. x 6 m. long.

1 Water cooler - Horizontal double-pipe unit consisting of 4 rows in parallel, 10 pipes high. The inside pipes, 45 mm. I.D. x 8 m. long, carry the high pressure gas while water is circulated counter-currently in the outside pipes which have an I.D. of 120 mm. The total surface of 1 unit is approximately 260 sq. m. The inside pipes are made of N5 steel (3% Cr, 0.25% Mo, 0.1% C). It was found that severe corrosion took place at the inlets to the cooler and pieces approximately 1 ft. long of N8 steel (3% Cr, 0.5% Mo, 0.5% Wo) were welded to the N5 pipes at the inlet ends.

1 Interchanger - (Fig.2) This unit is of the shell and tube type. The shell is a steel forging made of S2 carbon steel (Siemens Martin steel with 0.2% C, having 40 to 45 Kg/sq. mm. tensil strength and 26% elongation), 800 mm. I.D. x 12 M. long. It has a 10 mm. thick liner of N5 (3% Cr, 0.25% Mo, 0.1% C) or N8 (3% Cr, 0.5% Mo, 0.5% Wo) special steel protected by a 2 mm. thick brass (63% Cu, 37% Zn) liner. The two heads are also protected with 2 mm. thick brass plates. The tube bundle consists of 757 copper manganese alloy (Cu + 1.5% Mn) tubes, 8 mm. I.D. x 14 mm. O.D. x 10.34 m. long, rolled and silver soldered into copper manganese tube sheets. The total surface is 265 sq. m. There are 57 baffles each with circular holes 51 mm. dia. giving a total gas passage area of 285 sq. cm. The tube bundle is surrounded by a 2 mm thick copper manganese plate on the outside of which a 125 mm. thick

kieselguhr brick lining is installed, held in place by a 2 mm. thick brass shell. The tube bundle has funnel-shaped heads at each end made of copper manganese, the lower funnel being bolted to the bottom head of the vessel while the upper funnel is provided with a stuffing box which permits the tube bundle to expand. To prevent gas from by-passing the tube bundle, 5 asbestos packing rings are provided along its length as well as stuffing boxes at each end.

1 Converter - (Fig. 3). The shell is a steel forging 800 mm. I.D. x 12 m. long. The inside linings of the converter, similar to those of the interchanger, are indicated on Fig. 4. For installing the 10 mm. thick special steel liner the forging is heated with steam to a temperature of 250°C. and then the liner is inserted. The method used for inserting the 2 mm. thick brass liner is indicated on Fig. 4. The bulged portion of the liner is pressed against the shell with a jack and the whole liner is then hammered.

The present methanol converters in use at Oppau have old type catalyst baskets. Gas is introduced into the bottom of the converter and rises through a central tube in which a heating element is inserted. The gas then flows downward through the basket, which is completely filled with catalyst. Inserted into the catalyst mass are five equally spaced perforated pipe rings, made of N8 or copper manganese alloy, through which cooling gas is introduced. This converter is charged with approximately 2.6 to 2.7 cu. m. of catalyst, having a specific gravity of 1.4 to 1.5, and is said to have a capacity of 90 to 100 tons per day at 260 atm. pressure.

The newer type converters, such as were installed in the Hydebreck plant, have 6 catalyst beds. The cooling gas is introduced under each of the five top beds, the general arrangement being indicated on Fig. 4. The catalyst grate is made of N8 steel and is covered with a copper manganese screen, having 3 mm. openings, on which the catalyst rests. Four 3 point thermocouple leads are installed for measuring the temperatures in the converter. This type converter is charged with approximately 3 cu. m. of catalyst having a specific gravity of 1.4 to 1.5 and is said to have a normal capacity of 110 tons of raw methanol per day with a possible maximum of 150 tons per day at 300 atm. pressure.

Miscellaneous: In the more recent installations the starting heater is in a separate vessel as indicated on Fig. 1. The heating element consists of 40 mm. wide x 7 mm. thick copper bands wound around porcelain insulated pipes. Transformers for the starting heaters can be regulated to furnish from 80 to 400 KVA at 16 to 20 volts.

In recently built plants the shells of the high pressure vessels are of the wrapped or wound construction as described by Norman W. Krase in FIAT Final Report No. 611 dated December 12, 1945, entitled:

"Design and construction of high pressure compressors and reaction equipment". When built in this manner the special steel liner is 25 mm. thick and serves as a mandrel for the windings.

Piping in the synthesis loop, carrying hot gases, is made of N8 steel.

Another interesting feature in the newer plants is the provision made for the expansion of the interconnecting hot piping. Both the interchanger and the starting heater are supported by 10 cm. diameter rolls and can move as the hot piping interconnecting them expands. This arrangement obviates the necessity of long expansion bends.

Operating Data, Yields and Utilities.

a. Operating Conditions

A typical analysis of gas at the inlet of the converter is as follows: 18.4% CO, 67.2% H_2, 0.7% CO_2, 0.6% CH_4 and 13.1% inert gases. Plant experience has indicated that the percent CO in the gas entering the converters must be less than 20% in order to prevent the formation of appreciable quantities of higher alcohols.

The maximum operating temperature in the catalyst bed is between 360 and 390°C. The normal pressure drop across the converter with a new catalyst charge is 12 to 14 atm. After about 6 months of operation this pressure drop increases to about 20 atm. It was pointed out by the operating personnel that it is very important to maintain a constant pressure drop across the converter, as a sudden variation of even a few atmospheres increases the amount of undesirable components in the raw methanol. As the catalyst gets older in order to maintain a desired production rate, the pressure drop is increased very gradually by regulating the by-pass valve across the circulator.

The raw methanol leaving the synthesis loop has the following approximate composition: 1 to 2% $(CH_3)_2O$, 6 to 8% H_2O, 90% CH_3OH and 0.8 to 1.0% higher alcohols and ketones. The following information on the composition and properties of raw methanol was obtained from operating data for the Waldenburg plant:

Appearance	clear and colorless
Specific weight at 20°C	0.821
Water per cent	10 to 13
Dimethylether	10 to 12 c.c./500 c.c.
Free acid	2 to 5
Saponification number	5 to 8
Bromine number	2 to 3

According to the operators the bromine number of the raw methanol should be as low as possible. A high number indicates the presence

of unsaturated alcohols and ketones. The upper limit is from 5 to 7. Good quality product should have 3 and excellent product 1.

b. Material quantities.

Approximately 3000 cu. m. of fresh feed are required per ton of raw methanol. The circulation rate is about 8 times the make-up or approximately 100,000 cu. m. per hour. The average bleed from a loop is about 15% of the fresh feed or 450 cu. m. per ton of raw methanol.

c. Production capacity and yields.

A synthesis loop as described above, with the new type converter, is said to have a normal capacity of 110 tons of raw methanol per day. The conversion per pass is between 12 and 16% of the amount of CO fed to the converter. The yield of methanol contained in the raw product based on the CO fed into the system is approximately 72%. This yield based on the H_2 fed into the system is approximately 62%.

d. Utilities.

It is estimated that, under normal operating conditions one methanol synthesis loop as installed at Oppau, producing 100 tons of raw methanol per day, requires the following utilities per ton of raw methanol:

Electricity	25 kwh.
Steam	0.3 tons
Cooling water	130 cu. m.
Operating labor	1.54 man hours.

Catalysts.

The activated carbon (M Kohle) used for the removal of sulfur compounds and iron carbonyl from the fresh feed is prepared in the following manner: Ruhr anthracite 1 to 10 mm. in size is used as raw material. 400 liters of this material are charged into a special brick-lined furnace and the charge is ignited. Air, water gas and enough steam for temperature control are introduced into the bottom of the furnace. A temperature of 920°C, (not to exceed 950°C) is maintained for 3 hours. During this time the bulk density of the raw material, which at the start is 700 gm/liter, increases to 900 gm/liter and then decreases to 550 gm/liter which should be the density of the final product. The resulting product is screened and the 7 to 10 mm. material is used for the activated carbon vessels.

The catalyst used for methanol synthesis is a zinc chromate having the following composition before reduction: 26 to 30% Cr_2O_3, 59 to 64% ZnO, 1 to 1.5% graphite and 9 to 10% H_2O.

This catalyst is prepared at the I.G. plant at Leuna as follows: 100 kg. of zinc oxide in fine powdered form are mixed with 240 liters of water to form a suspension. Then 50 kg. of chromic oxide are added. According to Leuna this addition should be very rapid as the zinc chromate mixture has thixotropic properties and a non-homogeneous product may result, giving a poor quality catalyst. Approximately 150 liters of the water is then removed in a press. The material is dried in a shelf dryer with air at 110°C, pulverized in a mill, mixed with graphite, and then tabletted. The finished product is in the form of small cylinders 10 mm. diameter x 10 mm. high.

At present a new and simpler method is employed at Oppau for the preparation of this material: 100 kg. of pure powdered zinc oxide and 40 kg. of pure crystalline chromic oxide are mixed in a stainless steel (18-8) mixer and 40 liters of water are added, as well as 2 kg. of graphite. The temperature must not exceed 30°C. when graphite is added, otherwise lumps are formed. From the mixer the material is sent to the pelleting machine. The specific gravity of the pellets is 1.7 to 1.75. The catalyst made according to this method has not yet been employed on a large scale.

The normal catalyst life was said to be from 6 months to 1 year. On removal of a spent charge about 60 to 70% is found to be pulverized. A change of catalyst is made when the pressure drop across the converter reaches approximately 20 atm. and the spent catalyst is pneumatically removed from the converter. New catalyst should be carefully charged to avoid breakage.

A new catalyst charge is reduced in the following manner: The synthesis loop is purged with nitrogen and a pressure of 2 to 3 atm. of nitrogen is applied. The circulator is started at about 1/3 of the normal rate (30,000 cu. m. per hour), and fresh gas is slowly fed to the system. The temperature is slowly raised by means of the starting heater to 100 to 110°C, and the pressure to 260 atm. These conditions are maintained for 30 to 48 hours, during which time water separated in the product drum is measured. In the next 24 to 36 hours the temperature in the converter is raised until the entire catalyst bed is at a temperature of 250°C. At this stage the temperature can be raised to the normal operating temperature in 2 to 3 hours.

PART II - METHANOL DISTILLATION.

Process description.

Fig. 5 gives a flow diagram of the methanol distillation system. Raw methanol from the synthesis system is expanded into the raw product storage tank which operates at 12 - 15 atm. Dissolved gases are thereby released and are vented. The liquid flows through a second expansion valve which reduces the pressure to 6 - 8 atm., is preheated and introduced into the 1st rectification column. In this column the dimethylether is distilled

off, condensed, and sent to a storage tank, 98% pure dimethylether is obtained and is used for making dimethyl sulfate and dimethyl aniline.

The bottoms, free of methylether, are sent to a 2nd rectification unit. In this unit "V" methanol (Vorlauf methanol), consisting of 95% methanol and 5% methyl isobutyl ether, methylal, methyl formiate, etc., is separated and goes to a "V" methanol storage tank. The bottoms are cooled and introduced into settling and intermediate storage tanks. In the line going to these tanks a 1% solution of potassium permanganate in water is added to the stream in the amount of 0.3% of the product flow. The purpose of this addition is to oxidize any organic compounds and decompose the iron carbonyl contained in the product. The temperature at the mixing point should not exceed 30°C. otherwise oxidation of methanol takes place.

The liquid is allowed to stand in the intermediate storage tanks for at least 8 hours and preferably 24 hours for settling to take place. The clear liquor is decanted and conducted to the 3rd rectification unit. The sludge settled on the bottom of the intermediate storage tanks goes to a filter press. The filtrate is also sent to the 3rd rectification unit and the filter cake is discarded. The side stream of the 3rd rectification column is the pure product and goes to the product measuring tank where it is analyzed for purity. If it meets the specifications it is sent to the final product storage. A portion of the reflux is sent to the "V" methanol storage tank. The total production of "V" methanol from the 2nd and 3rd rectification units amounts to 3 - 10% of the crude methanol. This product is injected into the isobutyl alcohol synthesis system or used as fuel.

The bottoms from the 3rd rectification column are sent to a residue storage tank and from there are fed into the reboiler of the 4th rectification column which operates in a batchwise manner. The first overhead from the 4th rectification column is pure methanol and is sent to the product measuring tank. After a certain time the purity of the overhead is such that it must be sent to the raw methanol storage tank. Finally, when ethyl methyl ketones, di-isobutyl ketones, diisopropyl alcohol and mostly isobutyl alcohol begin to boil off, the overhead is sent to the higher alcohols storage tank. This product is used in the isobutyl plant. The residue in the reboiler, which is mainly water, is discarded.

The elaborate methanol distillation system described above is considered necessary at Oppau in order to obtain a product pure enough for formaldehyde manufacture.

Description of equipment

The following tabulation presents the principle information on the various rectification columns:

Rectification Column No:	1	2	3	4
Diameter	Top Sect. 0.6m. Bot.Sect. 1.0m.	1.5m.	2.9m.	1.5m.
Height	8.5m.	22.5m.	23.6m.	22.5 m.
Material of construction: column	steel	steel	steel	steel
Bubble caps	-	cast iron	cast iron	cast iron
Type of plates:	Bamag sieve type	Bubble caps	Bubble caps	Bubble caps
Number of plates:	Top Sect.23 Bot.Sect.21	70	70	70
Distance between plates	-	30 cm.	-	-
Feed injection point from bottom:	8th,12th and 18th plates	16th,20th and 28th plates normally 20th	17th,21st and 27th plates normally 21st	16th,20th and 28th
Side stream take off point from bottom:	-	-	52nd,56th and 60th plates normally 60th	31st,37th and 41st plates

The above information was given from memory by Dr. E. Haarer and since the detailed drawings for this equipment could not be located, the accuracy of this information cannot be vouched for.

Operating data, Yields and Utilities

The distillation system as described is said to be suitable to handle normally 160 to 190 tons of crude methanol per day, with a maximum of 240 tons per day.

The following tabulation presents the principal operating data for the various distillation columns:

Rectification column No.:	1	2	3	4
Operating pressure (absolute):	6 to 8 atm.	1 atm.	1 atm.	1 atm.
Temp. at the bottom of the column:	110° C..	68 to 70° C.	89 to 90° C.	72 to 100° C.
Temp. at the top of the column:	30 to 35° C.	62° C.	64° C.	46 to 98° C.
Ratio of reflux to distillate:	10:1	6:1	-	3:1 to 1:1
Ratio of reflux to side stream:	-	-	2.5:1	-

As the operation of the 4th rectification column is batchwise, operating conditions at the beginning and end of the cycle are given.

The above information was also given from memory by Dr. E. Haarer and its accuracy cannot be vouched for.

One ton of raw methanol furnishes the following products:

Pure methanol	780 to 830 kg.
"V" methanol	30 to 100 kg.
Dimethylether	20 kg.
Higher alcohols	0.2 to 0.3 kg.

The yield of pure methanol, based on the methanol content of raw methanol fed to the system, is approximately 89%.

In the methanol distillation system the following utilities are required per ton of pure methanol produced:

Electricity	17.0 kwh.
Steam	2.7 tons
Cooling water	163.0 cu.m.
Operating labor	0.7 man hours

Analytical methods

The distilled methanol is subjected to the following chemical tests:

1. Sulfuric acid test - To 5 c.c. of methanol cooled to under 5°C. is added 5 c.c. of pure concentrated H_2SO_4. The resulting mixture is shaken and its temperature should not exceed 5°C. A dark coloration of the mixture indicates the presence of traces of olefines, which are very poisonous to formaldehyde catalyst. A slight coloration is acceptable. If the solution remains white, the product is of excellent quality.

2. Boiling point test - An entire sample of methanol must distill off without a temperature increase of more than 0.3 to 0.4° C.

3. Potassium permanganate test - 1.3 c.c. of 0.1% $KMnO_4$ solution in water are added to 100 c.c. of the product. The mixture must be placed in a water bath and maintained at 17 to 18° C. The color should change from violet to brown in not less than 20 minutes. A longer period indicates a better product, while a shorter period indicates that an insufficient amount of $KMnO_4$ has been added in the process.

4. Test for iron - 10 c.c. of 25% NH_4OH and 10 c.c. of 30% H_2O_2 are added to 100 c.c. of methanol. The mixture is boiled with a reflux cooler for 30 minutes. The flocculent iron compound is filtered out, dissolved in hydrochloric acid, and a standard colorimetric test for iron is applied. Traces of iron in the product indicate that an insufficient amount of $KMnO_4$ has been added in the process for breaking up the iron carbonyl.

5. Bromine number - This test is applied to the raw methanol. To 100 c.c. of product, the bromine solution is slowly added until a yellow coloration identical to the standard solution is obtained. The number of c.c. of bromine solution added is the bromine number.

The bromine solution is prepared by adding 4.2 c.c. of concentrated bromine to 1000 c.c. of 50% acetic acid and the resulting mixture well shaken.

The standard solution is prepared by adding 0.05 gr. of potassium dichromate to 1 liter of water.

APPENDIX 1

LIST OF GERMAN PERSONNEL INTERVIEWED

AT THE I.G. FARBENINDUSTRIE PLANTS AT LUDWIGSHAFEN AND OPPAU:

Name	Position	Location
Dr. K. Goeggel	Chief of High Pressure Department	Ludwigshafen
Dr. D. Timm	Assistant to Dr. Goeggel	Ludwigshafen
Dr. H. Soenksen	Head of Organic Department	Oppau
Dr. H. Rabe	Head of Catalyst Preparation Plant	Oppau
Dr. E. Haarer	Superintendant of Methanol Distillation Plant	Oppau
Dr. F. Duerr	Chemist	Oppau
Dr. F. Winkler	Head of CO and H_2 synthesis experiments	Oppau
Mr. G. Schulze	Engineer	Ludwigshafen
Mr.K. Bossert	Superintendant of isobutyl synthesis plant	Oppau

APPENDIX 2

BIBLIOGRAPHY

Copies of the reports listed below were transmitted to Washington D.C. Inquiries should be addressed to:

Office of Publications Board
U.S. Department of Commerce
Washington 25, D.C.

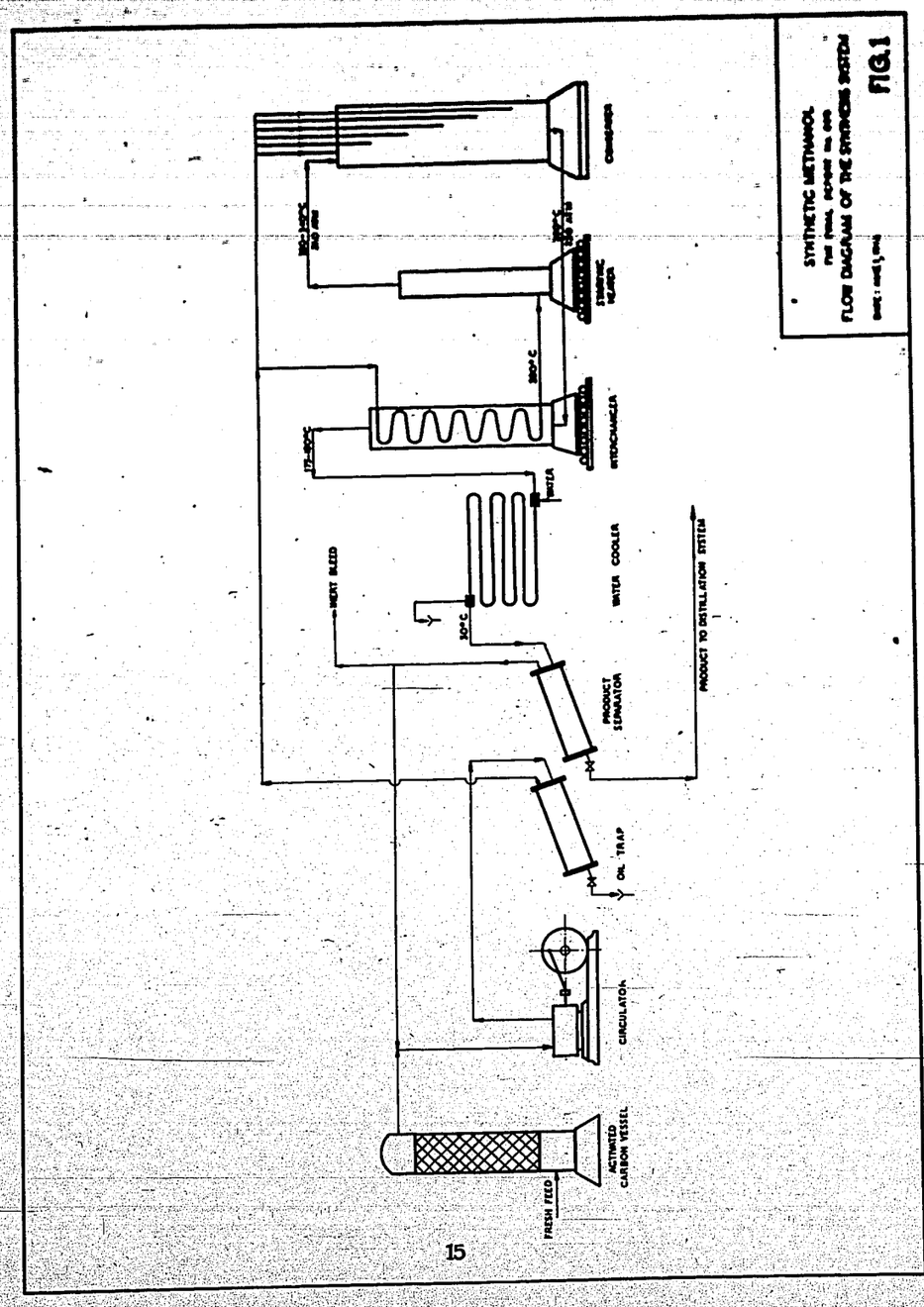
1. Related Reports Published by Allied Intelligence Agencies:

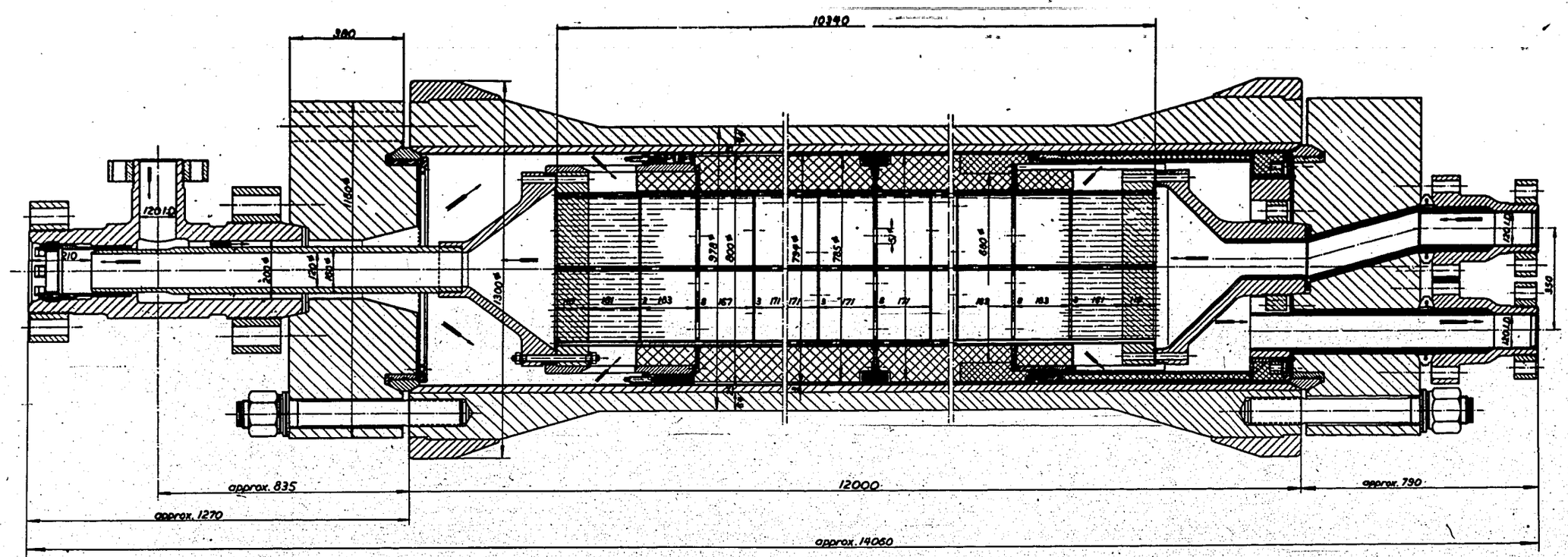
CIOS Report, File No. XXVIII-27
FIAT Records Branch File No.
17961/TP200/P964
Leuna Works near Merseburg.

CIOS Report, File No. XXX-103
FIAT Records Branch File No.
14088/TP200/P705
I.G. Farbenindustrie A.G. Works,
Ludwigshafen and Oppau.

CIOS Report, File No. XXVII-85
FIAT Records Branch File No.
13400/TP200/P683
I.G. Farbenindustrie A.G. Works,
Ludwigshafen and Oppau.

CIOS Report, File No. XXXII-107
FIAT Records Branch File No.
9351/TP200/P435
I.G. Farbenindustrie A.G. Works,
Leuna.



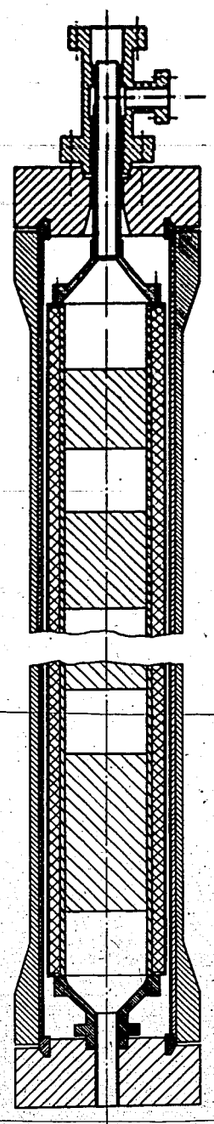


SYNTHETIC METHANOL

FIAT FINAL REPORT No. 888

INTERCHANGER

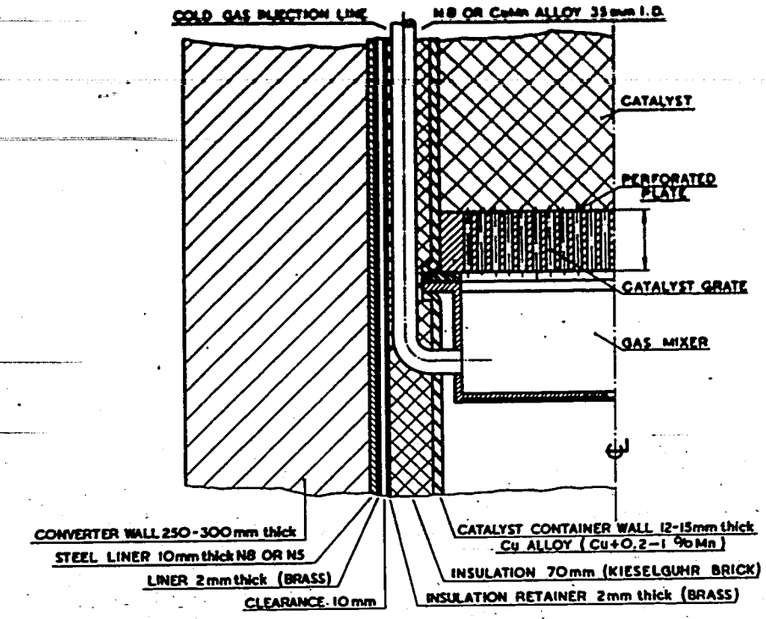
DATE: AUG. 1, 1946 **FIG. 2**



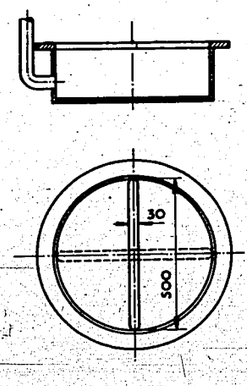
NOTE:
QUENCH LINES,
CATALYST GRATES
& MINOR DETAILS
NOT SHOWN.

SYNTHETIC METHANOL
FIAT FINAL REPORT No. 888
CONVERTER
DATE: AUG. 1, 1946 FIG. 3

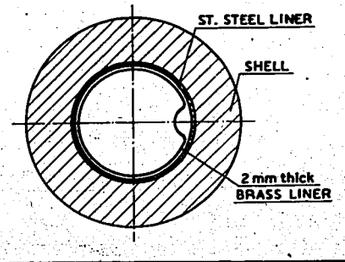
SECTION THROUGH CONVERTER



GAS MIXER



METHOD OF INSTALLING COPPER ALLOY LINER



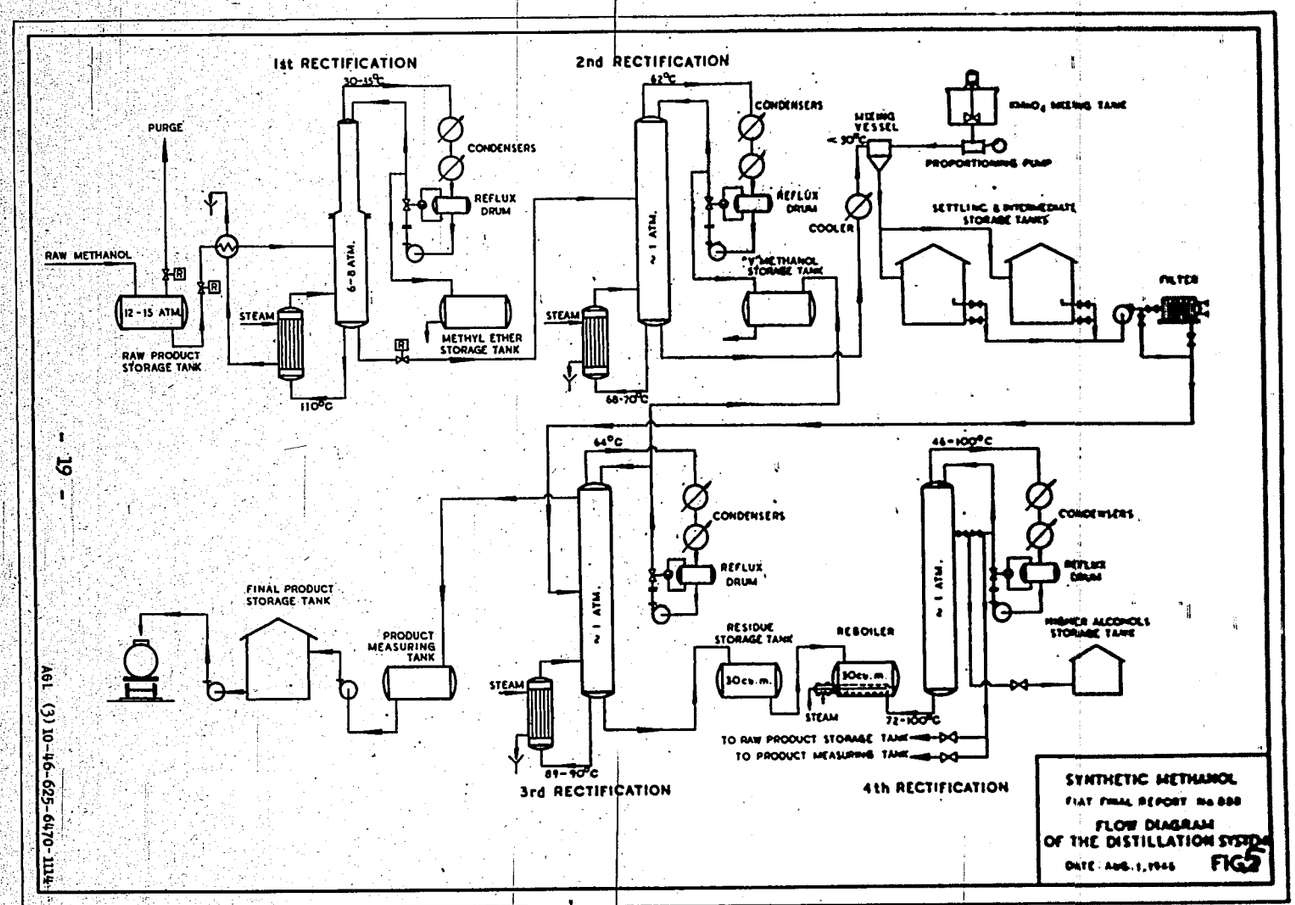
SYNTHETIC METHANOL

FIAT FINAL REPORT No. 888

CONVERTER DETAILS

DATE : AUG. 1, 1946

FIG.4

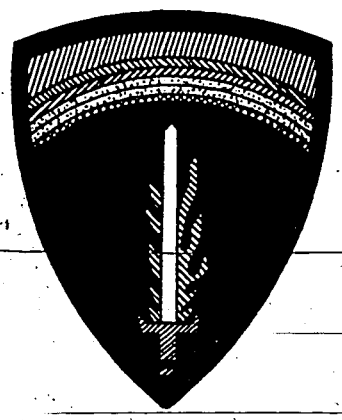


Copy 1

FIAT FINAL REPORT No. 856

MANUFACTURE OF POLYVINYLETHERS

Rosenquist, E. N.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 856 9 July 1946

MANUFACTURE OF POLYVINYLETHERS

BY

E. N. ROSENQUIST

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U.S. DEPARTMENT OF COMMERCE

A B S T R A C T

Detailed procedures are given for the preparation of the commercially important polyvinylethers, including the solid, oily, resinous and waxy Igevins.

PERSONNEL OF MISSION

Dr. E. N. Eosenquiste, TIIB
Mr. W. E. Alexander, TIIB

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The purpose of the investigation was to determine the detailed operating conditions for the preparation of the various Igevins or polyvinylethers.

Evaluation:

The entire series of polyvinylethers are prepared by rather simple mass polymerization methods using acidic catalysts, particularly boronfluoride dehydrate in dioxane.

Guide to the Reader:

Included in this report are the detailed procedures for the preparation of the solid polymers designated as Igevin M40, A50, J60, JZR, and Bindemittel Li 10; the oily Igevins A25, J30, J20 and Densodrin NW; and the waxy and resinous polymers designated as Igevin Z, ZJ, Densodrin V, W, H, and I.G. Wax V.

GENERAL SUMMARY

At Ludwigshafen at the present time, there is existing capacity for a monthly production of 100 tons of solid Igevins, 120-150 tons of oils and a maximum of 40 tons of the specialty resins and waxes. The solids are frequently sold to the trade in solution. For example Igevin M40 in 50% and 25% aqueous solution is sold as a textile finishing agent under the names Aggretan WL conc. and Appretan WL 25 respectively. The solids have found application as thickeners, textile finishing agents, adhesives, plasticizers, and paints for masonry. The oils have been used rather extensively as shoe and leather impregnating agents. The waxes and resins have had limited applicability to date.

The majority of the polymers are prepared in the presence of a boron trifluoride dehydrate catalyst. In one instance tin tetrachloride is the preferred catalyst. Depending on the boiling point of the monomeric ethers employed, the polymerizations are conducted at pressures up to four atmospheres gage.

DESCRIPTION OF EQUIPMENT

A. Solid Igevins

The monomers, prepared in another plant, are stored in a steel kettle of 2 cbm. capacity. The vessel is provided with brine cooling coils and a brine cooled V2A reflux condenser. This unit can be operated at up to five atmospheres gage pressure. Provision for agitation is made.

The polymerizer is "Remanit" lined (13-15% chromium steel) and has a capacity of 2 cbm. The unit is jacketed for brine cooling and in addition is equipped with an internal cylindrical shell cooler, fabricated from V2A steel. A double anchor type agitator is installed. A V2A reflux condenser having 6 sq. meters of cooling surface is attached. The maximum working pressure is 6 atmospheres gage. Provision is made for either draining the hot polymer directly to drums or to a Werner-Pfleiderer type mixer for the preparation of solutions.

Addition of raw materials is made by gravity flow through meters.

B. Igevin Oils

The starting materials are stored in the same equipment used above. A smaller 1 cbm. enamelled steel kettle equipped with a blade stirrer is employed as the polymerizing kettle. An interchangeable, heating or cooling jacket is provided. The tested working pressure is 6 atmospheres gage. A reflux condenser with 6 sq. meters of surface is installed.

For continuous polymerization a second agitated polymerizer of 150 liters capacity equipped with a heating jacket is provided. This unit is also enamel lined and has a working pressure of 6 atmospheres gage. Material overflows from the main polymerizer and is finished in the second smaller unit. The product is cooled in a 1 cbm. capacity jacketed steel kettle and finally is stored in a steel kettle of 5 cbm. capacity equipped with jacket for heating.

C. Igevin Oils and Waxes

The raw materials are stored in a 2 cbm. enamelled, agitated, kettle, provided with a V2A heating coil. For polymerization two kettles are available, both of 2 cbm. capacity. One is enamelled and equipped with a double anchor type stirrer while the other is stainless steel lined and has a blade stirrer. Each is equipped with a reflux condenser. The finished product is obtained in flake form by cooling on a revolving drum.

DETAILED POLYMERIZATION PROCEDURES

A. Solid Igevins

1. Igevin M40 - Polyvinylmethylether K value 45-50.

Monomeric vinylmethylether boiling within 6 to 9°C. is stored in the previously described vessel. The $CaCl_2$ brine temperature is maintained at -20 to -15°C. Seventy liters of the ether are introduced to the kettle. At a temperature of 3-5°C. and during the course of 30 minutes, 100 to 150 cc. of a 3% solution of $BF_3.2H2O$ in dioxane are added. Polymerization begins as evidenced by vigorous

boiling and a temperature rise to 12°C. The reaction is controlled by cooling to 7°C. Maintaining this temperature, 1130 liters of ether are added simultaneously with 800-1000 cc. of catalyst solution. The exact volume of catalyst is determined in a laboratory test polymerization of the particular lot of monomer available. The addition requires 3 to 4 hours and is done at atmospheric pressure. The kettle is closed to the atmosphere after addition is complete. The agitated mass is allowed to heat up at a rate of about 3°C. per hour. During this phase of the process the final pressure reaches 4 atmospheres. The viscosity of the polymer also increases steadily as noticed by the current requirements on the stirring motor. Initially 15 amperes are drawn and when the load amounts to 40 amperes (after 20 hours approximately), the motor is stopped. The temperature may rise at a faster rate at this point and may finally reach 100°C. The end of the reaction is observed by pressure drop and constant temperature. Unpolymerized material is distilled out of the mass to the storage tank. As mentioned above, the product can be drained directly to drums or run into a Werner-Pfleiderer type mixer for the preparation of solutions. The Igevin M40 is soluble in water and the lower alcohols, but is insoluble in naphta. It has been used as thickener, adhesive, textile finishing agent and a plasticizer for nitrocellulose lacquers.

2. Igevin A50 - Polyvinylethylether - K value 50-60.

Monomer boiling within the range of 35-37°C. is preferred although material boiling up to 38°C. can be used in an emergency. As in the case of Igevin M40, a batch is started with 70 liters of ether. This quantity is added to the kettle and is then cooled to 25-30°C. Gradually 300-400 cc. of a 0.5 to 1.0% solution of $BF_3.2H2O$ is added to initiate polymerization. The exact amount and concentration are determined for each lot of monomer by a laboratory test polymerization. The balance of the ether amounting to 1430 liters are introduced simultaneously with the remainder of the catalyst solution, of which a total of 1500 cc. is required. The addition requires 3 hours at 25-30°C. after which the kettle is closed and a 6 to 8°C. per hour temperature rise is permitted. After about seven hours the motor reaches its peak load and is shut off. At this point the temperature is about 60-70°C. and the pressure is 2 to 3 atmospheres gage. When the pressure begins to drop the polymerization is considered to be complete. The final temperature reached after stirring is discontinued may amount to 120°C. No unchanged monomer is present and the yield amounts to 97-98%.

Igevin A50 is water insoluble but can be dissolved in alcohols and naphtha. Its principal application is as a plasticizer for nitrocellulose and natural resin base lacquers.

3. Igevin J.60 - Polyvinylisobutylether - K value 55-60.

Monomer boiling between 82 and 84°C. is required. As before, an initial charge of 70 liters is employed and a total batch of 1500

liters is polymerised. Polymerisation is initiated at room temperature by the addition of about 300 cc. of the 1% catalyst solution. The reaction begins suddenly with a rapid temperature rise to 70-80°C. At this point the balance of the ether is introduced simultaneously with 3500 cc. of a 1% solution of tin tetrachloride in ethylbutylether. This addition requires three hours and is carried out at 30°C. The kettle is then closed and during the next 10-12 hours the temperature rises gradually to 90-100°C. As before, the stirrer is shut off when the load reaches 40 amperes. In the next two hours the temperature may go as high as 180°C. The yield of polymer amounts to 98%. Traces of monomer are distilled out of the mass and collected in the storage tanks. Igevin J50 is soluble in naphtha but is water and alcohol insoluble. Its chief application has been as a plasticiser.

4. Igevin JZR 80% Polyvinylisobutylether
20% Polydekalolvinylether K value 18-25,

The boiling range of the dekalolvinylether used is 230-245°C. As usual a batch is begun with a 70 liter initial charge. A total of 1200 liters of the mixture is prepared per batch; this requires 3 to 4 liters of 1% catalyst solution of which about 400cc. are needed to initiate reaction. The exact catalyst requirement is determined from a laboratory test polymerization as in the case of the other products. In this polymerization the ether mixture is warmed to 70°C. and the initial amount of catalyst is added. When reaction begins the rest of the ether mixture and catalyst are added during a three hour period. Water is used as the cooling medium instead of brine. When the addition is complete the kettle is closed and the contents are allowed to reach 110-120°C. This temperature is maintained for an additional hour. Agitation is continued during the entire polymerization. The end of the reaction is indicated by a temperature fall of the contents with an empty cooling jacket. A yield of 97-98% is obtained. This material has been used as a surface coating for masonry.

5. Bindemittel Li 10.

Approximately 100 liters of a mixture comprising 600 liters of vinylmethylether, 300 liters vinylisobutylether, 30 liters diglycol divinylether and 100 liters vinylester tall oil acids are added to the polymerizer and maintained at 6°C. Addition of 250 cc, of the 1% catalyst solution, $BF_3.2H_2O$ in dioxane, during a 30 minute period initiates the reaction. During a 3½ hour period the balance of the mixture and 900 cc. of catalyst are added. A temperature rise to 12-14°C. is permitted. During the next 5-6 hours the temperature is permitted to reach 80-90°C. after which it is cooled to 50°C. and discharged from the kettle with nitrogen. Polymerization is not completed in the polymerization kettle but is finished in a Werner-Pfleiderer type mixer. A 200 kg. batch from the kettle is heated to 90-100°C. for an additional 12 to 14 hour period. The yield of this product amounts to only 80%. It is definitely a

specialty type adhesive of little technical importance.

B. Igevin Oils

1. Igevin A25. Polyvinylethylether. K. value 15-18.

A 100 liter charge is introduced into the smaller 1 cbm. polymeriser. At 35°C. polymerisation is initiated by the addition of 400-500 cc. of 1% $BF_3.2H_2O$ solution. When the temperature reaches 40°C. continuous addition of ether and catalyst is begun at hourly rates of 230 liters and 800 cc. respectively. During the next 2 hours the temperature is allowed to reach 95-100°C. and is maintained at this point thereafter. The product overflows into the small "afterpolymerizer" where the contents are finished at a temperature of 150°C. From here the oil goes through the water cooled kettle to eventual storage.

A yield of 95-96% is obtained and the product is used as a leather impregnant.

2. Igevin J30 - Polyvinylisobutylether K value 18-20.

A 100 liter charge is introduced into the small polymerizer, heated to 82°C. and initiated with 500-600 cc. of a 0.5% $BF_3.2H_2O$ dioxane solution. At 90°C. continuous addition of 280 liters of ether per hour and 800 cc. of catalyst per hour is begun. After one hour the temperature reaches 110-115°C. By controlling the amount of cooling water the temperature is allowed to reach 150°C. and is maintained at this point thereafter. The balance of the process is carried out as described under Igevin A25. The yield amounts to 97% and the chief use of the product is in leather impregnating.

3. Igevin J30 Polyvinylisobutylether K value 15.

This material is prepared in 97% yield under the conditions described for J20 except that a 1% catalyst solution is employed and a final reaction temperature of 120°C. is maintained.

N.B. A mixture of 3 parts of Igevin J20 and 10 parts of Igevin J30 is sold under the name Densodrin N.W.

C. Igevin Resins and Waxes

1. Densodrin NH
or Polydekalolvinylether
Igevin Z.

The monomer used boils within the range 230-245°C. A batch amounts to 800 liters of which 200 liters are used at first. This amount is heated to 80°C, after which 800-1000 cc. of 1% $BF_3.2H_2O$ in dioxane are added during a 20 minute period. A temperature rise to 140°C. indicates that reaction has begun. The balance of the ether and the catalyst solution (2000-2500 cc. total volume) are added during the next hour maintaining the temperature at

140-160°C. The temperature is then allowed to go to 180° or even 200°C. No pressure is employed. Reaction is considered complete when the temperature drops of its own accord. The yield amounts to 99%. The total production of resinous and waxy Igevins amounts to only a few tons per month. This product and Igevin ZJ were used as substitutes for natural resin in the compounding of driving belt dressings.

The following specifications for the product are used: The product should be soluble to the extent of 10% in 65-95°C. naphtha, benzene and methylenedichloride. A 10% solution in naphtha should be compatible with an equal volums of a 10% solution of Oppanol B (polyisobutylene) in naphtha. A 30% solution in a 1 to 1 by volume mixture of naphtha and methylene dichloride should be compatible with an equal volume of a 10% solution of Oppanol C in the same solvents. The softening paint by the Kraemer-Sarnow method should be at least 70°C.

Igevin ZJ { 60% Polydekalolvinylether
{ 40% Polyvinylisobutylether

One sixth of the total 600 liter charged are introduced into the polymerizer and heated to 80-90°C. The polymerization is initiated by the addition of 400-500 cc. of a 1% $BF_3.2H2O$ catalyst solution. A sudden temperature rise to 100°C. indicates the start of reaction. The balance of the ether mixture and 2500-2600 cc. of catalyst solution are added during a 2 hour period at 90°C. The kettle is then closed to the atmosphere and during the next 4-5 hours a temperature of 130°C. is gradually attained. The reaction is considered complete when the temperature drops. A 97-98% yield is obtained.

The following specifications are employed: Softening point- 65-70°C. by Kraemer-Sarnow method. Solubility in 65-95°C. naphtha, benzol and methylene dichloride - at least 10%. A 10% solution in naphtha must be compatible with an equal volume of a 10% solution of Oppanol B 100 in naphtha. A 33⅓ solution in equal volumes of naphtha and methylene dichloride must be compatible with an equal volume of a 20% Oppanol C solution in naphtha. Oppanol C is merely another designation for polyvinylisobutylether. A 10% solution in naphtha must be compatible with an equal volume of a 10% solution of Oppanol C in naphtha.

3. I.G. Wax V. Polyoctadecylvinylether

A 300 liter portion of the 800 liter total batch is added to the polymerizer and heated to 70°C. Gaseous BF_3 is employed as the catalyst. The gas is introduced to the kettle through a wash bottle filled with a parafin oil at a rate of one bubble per second. Ten volumes of nitrogen per volume of BF_3 is used as a diluent. The nitrogen is introduced through a tee in the line after the gas washing bottle. The kettle contents are gradually heated to 90°C. at which point polymerization begins. The temperature is allowed to go

to 95°C. and the balance of the monomer is started in. In order to obtain a satisfactory product rigid control is necessary. The temperature must not be allowed to exceed 95°C. On the other hand the polymerization must not be permitted to stop. The rate of polymerization is checked by titrating samples with 0.5N bromine solution in CCl4.

Prior to each large run a laboratory test polymerization is made to determine the characteristics of the particular monomer available. The monomer employed must not melt below 20-22°C., and its boiling range should be within 160-200°C. at 6 to 8 mm. It is distilled twice over KOH before use. The quality of the octadecyl alcohol used in the preparation of the ether is also controlled. The following specifications must be met: acid number below 1; saponification number below 2; hydroxyl number about 210; iodine number below 5; and a melting point not below 50°C.

The finished wax must produce a clear solution in 4 parts of 80-120°C. solvent naphtha. This solution must retain its clarity for one hour at 0°C. The wax has a melting point of about 50°C. and a flash point of 180°C.

A yield of 97% can be expected. The wax is claimed to have superior properties over the natural waxes particularly for use in polishes.

Other waxy polymers were produced on relatively minor scale. For example Densodrin V, the polymer of the vinylether of wax alcohols, is prepared at 90-95°C. in 99% yield under conditions similar to those described above. Densodrin W is a mixture of 7 parts polyvinylether of wax alcohols and 3 parts of polyvinylether of coconut fatty alcohols. It is obtained in practically quantitative yield at a polymerization temperature of 50-52°C. Densodrin H is a 2 to 1 mixture of Densodrin and Colophonium. The melting points and flash points of the above waxes are listed below:

	Melting Point	Flash Point
Densodrin V	48-40°C.	213°C.
Densodrin W	35-36°C.	180°C.
Densodrin H	-	207°C.

D. Igevin Solutions

Igevin M40 is sold in 50 and 25% aqueous solutions under the name Appretan WL conc. and Appretan WL 25 respectively. These are used as textile finishing agents. Solutions of this polymer in methyl and ethylacetate are also produced. The latter is a 50% solution while the former is 70%. Igevin A50 is prepared in 70% naphtha solution and as 70 and 50% solutions in ethanol and methanol respectively. Igevin J60 is sold as an 80% solution in naphtha and a 70% solution in ethylacetate.

E. Applications

In addition to the applications mentioned under the preparation of the individual polymers, the following uses may be noted:

Igevin M40	Paper to metal adhesives, gasoline proof gasket constituent.
Igevin A50	Paper impregnation, paper to metal adhesives, fly paper.
Igevin J60	Paper impregnation, shoe adhesives and in bookbinding, fly paper.
Igevin Z	Paper impregnation, cable insulation.
Igevin ZJ	Paper impregnation, cable insulation.

F. Softening Point Method of Kraemer-Sarnow

A special glass tube of 0.5 cm.I.D. with a conical constriction to 0.3 cm. at the closed end beginning 1 cm. from the end is employed. The finely powdered sample is tamped into the tube with a wooden plug so that its upper surface is at the 1 cm. level. Five grams of mercury are poured on top of the sample, the loaded tube plus inserted thermometer are heated in an air bath within a glycerine bath. The temperature is rapidly brought to within 25°C. of the expected softening point, after which the heat source is removed for 15 minutes. Heating is then restored so that the rate of temperature rise is exactly 1°C. per minute. The softening point is taken at the temperature at which the mercury breaks through the sample.

APPENDIX 1

LIST OF GERMAN SCIENTIFIC PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Hambsch	Department Head	Ludwigshafen
Dr. Schultz	Supervisor	Ludwigshafen

APPENDIX 2

LIST OF GERMAN TARGETS VISITED

Name	Location
I.G. Farbenindustrie A.G.	Ludwigshafen

APPENDIX 3

BIBLIOGRAPHY

Brief and general accounts of the polymerization of vinylethers are given in the following publications.

1. "Plastics in Germany 1939-1945" by Dr. Gordon M. Kline, O.P.B. Dept. of Commerce, Washington, D.C.

2. "The Manufacture of Thermoplastics in Plants of the I.G. Farbenindustrie A.G., Germany" by Ray H. Boundy and R. Leonard Hasche, Combined Intelligence Objectives Committee.

3. C.I.O.S. Report, Item No.9,22, File No.XXIX - 62. Investigation of German Plastics Plants by D.G.M. Kline et al.

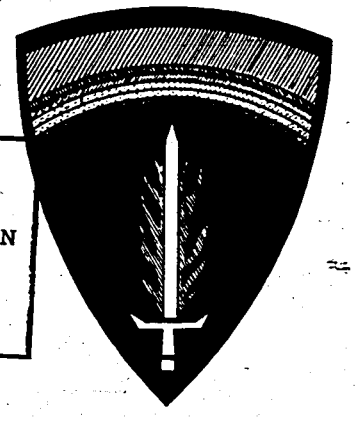
Specific manufacturing details and control methods included in this report were obtained in part from "Betriebsvorschriften für Igevine" prepared by Dr. Hambach.

Copy 1

FIAT FINAL REPORT 867

THE PRODUCTION OF MONO-VINYL CHLORIDE

Rosenquist, E. N.



OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIELD INFORMATION AGENCY, TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 867 — 22 July 1946

THE PRODUCTION OF MONO-VINYL CHLORIDE

BY

E.N. ROSENQUIST

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U.S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

This report covers the production of mono-vinyl chloride from anhydrous hydrogen chloride and acetylene using a mercuric chloride promoted, barium chloride on activated carbon catalyst. The preparation of the activated carbon itself is also included.

PERSONNEL OF MISSION

Dr. E. N. Rosenquist, TIIB
Mr. W. E. Alexander, TIIB

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The purpose of the investigation was to obtain details on operating procedures and equipment employed in the catalytic production of vinyl chloride using the mercuric chloride promoted barium chloride on activated carbon catalyst.

Evaluation:

The process studied has the advantage of long catalyst life with corresponding low mercury consumption. On the other hand the process operates at a low conversion, about 25%, and considerable amounts of accessory equipment are required for recovery of product.

Guide to Reader:

This report gives operating and equipment details to supplement earlier investigators' reports on the Wacker vinyl chloride process. Details of manufacture of the activated carbon employed as the carrier are also included.

SUMMARY OF PROCESS

At the Burghausen plant of Dr. Alexander Wacker, Gesellschaft für Elekrochemische Industrie G.M.B.H, there is installed capacity for a monthly production of 200 tons of monomeric vinyl chloride. Anhydrous hydrogen chloride and dry acetylene are converted to vinyl chloride over a catalyst consisting of 30% barium chloride and 1% mercuric chloride or activated carbon. Conversion at 100-180°C amounts to about 25% in a single pass. The converted gases are scrubbed with trichlorethylene to remove vinyl chloride. The gases are recycled and the vinyl chloride is recovered from the trichlorethylene by distillation at elevated pressure. Two identical banks of converter and accessory equipment are installed but only one series of columns.

Catalyst life is as yet undetermined. One batch had operated for 8000 hours when the unit was shut down for overhaul and was still active. A second batch has now been used for 5000 hours and is still performing satisfactorily.

Yields are 96-97% of which 2-3% is mechanical loss. The principal by-product formed is ethylidenedichloride.

Per ton of vinyl chloride produced there are required:

420 cbm acetylene
600 Kg. hydrogen chloride
1 Kg. of catalyst (690 g carbon
(
(
(300 g $BaCl_2$
(
(
(10 g $HgCl_2$

Usually the entire output of the plant is used at Burghausen mainly for the preparation of high molecular weight polyvinyl chloride ultimately reaching the consumer in the form of bicycle tires and shoe soles.

DETAILED DESCRIPTION OF PROCESS

Hydrogen chloride obtained by the cracking of tetrachlorethane is required at an hourly rate of 50 cbm. This material enters the process through a tangential mixer with the recycle gas leaving the absorption tower. The mixed gas is delivered to the reactor at a pressure of 0.16 Kg. per square cm.

An equal volume of acetylene is required per hour. This gas is generated in a dry Herreshof type reactor. It is then scrubbed with 20% H_2SO_4 to remove ammonia, next with sodium hydroxide solution, 350 g/l., to remove acids and aldehyde and finally dried in a packed tower by contact with a 5% solution of methyl pentandiol-2,4 in trichlorethylene at a final temperature of -5°C. This gas is delivered to the vinyl chloride absolutely anhydrous; i.e. free from moisture as determined by the sensitive Karl Fischer method. Acetylene received at the vinyl chloride plant enters the system first via a dry purifier where it is mixed with 200 liters per hour of chlorine gas to oxidize phosphine and silane. It then enters the absorption tower one third of the way up from the bottom and leaves at the top of the tower with the 300 cbm per hour of recycle gas. This gas then enters the suction side of a Roots-Connersville type blower with the incoming fresh hydrogen chloride. In normal operations the analysis of the gas to the converter is 30% N_2, 35% HCl and 35% C_2H_2. The gas contains 150 grams per liter of trichlorethylene and 800 grams per liter of vinyl chloride. Operation is satisfactory with a nitrogen content of 15-30%. Below 15% N_2, control difficulties are encountered. In particular there may be local zones of overheating in the catalyst bed. With a fresh catalyst a nitrogen content of about 40% is required for the first day or two of operation. When the catalyst is broken in this can be reduced to 15-30%. On the recycle gas line there is attached a safety bottle containing a 20 cm. depth of trichlorethylene mixture sp.g. 1.68.

If pressure ever builds up in the converter system to this extent because of improper valve setting on the bleed line or poor conversion the excess pressure is automatically released here. Approximately 500 liters of nitrogen per hour are released from the system at the brine cooler above the absorption tower. The incoming gases after mixing are preheated from 80 to 120°C and then enter the top and bottom of the converter and leave through a collecting manifold at the center circumference of the unit (see diagrammatic sketch, Figure 2, appended). Formerly the gases fed at the bottom and left at the top, but the above change was made to reduce pressure drop through the unit. The weight of catalyst employed amounts to 1.2 tons and is placed outside the cooling tubes. The cooling is accomplished by evaporation of water in the tubes and jacket which gives thermosyphon and gas lift action for circulation. A pump circulating 10 cbm. per hour supplements the above. The steam produced is condensed and recirculated. Water circulated through the tubes is collected in a manifold in the longitudinal center of the unit and returns to the pump. Water from the jacket passes through a steam release then to the condenser then back to the pump. The condenser is tapped to vacuum and nitrogen pressure lines. By varying the pressure the boiling point of the water, and therefore the temperature of the catalyst mass can be varied. Throughout a cycle the temperature is gradually increased from 110° to 180°C.

Product gases leave the converter at 100-140°C and pass through 4 precoolers operating in series. These water cooled units are supplemented in summer by 2 additional brine coolers, using -30 to -36°C. K_2CO_3 brine. The gases then enter the trichlorethylene absorption tower at about 10°C, and at a point one meter above the bottom. At a point 2 meters from the bottom the chlorine treated acetylene is introduced. Also at this point 365 Kg. per hour of fresh trichlorethylene is added. An equivalent amount is withdrawn hourly from the stream leaving the heat exchanger. This stream originates in the pot of the first distilling column, designated as the crude column. This withdrawal serves to cleanse the trichlorethylene of the impurities built up therein including the by-products formed in the converter and the phosphorous and silicon chlorides formed in the acetylene purifier. The trichlorethylene bottoms, as mentioned above, go through a heat exchanger after which a portion is removed and sent to the trichlorethylene plant. The balance goes through a "Heliflo" type exchanger, then a brine cooler and finally enters just below a brine cooler on top of the absorber at a rate of 3000 Kg. per hour. Bleed gas 500 liters per hour of essentially pure nitrogen leaves the top of the cooler mentioned above at -30°C, while the recycle gas leaves the top of the column at 0°C. The pot bottoms leaving at 35°C consist of 3000 Kg. of trichlorethylene and 140 Kg. of dissolved vinyl chloride.

This mixture and an equal amount from the second converter pass enter the mid-point of the first or crude column operating at 3.5 atmospheres gauge. Overheads leave the column at 80°C, pass through a dephlegmator from where a portion is returned as reflux while the remainder, 240-300 Kg. per hour, goes to storage tanks. A reflux ratio of 3 to 1 is normally maintained in this column. Approximately 0.5 to 1 cbm. per hour of gas from the dephlegmator returns to the absorption tower. The stripped trichlorethylene leaves the reboiler of this column and returns to the absorption tower through a constant level float valve. The coils in the crude column must be cleaned annually. This is done at the annual inspection of the equipment.

The crude vinyl chloride is next stripped of dissolved gas. The degassing column operates in 4 atmospheres gauge. Bottoms at 55°C go to the pure vinyl chloride column. The overheads at 38°C enter two dephlegmators and a brine condenser in series. Vinyl chloride is condensed and returns to column as reflux at 800 Kg. per hour. Approximately 2 cbm. of gas at -10°C. returns to the absorption tower.

The pure column operates at 3.5 atmospheres gauge with a 30°C, head temperature and a reflux ratio of about 6-8 to 1. The reboiler temperature is not constant since withdrawal of bottoms is semi-continuous. When the reboiler temperature amounts to 120°C. approximately one half the contents are withdrawn for clean up in a batch still. The usual temperature spread is 40-120°C. in the reboiler. The average withdrawal rate of bottoms is 25-60 kg. per hour containing 10-20% monovinyl chloride. Between 240-300 Kg. per hour of overheads at 30°C. are sent to a caustic scrubber where at 40°C. 1 cbm. per hour of 15% aqueous NaOH is recirculated. The vinyl chloride from this unit passes through a $CaCl_2$ drying tower, then into a chromium-steel condenser from which it is delivered to one of 3 enamelled storage tanks. After assay the product is transferred to a larger underground storage tank. In the event of pressure loss, emergency equipment is available to prevent loss of product at this point. Following the chrome-steel condenser is a brine cooled condenser through which the vinyl chloride could be condensed and held for clean up in the batch still.

The batch still operates at 3.5 atmospheres gauge with a reboiler temperature of 35-130°C. Reflux ratios of 1 to 1 and 3 to 1 are used depending on the nature of the fraction. Vinyl chloride overheads cooled to 20°C. are then caustic washed and dried in duplicates of the equipment used on the overheads from the pure column. The dried product is delivered to the above ground hold tanks and then stored below ground after assay.

The catalyst is prepared by charging activated carbon, e.g. Lavinson Taf III grade, to the empty converter. The carbon is dried to less than 0.5% H_2O by blowing with air at 150°C. for twelve hours. The dry carbon is now placed in a kettle and agitated manually with a wooden paddle while a solution, containing the 30 parts of BaCl and 1 part of $HgCl_2$ per 69 parts of carbon, are sprayed on. The salt solution is preferably at about 90°C. and close to saturation at that temperature. The wet mass is recharged to the converter and redried as before.

The quantity of barium chloride is not critical. A 20 to 40% $BaCl_2$ catalyst would be satisfactory. Unpromoted $BaCl_2$ on carbon has been tested but reaction temperature must be approximately 100°C. above the operating temperature feasible using the $HgCl_2$ promoted material. Mercuric chloride alone could be used but in that case control of temperature would be difficult because of localised overheating. Other halides than $BaCl_2$ were investigated but it seemed to be the most specific for the mono-vinyl chloride reaction. In the case of zinc chloride for example, considerable quantities of ethylidene dichloride were obtained.

The underground storage tank is equipped with a wire basket containing hydroquinone. This is still used but believed to be superfluous. The product is used entirely at Burghausen hence not very complete product specifications are available. It is required that the product be free from acetylene by the ammoniacal cuprous chloride test and free from HCl by silver nitrate test. A boiling range specification was formerly used but this has been abandoned.

Prior to installation of the dry chlorine purifier catalyst life was about 1000 hours. With this equipment life is 8000 hours minimum. Previous operations have indicated that the widely used chlorine-water treatment for the crude acetylene is not adaptable to this process. Apparently in this treatment by-product materials are formed which interfere with the methylpentandiol acetylene drying operation. The operating staff believe that an acetylene purification treatment with a Kieselguhr - H_2SO_4 - $Na_2Cr_2O_7$ might be equally satisfactory as the present dry chlorine treatment. However the latter is particularly suited for this operation.

DESCRIPTION OF EQUIPMENT

Unless otherwise stated all equipment is ordinary steel. The numbers identify the various pieces of equipment in the appended flow sheet, Figure 1.

1. Mixer Tangential type

2. Recycle Gas Blower - A Roots-Connersville type blower operating at a constant rate of 400 cbm. per hour delivers gas to reactor at a pressure of 0.16 Kg/cm^2.

5. Reactor Preheater - heated with steam at 45 lbs. gauge. Total heating surface 3 square meters.

4. Reactor - (See diagrammatic sketch, Figure 2) Overall height 6 meters including conical bottom. Diameter 1.5 meter. Contains a jacket for cooling together with 400 cooling tubes 4.5 meters long by 46 mm. o.d. (38 mm. I.D.). Four mercury thermometers are inserted equidistantly through side wall. Six thermocouples operating on a recorder indicate the temperature at various levels within the bed. Catalyst volume 4 cbm. Mixed gas enters the catalyst bed from top and bottom and product gas is withdrawn from the middle. Cooling water enters at the bottom and is collected and withdrawn in a main through the longitudinal centre.

5. Steam Condenser - Total surface 2 sq. meters provided with tap for vacuum or N_2 pressure.

6. Water Pump - Capacity 10 cbm. per hour.

7. Off Gas Coolers - 6 total, each with 4 sq. meter surface, four are water cooled, last two are brine cooled.

8. Absorption Tower - Height 8 meters by 600 mm. diameter. Packed with 20 mm. Raschig rings. Reboiler has capacity of 1.5 cbm. and contains a steam coil with 0.5 sq.meters surface. Atmospheric pressure steam is used. Above the tower is a smaller section 1.5 meters high by 300 mm. diameter containing a brine cooler. Gas goes through tubes cooled by brine outside. Cooling surface is 0.5 sq. meters in the brine cooler.

9. Chlorine Purifier - Height 2 meters by 150 mm. diameter. A graphite injector introduces the chlorine to fresh acetylene stream, the tower is packed with 20 mm. Raschig rings.

10. Safety Bottle - Glass, filled to 20 cm. depth with trichlorethylene mixture s.g. = 1.68

11. Pump - Operating against 3.5 atmospheres gauge

12. Crude Column - 6 meters high by 400 mm. diameter for lower half and 160 mm. diameter for upper half. The two sections are packed with 35 and 20 mm. Raschig rings respectively. The reboiler has a capacity of 1.2 cubic meters with 15 sq. meters of heating surface, coils and jacket, and has a float valve level controller.

13. Feed Preheater - Bottoms Precooler - Heat transfer surface 14 sq. meters.

14. Secondary bottoms Cooler - Water cooled "Heliflo" type Exchanger with 24 sq. meters surface.

15. Final Bottoms Coolers - Three brine coolers with 4 sq. meters surface each.

16. Float Valve Level Controller

17. Dephlegmator - Cooling surface 35 sq. meters.

18. Crude Vinyl Chloride Storage - three enamelled 5 cubic meter tanks

19. Degassing Column - Height 3 m. by 300 mm. diameter packed with 20 mm. Raschig rings. Feed point at center. Reboiler is 0.9 m. high by 800 mm. diameter and is jacketed. A steam coil is also available.

20. Dephlegmators - Two each with 4 sq. meters of surface.

21. Brine Condenser - Surface 4 sq. meters.

22. Pure Column - Height 6 meters by 400 mm. diameter packed with 20 mm. Raschig rings. The reboiler has a capacity of 1 cbm. and contains 10 sq. meters of heating surface.

23. Dephlegmator - Cooling surface 35 sq. meters.

24. Caustic Scrubber - Height 5 meters by 600 mm. diameter packed with 20 mm. Raschig rings.

25. Caustic Cooler - Jacketed pipe section.

26. Caustic Storage Tank - Capacity 1 cubic meter.

27. Pump - Working capacity, 1 cubic meter per hour.

28. Calcium Chloride Drier - Height 3 meters by 600 mm. diameter packed with granular calcium chloride.

29. Condenser Chrome-Steel - Surface 35 sq. meters.

30. Pure Vinyl Chloride Tanks - Three enamelled tanks each of 5 cubic meters capacity.

31. Underground Storage Tank - One enamelled 30 cubic meter container

32. Emergency Brine Condenser - Stainless steel with 10 sq. meters surface.

33. Emergency Hold Tank - Stainless steel capacity 1 cubic meter.

34. Feed tank batch still - Capacity 5 cubic meters.

35. Batch Still - Height 45 meters by 400 mm. diameter. Reboiler capacity 6 cubic meters. Column packed with Raschig rings.

36. Dephlegmator, 37, Caustic scrubber, 38. Tank, 39. Pump, 40. Drier, and 41. Condenser.
Identical with pure column accessory equipment, items 23, 24, 26, 27, 28 and 29.

ACTIVATED CARBON

a. General:

The activated carbon used in the preparation of the catalyst for vinyl chloride production at Burghausen is a Leverkusen product designated as Tdf III. Formerly carbons AKT III and AKTd III were used. These were preferred in that order over the present product. These carbons are also employed as catalyst supports in the monovinyl acetate operations at Höchst and Burghausen.

Accordingly the preparation of these carbons was investigated at the Leverkusen plant. It was learned that all these carbons are essentially the same. The significance of the letters and numerals in the code is as follows:

A - Adsorbent grade
K - Prepared using Zinc Chloride
T - Peat base
d - Steam treated
f - Formed
III, IV etc. - Size in mm.

All carbon prepared at the present time is given a steam treatment to remove last traces of acids, hence an AKT grade is now unavailable. In normal operations dies with 6 mm. holes are used in the extrusion equipment. The material after carbonization shrinks to a 4 mm. size. When 3 mm. size is required the material shipped is that obtained from the screening of the 4 mm. carbon. Frequently, however, orders for the smaller size exceed the amount of fines available. When this occurs, dies with 4 mm. holes are substituted to give a dry product of about 3 mm. diameter. This latter material has the "f" in the code designation.

b. Production

For the production of these carbons black peat with a moisture content of 25-35% is received in the form of bars. These are ground in hammer mills and sieved to 2-3 mm. particle size. The sieved material is mixed with 2 parts of 50% aqueous zinc chloride in a continuous mixing screw which then conveys the pasty mass to the extruders. Extruded material drops onto a moving belt where it breaks up into irregular lengths. The continuous belt delivers the particles to a rotary kiln where they are ignited by a gas flame and heated to 700°C. Only enough air is admitted to burn the volatile matter. The high zinc chloride content also protects the carbon. A sojourn time of 45 minutes in the kiln is maintained. The gases leaving the kiln are water scrubbed thereby recovering about 30% of the zinc chloride. This dilute solution is concentrated and re-used.

The hot particles leaving the kiln are cooled in covered iron boxes. When cool the material is washed countercurrently with 3% aqueous hydrochloric acid in a series of three tanks. The wash liquor leaving the final tank has a 50% zinc chloride content and is re-used. A total of six acid proof brick tanks are installed. The zinc chloride recovered at this point is about 55-60% of the original amount used.

The leached material is now heated with 3% hydrochloric acid for one hour at 80-90°C to remove last traces of metallic compounds. In certain instances it may be necessary to reboil the carbon to reduce the metal content to the desired extent. Normally the dilute acid from the boil tank is used in the leaching operation but when a second boiling is required this acid is discarded to avoid contaminating the carbon. As stated above the 50% zinc chloride solution from the final leach is re-used normally. However after continued re-use impurities may build up to such an extent that is impractical to re-use it. In this event the solution is sent to the lithopone plant. Impurity build up is noticeable by definite changes in the density of the solution as well as by changes in the adsorbtive power of the final product.

After the acid boil, the carbon is washed with water countercurrently in a series of three towers. Next the material is dried with hot air in a rotary iron kiln. Hot air enters concurrently at 300-400°C and leaves at 100°C. Initially the water content is about 100°C, and is reduced to about 15%. This drier is 16 meters long by 1.5 meters diameter and rotates at about 1 RPM. The partly dried product next goes to a brick lined rotary countercurrent steamer 15 meters long by 1 meter diameter where final traces of hydrochloric acid are expelled. A gas flame with no excess air supplies heat to the unit. The steam is at 500-600°C. This stage of the process is checked in the laboratory. A sample from the steamer is heated to 300°C during a one hour period. No evolution of acid is permitted. Moist indicator paper is used to qualitatively determine acid.

The steamed product is sieved on vibrating screens. A typical screen analysis is:-

4 mm.	65-70%
2 mm.	15%
(2	
(1 mm.	5%
fines	10%

All equipment contacting acid at temperatures up to 80°C. is rubber lined. Above 80°C. acid proof brick is employed. Metallic zinc is added to the zinc chloride storage tanks.

c. Product Evaluation

"Black" peat with an ash content of about 1% and 56% total carbon is employed as the raw material. The finished product has an apparent density of 0.38 to 0.42.

The quality is checked by adsorption of benzene vapour from a stream of air at various saturation levels. A typical carbon has the following adsorption characteristics.

Benzene in air % saturation	18°C constant weight benzene adsorbed	100°C. constant weight benzene adsorbed
90	48.8%	19.5%
10	39.0%	15.6%
1	22.2%	8.9%
0.1	11.2%	4.5%

The test with 0.1% saturated air is rarely used because of its time consuming nature. Five days may be required for the carbon to reach constant weight.

This carbon is used mainly for adsorption processes. For catalytic work involving acetylene, it is specified that the copper content be below 0.08%. The only way of maintaining this low copper content is to employ a copper free zinc chloride since copper removal by the acid boil is not very effective.

A typical carbon of 6-6.5% total ash might have the following ash analysis. This carbon although suitable for adsorption processes would not be acceptable for catalytic work.

Total ash 6.64% of which =

SiO_2	68.8%
Fe_2O_3	1.82
Al_2O_3	5.52
CaO	1.56
MgO	0.46
Pb	3.14
Cu	2.1
Zn	6.1

One liter samples of AKTd IV and AKTd II/III were obtained at Leverkusen for transmittal to Washington. From the Burghausen plant approximately three liters of Tdf III were obtained.

APPENDIX I

LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Norbert Platzer	Assistant Director	Burghausen
Dr. E. Schaeffer	Department Head	Burghausen
Dr. W. Niemann	Department Head	Leverkusen

APPENDIX II

LIST OF GERMAN TARGETS VISITED

Name	Location
Dr. Alexander Wacker, Gesellschaft für Elektrochemische Industrie G.M.B.H.	Burghausen
I.G. Farbenindustrie A.G.	Leverkusen

APPENDIX 3

BIBLIOGRAPHY

The manufacture of mono-vinyl chloride at Burghausen has been briefly described in two previous reports, namely:-

C.I.O.S. Item No.22 File No XXV - 20 "Dr. Alexander Wacker Gesellschaft fur Elektrochemische Industrie G.M.B.H., Burghausen, Germany", by V.C. Bidlack, F.C. Curtis and J.M. Harris.

C.I.O.S. Item No. 9822 File No XXIX - 62 "Investigation of German Plastic Plants" by Dr. G.M. Kline, et al.

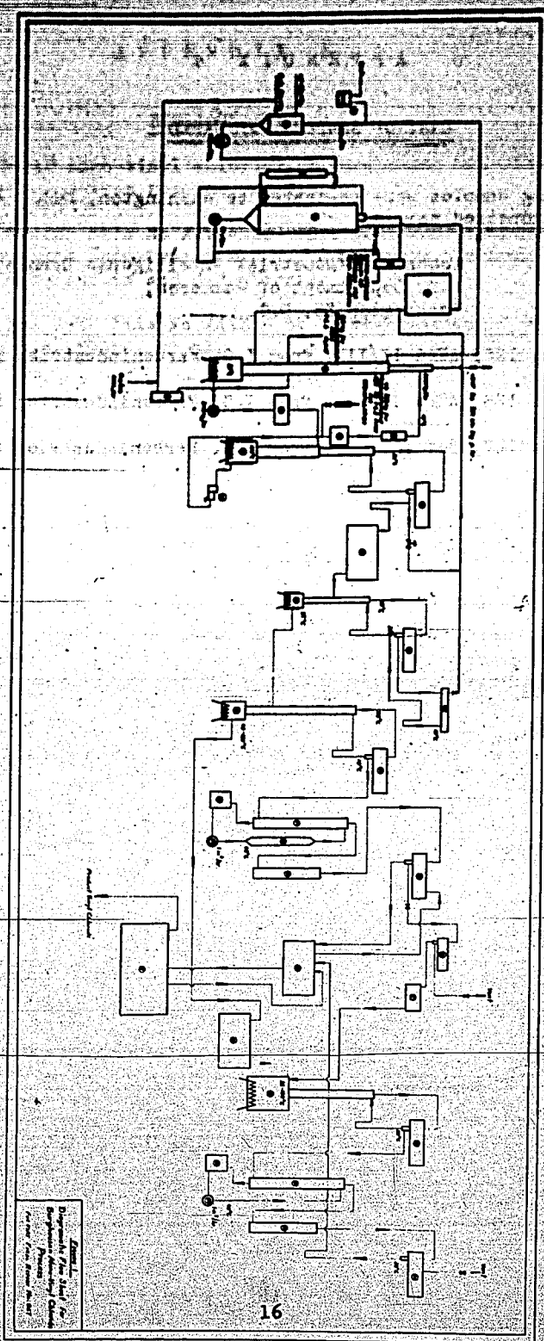
APPENDIX 4

LIST OF SAMPLES EVACUATED

The following samples were evacuated to Washington, D.C. Inquiries should be addressed to:

Technical Industrial Intelligence Branch,
U.S. Department of Commerce,
Washington 25, D.C.

1. M.C. No. 125, AKTd II/III, from I.G. Farbenindustrie, Leverkusen.
2. M.C. No. 126, AKTd IV, from I.G. Farbenindustrie, Leverkusen.
3. M.C. No. 127, Tdf III, from I.G. Farbenindustrie, Burghausen.



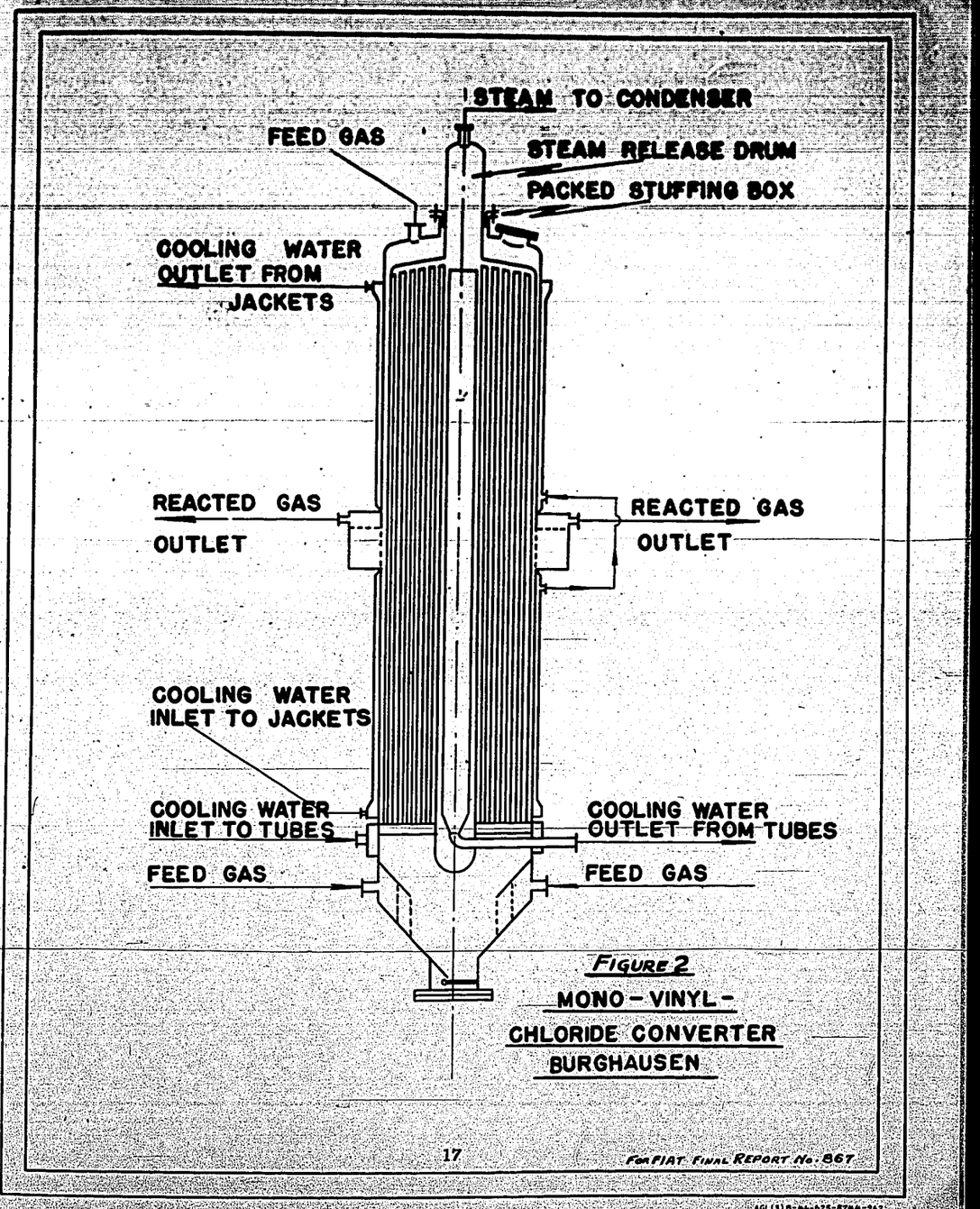


FIGURE 2

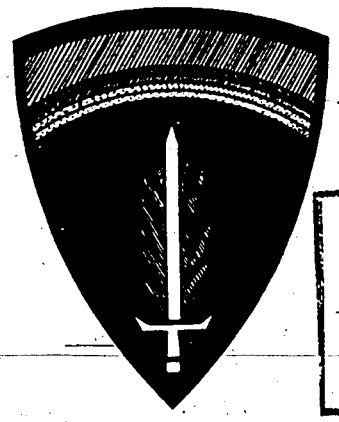
MONO-VINYL-CHLORIDE CONVERTER BURGHAUSEN

Copy 1

FIAT FINAL REPORT 861

PLASTICIZERS FOR POLY-VINYL CHLORIDE

Smith, A. F.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 861

23 July 1946

PLASTICIZERS FOR POLY-VINYL CHLORIDE

BY

A. F. SMITH

TECHNICAL INDUSTRIAL INTELLIGENCE BRANCH

U.S. DEPARTMENT OF COMMERCE

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

Reviews German efforts to produce a group of plasticizers for poly-vinyl chloride that would fit into German economics and still satisfy the demands of the applications. Contains a theoretical discussion on plasticizer constitution and details of manufacture of several important plasticizers.

TABLE OF CONTENTS

I N T R O D U C T I O N

Objective:

The purpose of the investigation was to determine what German developments in the field of poly-vinyl chlorids and poly-vinyl chlorids co-polymer plasticization had taken place during the war years, and to obtain the manufacturing data on their plasticizers.

Evaluation:

While Germany had developed several new types of plasticizers it is doubtful that any of immediate economic significance to the United States have been found. This is due to the difference between German and U.S. raw materials.

Guide to the Reader:

This report presents the information gathered from the investigation of the German plasticizer industry in the U.S., French and British Zones. It was not possible to obtain information on the operations at Bitterfeld and Elberfeld. Application of plasticizers is covered in Quartermaster Corps Technical Intelligence Report #5, "The German Plastics Industry" and in CIOS Report No. XXVII-85.

Significant points in German plasticizer technology:

1. The lack of an 8 - 10 carbon aliphatic dicarboxylic acid such as sebacic acid for the preparation of esters was felt. The final approach to a solution of this problem was made with thio-dibutyric acid with raw materials from the Reppe synthesis. With an ester based on this type of acid, good low temperature and good electrical properties are at a maximum. The lack of castor oil, the common source of sebacic acid, contributed to this condition.

2. The abundance of Fischer-Tropsch acids suggested these materials as raw materials. As a result large quantities of plasticizers were so based.

PLASTICIZER STUDIES

RELATIONS BETWEEN CHEMICAL CONSTITUTION AND SOFTENING EFFECT OF PLASTICIZERS

Search for Usable Plasticizers for Poly-vinyl Chloride

A discussion was had with Dr. Kling at Ludwigshafen and an examination was made of notes on plasticization prepared by Dr. Kling.

There was an interest in the question as to whether it would be possible to determine the relationship between the constitution of a plasticizer and its plasticizing properties, that is, whether it would be possible to determine without experimental tests on the plasticized mass, the properties of the plasticizer; therefore predicting the properties of the plasticizers solely from the known constitution of the material. Determining the existing relations between constitution and plasticizing properties is of course only possible on the basis of many tests of substances which belong to various chemical groups. As early as 1938 a program to determine existing relations between plasticizer constitution and performance was started. Factors having a definite influence on the plasticization were found to be:

1. The size of the molecule
2. The form of the molecule
3. The polar concentration of the plasticizer molecule.

To be a satisfactory plasticizer for poly-vinyl chlorides, the plasticizer must have many properties, i.e.:

1. It must swell poly-vinyl chloride and possess a dissolving power so that at a processing temperature of 160°C. gelatinization will result on a two roll mill, with a formation of a stable gel.
2. The plasticizer must have a low volatility index, so that it will not evaporate out of the mass.
3. It must impart good physical properties with respect to elongation and tensile strength.
4. In the case of electric appliances it must possess a specific resistance as high as possible.
5. It should have a low toxicity value.
6. It should have low water absorption.
7. It should have good light and heat stability.
8. It should have chemical stability, particularly with regard to hydrolysis.

The most important factor as a guide in constitution study is polarity. It is essential that polar groups exist in the molecule, because only these groups can effect affinity between the poly-vinyl chloride molecule and the plasticizer molecule.

By and large, tests revealed that the most usable plasticizers can be found most readily among the esters. Usable others are much more difficult to find. The prospect of finding plasticizers among the ketones, alcohols and pure hydrocarbons is almost negligible.

Hydrocarbons

In addition to the basic requirement for a substance acting as a softener having a polar group, there is also a basic requirement that the substance possess a definite solvent action on the polymer. Aliphatic hydrocarbons hardly swell poly-vinyl chloride, while aromatic hydrocarbons possess strong swelling power. As a result, aromatic hydrocarbons, providing a low volatilization rate can be selected that will gelatinize a mass at 160°C. However these straight hydrocarbons do not possess all the desirable properties consistent with a good plasticizer. Their drawbacks are:

1. Too low compatibility. They sweat out of the mass too easily.
2. Poor cold flexibility.
3. Poor heat stability.

The best known plasticizer of the hydrocarbon group was benzyl naphthalene. The limit of compatibility of this material is 30 parts of plasticizer (Vulcanol B) to 70 parts of polymer. In contrast, the common ester type plasticizer is still compatible when used in the ratio of 85 parts plasticizer to 15 parts of polymer.

The introduction of chlorine atoms to the hydrocarbon molecule satisfies the polar group requirements. A plasticizer of this type is the chlorinated diphenyl. No product suitable as a plasticizer was found among the purely aliphatic hydrocarbons.

Chlorinated aliphatic hydrocarbons exhibited suitable solvent action. It was therefore expected that chlorinated aliphatic hydrocarbons with sufficiently long chains to reach a high boiling point might find use. Plasticizers such as chlorinated octadecylene and chlorinated diesel oil from the benzene synthesis were tried. These, however, failed, due to poor physical properties in the mass. Here the relationship between the viscosity of the plasticizer and cold resistance of the plastic mass was demonstrated. The higher the plasticizer viscosity the poorer the cold temperature stability will be. The higher the chlorination of the hydrocarbons, the more viscous the resulting chlorinated hydrocarbon will be. The desirable high boiling point was only realisable by higher chlorination.

The lower chlorinated hydrocarbons were much too volatile, had much too low compatibility and tended to sweat out. Also the complete

chlorination of the hydrocarbon resulted again in insufficient polarisation. For example, methylene chloride is polar, while carbon tetrachloride is non-polar. Correspondingly, methylene chloride is a relatively potent dissolving and swelling agent for poly-vinyl chloride, while carbon tetrachloride has no solvent action on this polymer.

Alcohols and Phenols

With these materials it is also possible to attain gelatinization only with phenols and aromatic alcohols. Purely aliphatic alcohols have no swelling properties. Phenylglycol, dicyclohexylmethyl-carbinol etc. possess good gelatinising properties at 160°C. Films obtained from these combinations, however, are not usable because they are too hard and these plasticizers are too volatile. To a degree, an exception might be granted for dicyclohexylmethyl-carbinol, the film of which has a cold stability of about -10°C. It is still a poor plasticizer when used above 25% because of its high volatility.

Ketones

The ketones exhibit good solvent action and will severely swell poly-vinyl chloride. Poly-vinyl chloride can be gelatinized by several of the ketones, even though these materials are low from the standard of polarity. Very little work was done on the development of a ketone plasticizer.

Ethers

The properties of ethers with regard to poly-vinyl chloride are quite similar to those of the ketones. Purely aliphatic ethers have negligible swelling properties, while the aliphatic aromatic mixed ethers do have sufficient swelling powers, and it is possible to form a gelatinized sheet with these materials. Among the many ethers tested, the following four are found most suitable:

1. 2.3 dioxydioxene-diethyleneglycol ether
2. Dicresyldiglycol ether
3. Dixyleneglycol ether (Plastol DG)
4. β-phenoxy-methyltetralin (Teolan P)

Of interest is a comparison between dixyleneglycol ether and β-phenoxy-methyltetralin. Both are ethers. In the latter only one ether group exists in the molecule, while in the former there are three ether groups. The polarity of the former, dixyleneglycol ether, is therefore much greater

than that of the β-phenoxy-methyltetralin, which leads to the conclusion that this material should be more suitable as a softener, and no doubt it does exert a greater attraction for the poly-vinyl chloride molecule. Evaporation rate is much lower with this material than for the β-phenoxy-methyltetralin, even though the evaporation rate of the pure material is higher.

Esters

As already mentioned, the largest group of good plasticizers can be drawn from this group of compounds. The abundance of polar groups fulfills one major requirement for a suitable plasticizer. Also, the strong swelling properties of the esters make them ideal for poly-vinyl chloride plasticizers.

A large group of ester plasticizers were manufactured in Germany known under the trade name of "Palatinols". Dimethyl phthalate (Palatinol M) was produced in some quantity, but was too volatile to process on a 2 roll mill at 160°C. Dibutyl phthalate (Palatinol C) with its higher boiling point was readily processed, but is generally considered too volatile. Palatinol V, which is a $C_5 - C_6$ Fischer-Tropsch fatty acid alcohol ester of phthalic acid, has properties quite similar to dibutyl phthalate, being slightly too volatile, but otherwise satisfactory. The first running C_7 to C_9 alcohol produces the most satisfactory esters with phthalic acid. This plasticizer offers the best cold resistance and heat resistance, having the ideal alcohol chain length. If a longer chain alcohol is esterified with phthalic acid, the compatibility is reduced and also the low temperature flexibility. This is exhibited by the lorol alcohol esters which tend to sweat out of poly-vinyl chloride and have poor cold stability.

The phthalate acid esters from aliphatic alcohols can make excellent plasticizers. All the desirable properties occur when the aliphatic alcohols have a chain length of from C_7 to C_{10}, the lower alcohols imparting too great volatility and the higher alcohols decreasing the compatibility. Esterification of phthalate acid with aromatic or araliphatic alcohols will effect a decrease in the plasticizing action of the ester. An example of this difference is well shown by comparison of normal octyl phthalate and methyl-cyclohexyl phthalate. Normal octyl phthalate is an excellent plasticizer, while methylcyclohexyl gelatinizes badly and has only slight softening action This shows that the accumulation of ring systems in the plasticizer molecules effects a decrease in the plasticizing action.

Replacing the benzene ring nucleus by the naphthalene nucleus decreases the plasticizing action of the corresponding esters. These esters have poor cold flex properties. Some of the benzoic acid esters have been studied. The chloro amyl esters have very good cold stability, but offer very high volatility. The diglycol benzoic acid esters have poor cold stability, but have fair heat stability. An interesting plasticizer that has been used

in the cable industry is tetrahydrofuryl oleate. Here we have a chain length greater than C_{12}, but a plasticizer with very strong plasticizing action when used in small amounts of 10 - 20%. Beyond this amount sweating out was experienced. In general, esters with an aromatic nucleus and aliphatic side chains are very suitable as poly-vinyl chloride plasticizers. Phthalic acid is a superior acid for plasticizer manufacture from several points. It has a relatively low cost, is generally available and is a dicarboxylic acid, which is favorable. An agglomeration of ring systems, such as one finds in diphenyl phthalate causes reduced plasticizing action. In addition to esters in which we have aromatic groups, we may have straight aliphatic esters. These are also excellent plasticizers. A good example of this plasticizer is dioctyl sebacate.

Some of the alcohols and acids that are considered suitable as plasticizer components are as follows:

(a) Acids - succinic
glutaric
adipic
sebacic
thiodibutyric
Fischer Tropsch acids $C_6 - C_{12}$, etc.

(b) Alcohols - diglycol
butanediol
propylene glycol
Fischer Tropsch $C_4 - C_1$

The esters of adipic acid first running Fischer Tropsch fatty acid alcohols reveal a diminishing volatility with a lengthening of alcohol chain. The same is of course generally true for all esters of this type. With the first running fatty acid ester with triglycol, loss of compatibility with sweating out begins at C_9 to C_{11}. C_9 to C_{11} alcohols also represent the limit of chain length in the esters of thiodibutyric acid. In the case of aliphatic acid alcohol esters, it has been determined that the compatibility limit lies with a total length of 26 carbon atoms. This 26 carbon atom limit was based on observations made in connection with several types of esters, dibasic acids of monohydric alcohols, model basic acids and polyhydric alcohols, and dibasic acids and polyhydric alcohols.

Little work on polyhydric alcohols and dibasic acids was done. In this group of poly esters it was found that a too short limit of polymer chain resulted in water sensitivity, while a too long chain resulted in lack of compatibility. One such poly ester was manufactured - Plastomoll TB. This was thiodibutyric acid - butylene glycol ester. The specific plasticizing action of this poly ester is not very good. However it is gasoline proof.

In general it was observed that better cold flex resistance can be achieved with aliphatic chains than with branched chains. This is illustrated by the greater cold resistance of Palatinol F as against Palatinol HS. Palatinol F is $C_7 - C_{10}$ Fischer Tropsch diester of phthalic acid. It has also been found that the low temperature flexibility of a polyvinyl chloride plasticized mass, once gelatinizing power and compatibility of a substance are established, depends to a great extent upon the viscosity of the plasticizer. Dr. Wuerstlin at Ludwigshaven made elaborate tests proving the relationship between plasticizer viscosity and low temperature flexibility. He proved a direct connection in almost every case, but did find a few exceptions. One exception was the case of tricresyl-phosphate and triphenyl phosphate. Tricresyl phosphate is an oily liquid at 20°C., while triphenyl phosphate is a solid. In spite of this, these two materials exhibit practically the same plasticizing curves.

In 1939 it was recognised that large quantities of a suitable plasticizer for use in cable installation in connection with poly-vinyl chloride would be required. In this case low temperature properties would be very important. At the same time the electric properties should be kept at a maximum. It was proved that polyglycols and ether carbonic acids with the replacement of the oxygen by a sulfur atom substantially improved the electric properties of poly-vinyl chloride films produced from these esters without impairing the cold-flex resistance. Prominent among the sulfur containing esters were the esters based on thiodybutyric acid and thiodiglycol. The sulfur containing esters resulted in poly-vinyl chloride films having a specific resistance lying about a tenth power higher than the normal esters. It was also assumed that branching of the aliphatic acid chains was favorable in respect to electric properties of the films. In many cases it was found advantageous to sacrifice the low temperature flexibility in favor of better electric properties.

A comparison of electric properties of the films made from esters of the first running fatty acids with glycols indicates that like low temperature resistance, the electrical resistance increases from the lower glycol ester on, via butanediol ester to the octanediol ester. The esters of succinic and maleic acids were checked. A long chain of alcohol was esterified with these two acids. Film made with the maleic acid esters showed a higher specific resistance. The dichloromaleic acid esters were then made up. With a C_{10} fatty acid alcohol esterified with dichloromaleic, an excellent plasticizer was produced. It was believed to be the best plasticizer for the cable industry thus far investigated.

MANUFACTURE OF PLASTICIZERS (LUDWIGSHAFEN)

One large group of plasticizers is known under the trade name of Palatinol. Fig. I shows the plant lay-out at Ludwigshafen for these esters. They are all neutral esters. The formulation of the reaction proceeds

according to the general ester equation

$$R{\cdot}COOH + R{\cdot}OH \longrightarrow R{\cdot}COO{\cdot}R + H_2O$$

In this reaction both of the esterification components are brought together in the presence of an acid catalyst, for example sulfuric acid, p.toluene sulfonic etc. In order to shift the equilibrium during reaction to the side of the esters, the water formed during reaction must be removed as it is formed. In the manufacture of the Palatinols the removal of the water was carried out by three different processes.

1. The water is linked on to an inorganic solid such as sodium bisulfate. The sodium bisulfate at the same time acts as an esterification catalyst due to its acidic nature. This is the Bisulfate Process.

2. By means of carrying out azeotropic distillation using a hydrocarbon or a chlorinated hydrocarbon as the medium. This is the Circulation Process.

3. By vacuum distillation, in which the water is swept out by a gas stream as it is formed. After formation of the esters they are alkalized with soda solution, neutrally washed with water, blown out with steam to remove readily volatile portions, clarified with active decolorising carbon dehydrated under vacuum and filtered. This is the Vacuum Process.

It was not the practice in the Ludwigshafen Palatinol Plant to distill the esters, in as much as they could realize no gain that would justify the expense of this additional process. The color of the esters was often improved by the addition of 0.002% potassium permanganate to the finished ester.

DESCRIPTION OF THE PROCESSES AND APPARATUS

Bisulfate Process

This process can be advantageously applied when the acid used is the anhydride, and only half the amount of water must be bound by the bisulfate. It is also most active where the lower alcohols are esterified, the lower alcohols having a higher degree of re-activity. When one reaches an alcohol such as isoamyl with its lower activity, this process is no longer advantageous.

The proper quantities of alcohol, acid anhydride and sodium bisulfate are filled into a homogeneously lead-lined wrought-iron kettle of 6 m^3 capacity. This vessel is provided with a steam jacket capable of

operating at 75 lbs. steam pressure. The kettle is provided with a lead-lined stirrer of anchor type revolving 27 r.p.m. The time of reaction for such a process is generally about 5 hours. In order to avoid crystallisation of the sodium bisulfate during the cooling period following esterification, it is necessary to add additional water. After cooling, the contents of the kettle are pressed by an air head through a lead riser in the vessel to a so-called Spitz cylinder, passing from the Spitz cylinder to the settling tank which is a cylindrical enamelled vessel with a pointed bottom equipped with an agitator. This vessel is 2400 mm. high and 1800 mm. in diameter. The agitator is an anchor type, revolving 54 r.p.m. Here the raw ester and bisulfate solution are dissociated from each other by letting the lower layer drain off. This vessel is valved at the bottom by a rubber-lined squeeze type valve similar to the Hills McCanna valve. A volume of water equivalent to the volume of the ester remaining in the kettle is added, and sufficient solid soda is added to bring the pH slightly above 7. The alkaline pH should be maintained after one hour's stirring. The esterification by this method cannot be brought to 100% completion, with the result that 8 - 12% of monoester still remains. This is soluble in the soda solution and can be isolated by acidification. The monoester is collected in a lead-coated receiver and used later. The alkalized crude ester is now passed to the second 6 m^3 kettle. This kettle is provided with a steam jacket having a heating surface of 6 m^2. This vessel is equipped with a steam line to enable the carrying out of steam distillation. To this vessel is connected a vacuum condenser. 1 - 3% decolorising carbon is then added and a small quantity of solid soda. The temperature in this vessel is brought to 100° - 120°C. and then a vacuum is applied. This will remove the last traces of water and unreacted alcohol. When nothing more can be pulled over through the condenser, the temperature is allowed to fall to 80°C. The ester is then pumped through a filter press having 34 frames 800 by 800 mm. This press is of Sperry type. The filtering material is jute cloth backed filter paper. The advantages of this type of esterification process are its simplicity, its relatively high space time yield and its ability to produce light colored esters. The disadvantages are on the economic side, in as much as great quantities of sodium bisulfate are involved. The corrosive action of the bisulfate solution also brings up the cost of equipment maintenance. Renewal of the lead-lined apparatus in such a plant must be made on an average of every three months. Using refined lead was found to double this life expectancy. Vessels lined with ferrous silicon plates are going to be tried. Gaskets used in the equipment are lead.

Circulation Process

This process can be used in the manufacture of almost any ester. It has the disadvantage of low yield per unit volume of reactor space, and the color of the esters are affected by the increased time of reaction. In this reaction the 6 m^3 enamelled kettle is employed. The enamelled kettle is equipped with an agitator of anchor type turning 54 r.p.m. The vessel is

steam jacketed and is equipped with a condenser and Florentine bottle to separate the water carried off. During the war, ethylene dichloride was the common material for making up the azeotropic mixture. This was due to the shortage of hydrocarbons and would not generally be practised. As a result some ethylene dichlorides was continually lost by water solution, and its toxic nature was not appreciated in the plant. To carry out the reaction, the acid, the alcohol, the catalyst and the ethylene-dichloride were added to the kettle. The mixture is passed through the condenser and separated in the Florentine bottle. The condenser was of the 6 m^2 condensing area and was of shell and tube construction. The ethylenedichloride condenses, returning to the kettle from the Florentine separating bottle, the water being discharged to a measuring vessel. In these lines are glass sections to check the flow visually. The capacity of the measuring vessel for water was 1.5 m^3. The rate of reaction was checked by the rate of flow of the water from the Florentine bottle and also by the acid titer.*

This distillation will normally be run with a vessel temperature between 90 and 110°C. As soon as the titer has fallen to about 1, the esterification is regarded as complete. The distillation is then switched over to a vacuum condenser and a slight vacuum applied. The ethylene dichloride is pulled off under these conditions and stored in a separate receiver to be re-used. The ethylene dichloride has another disadvantage. Hydrogen chloride is gradually liberated, which results in equipment corrosion. To combat this, lead-lining of the pipes is generally practised.

Vacuum Process

A 6 m^3 kettle equipped with a steam jacket and an agitator are used in this process. To the kettle is connected a vacuum line and a condenser. The acid alcohol and catalyst are added to the kettle and the mass heated up to 100°C. and held at this temperature for 1 hour. The vacuum is then slowly applied, and a moderate air stream sucked through the mass in the kettle. Nitrogen was used at first, but was discontinued when air was found satisfactory. The temperature is slowly raised to 120°C. The termination of the reaction is determined by titration. This process unfortunately can only be applied when the components of the reaction boil sufficiently high that they do notpass over with the liberated water to any extent. The economic side of this reaction can be appreciated, when it is realised that no water carrier or absorber is required. Also, esters of particularly good electric properties can be produced by this method, in as much as no traces of undesirable impurities are present to be left behind, such as ethylene dichloride and sodium bisulfate. Also, the space time yield of this reaction

*Titer here means the quantity of a normal NaOH solution in cm^3 necessary to neutralize 10 cm^3 of a reaction mixture against phenol phthalein indicator.

is higher. Furthermore, hydrocarbons, olefines, etc. present in the alcohols are readily distilled off with the water, so that a subsequent blowing out with steam is often not necessary.

MANUFACTURE OF INDIVIDUAL PLASTICIZERS

Palatinol HS

Process - Circulation

Kettle Charge

1210 kg. phthalate anhydride
2200 kg. heptyl hexyl alcohol from Leuna synthesis
1000 kg. ethylene dichloride
20 kg. paratoluene sulfonic acid
9 kg. concentrated sulfuric acid

As in the general description, this reaction is run in a 6 m^3 capacity kettle and the water is continuously removed during the azeotropic distillation. After 10 - 12 hours, no more water can be collected in the water receiver, and the titer will have fallen to about 1. The excess of ethylene dichloride and non-esterifiable portion are pulled over by vacuum distillation and the temperature of the vessel is raised to 120°C. The crude ester is now alcoholised with solid soda, after having been passed into the separatory vessel with a pointed bottom, and containing 2½ m^3 of water. The watery portion is drained off and the ester blown out with steam in the steam still under a vacuum. 60 kg. of de-colorising carbon and 5 kg. of soda are added and the ester stirred for two hours at 120°C. with the vacuum on full. The ester is then pumped through the filter press.

Yield

2350 kg. Palatinol HS (88.2% based on phthalate acid)

Physical Data: Color: 10 - 30 iodine No.

Boiling Point: 230 - 245°C. at 20 mm. Hg.

Specific Gravity: 20°C. (.995 - .1010)

Acid No: 0.2

Saponification No: 310 - 340

Palatinol BB

Process - Bisulfate

Into a 6 m^3 lead-lined vessel were added the following:

1250 kgs. phthalic anhydride
1040 " benzyl alcohol (1000 liters)
600 " butanol pure (740 liters)
1500 " sodium bisulfate (pulverised)

The mixture is heated to 100°C. and held at this temperature for five hours. Then 2 m^3 of water is added and the mixture allowed to settle in the pointed separatory cylinder. The aqueous bisulfate layer is then drained from the separatory vessel. It is then blended with 2½ m^3 of water and alkalized by the addition of solid soda. The aqueous solution must remain alkalized after stirring for one hour. The aqueous part is drained off and the crude ester transferred to an enamelled agitator kettle equipped for steam distillation. This kettle is also equipped for vacuum distillation. In this kettle the ester is blown out with steam under vacuum for one hour at 100°C. 30 kg. of decolorising carbon and 5 kg. of solid soda are added and the vacuum again applied. The ester is agitated and heated to 120°C. After 1 - 3 hours the ester is allowed to cool to about 80°C. and pumped to a filter.

Instead of adding both alcohols simultaneously, the benzyl alcohol may be added first, and after completion of the formation of the monoester the butyl alcohol may be added. This procedure will result in less formation of dibenzyl and dibutyl esters.

Yield

2360 kg. Palatinol BB (70.5% yield based on phthalic acid)

Physical data: Color 2 - 10 mg. iodine

Boiling Point: 200 - 280°C. at 20 mm. Hg.

Specific Gravity: (20°) 1,080 - 1,090

Acid No: 0.2

Saponification No: 360 - 375

Diamyl Phthalate

Process - Bisulfate

Kettle Charge

1260 kg. phthalate anhydride
1980 kg. (2300 liters) isoamyl alcohol (OH No. 584)
1500 kg. sodium bisulfate

The mixture is heated to 100°C. in the 6 m^3 lead-lined agitator kettle and held at this temperature for five hours. 2 m^3 water are then added and the mixture allowed to settle in the large pointed-bottom separatory vessel. The bisulfate solution is then drained off and 2½ m^3 more water added to the ester. Solid soda is then added to raise the pH slightly above 7, and the pH maintained during one hour of stirring. After the ester is separated from the water layer, it is transferred to the enamelled 6 m^3 steam still and blown out with steam under vacuum for two hours at 100°C. 50 kg. of decolorising carbon and 5 kg. of solid soda are added and the temperature raised to 120°C. under full vacuum. After 1 - 3 hours the temperature is allowed to fall to 80°C. and the ester pumped through the filter.

Yield

2100 kgs. diamyl phthalate (77.9% yield based on phthalate acid)

Physical Data: Color 5 - 20 mg. iodine

Boiling Point: 218 - 230°C. at 20 mm. Hg.

Specific Gravity: 20°C. (1.020 - 1.024)

Acid No: Less than .2

Saponification No: 350 - 360

Dicyclohexylphthalate:

Process - Circulation

Kettle Charge

1500 kg. phthalate anhydride
2250 " cyclohexanol
1000 " ethylene dichloride
5 " sulfuric acid (concentrated)

The mixture is heated in a 6 m^3 enamelled azeotropic distillation unit. The esterification is continued for approximately 48 hours, by which time the titer will have dropped to approximately 1. The ethylene dichloride

is then pulled off under vacuum. The temperature inside the kettle is raised to 120°C; after a short period of 120°C. the crude ester is transferred to the large separatory vessel and mixed with 2½ m^3 of warm water. Solid soda is added to raise the pH above 7. The mixture is kept constantly above 90°C., as otherwise the ester will become viscous and ultimately solid. After separating the aqueous solution, the ester is washed clean with hot water, separated again and transferred to the steam and vacuum still to be blown out with steam and dehydrated under vacuum at 120°C. after the addition of 5 kg. of solid soda. The hot product is transferred to barrels for further process. The yield at this point is 2850 kg. dicyclohexyl phthalate crude (86.5% yield based on phthalate acid).

The barrelled product is further purified by re-crystallising from an almost saturated spirit solution. In this process the dicyclohexylphthalate is mixed with the spirit and 5 kg. of decolorising carbon per 300 kg. of dicyclohexyl phthalate.

The mixture is stirred in a small steam kettle at 75°C. for 1 hour. The ester is then passed through a filter up to the crystallising pans. Crystals are collected and further dried in a circulating air type dryer.

Yield

250 kg. dicyclohexylphthalate per 300 kg. of raw product (71% yield based on phthalate acid)

Physical Data: Color: Colorless crystals

Melting Point: 63 - 65°C.

Acid No: Less than 2/10

Saponification No: 340

Plastomoll KF

Process - Circulation

Kettle Charge

2300 kg. first running Fatty acid C_7 - C_9 (Acid No. 400)
1200 kg. triglycol
1500 kg. ethylene dichloride
5 kg. sulfuric acid (concentrated)

The mixture is heated and agitated in a 6 m^3 enamelled azeotropic

distillation unit. After 10 hours of distillation the titer will have dropped to about 1, and the excess ethylene dichloride is distilled off from the vacuum and the temperature raised to 120°C. in the kettle. The crude ester is transferred to the separatory vessel and 2½ m^3 of water are added. Solid soda is then added to neutralize the acid. Severe foaming will be encountered in this step and care must be taken to avoid over-flowing. A small amount of sodium chloride may here be added to aid in dissociation of the ester and water layers. The crude ester is again washed with 2½ m^3 water, separated again and then transferred to the steam distillation unit, where an additional 60 kg. of de-colorising carbon and 5 kg. solid soda are added. The temperature is raised to 120°C. under vacuum, and after 1 - 2 hours cooled to 80°C. and pumped through the filter.

Yield

2500 kg. Plastomoll KF (79.5% yield based on triglycol)

Physical Data: Color: 20 - 40 mg. iodine

Boiling Point: 200 - 290°C./ 20 mm.Hg.

Specific Gravity: (20°C.) 0.980 - 0.990

Acid No: 0.3

Saponification No: 266 - 306

Plastomoll TAH (diethylhexylthiodibutyric acid ester)

Process - Vacuum

Kettle Charge

2000 kg. of thiodibutyric acid pure
2670 " ethylhexanol
70 " decolorising carbon
5 " sulfuric acid (concentrated)

This mixture is heated to 100°C. in the steam vacuum distillation unit with enamelled kettle and kept at 100°C. for one hour. The vacuum is then gently applied and brought to a point where an intensive air stream is sucked through the mixture. The temperature of the vessel is slowly allowed to rise to 120°C: after 6 - 7 hours the titer willhave dropped to 1. The reaction will then be considered finished. The crude ester is then alkalized in the pointed separatory vessel with 2½ m^3 water and solid soda; it is separated, transferred to the steam still, blown out with steam for two hours under vacuum at 120°C., after the addition of 5 kg. more of solid soda. The ester is then pulled through the filter.

Yield

3470 kg. Plastomoll TAH (diethylhexylthiodibutyric acid)
(83% yield based on phthalic acid)

Physical Data: Color: 10 - 100 mg. iodine

Boiling Point: 230 - 297°C. / 20 mm. Hg.

Specific Gravity: (20°C.) 0.964 - 0.967

Acid No: 0.2

Saponification No: 250 - 270

Plasticizer 1980 Special

Process - Vacuum

Kettle Charge

3200 kg. first running fatty acid. $C_7 - C_9$
1500 kg. thiodiglycol
40 " decolorising carbon
20 " para toluene sulfuric acid
7 " sulfuric acid (concentrated)

This mixture is introduced in a 6 m^3 enamelled kettle equipped for steam distillation with a condenser and vacuum receiver and heated to 100°C. for one hour. After one hour the vacuum is gently applied until an intensive air stream is sucked through the mixture. The temperature is slowly raised then to 120°C. Besides the removal of reaction water, volatile thionyl compounds are distilled over some dithiam with melting point 111°C., passing over into the condenser. Care must be taken not to allow this material to crystallize on the surface of the condenser and in this way clog the condenser. The esterification is usually completed after 35 - 40 hours, when the titer has dropped to approximately 2. The crude ester is then transferred to the separatory vessel and alkalised with solid soda, after the addition of 2⅓ m^3 of water. Some sodium chloride may be needed to effect better separation of the two layers. After two washings with warm water and separation of the water, the ester is transferred to the steam distillation unit and 50 kg. of decolorising carbon is added, and it is subjected to vacuum steam distillation for ½ hour. 5 kg. of solid soda are then added to the ester and the mass is dehydrated by vacuum at 120°C. After cooling to 80°C., the ester is pumped through the filter.

Yield

2900 kg. plasticizer 1980 Special
(70% yield based on first running fatty acid)

Physical Data: Color: 30 - 200 mg. iodine

Boiling Point: 205 - 295°C./20 mm. Hg.

Specific Gravity: (20°C.) 0.995 - 1.005

Acid No: 1.0

Saponification No: 280 - 310

Plasticizer ELAOL 3

Process - Circulation

Kettle Charge

590 kg. pentaerythritol
2500 " first running fatty acid $C_4 - C_6$ (Acid No. 488)
1000 kg. ethylene dichloride
10 " sulfuric acid (concentrated)

The mixture is charged into a 6 m^3 enamelled kettle equipped for azeotropic distillation. The temperature of the mixture is raised until distillation is started. The esterification is completed after 70 - 75 hours, when the titer will have dropped to about 8 - 9. The excess ethylene dichloride is distilled off under vacuum, and the temperature gradually raised to 120°C. The crude ester is then sent to the pointed bottom separatory vessel. To the separatory vessel is added 2½ m^3 water and sufficient solid soda to alkalize the mixture. The water layer is separated and the ester is washed once more with warm water and again separated. The ester is then passed to the steam distillation kettle, and blown out with steam for about 2 hours. 50 kg. of decolorising carbon and 5 kg. solid soda are added and the temperature raised to 120°C. The ester is then cooled and pumped through the filter press.

Yield

1870 kg. of Elaol 3 (82% yield based on pentaerythritol)

Physical Data: Color: 100 - 300 mg. iodine

Boiling Point: 185 - 330°C./.20 mm. Hg.

Specific Gravity: (20°C.) 1.036 - 1.066

Acid No: 1.0

Saponification No: 437 - 440

Plasticizer ELAOL 4

Process - Circulation

Kettle Charge

700 kg. pentaerythritol
3500 " first running fatty acid C_7 - C_9 (Acid No.410)
1000 " ethylene dichloride
10 " sulfuric acid (concentrated)

The mixture is charged into the 6 m^3 enamelled azeotropic distillation unit and the distillation started. The esterification is generally finished after 75 - 80 hours, when the titer will have fallen to 7 - 8. The excess ethylene dichloride is distilled off under vacuum and the ester slowly brought up to a temperature of 120°C. The ester is then transferred to the pointed separatory kettle and 2½ m^3 water are added. To this sufficient solid soda is added to alkalize the mixture. This mixture must be kept warm in order to separate the two layers. After the two layers have separated, the ester is again washed with warm water, again separated and then transferred to the steam distillation kettle, where it is blown out with steam for about 2 hours. 50 kg. of decolorising carbon and 5 kg. of solid soda are added and the temperature brought up to 120°C. under full vacuum. After slight cooling, the ester is pumped through a filter.

Yield

2570 kg. of ELAOL 4 (80% yield based on pentaerythritol)

Physical Data: Color: 100 - 300 mg. iodine

Boiling Point: 217 - 350°C / 20 mm. Hg.

Specific Gravity: (20°C.) 0.980 - 1.000

Acid No: 1.0

Saponification No: 355 - 365

Plasticizer OX (Dixyloloarbonate)

Apparatus:

1. 1 Storage Tank: 10,000 liter capacity
2. 1 Reaction Kettle: 10,000 liter capacity, lead-lined with titrator and jacketed for heating and cooling.
3. 1 Pressure Filter of Sperry type.
4. 1 Vacuum Distillation Unit with 2500 liter retort vanadium alloy, plated, fitted with heating coil. Designed for 65 atmospheres steam pressure.

Kettle Charge

2000 kg. xylol
1800 kg. sodium hydroxide (50%)
4500 kg. water

These materials are charged into the one 10,000 liter lead-lined reaction vessel and the temperature slowly raised to 35 - 40°C. When this temperature is reached, 1200 kg. of phosgene are pumped in. The sodium hydroxide must be consumed after phosgenization to a point where less than ½% free NaOH remains. The reaction, however, never should be allowed to go over on to the acid side. The resulting compound is then drained into the vacuum distillation unit and subjected to vacuum distillation. From 3000 kgs. raw product, the following fractions are obtained:

900 kg. of first running
200 " of intermediate running
1600 " of main running

Boiling point: 230 - 245°C. at 15 mm. Hg. 300 kg. high boiling residue. The first runnings and the intermediate runnings are returned for subsequent distillations.

Plasticizer NP at Leverkusen
(Diisopropylnaphthalene)

Apparatus:

1. 1 Agitated Autoclave 1 m^3 capacity designed for 50 atmospheres w.p.
2. 1 Naphthalene Melting Vessel constructed of iron

3. 1 60 liter capacity Centrifuge

4. 1 Vacuum Distillation Unit 3 m. capacity, equipped for direct gas heating; fabricated from iron.

5. 1 Storage Tank for propylene; capable of operating at 20 atmospheres pressure, with indicator, fabricated from steel.

Operation:

Into the autoclave are charged the following:

600 kg. pure naphthalene
800 liters of propylene
10 kg. tonsil
5 " zinc chloride (water free)

The molten naphthalene is sucked into the autoclave by drawing a vacuum on the autoclave. Zinc chloride and Tonsil are added with stirring and the temperature of the mixture brought up to 150°C. The propylene is then led in, in a liquid state. After about 2½ hours the propylene will have reacted and the temperature will have risen to 250°C. The reaction mixture is then cooled down to 100°C. and passed to the centrifuge. 1000 kg. of raw product is obtained from the centrifuge. The raw product is now subjected to distillation.

Raw diisopropylnaphthalene is charged into the 3 m^3 vacuum distillation unit and 2 kg. of dry soda are added. The first fraction of the mixture to pass over contains a high percentage of naphthalene and monoisopropylnaphthalene. 15% of the raw product passes over in this form. The next and main fraction, (about 70%) is then collected. The final third running (about 12%) is solid and constitutes higher propylated naphthalenes. The remaining 2 - 3% is washed out of the still with steam and discarded.

Specifications of Product:

Color: Water-clear to light yellow

Odor: Free of naphthalene

Average Specific Gravity: at 20°C. 0.945 - 0.955

Ignition Point: Not below 175°C.

Flash Point: Not below 150°C.

Solidifying Point: Below minus 30°C.

Viscosity: at 20°C. 6 - 7°E.

Plasticizers ELOAL Type at Leverkusen

ELAOL type plasticizers are manufactured at Leverkusen as well as at Ludwigshafen. They are esters manufactured from first-running Fischer Tropsch fatty acids condensed with hexantriol.

ELAOL 1 is made with first-running fatty acid, having chain length of $C_3 - C_6$.

ELAOL 2 has a fatty acid with chain length $C_6 - C_9$

ELAOL 12 has a fatty acid of $C_8 - C_{12}$ chain length

Operation

3400 kg. of first-running fatty acid and 1225 kg. of hexantriol are charged into a stainless steel re-action vessel with equipment for gas heating and vacuum distillation with air agitation. The temperature of the mixture is heated for 8 hours at 190°C. The mixture of fatty acid and water are passed up through the connecting column to be condensed in the condenser and separated in a Florentine bottle, the fatty acid returning to the reactor and the water being discarded. After about 12 hours the titer will have dropped to 1 and esterification is considered completed. The crude ester is then cooled off and run into a 5 m^3 separating vessel with conical bottom. 5 kg. of solid soda and 1 m^3 of water are then added. The water-ester mixture is dissociated by centrifuging in liquid centrifuge turning 6000 r.p.m.

ELAOL is then sent to a vacuum distillation unit, and after 20 kg. of active carbon are added, it is subjected to vacuum and agitated at 100°C. for one hour. The mixture is then pumped through a Sperry type filter and stored in drums.

Desavin at Leverkusen
(Diphenoxydiethanolformal)

Diphenoxydiethanolformal is an ether made by reacting dichloracetal with sodium phenoxide according to the following equation:

$$2(C_6H_5ONa) + \begin{matrix} ClCH_2 - CH_2O \\ ClCH_2 - CH_2O \end{matrix} \diagdown CH_2 \rightarrow \begin{matrix} C_6H_5O-CH_2-CH_2-O \\ C_6H_5O-CH_2-CH_2-O \end{matrix} \diagdown CH_2 + NaCl$$

The main reaction is carried out in equipment illustrated in Print No. 2.

Process

420 kg. phenol
358 kg. 50% caustic soda

are accurately weighed out and charged into the autoclave. The reaction is exothermic, and the water formed is allowed to evaporate. After the reaction the apparatus is allowed to cool down to 128°C. and is held at this temperature evenly for about 5 minutes in order to give a uniform temperature throughout the mass. 392 kg. of dichloracetal are then filled into the measuring container and pumped from the measuring container into the autoclave in a slow stream. The autoclave at this time is connected to a reflux condenser, which allows for refluxing of the dichloracetal. The reaction is violently exothermic. The rate of reflux of dichloracetal is so adjusted that the reaction mass temperature does not exceed 135°C. If the temperature should start to rise, the flow of dichloracetal to the autoclave is shut off until the temperature again normalizes. After 70 kg. of dichloracetal have flowed in, steam is applied to the autoclave heating system, sufficient to keep the temperature of the mass at 135°C. For about 10 minutes the temperature of the mass is closely watched. Should no further rise in temperature be observed the dichloracetal is again slowly added. After the entire quantity of dichloracetal has been admitted, the steam is raised slightly until a temperature of 150°C. is reached. The reaction is complete when the temperature of the mass no longer exceeds the steam heating temperature. A test for reaction progress is made by sampling 20 gms. of the reaction mass. To do this the 20 gms. sample is stirred well with 500 ml. of water and titrated against a normal H_2SO_4. A solution of not more than 0.4 of ml. of normal H_2SO_4 should be required for titration. If the batch is still too alkaline, it is heated for another two hours at 150°C. and again checked. When the reaction is completed by test, it is cooled off to 120°C. and placed in a vacuum distillation unit and distilled under 1 mm. Hg. The melting point of Desavin should be 18 - 18.9°C. The yield based on phenol is 87.4%.

Plasticizer N
(Tetrachloronaphthalene)

The chlorination of naphthalene is carried on in a 8000 liter cast iron kettle equipped with an agitator, of Anchor type, turning 60 r.p.m. The kettle is jacketed, the jacket capable of 4 atmospheres working pressure. Two chlorine inlet pipes are provided.

6000 kg. naphthalene
5 " antimony metal (finely ground)

are charged into the kettle. The naphthalene is melted by raising the temperature to 80 - 90°C. 120 - 200 kg. of chlorine are then introduced hourly. The temperature is slowly raised to 110°C. and after 8 hours to 130°C. After 10 hours a melting point test is run on the mass. This test is repeated over 8 hours until a melting point of 40°C. is obtained. The test is then carried out every 4 hours. The input of chlorine is determined by the melting point. The melting point for tetrachloronaphthalene is 93°C. The chlorination is usually completed in about 100 hours. When completed the mass is

blown out with warm air. After 1 - 2 hours of air blowing, the molten material is transferred to a 7000 liter nickel-lined neutralizing vessel. Here 1% NaOH in the form of a 50% water solution is added and the mass is stirred at 140°C. for 10 hours. The mixture then should have a pH above 7. The alkaline tetrachloronaphthalene is now continually washed with hot water until the washing water runs neutral. About 20 hours of washing will be required. The mass is then heated to 140°C. for drying.

Molten tetrachloronaphthalene is now drained into a 4000 liter agitated oil bath heated vacuum distillation unit. 10 kg. of Fullers Earth and 40 kg. of solid soda are added. The temperature is raised via the oil bath to 190°C. and a vacuum of 4 - 5 mm. Hg. applied. Distillation will actually start at about 170°C. in the tetrachloronaphthalene and at about 200°C. in the oil bath. The apparatus is capable of distilling 200 liters per hour. The distillation is considered complete as soon as a yellow tinted product begins to come over into the receiver. This happens when the tetrnaphthalene temperature in the evaporation kettle reaches 230°C. The oil bath at the end of the distillation will have a temperature of 280°C. The product remaining undistilled in the distillation kettle is marketed as scrap.

APPENDIX 1

LIST OF GERMAN SCIENTIFIC AND TECHNICAL PERSONNEL INTERVIEWED

Name	Position	Location
Dr. O. Helscher	Assistant in charge of plasticizer plant	I.G. Farben A.G. Ludwigshafen
Dr. H. Kling	Director of plasticizer laboratory	I.G. Farben A.G. Ludwigshafen
Dr. Tweister	Assistant Director	I.G. Farben A.G., Leverkusen

APPENDIX 2

LIST OF GERMAN TARGETS VISITED

Name	Location
I.G. Farben, A.G.	Ludwigshafen
I.G. Farben, A.G.	Leverkusen

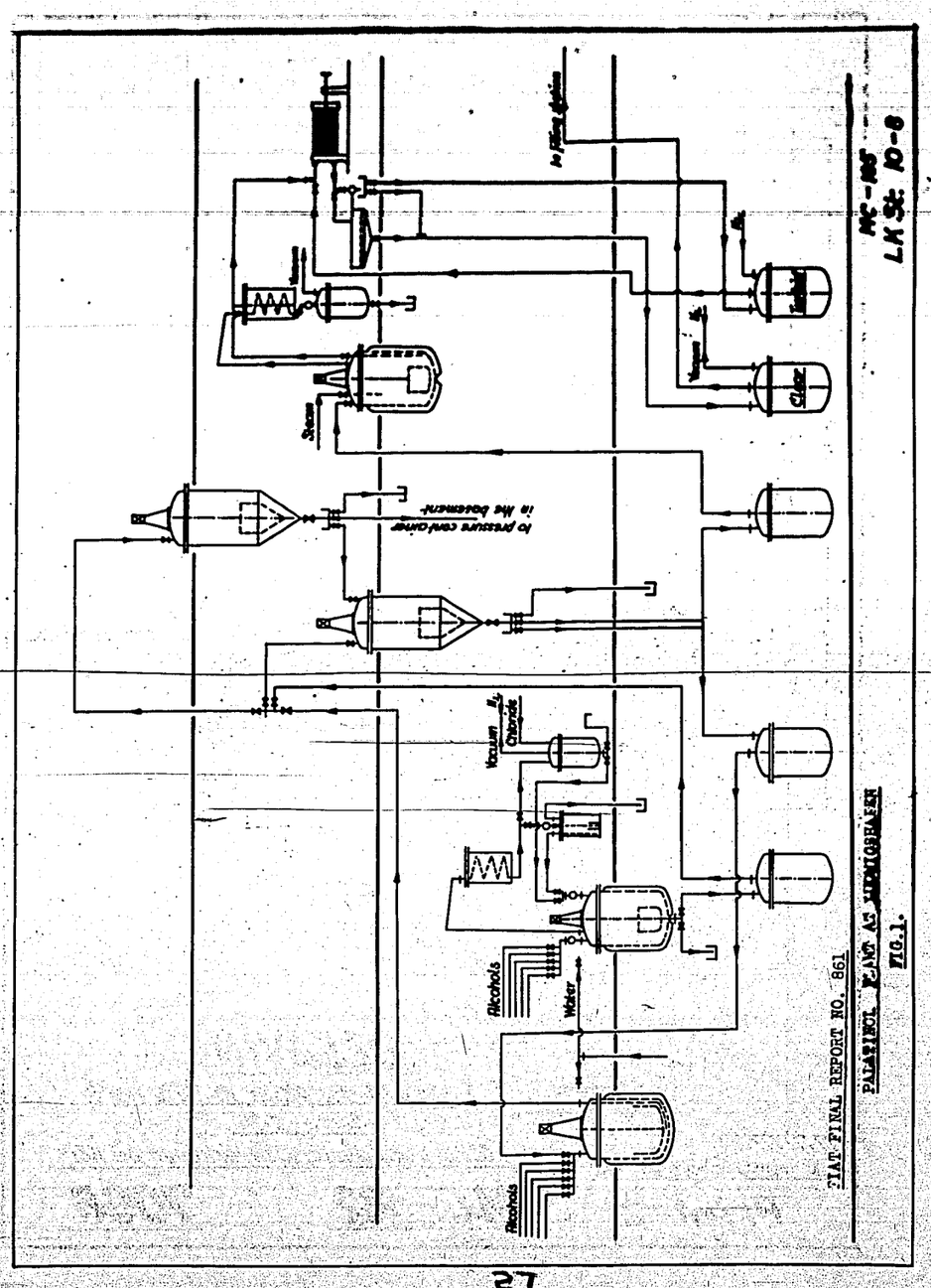
APPENDIX 3

LIST OF SAMPLES EVACUATED

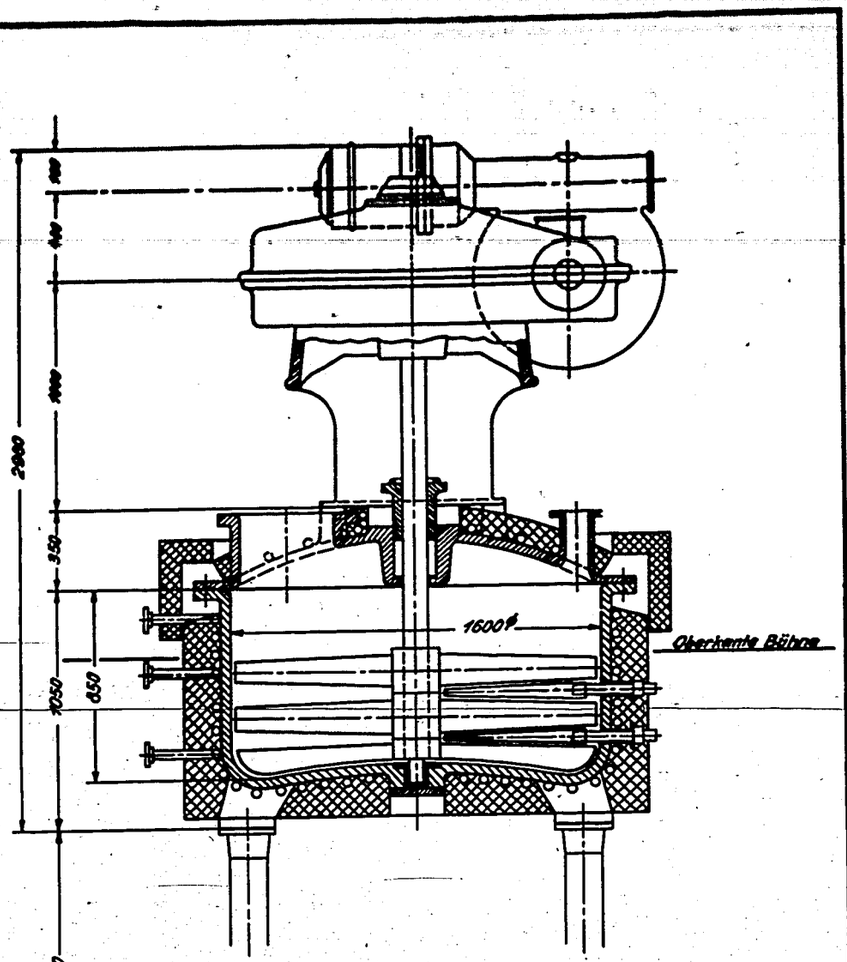
The following sample was sent to Washington, D.C. Inquiries should be addressed to:

Technical Industrial Intelligence Branch,
U.S. Department of Commerce,
Washington 25, D.C.

MC No. 117. Plastomoll TAH (Diethylhepylthiodibutyrate), from I.G. Farbenindustrie, Ludwigshafen.



FIAT FINAL REPORT NO. 861
PLASTOMOL TAH PLANT AT LUDWIGSHAFEN
FIG.1.



DESAVIN

1,6 m Stg.-Autoklav m. Rührwerk

Scale: 1:20

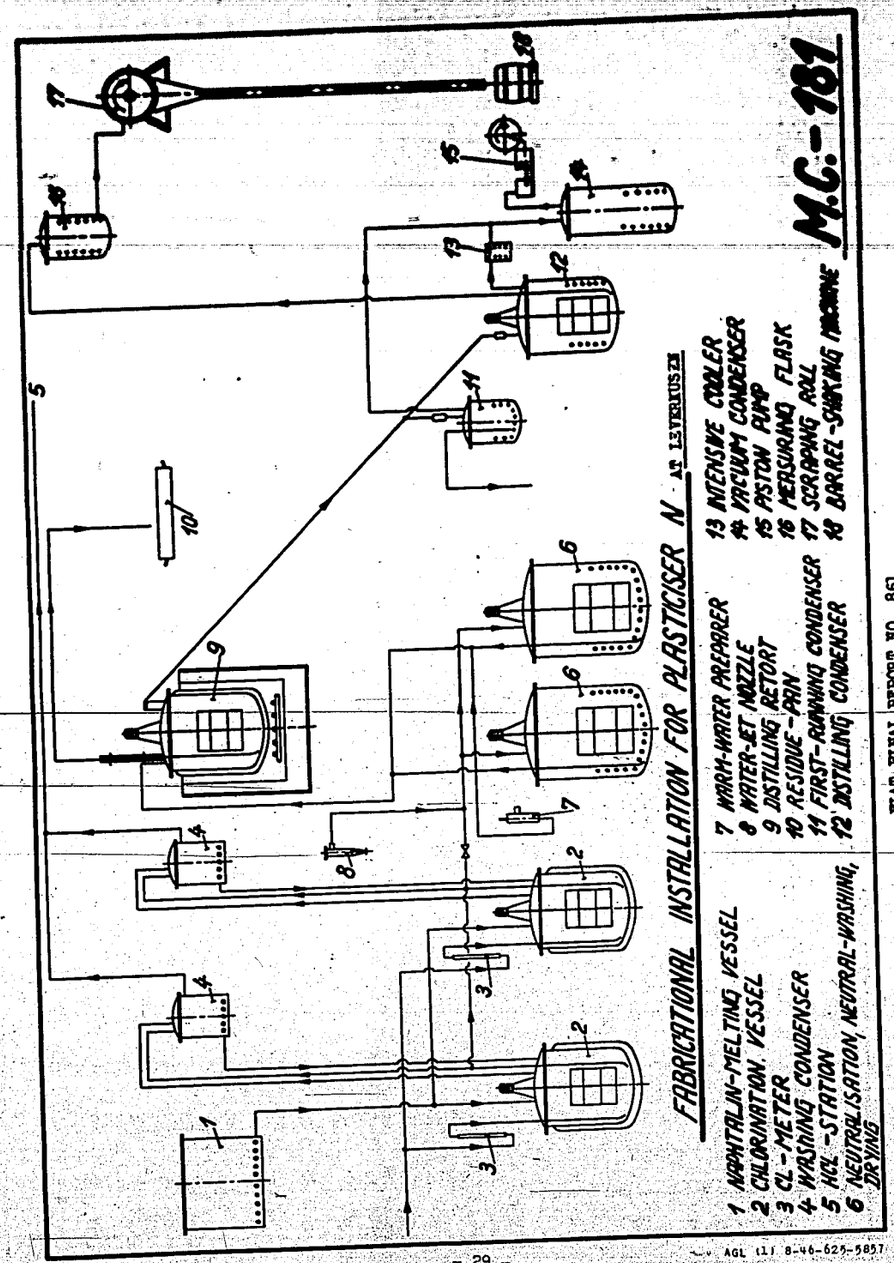
I.G. Farbenindustrie, Leverkusen bei Köln

FIAT FINAL REPORT NO. 861

Print 2

M.C.-182

7066



FABRICATIONAL INSTALLATION FOR PLASTICISER N - Ar 1.5 VERLUSTE

1 NAPHTALIN-MELTING VESSEL
2 CHLORINATION VESSEL
3 CL-METER
4 WASHING CONDENSER
5 HCL-STATION
6 NEUTRALISATION, NEUTRAL-WASHING, DRYING
7 WARM-WATER PREPARER
8 WATER-JET NOZZLE
9 DISTILLING RETORT
10 RESIDUE-PAN
11 FIRST-RUNNING CONDENSER
12 DISTILLING CONDENSER
13 INTENSIVE COOLER
14 VACUUM CONDENSER
15 PISTON PUMP
16 MERCURING FLASK
17 SCRAPING ROLL
18 BARREL-SHAKING MACHINE

M.C.-181

FIG. 3.

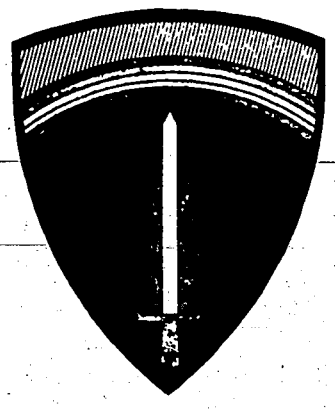
FIAT FINAL REPORT NO. 861

Copy 1

FIAT FINAL REPORT 754

VIBRATING BALL MILL FOR PULVERIZING FINE MATERIALS

Tyler, Paul W.



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

FIAT FINAL REPORT 754

VIBRATING BALL MILL FOR PULVERIZING FINE MATERIALS

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)
FIELD INFORMATION AGENCY, TECHNICAL

FIAT FINAL REPORT NO. 754 25 April 1946

VIBRATING BALL MILL FOR PULVERIZING FINE MATERIALS

By

PAUL M. TYLER

Joint Intelligence Objectives Agency

THIS REPORT IS ISSUED WITH THE WARNING THAT, IF THE SUBJECT MATTER SHOULD BE PROTECTED BY U.S. PATENTS OR PATENT APPLICATIONS, THIS PUBLICATION CANNOT BE HELD TO GIVE ANY PROTECTION AGAINST ACTION FOR INFRINGEMENT.

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

A ball mill operated by an unbalanced eccentric is described. Such a mill gives a very close sizing and will pulverise down to 1 micron.

Data on the pulverization of aluminum and alloys of silver are given, along with 17 illustrations.

TABLE OF CONTENTS

VIBRATING BALL MILL FOR PULVERIZING FINE MATERIALS

By Paul M. Tyler

I. INTRODUCTION

The investigator first saw the mill described in this report in a hard-carbide manufacturing plant. It is the standard grinding and mixing machine in Germany for tungsten carbide and certain other powder metallurgy products and is reported as being used extensively by pencil lead manufacturers and more or less generally in processing cosmetic talc and to some degree for grinding dyes, lacquers, paint pigments, silica flour, clay, ceramic batch materials, sulphur, gypsum, graphite, chalk, rubber waste, wood meal, lignite and other minerals, pharmaceuticals, and "all kinds of food products."

FIAT Final Report No. 617 (p. 9) records laboratory tests by a Dr. Ryschkewitsch at Degussa, Frankfurt/Main, employing a non-revolving ball mill subjected to vibration. Dr. Ryschkewitsch believed the method would be even more efficient on a large scale and that it had much commercial promise. It was further stated that, according to Dr. Ryschkewitsch, "this method is unknown in Germany and has never been developed commercially." The essential principle of this experimental mill, however, is apparently identical with that of the mill herein described.

Actually, the novel principle of this mill is covered by German and foreign patents (taken out by I. G. Farben) and the mill has been on the market for about 10 years. Small units made by the same manufacturer were advertised and sold in the United States before the war for laboratory work but the investigator is not aware of any mill of similar type being employed by American mineral industries. Inquiry among mining men and metallurgists in Great Britain indicated that it is not generally known in that country except perhaps in the powder metallurgy field.

II. DESCRIPTION

The mill itself is a cylindrical or semicylindrical shell of steel or porcelain partially filled with steel or porcelain grinding balls. The balls in the smaller mills are 12 mm. in diameter but the sintered carbide industry uses tungsten carbide balls having an initial diameter up to 1½ inches or more. Passing through the entire length of the shell is a sleeve bearing in which revolves an eccentric shaft rotated by a suitable motor, usually direct-connected by a flexible coupling. The motor is rigidly mounted but the weight of the mill is supported by suitably shaped leaf springs.

Rotation of the unbalanced shaft, combined with the action of the springs, vibrates the mill at high speed. Laboratory sizes operate at 1450 r.p.m. The motion corresponds exactly with that obtained in a vibrating screen actuated by an unbalanced flywheel; in fact, the company manufactures a vibrating screen using the same unbalanced shaft and a similar spring suspension.

The mill is known as Schwingmühle "VIBRATOM." It is manufactured by Siebtechnik G.m.b.H., Bleichstrasse, 23, Mülheim-Ruhr, which also manufactures a general line of screening equipment, centrifugal separators, and pumps. Information was furnished the writer and Dr. Pollitzer (who accompanied him on the visit to the plant) by Dr. Wilhelm Sticker, Technical Director, and Dr. Ing. Robert Olbrich, consulting engineer. Various castings and machined parts are supplied by outside plants (probably contract work) and screen cloth and plate are obtained from an allied concern so factory operations at the above address are principally assembling and testing. Export sales are handled by a Dutch firm, Tema Technischmaterial, Nassaulaan, 1, La Hague.

The most popular size is the small laboratory mill of 0.3 liter capacity but larger mills up to 250 liters capacity are made and sold. The largest size requires a 16 H.P. motor when porcelain balls are the grinding media and a 20 H.P. motor when steel balls are used. The volume of balls (12 mm. diameter) is 650 liters in either case. Even on this large size, the rotation speed is high, 1,000 R.P.M. The complete machine weighs around 3,000 kg. and is listed at RM 7,280, net F.O.B. works, without motor. Capacities in all cases are given in net volume of material that can be charged at one time and so do not include volume of ball load which is much larger.

III. GRINDING ACTION

The effect of the peculiar agitating motion characteristic of this mill is to cause the balls to dance up and down in full teeter and to rotate, individually and also as a mass, slowly around the shell. The action was demonstrated to this investigator by resting a glass fruit jar filled with marbles on the frame of a small mill. Although the relative movement of the balls is slight, it is positive and no dead spots were observed at any point. The rapid beating action of the balls against one another, combined with friction, is claimed to constitute a highly efficient means of reduction.

Owing to the small amplitude of movement of the balls, the mill cannot ordinarily handle feed coarser than 0.5 mm. For a few exceptionally friable materials this top limit may be raised slightly but not above a maximum of about 0.7 mm. The real field of the mill is in superfine grinding and it will grind most materials down to one micron (0.001 mm.) in a single batch operation. The manufacturers claim that it will handle materials

SCHWINGMÜHLEN „VIBRATOM"

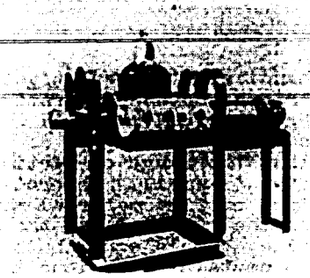


Abb. 1. 6-Ltr.-Tischmühle (4 Gefäße je 1,5 Ltr.. Kleinste Betriebsmaschine oder größeres Labor Modell.

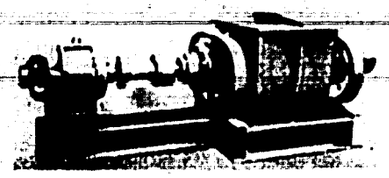


Abb. 2. 50-Ltr.-Mühle.
Kleine Betriebsmaschine mit meist gummiertem Mühlentrog.

Weitere Typen
20-Ltr.-Mühle (ähnlich Abbildung 3)
125-Ltr.-Mühle (ähnlich Abbildungen 2 u. 3)

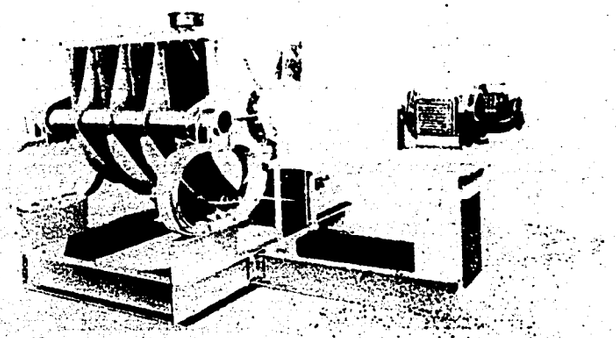


Abb. 3. 250-Ltr.-Mühle.
Größere Betriebsmaschine mit meist gummiertem Mühlentrog, auch für kontinuierliches Mahlen

***Labor*-Schwingmühle „Vibratom"**
mit 0,3 Ltr. Nutzinhalt

Besonders empfehlen wir die nebenstehend abgebildete Labor-Schwingmühle mit 0,3 Ltr. Nutzinhalt, die es jedem Betrieb ermöglicht, selbst die verschiedensten Mahlversuche durchzuführen. Die hiermit erzielten Ergebnisse sind insofern besonders wertvoll, als sie sich infolge weitgehend erforschter Modellgesetze mit 10% Genauigkeit auf alle unsere großen Mühlen übertragen lassen.

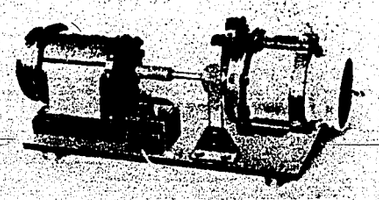


Abb. 4. 0,3-Ltr.-Labor-Schwingmühle

which no other machine will pulverise satisfactorily and also that the economy is greater than that of "any other process." Grinding may be either wet or dry.

IV. PERFORMANCE

Possibly by reason of language handicaps the investigator failed to obtain any quantitative comparisons between operations of this mill and other machines grinding identical material. However, he was shown various screen analyses and samples of powders which substantiated the claim that the range of particle size of material at any stage of reduction is small. Theoretically, the absence of excessive quantities of fine material which might cushion the impact of the balls on the material and the uniform quality of the product at all times should contribute to great efficiency. It was stated that on certain reductions the "Swing mill" saved 50 percent of time and roughly the same percentage of power. Grinding granulated aluminum from 0.5 mm. to powder (80 percent under one micron) took 22 hours in a 6-liter mill (about 4 kg. of material) operated by a 2 H.P. motor which probably consumed actually only 1.2 H.P.

Another advantage is that screen- or air-sizing of the product is unnecessary because there never are any particles much larger than the average of the whole batch.

The shape of ground particles tends to be flaky rather than cubical or round--a factor of importance in the paint and graphite industries and probably also in the talc trade and other special fields.

Hitherto the mill has operated only on a batch basis but the manufacturers are experimenting with continuous operation which appears feasible.

Available data on grinding aluminum and certain other specified powders are contained in an article contributed by Dr. Olbrich to a German trade journal and reproduced as an appendix to this report.

APPENDIX A

FINE GRINDING OF METAL POWDERS IN VIBRATING BALL MILLS

By Dr. Ing. Robert Olbrich, Mülheim/Ruhr

Tests prove beyond doubt the fact that even brittle and very hard materials, such as metals, can in most cases be successfully pulverized in vibrating mills. An effective pulverization is achieved, however, only with the proper balls and frequently only by the assistance of suitable addition agents. 1/

The good performance of the vibrating mills in the field of pulverization of many nonmetallic materials made it necessary to look into the possibility as to adapting the vibrating mills for pulverization of pure metals also.

The vibrating mill could hitherto successfully deal with the solution of difficult pulverization problems in numerous industries. Comprehensive investigations relating to vibrating mills have been conducted hitherto by Bachmann, Gründer, Kiesskalt, and Meldau.

Metal Pulverization

The pulverization of metals must be regarded as a new process in grinding technique and has experienced a considerable upswing in the last few years. Powder metal is being processed today for manifold purposes. The bronze and pyrotechnical industries are leading as main producers and consumers. But also numerous other applications, such as cemented carbides or high-speed steel industry, strive more and more to bring about the highest possible degree of fineness of the matrix metal or of the carbides and of the various addition substances, prior to processing. To reach this goal, one is even willing to take into account the unusually long duration of pulverization.

The question as to how far the pulverization of the metal powders will be carried out depends, of course, entirely upon the ultimate use of the powder concerned. Thus, for example, an initial product serving for the manufacture of a cemented carbide is being pulverized for 75 hours in the vibrating mill of a cemented carbide plant, in order to attain a grain fineness of at least 90 percent below 4 microns. Since even a trace of iron is objectionable in the finished samples, it is necessary to resort to porcelain balls without considering the higher abrasion of the pulverizing medium.

1/ Lecture at a meeting of the Working Committee "Technique of Dust-Production" of the VDI (Society of German Engineers), on May 6, 1941, in Berlin. The tests were carried out in the Research Laboratory of the Firm Siebtechnik, G.m.b.H., in Mülheim/Ruhr. I thank Frau Dr. Teichmüller and Herrn Dr. Meldau, both of Berlin, for their assistance in preparing the microscopic part of the work.)

The wear of the mill and pulverizing body constitutes an essential factor in metal dust production. The pulverizing media of vibrating mills consists in most cases of hard porcelain, which serves excellently for numerous materials to be pulverized. But there are also many cases in which the application of porcelain balls would not lead to favorable results because of their low hardness and of their low dead-weight, as compared with steel balls, and thus a conversion to harder pulverizing bodies with a higher gravity becomes indispensable. One will therefore resort to steel balls, providing that iron abrasion does not prove harmful in the finished pulverized product.

Aluminum Powder

Since aluminum occupies a leading role today in the great series of metals in its compact as well as powdered state, primary tests have been directed to the capacity for pulverization of this important light metal. Powdered aluminum is processed in large quantities in the paint industry, in the production of bronze colors, and in the pyrotechnical and chemical industry. In aluminum pulverization a granular form, or more frequently, a lamellar structure of the dust particles is being sought. The use of the vibrating mill proved very favorable in attaining both of these types of dust.

The starting material for Al-dust pulverization is either aluminum foil or granular aluminum. The processing from the solid, compact Al to the preground starting product may be variable, but since they concern only preparation, these processes will be omitted.

Production of Al-Dust in the Vibrating Mill

Experimental pulverizations were carried out in a laboratory vibrating mill with a capacity of .3 ltr. at a frequency of 24 Hertz and of an average amplitude of 4.5 mm. The pulverizations were made in three experimental series, which were based on the following conditions:

(1) Dry pulverization in the porcelain mill with hard porcelain balls of about 12 mm. in diameter.

(2) Dry pulverization in the steel mill with steel balls made of chromium steel of about 12 mm. in diameter.

(3) Experimental set-up like under (2), but with grease and stearine addition.

In all the tests the same starting material was used which consisted of tightly compressed aluminum foil below 2 mm. in size. The pulverization lasted for 10 hours. For simultaneous determination of the maximum grain size in Al-pulverization,

a somewhat coarser grain has been intentionally started with. Hitherto, it has been taken for granted, quite wrongly, that the most suitable or admissible grain size for feeding the vibrating mill lies at .5 mm. as a maximum, i.e., the grain is to lie if possible below the .5 mm. limit.

In contrast to this claim, numerous tests indicated the fact that the admissible grain size for numerous substances does not lie in any case at .5 mm., but, moreover, at 1 mm., in some cases even at 1.5 mm. for the same pulverizing medium with a diameter of 12 mm. Even the grain fraction 1-2 mm., amounting to almost 50 percent, was represented to a large extent in the Al initial product. Ill. 1 shows a powdered grain of the charge. The greatly magnified grain possesses actually a length of about 1 mm. The lamellar structure of the initial material is shown much more distinctly in the polished section, according to Ill. 2, which shows an Al-grain in section. This illustration indicates clearly the size of the actual surface and it must be taken into account under all circumstances when evaluating the progress of pulverization.

First Test

The progress in pulverization of Al with hard porcelain balls in the porcelain mill is shown by Ill. 3. The trend of the curves points to considerable pulverization during the first 3 hours; prolonging the time by another 7 hours could not bring about a further marked pulverization of the material; only the medium grain fractions were further reduced in size. The portion of the grains above 1 mm. decreased after 10 hours from 50 percent in the initial material to about 7 percent. It is noteworthy that a decrease of that portion of the grains has occurred by increasing the duration of grinding from 3 to 10 hours, which is indicated by the intersecting of curves I and II in the graphical illustration. This characteristic can be observed quite frequently in the pulverization of metal dusts and is principally caused by a baking together or sintering of the fine grains at increasing temperature. The grain structure of the Al-dust ground with hard porcelain balls is predominately granular and is shown in Ill. 4. The two foreign particles (roundly polished) seen in the picture are abraded particles of the porcelain balls.

Second Test

More favorable results were obtained in the second test in which the grinding was carried out in a steel container with steel grinding balls. Ill. 5 shows the results of this test. After 10 hours of grinding, a fineness of 60 percent below 0.1 mm. has been attained, 32 percent of which shows a fineness of below 60 microns. The considerably heavier mass of the pulverizing balls brought about a more effective pulverization as compared with the first test. The dust particles have a partial lamellar structure as indicated by Ill. 6.

Third Test

A quite considerable increase in performance was achieved in the third test. Here, too, the grinding was carried out in a steel container with steel balls; however, differing from the other tests in that the balls were greased prior to the grinding process, and some stearine had been added to the material to be pulverized. By this method, which is used to some extent in the bronze-color industry for grinding of bronzes, it has been made possible to achieve an extremely favorable degree of grinding efficiency. Picture 7 indicates quite distinctly the very favorable grinding progress. After 5 hours, a grain fineness of 87 percent below 60 microns was attained; after another 5, or a total of 10 hours, all the dust particles passed through the sieve with 10,000 meshes per cm^2 (width of mesh = 60 microns).

The microscopic determination of the grain size resulted in an average grain between 1 and 10 microns; thus it is evident that a considerable portion of the dust lies in the submicroscopic range. In view of the fact that today 24 to 36 hours are necessary for pulverization of Al by the stamping process, the results achieved with the vibrating mill can be evalnated as very high. In repeating the same test several times it was possible to establish the most favorable amounts of grease and stearine to be added. It proved most suitable to add the previously calculated quantity of grease not all at once but at definite intervals. As a rule, a quantity of grease amounting to .1 to .3 percent, based on the charge weight of the material to be ground, is considered as being adequate. The stearine content, on the other hand, may lie somewhat higher. Moreover, definite guaranties are asked for the Al-dust in respect to the grease content; a definite percentage of grease should not be overstepped.

In order to illustrate better the pulverization progress of the 3-test series described above the curves have been plotted in Illustration 8 after 10 hours' grinding time. The dust particles have obtained a pronouncedly lamellar structure by grinding with grease and stearine additions. Furthermore, it could be observed that, as soon as the grease and stearine was consumed by the heat of working, the particles had a tendency to assume again a granular form. At the same time, the dust adopted a matt appearance in place of the silvery gloss. A renewed grease addition, however, eliminated completely this attendant phenomenon; the lamellar form as well as silvery gloss returned after a short grinding time.

Illustrations 9 and 10 show quite distinctly the lamellar structure. Illustration 11, on the other hand, indicates the partially returned granular structure. It was through the renewed grease addition that the lamellar form could again be attained; Illustration 12.

In another test, the problem was to convert a pronouncedly granular Al-dust into a dust of a lamellar condition by means of the vibrating mill. The problem could be solved with an additional grinding time of 1 hour, Illustrations 13 and 14.

Grinding of Silver Solders

The process of silver solders pulverization in the vibrating mill will now be briefly illustrated. Here, too, the grinding was carried out once with porcelain balls and, at a second comparative test, with steel balls. The processes of pulverization are illustrated by Illustrations 15 to 17. The rather constant course of the characteristics inherent to both tests indicates clearly that it does not make any difference whether the pulverization is carried out with porcelain or steel balls. A rather constant grinding performance has been achieved in both cases. The dust has a granular structure in both cases. It is advisable in practice, however, to perform the grinding with steel balls instead of with porcelain balls on account of the greater abrasion of the porcelain balls.

Wear of Mills and Milling Bodies

The wear is considerably higher with porcelain ball grinding compared with steel ball grinding. With regard to steel ball grinding, for example, the wear of the grinding container was established as .5 gm. weight after a duration of grinding of 10 hours. The container itself had a net weight of 1560 gm. Considering only the effective grinding surface, a wear factor of .04 percent is obtained. The wear of the grinding balls has been figured as .02 percent.

Operational Grinding

With metal grinding, especially with Al-grinding, a very high heat of work has to be dealt with. It is necessary to provide an effective cooling for operational pulverization in the large vibrating mills. As is known, Al-dust is highly explosive, and spontaneous combustion is very likely to occur at high temperature and in the presence of oxygen. In order to eliminate the danger of explosion, it is advisable to perform the grinding in an atmosphere of inert gas. Both operational methods--an adequate cooling as well as the use of inert gas--are readily applicable to the vibrating mill.

Table 1. Loose weights with vibrating pulverizing of aluminum and silver solders

	Material charged kg. per ltr.	Grinding time: After 1 hr.	After 3 hrs.	After 5 hrs.	After 10 hrs.
Aluminum pulverization					
Pulverizing with porcelain balls.	.440	---	1.082	---	1.320
Pulverizing with steel balls	.440	.998	---	1.240	1.240
Pulverizing with steel balls and grease and stearine addition ...	.440	.403	.436	.808	---
Silver-solder pulverization					
Pulverizing with porcelain balls.	.815	2.578	2.892	2.924	2.982
Pulverizing with steel balls	.815	2.638	2.815	---	---

In the above table, the loose and packed weights of the metal dust samples, removed after a definite time of grinding, have been enumerated. It is worthy of note that the metallic dusts, in contrast to most minerals, increase in loose weight with increasing fineness. Thus, for example, the loose weight of Al-dust increased from .440 kg. per ltr. to 1.320 kg. per ltr. after a grinding time of 10 hours by grinding with porcelain balls. Considering Al-dust produced with steel balls, the loose weight is somewhat less after 10 hours. A decisive factor seems to be the structure of the dust particles. The grain distribution is more favorable with the spherical or cubical form than with the lamellar form.

There was a strikingly high loose weight increase during silver solder pulverization. The loose weight increased from .81 kg. per ltr. in the material charged to 2.98 kg. per ltr. after 10 hours of pulverization.

ILLUSTRATIONS

1. Al-grains of the material charged. Magnification 110 x, reproduction 4/5.

2. Al-grains (compressed Al-foil) from the material charged, in polished section. Magnification 110 x, reproduction 4/5.

3. Granulation characteristics of the Al after pulverization with hard porcelain balls of 12 mm. in diameter.

   Initial grain size smaller than 2.0 mm.; total pulverizing time: 10 hours. Structure: granular. The two smoothly rounded particles in the middle of the picture are porcelain abrasion of the balls.

4. Al-dust pulverized with porcelain balls, in polished section. Pulverizing time: 10 hours. Structure: granular. The two smoothly rounded particles in the middle of the picture are porcelain particles.

5. Granulation characteristics of Al after pulverization with steel balls of 12 mm. in diameter. Total pulverizing time: 10 hours.

6. Al-dust with predominating leaf-like structure after 10 hours. Polished under oil.

7. Granulation characteristics of Al after pulverization with steel balls of 12 mm. in diameter under addition of grease and stearine. Time: 10 hrs.

8. Combined graphs of the granulation characteristics of Illustrations 3, 5, and 7 after 10 hours. Initial material smaller than 2.0 mm.

   A: Material Charged
   I: Pulverized with porcelain balls.
   II: " " steel balls.
   III: " " " and addition agent.

9. Al-dust pulverized in vibrating mill with steel balls and addition of grease and stearine, for 5 hours.

10. Lamellar Al-dust, pulverized in vibrating mill with addition of grease and stearine, for 5 hours.

11. Al-dust with partly granular structure. Time: 8 hours, with slight grease and stearine addition.

12. Al-dust with predominate lamellar structure. Time: 10 hours, with addition of grease and stearine.

13. Granular Al-dust prior to vibrating pulverization.

14. Al-dust converted in vibrating mill into lamellar structure by grease and stearine addition.

15. Granulation characteristics of silver solder after pulverization in the vibrating mill with hard porcelain balls of 12 mm. in diameter. Initial material smaller than .5 mm. Time: 10 hours.

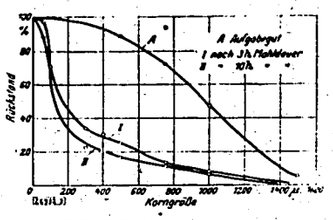
16. Granulation characteristics of silver solder after pulverization in the vibrating mill with steel balls of 12 mm. in diameter. Initial material smaller than .5 mm.; time: 3 hours.

17. Combined graph of the granulation characteristics of the silver solder from Illustrations 15 and 16 after a time of pulverization of 1 to 3 hours. Initial material below .5 mm.

ILLUSTRATIONS

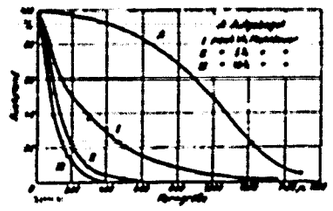
1. Al-grains of the material charged. Magnification 110 x, reproduction 4/5.

2. Al-grains (compressed Al-foil) from the material charged, in polished section. Magnification 110 x, reproduction 4/5.



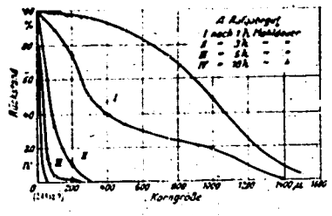
3. Granulation characteristics of the Al after pulverization with hard porcelain balls of 12 mm. in diameter. Initial grain size smaller than 2.0 mm.; total pulverizing time: 10 hours. Structure: granular. The two smoothly rounded particles in the middle of the picture are porcelain abrasion of the balls.

4. Al-dust pulverized with porcelain balls, in polished section. Pulverizing time: 10 hours. Structure: granular. The two smoothly rounded particles in the middle of the picture are porcelain particles.

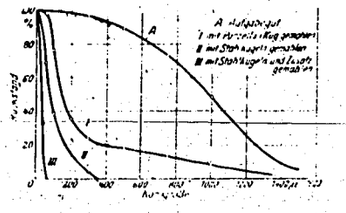


5. Granulation characteristics of Al after pulverization with steel balls of 12 mm. in diameter. Total pulverizing time: 10 hours.

6. Al-dust with predominating leaf-like structure after 10 hours. Polished under oil.

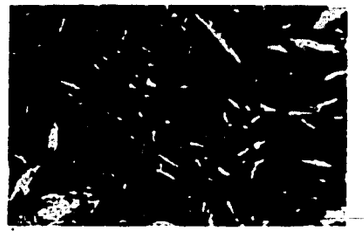


7. Granulation characteristics of Al after pulverization with steel balls of 12 mm. in diameter under addition of grease and stearine. Time: 10 hours.

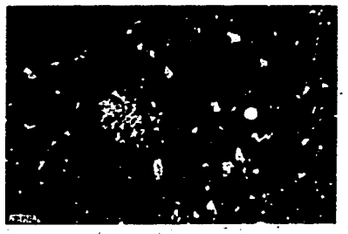


8. Combined graphs of the granulation characteristics of Illustrations 3, 5, and 7 after 10 hours. Initial material smaller than 2.0 mm.
A: Material charged.
I: Pulverized with porcelain balls.
II: Pulverized with steel balls.
III: " " " "
and addition agent.

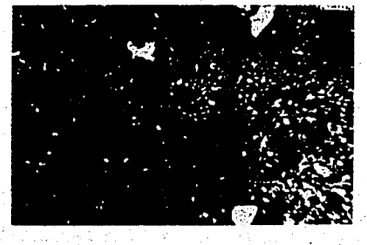
9. Al-dust pulverized in vibrating mill with steel balls and addition of grease and stearine, for 5 hours.



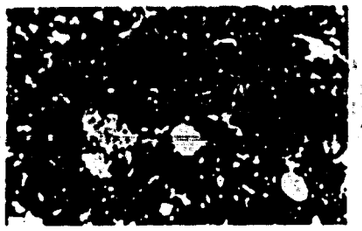
10. Lamellar Al-dust, pulverized in vibrating mill with addition of grease and stearine, for 5 hours.



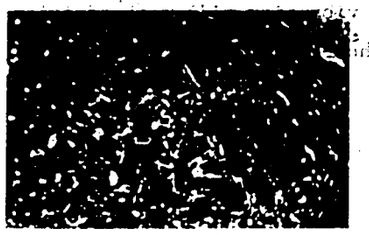
11. Al-dust with partly granular structure. Time: 8 hours, with slight grease and stearine addition.



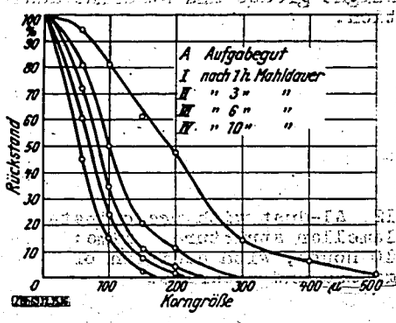
12. Al-dust with predominate lamellar structure. Time: 10 hours, with addition of grease and stearine.



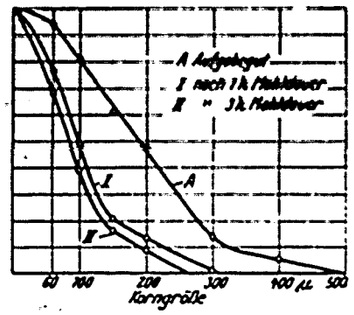
13. Granular Al-dust prior to vibrating pulverization.



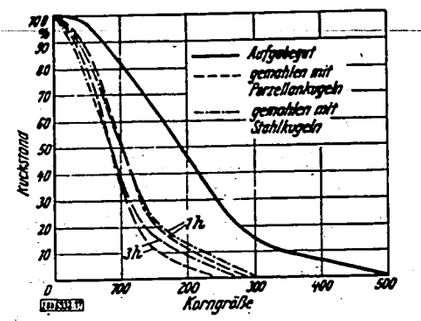
14. Al-dust converted in vibrating mill into lamellar structure by grease and stearine addition.



15. Granulation characteristics of silver solder after pulverization in the vibrating mill with hard porcelain balls of 12 mm. in diameter. Initial material smaller than .5 mm. Time: 10 hours.



16. Granulation characteristics of silver solder after pulverization of the vibrating mill with steel balls of 12 mm. in diameter. Initial material smaller than .5 mm.; time: 3 hours.



17. Combined graph of the granulation characteristics of the silver solder from Illustrations 15 and 16 after 1 to 3 hours. Initial material below .5 mm.

Do Not Reproduce
Copy 1

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 730 January 1946

REGISTER OF NOW I. G. FARBEN CHEMICAL PLANTS IN GERMANY

BY

J. P. WILKINS

Joint Intelligence Objectives Agency

TABLE OF CONTENTS

INTRODUCTION

Dr. Mathias Pier of I. G. Farbenindustrie A.G., Ludwigshafen/Rhine in the Division of High Pressure Research at Heidelberg was requested to prepare a directory or register of non-I. G. Farbenindustrie chemical plants in Germany. The following is the report furnished by Dr. Pier.

The I. G. Farbenindustrie A.G. was not included because its organization, location of plants, and products produced by each plant, has been adequately covered by other reports already issued or in preparation.

From observations made through the use of this document to date, it appears that is is satisfactorily complete. Of course, it is intended for use in the field of industrial chemistry and, consequently, may not include all new German war plants - for instance, in the field of ordnance items such as high explosives, propellants, and war gases.

The page of the report dealing with the source of information and the key to the numbering system has been translated. Since the remainder of the report is concerned with names of plants, and towns in which they are located, no further translation is needed.

Verzeichnis chemischer Fabriken

nach folgenden Quellen:

Handbuch der Aktiengesellschaften 1939
Mitgliederverzeichnissen des Vereins deutscher Chemiker
(der deutschen Bunsengesellschaft
(1931-1933) (der deutschen Gesellschaft f.technische
(Physik

Handbuch der Internat. Petroleumindustrie 1938/39
Deutsches Reichsadressbuch f. Industrie, Gewerbe und Handel 1941
Die chemische Industrie im deutschen Reich 1939/40.

Die Nummern im Anschluss an die Firmen geben die jeweiligen Arbeitsgebiete an und bedeuten:

1 ..... Grundchemikalien (Schwer-u.Feinchemikalien)
2 ..... Pharmazeutische Erzeugnisse
3 ..... Pflanzenschutz-, Schädlingsbekämpfungs-, Desinfektions- und Konservierungsmittel
4 ..... Ätherische Öle, Riechstoffe und Essenzen
5 ..... Körperpflegemittel, Seifen und Waschmittel
6 ..... Farben, Farbstoffe und Farbwaren
7 ..... Lacke, Firnisse, Polituren, Beizen, Trockenmittel
8 ..... Chemische Herstellung von Fasern
9 ..... Kunststoffe
10 ..... Gummi und Gummiwaren
11 ..... Chemische Erzeugnisse für photographische Zwecke
12 ..... Dünge-und Futtermittel
13 ..... Mineralöle und Mineralölprodukte
13a .... Kraftstoffe und Schmiermittel
14 ..... Sprengstoffe, Schiesspulver, Zündmittel, pyrotechnische Erzeugnisse
15 ..... Leim, Klebestoffe, Kitte, Gelatine, Appreturen, Gerbstoffe, Gerberei-, Textil- und Druckerei-Hilfsstoffe
16 ..... Tierische und pflanzliche Fette und Öle, Wachse, Wachs- und Stearinwaren
17 ..... Reinigungs-, Putz, Polier-, Schleif, Oberflächenbehandlungsmittel
18 ..... Asphalt, Dachpappe, Isolier- und Schutzmittel
19 ..... Asbest und Asbest-Erzeugnisse, Wärme- und Kälteschutz, Schall- und Erschütterungs-Isoliermittel
20 ..... Harze, Peche, Teer
21 ..... Sonstige Erzeugnisse.

(Translation of preceding page)

According to the following sources:

Handbook of the joint-stock companies 1939
Register of the members of the Society of German Chemists
(1931 to 1933) (of the German Bunsen Society
(of the German Society for Technical Physics
Handbook of the International Petroleum Industry 1938/39
German Reichs address director for Industry, Trade and Commerce, 1941
The Chemical Industry in Germany, 1939/40

The numbers behind the names of the firms indicate the respective spheres of work and mean:

1 .... fundamental chemicals (heavy and fine chemicals)
2 .... pharmaceutical products
3 .... plant protection agents, agents for spreading of insecticides, disinfectants, and preservatives
4 .... ethereal oils, odoriferous substances, and essences
5 .... physical culture agents, soaps, and washing agents
6 .... pigments, dyestuffs, and dyeing materials or paints
7 .... lacquers, varnishes, polishes, mordants, drying agents
8 .... chemical production of fibres
9 .... synthetic substances
10 ... rubber and rubber goods
11 ... chemical products for photographic purposes
12 ... fertilizers and feeds
13 ... mineral oils and mineral oil products
13a .. fuels and lubricants
14 ... explosives, gunpowder, fuse agents, pyrotechnical products
15 ... glue, adhesive substances, putties, gelatin, finishes, tannins, and tannery-, textile-, and printing-auxiliary substances
16 ... animal and vegetable fats and oils, waxes, wax- and stearin-goods
17 ... detergents, cleaning agents, polishing agents, abrasives, surface treatment agents
18 ... asphalt, roofing paper, insulation agents and preventives
19 ... asbestos and asbestos products, heat and cold protection, sound insulating materials and shock insulating materials
20 ... resins, pitches, tar
21 ... other products

Verzeichnis chemischer Fabriken

Amerikanische Zone:

Aschaffenburg,	Aschaffenburger Zellstoffwerke A.G.	1
Augsburg,	Chemische Fabrik Silbermann	1,12,21
	Chemische Fabrik Pfersee G.m.b.H.	15
Bad Homburg	Chem. Pharmazeut. A.G.	2
Darmstadt,	Merck, Chem. Fabrik	1,2,3,21
	Röhm & Haas G.m.b.H.	2,6,9,15
Eberbach,	Chemische Werke Odin G.m.b.H.	15
	Chem. Werke Stoess & Co. G.m.b.H.	11,15
Hilenburg	Deutsche Celluloid-Fabrik A.G.	9
Hislingen,	Zeller & Gmelin	13,18,20
Ergelding	Chem. Fabrik Ergelding A.G.	9
Flörsheim	Chem. Fabrik Flörsheim A.G.	2,3,13a
Frankfurt	Andreae-Noris Zahn A.G.	2
	Degussa	1,3,6
	Lurgi, Ges.f.Warmetechn.m.b.H.	13,13a
	Metallgesellschaft A.G.	1,17
	Merz & Co., Chem. Fabrik	2
	Odisalla A.G., Fabrik f.chem.pharm. Bedarf	2,5
	Vial & Uhlmann, Fabrik chem.pharm. Präparate	2
Göppingen	Chem. Fabrik Gentner, Migrin-Werke	5,17
Hanau	Heraeus-G.m.b.H.	1,6
Heidelberg	Deutsche Bergin A.G. für Holzhydrolyse	21
Heilbronn	Knorr	21
Henfeld	Bayer A.G. f. chem. Fabrikate	1,12,21
Höllriegelskreuth,	Elektrochem. Werke München A.G.	1
	Ges. f. Lindes Eismaschinen A.G.	21,1

Amerikanische Zone:

Hof	Nordbayer. Farben-u.Mineralwerke	1,6
Kassel	Wintershall A.G.	1,12,13,13a
Kelheim	Süddeutsche Zellwolle A.G.	8
Kempen	Elektrochem. Fabrik Dr. Brandenburg & Weyland, G.m.b.H.	15,21
Mannheim	Böhringer & Söhne	2
	Chem. Fabrik Weyl	1,13a
	Rhein.Gummi-u. Celluloidfabrik	9,10
	Sunlicht Gesellschaft	4,5,17
	Kalichemie A.G. Wohlgelegen	1,2,3,6,10,12
	Zellstoffabrik Waldhof	1,5,13,15
Marktredwitz	Chem. Fabrik Marktredwitz A.G.	1,2,3,6
München	Bayerische Stickstoffwerke A.G.	12
	Chem. Fabrik Dr. G. Rebisch K.G.	2
	Chem. Fabrik Zyma A.G.	2
	Chem. Werke Otto Bärlocher G.m.b.H.	1,5,14,15,17
	Diamalt A.G.	15
	Luitpold Werk, Chem.pharm. Fabrik	2
	Vereinigte Bleicherdefabriken A.G.	1,12
Niederwalluf	Chem. Werke Breckhues A.G.	6,21
Nürnberg	Rhein. Westf. Sprengstoff A.G.	14
	Sandoz A.G.	2
Oberlahnstein	Farbwerke Schroeder & Stadelmann A.G.	6
	Fleischwerke A.G. für Gerbstoff-Fabrikation und chemische Produkte	15,16
Oestrich/Rhein	Rud. Koepp & Co., Chem. Fabrik A.G.	1,15,21
Regensburg	Ico-Werk A.G. Fabrik chem.pharm. Präparate	2
	Vereinigte Holzverzuckerungs A.G.	12,21
Schweinfurt	Vereinigte Ultramarinfabriken A.G.	6
Stuttgart	Robert Bosch G.m.b.H.	21
	Kast & Ehinger G.m.b.H., Druckfarbenfabrik	6,7,15

Amerikanische Zone:

Stuttgart	Öffentl.Chem.u.bakt.Labor, Schmiedel & Andreae	
	Öffentl.chem. Labor Dr. Mundshagen & Dr. Sieber	
	Siegle & Co., Farbenfabriken G.m.b.H.	6,7
Trostberg	Bayr. Kalkstickstoffwerke A.G.	12
Weinheim	Lederfabrik Freudenberg	9
Wiesbaden	Chem. Labor Fresenius	
Würzburg	Jordan & Co., K.G., Lackfabrik	7,17
Meitingen	Siemens Plania Graphit-Anoden	

Englische Zone:

Aachen	Aachener Chem.Werke f.Textilindustrie G.m.b.H.	5,15
Bielefeld	H. Stodick & Co. A.G.	1,12
Bochum	Benzolverband	13,13a
	Bergbau A.G.	1,13a,20
	Chemische Industrie A.G.	1,21
Bottrop/Westf.	Ruhröl G.m.b.H.	13a
Brackwede	Asta A.G., Chemische Fabrik	2
Braunschweig	Chemische Fabrik, Eisenbüttel G.m.b.H.	13,13a,16
	Chininfabrik Buchler & Co.	1,2
Castrop-Rauxel	Gewerkschaft Viktor	13,13,13a
Celle	Chr.Hostmann-Steinberg'sche Farben-fabriken	6,7,15,17
Dortmund	Gesellschaft für Kohlentechnik G.m.b.H.	
	Hoesch-A.G., Abt.Kokereianlagen	1,13a,20
	Hoesch-Benzin G.m.b.H.	13a
Duisburg-Meiderich	Aktienges.f.Steinkohleveredelung-und Verflüssigung	13,13a
	Gesellschaft für Teerverwertung	21

Englische Zone:

Duisburg-Hochheim	Chemische Fabrik Curtius A.G.	1
Düsseldorf	Chemische Fabrik Kossack A.G.	2,5,6,15,17
	Henkel & Co.	1,5,12,15,19
	Industrielackwerke A.G.	6,7,17
	Thompsons Werke G.m.b.H.	5,17
	Vereinigte Farbwerke A.G.	6
Elberfeld	Chemische Fabrik Herberts & Co.	6,7,9,15,17
Essen	Chem. Fabrik Dr. Reininghaus	1
	Chem.Werke, Essener Steinkohle A.G.	13a
	Essener Steinkohlenbergwerke A.G.	1
	Gewerkschaft Mathias Stinnes	1,13a,20
	Th. Goldschmitt A.G., Chem. Fabrik	1,5,6,15,18
	Krupp Treibstoff G.m.b.H.	13a
	Rhein. Stahlwerke A.G.	13,13a
Gelsenkirchen	Aktienges.f.chemische Industrie	1,6
	Gelsenberg-Benzin A.G.	13a
	Hydrierwerk Scholven A.G.	13a
Hamburg	Aktienges.f.Chem.u.Teerprodukten	3,13,13a
	Beiersdorf & Co. A.G.	2,5,21
	Bigot, Schärfe & Co., Chem.Fabrik G.m.b.H.	1,2,5,5,7
	Chem.Fabrik S.Kroch A.G.	13,15
	Chem.Fabrik Promonta	2,5
	Chem.Fabrik Billwärder, vorm.Hell & Sthamer A.G.	1,3
	Chem.Fabrik J.E.Devrient A.G.	1,3
	DAPG	3,4,5,13
	Deutsche Maizena-Werke A.G.	2,12,15,16,21
	Deutsche Vakuum Öl A.G.	13
	Ebano Asphalt Werke A.G.	13a
	Guano-Werke A.G.	1,12
	Hanseatische Teerproduktenfabrik Haltermann & Co. G.m.b.H.	1,13a,20
	Harburger Chemische Werke, Schön & Co.AG	6
	Norddeutsche Affinerie	1
	Ölwerke Jul.Schindler G.m.b.H.	2,13,13a
	Rhenania Ossag Mineralölwerke A.G.	13,13a
	Ernst Schliemanns Ölwerke	13,13a
Hannover	Chem.Fabrik Wülfel, Just & Dittmar	1,3,12
	Continental-Gummiwerke A.G.	10

Englische Zone:

Hannover	Gewerkschaft Deutsche Erdölraffinerie Deurag	15
	Siebelwerke A.G.	15,21
Homberg	Rheinpreussen G.m.b.H.	13a
Holzminden	Haarmann & Reimer, chem.Fabrik G.m.b.H.	4
Hüls-Marl	Chemische Werke Hüls G.m.b.H.	10
Köln	Chem.Fabrik u.Farbwerke Dr. Kell & Spitz A.G.	6,15
	Chem. Werke Lubszynski & Co. A.G.	17
	Chem.Fabrik Kalk G.m.b.H.	1
	Farbwerke F. Rasquin A.G.	6
	Martinswerk G.m.b.H. f.chem.u.metallurg. Produktionen (Bergheim-Erft)	1
	Lack-u.Farbenfabrik Court & Bauer A.G.	6,7
	Vereinigte Ultramarinfabriken A.G., verm. Leverkus, Zeltner & Co.	6
Krefeld	Chem.Fabrik Stockhausen & Co.	5,15
	Dreiring-Werke A.G.	5,15,16
Oberhausen	Chemische Fabrik Holten, G.m.b.H.	21
	Concordia Bergbau A.G.	1,13a,20
	Gutehoffnungshütte A.G.	13a,20
	Ruhrbenzin A.G.	13a
	Ruhrchemie A.G.	1,12
Oker a.H.	Chemische Fabriken Oker & Braunschweig A.G.	1,6,13a,18
Troisdorf	Dynamit A.G.	9,14
Wesseling	Chemische Fabrik Wesseling A.G.	1,6
	Union Rheinische Braunkohlen Kraftstoff A.G.	13a
Witten/Ruhr	Deutsche Fettsäurewerke G.m.b.H.	16,20
	Märkische Seifenindustrie	5
Wuppertal	Vereinigte Glanzstoffabriken Bemberg A.G.	8

Französische Zone:

Bad Kreuznach	Chem. Fabrik Jacob	1,7
Freiburg/Breisgau	Deutsche Acetat-Kunstseiden A.G. Rhodiaseta	8
Frendenstadt	Pino A.G., Chemische Fabrik	2,4
Gernsbach i.Murgtal	Louis Lutz	3,21
Grenzach/Baden	Chem. Werke Hoffmann-La Roche & Co. A.G.	1,2,4
Konstanz	Holzverkohlungsindustrie A.G.	1,3,6
Ludwigshafen	Chem. Fabrik Benckiser G.m.b.H.	1
	Gebr. Giulini G.m.b.H.	1,12
	Knoll A.G., Chemische Fabriken	1,2
	Dr. F. Raschig G.m.b.H.	1,3,4,7,9,13, 18,20,21
Mainz	Chem. Fabrik Budenheim A.G.	1
	Chem. Werke Albert	1,2,3,12,18
	Werner & Mertz A.G.	17
Speyer	Celluloid-Fabrik Kirrmeier & Scherer	9
Völklingen	Röchling'sche Eisen-u.Stahlwerke A.G.	20
Waldshut	Lonza-Werke, Elektrochem. Fabriken	1,9,12,17

Russische Zone:

Altherzberg	Chemische Fabrik Alwin Nieske G.m.b.H.	1
Ammendorf/Saale	Gebr. Hartmann, Druckfarben-Fabrik	6,7,15
	Chemische Fabrik Julius Jakob	1,15,21
Beraburg	Deutsche Solvay-Werke A.G.	13a
Breslau	Öffentl. chem. Labor Rud.Woy	
Brieg	Chemische Werke A.G.	13,20
Burg b.Magdeburg	Öffentl.chem.Labor Rogner & v.Graffenried	
Chemnitz	Böhme-Fettchemie	5,13,15

Russische Zone:

Chemnitz	Th. Böhme A.G.	2,7,15
	Zschimmer & Schwarz, Chem. Fabriken	1,2,5,7,13a
Coswig-Anhalt	Chemische Fabrik G.m.b.H. H. Schrumbe	1,2,17,21
Danzig	Chemische Industrie A.G.	1,12
	Chemische Fabrik Milch A.G.	1
Draschwitz (Zeitz)	Chemische Fabrik Draschwitz-Reuden, Weise & Co.	12
Dessau	Chemische Fabrik G.m.b.H.	15,17,21
	Dessauer Werke f.Zucker u. chem. Industrie A.G.	12,21
Dresden	A. G. Sächsische Werke	13
	Chemische Werke Aussig-Falkenau G.m.b.H.	1,6,11,12,15,21
	Chemische Fabrik Helfenberg A.G.	2
	Filsinger & Böttcher, vereinigt. chem. Labor	
	A.Th. Böhme, Chemische Fabrik	15
	Chemische Werke A.G. Postlerit-Werke	10,19
Eisenach	Böhlig & Roth, Chemische Fabr.	1
Freital	Kerkhof & Harzer G.m.b.H., Fabrik chem.u. pharm. Präparate	2,16
Fürstenwalde	Chemische Werke Dr. B. Hecker & W. Zeidler G.m.b.H.	1,7
Gleiwitz	Gräflich Schaffgotsche Werke G.m.b.H.	1,12
Görlitz	Th. Schuchardt G.m.b.H., chemische Fabrik	1
Goslar	Harzer Farbenwerke	6
	Gebr. Borchers A.G.	1,3,7
Greiffenberg/Schl.,	Chem.Fabrik Karl Koethen G.m.b.H.	12
Halle	Braunkohlenwerke Bruckdorf A.G.	13a
	Albert Binder, Chem.Fabrik u. Mineralölraffinerie	1,13,15,17,20
	Öffentl.chem.Labor Dr. Herrmann	
	Riebeck'sche Montanwerke A.G.	13,13a
	Werschen Weissenfelser Braunkohlen A.G.	13,13a,20

Russische Zone:

Hindenburg	Bersig Kokswerke A.G.	1,2,12,13,13a, 18,20
Hirschberg	Schlesische Zellwolle A.G.	8
Hirschfelde/Sachsen	Elektrochem. Ges. m.b.H.	1,12
Jena	Jenaer Glaswerk Schott & Gen.	
Königsberg	Königsberger Zellstoff-Fabriken u.chem.Werke Koholyt A.G.	
Kottbus	Öffentl.chem.techn.Labor Dr. Gebeck	
Küstrin	Zellwolle und Zellulose A.G.	1
Lauta/Lausitz	Vereinigte Aluminum-Werke A.G. Lautawerk	1
Leipzig	Chem.Labor f.Handel und Industrie	
	Heine & Co., A.G.Fabrik ätherischer Öle	4
	Langbein-Pfanhauser-Werke A.G.	1
	Röbel & Fedler G.m.b.H. Chem.Fabr.	5
	Farbenfabriken Springer & Möller A.G.	6,7
Lohmen i.Sachsen	Chemische Fabrik Dr. W. Miersch G.m.b.H.	1,3
Magdeburg	Fahlberg-List A.G. Chem. Fabr.	1,2,3,12
	Öffentl.chem.Labor Dr. Albert Schönn	
Miltitz	Schimmel & Co., A.G.	1,2,4,5,6
Meissen	Öffentl.chem.Labor Bobach	
	Staatl.Porzellan-Manufaktur	6
Mölkau b.Leipzig	Chem.Fabrik Atlas Ago A.G.	7,15
Mögeln b.Leipzig	"Lipsia" Chem.Fabrik A.G.	1,2,18,19,21
Oberschlema	Staatl.Sächs.Hütten-u.Blaufarbenwerke	3,6,11
Oranienburg/Berlin	Oranienburger Chemische Fabrik A.G.	12,15
Pirna	Chem.Fabrik Pott & Co.	15
	Friedr.Köttner A.G., Sulfit-zellulosefabrik	8

Russische Zone:

Pölitz	Hydrierwerke Pölitz A.G.	13a
Radebeul	Chemische Fabrik von Heyden A.G. Chemische Fabrik Pyrgos G.m.b.H.	1,2,3,9,11,21 15,31
Rodleben/Anhalt	Deutsche Hydrierwerke A.G.	1,3,16,21
Rudolstadt	Chemische Werke G.m.b.H.	2
Saarau	Silesia Verein chemischer Fabriken	1,3,6,10,12, 13a
Schönebeck a.d.Elbe	Chemische Werke Schönebeck A.G.	1,3,15,16,20
Stassfurt	Sodafabrik Stassfurt G.m.b.H.	1
Stettin	A.G. der chem.Produkten-Fabriken Pommeronsdorf-Milch	1,9,12
	Feldmühle, Papier-u. Zellstoff-werke A.G.	1,3,8,9
	Stettiner Kerzen-u.Seifenfabrik	5,16,17
	Öffentl.chem.Labor Mack & Wimmer	
	Union Fabrik chem.Produkte	1,12
Velten/Mark	Chemische Fabrik Stockhausen K.G.	5,15,21
Waldenburg	Waldenburger-Bergwerks-A.G.	1,12,13a,20
Westeregeln	Alkaliwerke Westeregeln G.m.b.H.	1,2,3,6,11, 14, 19,20,21
Wünschendorf (Elster)	A.G. für Lithoponefabrikation	1,6
Zwickau	Chemische Fabrik Louis Blumer	9,15

BERLIN:

A.E.G.	10
Auergesellschaft A.G.	1,2
Braunkohle-Benzin A.G.	13a
Bakelite G.m.b.H.	9
Byk-Gulden-Werke, chem. Fabr. A.G.	1,2,3,5,11, 15,18
Chemische Fabrik Oldin A.G.	14

BERLIN:

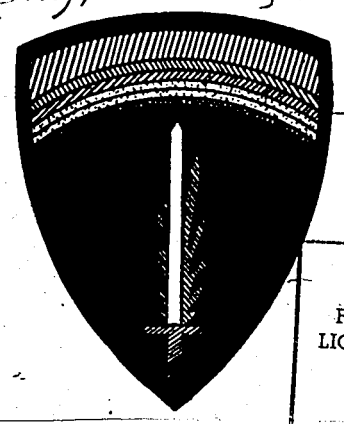
Chemikalien A.G.	1,3,12
Chemische Fabrik Weyl A.G.	1,13a
Chemische Grünau A.G.	1,2,5,11,15, 18,21
Chem. Fabrik f. zahnärztl. Bedarf Richter & Hoffmann, Howard Dentalges.	21
Chemische Fabrik Hydra, Dr. Petzold & Co.A.G.	3,17
Chemieprodukte K. G.	7,18,19
Deutsche Erdöl A.G.	13,13a
Edeleanu Ges.m.b.H.	13,16
Fattinger & Co. G.m.b.H., Werke f. chem. pharm. Präparate	2
C. F. Heyde, Chemische Fabrik A.G.	7,15
Kali-Chemie A.G.	1,2,3,6,10, 12,14,15,21
Kohlenveredelung und Schwelwerke A.G.	13a
Kokswerke und Chemische Fabriken A.G.	21
Dr. Labochin A.G., Fabrik chem.pharm. Präparate	2
Nitritfabrik A.G.	1,3
Olex Deutsche Benzin u. Petroleum G.m.b.H.	13a
Permutit A.G.	21
Pertrix, Chem. Fabrik A.G.	1,21
Pharmazeutikon A.G.	2,6
Pintsch-61 G.m.b.H.	13
Preussag, Bergwerk- u. Hütten A.G.	1,12,13,13a,20
Riedel-Haën A.G.	1,2,3,4,5,6, 7,21
Rütgerswerke A.G.	1,6,7,13a,18,20
Scheidemandel-Motard-Werke A.G.	1,12,15,16,20
Schering A.G.	1,2,3,4,5,6,8, 9,12,13a,15,20
Siemens Plania A.G.	21
Staatl. Porzellan-Manufaktur	6
Vereinigte Aluminiumwerke A.G.	1,6,21
Westfälisch-Anhaltische Sprengstoff A.G.	1,9,12,14

Copy 1

FIAT FINAL REPORT No. 916

ENGLISH TRANSLATION
OF
STUDIES ON CO-POLYMERS AND INGREDIENTS FOR CO-POLYMERIZATION

(Wolf, (Dr.), Berkes, (Dr.), Weissenborn, (Dr.))



OFFICE OF MILITARY GOVERNMENT

FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO. 916 — 20 August 1946

ENGLISH TRANSLATION
OF
STUDIES ON CO-POLYMERS AND
INGREDIENTS FOR CO-POLYMERIZATION
BY

GERMAN STAFF MEMBERS

I. G. FARBENINDUSTRIE

(Wolz, (Dr.); Bechd, (Dr.); Wiesemann, (Dr.)

FIELD INFORMATION AGENCY, TECHNICAL

A B S T R A C T

These various reports are on work done in I.G.Farbenindustrie in 1942 and 1945. They include studies on co-polymers and ingredients for co-polymerisation.

FOREWORD

This is a translation prepared in London from German documents evacuated in the early stages of Technical Industrial Intelligence operations. The selection of reports for translation was made by Sherlock Swann and N.M.Elias. The abstract was prepared in the office of the Chemicals Unit, Industry Branch, Field Information Agency, Technical.

AUTHORS

Dr. Wolz, Dr. Becker and Dr. Wiesemann of I.G.Farbenindustrie, Leverkusen.

TABLE OF CONTENTS

ANNUAL REPORT FOR 1942.

During the last year the following problems were investigated:

1. The continuous and discontinuous Polymerization of Buna M.

The Buna M types acquire greater importance because of the observation of various Buna testing departments that some butadiene-methacrylic acid methyl ester-co-polymerisates possessed good adhesiveness by themselves besides outstanding physical test values. To obtain the optimum conditions I performed a series of discontinuous experiments before working out a process for the continuous preparation of Buna M. These initial investigations were concerned with the two types Buna M 25 (butadiene : methacrylic acid methyl ester = 75 : 25) and Buna M-32 (butadiene : methacrylic acid methyl ester = 68 : 32). It could be confirmed that the activation of the Buna M-polymerization was catalyzed by triethanolamine, which was discovered by Ludwigshafen. To clarify the question of the Emulsifier I polymerized in a Nekal BX tr. mepasine sulfonate - and mersolate H - emulsion, and the various emulsifiers showed no noteworthy differences regarding the velocity of polymerization. Qualitatively the polymerisate obtained with Nekal BX tr. emulsion showed the best appearance; it had good adhesiveness and reached the top performances of Buna S at tire tests. The product obtained with mepasine-sulfonate approached the quality of the polymerisate from Nekal BX tr. Its tire qualities, however, were deficient by reason of its inferior adhesiveness. Compared with these two polymerisates the product from mersolate H was somewhat inferior.

The continuous trial was made for the above reasons with the emulsifier Nekal BX tr. and mepasine sulfate. With a time-space yield of 8-10 and a smooth polymerization a product was obtained, which was equal in its rubber qualities to the material produced discontinuously, but lacked much indeed in adhesiveness. The working up of the latex on the conveyor band machine encountered no difficulties whatsoever.

2. The continuous Polymerization of Buna SS and Buna S-acid.

The types Buna SS and Buna S acid, which were developed by the Rubber Central Laboratory were prepared by the con-

tinuous process. Polymerization proceeded smoothly with or without linoleic acid; at temperatures of 38-42° with a sulfuric acid ester-amine solution a timespace yield of 8.5 was obtained. The polymerisates produced in the presence of linoleic acid showed excellent rubber technological test values and were easily workable; the results of tire trials were only partly satisfactory by reason of the inferior adhesiveness of the products. The polymerisates obtained in the absence of linoleic acid were quite workable, but their rubber-technological test values were somewhat poorer than the polymerisates containing linoleic acid. For the present only the linoleic acid containing polymerisates could be worked up on the conveyor band. The pipe lines, which were "phenetalized" as a protection against corrosion by sulfuric acid were unaltered after a working period of 7 weeks.

3. Replacement of Ester-amine by Ether-amine as Acid Emulsifiers.

For the polymerization in emulsion in acid medium until now the ester-amine was used, an esterification product of a definite fraction of aliphatic fatty acids and diethylaminoethanol. The effectiveness of the ester-amine as emulgator depends strongly on the constitution of the fatty acid, and it is to be supposed that it will be difficult to secure a paraffin fatty acid of constant quality. For that reason the so-called ether-amines were investigated for their suitability as substitutes of ester-amines in the acid emulsion polymerization; they are synthesized by the hydration of the addition compounds of higher alcohols and acrylonitrile. The preparation of the ether-amines was performed by Dr. Koenig, (A. Labor.) in alkaline medium and the catalytic hydration of the alkoxynitrile thus obtained in presence of Raney-nickel (Dr. Wegner, A. Labor.). Of the amines investigated, decyl-oxypropylamine, nonypropylamine, octyl-oxypropylamine, and Leuna-C_8C_{10}-alkoxy-propylamine can replace the ester-amine in HCl as well as in H_2SO_4 emulsion; ethyl-hexyl-oxypropylamine, however, could be used in HCl emulsion only and a satisfactory polymerization obtained only when used as in double quantity. Qualitatively the polymerisates prepared with ether-amines were equivalent to those of the ester-amine products.

4. The discontinuous Polymerization of Buna S free from Linseed Oil.

I have already stated (report of 29th July 1940) that Buna S polymerization can be carried out with emulsifiers free from linoleic acid in the presence of a regulator. The necessity of changing the Buna S manufacture, due to the

scarcity of linseed oil, to a charge free from linoleic acid made further investigations in this direction necessary.

Whereas others investigated the polymerization without linoleic acid chiefly for the velocity of polymerization, I studied the question whether, and how far, the quality of the polymerisate in the absence of linoleic acid and with the addition of a regulator was dependant on the nature of the emulsifier. Polymerisates of practically equal quality were obtained in the Buna S polymerization in the presence of linoleic acid, with Nekal BX tr. as well as Nekal BXG. But Nekal tr. gave distinctly better products than Nekal BXG in the absence of linoleic acid. Apparently the regulating effect of the diproxide in Nekal BX tr. manifests itself better than in Nekal BXG.

It appeared to be more advantageous to add the paraffin fatty acid as its sodium salt to the emulsifier, so as to utilize the emulsifying power of the sodium salt for the polymerization, moreover it was necessary to add to the Buna S free of linoleic acid, some iron fatty acid salt as a degrading catalyst. The iron necessary for the degradation could be added to the polymerisate during the working up.

Contrary to linoleic acid the fatty acid does not act as a retardant in Nekal BXG but even slightly as an accelerator on the polymerization velocity. With Nekal BX tr. polymerisation is more strongly activated by fatty acid than with linoleic acid. With 0.5% paraffin fatty acid added a perfect progress of ploymerization can be achieved and after addition of iron a good degradation is achived.

The difficulties arising with latex free from linoleic acid or erucic acid could be eliminated by the addition of $CaCl_2$ to the brine or by precipitation with pure $CaCl_2$ solution.

Trials for replacement of linoleic acid by erucic acid, the fatty acid from corn germs or mixtures of corn germ acid-linoleic-acid showed that the mixture corn germ-linseed acid can fully replace linoleic acid; with corn germ-colza-acid about the same results were achieved as with paraffin fatty acid.

5. Perbunan Polymerization with Acrylonitrile from the VC Plant.

The acrylonitrile produced in the VC plant gave only cross-linked polymerisates of good working up qualities, but of extremely bad tear. Model experiments on the influence of impurities in the acrylonitrile, like acetaldehyde and divinyl-acetylene showed that a content of even 0.2% acetaldehyde

or 0.5% di-vinyl-acetylene resulted in a strongly stiffened polymerisate. The long latent period of the VC nitrile could be eliminated by the addition of activating catayste or by distillation of the nitrile over sodium hydrosulfite. The high velocity of polymerization, once started, could be reduced by the addition of a small quantity of aniline.

Further, a range of experiments for polymerization were made with samples of acrylonitrile purified in various ways. Only those samples of nitrile 23/o and 23oD, prepared by Dr. Heinen, and the VC nitrile, which was fractionated in the Rd plant until it gave a negative H_2SO_4 test, were useful.

6. Separation of the Di-vinyl-acetylenes from the VC-nitrile by Chlorination.

The acrylonitrile from the VC plant always contains a varying amount of di-vinyl-acetylene, which causes a stiffening of the polymerisate, which cannot be removed by increased storage. As the di-vinyl-acetylene adds chlorine very easily, whereas acrylonitrile is very resistant against halogens, chlorination of di-vinyl-acetylene so as to make possible its elmination from the VC-nitrile by distillation was tried.

It is possible, indeed, to achieve an effective purification of the di-vinyl-acetylene containing acrylonitrile by treatment with chlorine. The acrylonitrile distilled off from the chlorinated di-vinyl-acetylene gave with butadiene mixed polymerisates, which did not quite reach the quality of the products prepared from acrylonitrile-Lu, when they were polymerised to about 80%; when however polymerised up to 70-75%, or in admixture with acrylonitrile-Lu, suitable perbunans were obtained.

7. The mixed Butadiene-acrylo-nitrile Polymerization with extremely strong Activation.

It is possible to reach a normal polymerization velocity at relatively low temperatures by catalyzing the activation of the polymerization of vinyl compounds as well as of the mixed polymerization of dienes with vinyl compounds.

In the polymerization of vinyl compounds reasons for the limitation of the lower temperatures of polymerization can scarcely be found. Conditions are different with mixed polymerizations of dienes with vinyl-compounds. The following explanation can be given for the course of such polymerizations, based on the observation that the activation of the mixed polymerization proceeds via the vinyl compound:

In the first instance the vinyl compound is activated by the activator (persulfate). The direct activation of the diene by persulfate is of minor importance for the accomplishment of the mixed polymerization. The activation of the diene is initiated by the activated vinyl compound, which makes the diene receptive at the given temperature. Whereas, therefore, the vinyl compound, when catalyzed suitably, can be catalyzed at comparatively low temperatures, the activation of the diene, which would lead to a normal mixed polymerisate, occurs only at higher temperatures; the catalytic activation works primarily on the vinyl compound. If the temperature is too low to activate the diene usually the vinyl compound only will polymerise, whereas the diene will enter the mixed polymerisate in a much lesser amount than corresponds to the quantity of it which is present. To achieve a far-going mixed polymerization it is necessary not to understep a definite temperature at a definite activation.

Corresponding experiments with perbunan and perbunan extra has confirmed the validity of these considerations. If the activation of these polymerizations is catalyzed by the addition of 0.5% triethanolamine or diethylamine a strong pre-polymerization of the acrylonitrile starts with a batch of perbunan even at 28°, and with perbunan extra even at temperatures below 20°, leading to the formation of considerable quantities of material which separates out.

The addition of a regulator under these conditions of polymerization prevents the occurrence of increasing pre-polymerization of the acrylonitrile in perbunan, whereas they favor it with perbunan extra.

The catalysis of the activation of the butadiene-acrylonitrile mixed polymerisation and the lowering of the polymerization temperature connected with it can therefore be performed only within definite limits.

8. The Preparation of Benzene Resistant mixed Polymerisates from Butadiene, Acrylonitrile and Fumaric Acid Di-nitrile.

Since acrylonitrile bestows an improved resistance against benzene, when added to the mixed polymerisates with butadiene, as compared with the mixed polymerisates containing styrene, it was to be expected that the mixed polymerization of butadiene with fumaric acid di-nitrile would lead to products of further improved benzene stability. Unfortunately these mixed polymerizations yielded only hard products, which lacked every character of rubber. Only by mixed polymerization in the presence of a second vinyl component, like acrylonitrile, could

rubber-like products be obtained, which showed good manufacturing quality and real improved resistance against benzene (swelling in benzene after 48 hours at 50° 70%). The production of a larger quantity of this mixed polymerisate for further investigations had to be renounced, as the preparation of the fumaric acid di-nitrile met with difficulties.

Further experiments were carried out to replace the fumaric acid di-nitrile by the chloro-fumaric acid di-nitrile, prepared by Dr. Bollweg for the mixed polymerization just described. It was shown that chloro-fumaric acid di-nitrile could only partly replace the fumaric acid di-nitrile.

Polymerization proceeded satisfactorily only when freshly distilled chlorofumaric acid-di-nitrile was used, and the swelling in benzene with polymerisates tested so far was always 10-20% worse. The final estimation of these mixed polymerisates is still pending.

9. Improvements of certain Qualities of Polystyrene by Co-polymerization with Fumaric Acid Di-nitrile.

In the co-polymerization of styrene with fumaric acid di-nitrile the softening point of the polystyrene was increased, and the stability of the polystyrene film against chemicals and temperature was essentially improved. The hardness of the polystyrene (101° according to Vicat) which was too low for various application purposes, could be increased by co-polymerization of 20% fumaric acid di-nitrile to 130°, with 35% fumaric acid di-nitrile to 165°. The co-polymer containing 20% fumaric acid di-nitrile forms more brittle films than polystyrene; they are distinguished, however, by a special resistance against acids and alkalis and boiling water, and remain hard even at 150°. The continuation of the investigation into these co-polymers had to be stopped because of the lack of starting material.

10. Investigation of Latex by the Ultra Centrifuge and the Electronic Microscope. (Joint with Dr. Kircher & Dr. Sybertz.

After having reached the first goal of these investigations, the estimation of the dimension of the latex particles and the distribution curve characteristic of the various Buna latices, we tried to determine the relations between dimension of particles built up, and quality of the polymerisate.

Connected with the investigations on fractional creaming we were able, by investigating the cream and serum with the

ultra-centrifuge and the electronic microscope, to show conclusively that in the fractional creaming the large latex particles went into the cream, the small ones into the serum. By comparing the distribution curves of the sera it was possible to arrive at comparable relationships in latex fractionation. Besides, the electron-microscopic pictures of the cream and serum latices explained the mode of operation at the creaming operation.

As the dimension of the latex particles stands in a definite relation to the quality of the polymerisates, which shows itself distinctly in the fractional creaming, the quality of the polymerisate can be predicted from the distribution curve of a latex as obtained by means of the ultra centrifuge. It is not yet possible to establish detailed differences with this method. It is, however, quite possible that the usefulness of the ultra centrifuge will be increased.

We could distinctly ascertain differences in the structure of the particles by investigating the latex with the electronic microscope. Whereas, for instance the latex of non-regulated perbunan-extra consisted of small compact particles, the corresponding regulated latex contained considerably larger particles, which were built up less densely. Clear models could be developed from these investigations regarding structure of the latex particles.

Further by the investigation into the latex with the electronic microscope the validity of the law of Wintgen could be examined regarding the dependence of the dimension of the particles on the quantity of the emulsifier; we established in accordance with Prof. Wintgen, that the magnitude of the latex particles is inversely proportional to the quantity of emulsifier. Contrary to Wintgen we had to state that the ratio of the phases, too, with constant quantity of emulsifier, had an important influence on the magnitude of the particles. This influence of the phase ratio on the magnitude of the particles shows a reverse trend in the polystyrene polymerization as compared with the perbunan-extra polymerization.

11. Preparation of Plasticizers for Cellulose Tri-esters.

Investigations into the development of plasticizers for cellulose tri-esters led to the statement that compounds containing chlorine are especially good gelatinizing and softening means for cellulose tri-esters if they still contain one free OH group. As the chlorinated softeners mostly decompose at the high temperature needed for the manufacture of spray molded articles, the preparation of chlorine free plasticizers

containing OH groups, was investigated, which, too, have good gelatinising power for cellulose tri-esters. Of the products so far developed the best proved to be the plasticizers obtained by the interaction of dimethyl ester by phthalic acid with 1,4 or 1,3 butandiol. At the request of the varnish and plastics test department, larger samples have already been sent to Troisdorf and Ludwigshafen for testing. According to Troisdorf these products are good gelatinizers for cellulose-tri-esters with which outstanding clear spray mold articles can be produced with good electric qualities. The opinion of Ludwigshafen of these plasticizers has not yet come in.

TO:- Dir. Dr. Konrad
in/house.

9th January, 1942.

HIGH PRESSURE POLYMERIZATION.

Dr. Holzrichter informs me that much seems to be expected from the high pressure polymerization for rubber in respect to space and time saving. H. gave me the requisite details. If one compares these experiments with the polymerization experiments in the continuous flow pipe which we carried out about nine months ago, it will be found that these experiments, which were carried out at a pressure of approximately 20 atü maximum, exceeded the high pressure polymerization even in its present stage. With a phase proportion of 1:1.8 the space and time yield is 150-250 kg/cbm. effective. With a phase proportion of 1:1.2, as is technically used, one obtains a space and time yield of 250-350 kg/cbm. We obtained these high thruputs by using a combination of iron vanadate and persulfate and by charging with ester-amine. These space and time yields can, without a doubt, be considerably increased. We, however, interrupted the experiments at that time because the apparatus was too primitive to allow a (Durchfeilung) of the product. The new continuous apparatus should be at our disposal in about three weeks.

The experiments at that time were demonstrated to Dr. Klein, Dr. Meis and Dr. Holzrichter and the results surprised them very much. The resistance (Festigkeit) figures were lower than those of the present day Buna S, but it is our endeavour to bring these to a high level. Such polymerisates became interesting after trials at Hüls, because they can be mixed with Buna S-latex. This resulted in a resistance (Festigkeit) improvement, which was alo found to be the case when mixing high pressure latex with normal latex.

I would like to point out the results which we obtained at that time because I am of the opinion that the results in the high pressure autoclaves in respect to mixed polymerization of butadiene with styrene is over-estimated. The same results as far as quality and speed are concerned, can be obtained in the continuous flow tube.

We obtained the following average figures:-

	F.	D.	Bel.	E.	H.
	207	530	80	54/56	67
The optimal figures were:	244	640	57	54/54	66
The following optimal figures have so far been obtained with the high pressure polymerization	200	580	77	41/48	71

I. G. LEVERKUSEN.

RUBBER CENTRAL LABORATORY.
Group 1.

Signed:- Becker.

Name: Dr. Wiesemann Dept: Rubber Central Lab. Group 1.

Report of 31 January 1945. Rung No. 15

IRON SALTS AS DEGRADATION CATALYSTS

A product is contained in the paraffin fatty acid, which can be used for the thermal degradation of rubber. Experiments have been made with other iron salts in respect to their suitability as degradation catalysts, because a substitute product of equal quality must be at hand in case the paraffin fatty acid is unobtainable. The properties, which should be demanded from such a product, are, first, a good rubber solubility, and second, ease of production of the product. A number of substances were chosen according to this principle and were mixed into the material in the absence of fatty acid. We would like to refer to the report of Dr. Rathjen who, however, could not complete the work owing to a short holiday. The iron salts were produced from the following substances:-

Benzoic acid
Hydrobenzoic acid
Naphthalene 2-oxy-3-carboxylic acid
Isododecylphenoxy acetic acid
B-Phenylethylthioglykol acid, iron salt
Diisopropyldithiocarbaminic acid, iron salt
Diisobutylnaphthalenesulfonic acid, iron salt

The fatty acid-free material used as a charge for the iron salts was made up as follows:-

1.7	Nekal BX
1.7	Nekal BXG
0.25	NaOH solid
0.3	Ammonium sulfate
126	Water
0.03	Diproxide
30	Styrene
70	Buna

Degradation is naturally the most important criterion for the quality of such an iron salt. The deciding factor for this effect is, however, the absorption of the salt into the rubber, which can be ascertained from the iron content of the salt and the iron content of the rubber which has been tested with it, or from the solubility of this salt in the rubber solution medium. The iron salts can be charged to the latex

or to the precipitated crude, whereby difficulties may arise in both cases. The solution of the iron salts in toluene - as far as they are soluble in toluene - can, during the mixing into the latex, result in a precipitation of the salt and in a bad distribution if one does not observe the concentration of the solution and its pre-emulsification. If one desires for instance, to put the paraffin acid salt of iron into a toluene solution, the following proportions should be used:

10% Nekal BX-solution	20 ccm
Water	16 "
n NaOH	4 "
Fatty acid iron salt in toluene 0.5%	20 "

The mixture is well stirred and 40 ccm. latex are slowly added to it. This emulsion is added to the calculated quantity of latex.

This procedure can be used generally providing the solubility of the iron salts in toluene is sufficient. If this is not the case, suspensions of the salts in Nekal solution have to be produced. This can easily be done if the products are available in correspondingly small grain sizes. What kind of charge of iron salts is to be used must be decided in each case in order to obtain a good distribution as the basis for a good decomposition. The charging of the iron salts into the precipitated mass can be carried out in the same manner providing the precipitation has been undertaken in such a way that very small particles are obtained. The size of the particles must obviously be sufficiently large to allow the separation of the liquid and give no difficulties in washing.

The iron salts were produced after the clarification of these questions. The instructions given by Dr. Dennstedt for the manufacture of the paraffin fatty acid iron salts were generally observed. It was thereby shown that the difficult solubility of the iron salts in the case of benzoic acid, hydrobenzoic acid or naphthol carboxylic acid produced only a very dilute solution of the salts in toluene. The salts are obtained in solid form and are finely powdered after drying and they are then added to the latex or precipitated latex as suspensions in Nekal solutions.

The manufacture of the diisobutylnaphthalenesulfonic acid iron salts (Nekal iron) cannot be carried out according to the instructions for the manufacture of the paraffin fatty acid iron salts. Working according to these instructions would only produce a solution of the salt in toluene with a content of 0.01%. It is best to precipitate a concentrated Nekal solution with ferrous sulfate and to separate the precipitate of the Nekal

iron. The Nekal iron is easily soluble in toluene. Unfortunately this iron salt does not precipitate completely, but a further part can be salted out in the filtrate, which brings the yield to not quite 30%. The deposit dissolves again when hot and precipitates on cooling. This behavior could make it difficult for the absorption of the salt into the rubber.

As the results of the decomposition experiments with these iron salts are not completely at hand, we shall discuss them in our next report.

Copy 1

J.I.O.A.
Report No. F-79
No. corrected
as per audit 48

GERMAN

BULK STORAGE

OF

LIQUID FUELS

JOINT INTELLIGENCE OBJECTIVE AGENCY
WASHINGTON, D. C.

REPORT ON

GERMAN BULK STORAGE

OF LIQUID FUELS

Ost, R. E.

Maltzer, Arnold.

CIOS SECTION
INTELLIGENCE DIVISION
OFFICE, CHIEF ENGINEER, USFET
APO 887

2

CIOS SECTION
Intelligence Division
OCE, TSFET(Rear)
APO 887

Report No. SIII
15 November 1945

BULK STORAGE OF LIQUID FUELS

1. SCOPE

(a) Aboveground Installations:

1. Ebenhausen Bulk Storage Plant, Ebenhausen
2. Ebrach Bulk Storage Plant, Ebrach

(b) Underground Installations:

1. Freiham Fuel Storage Depot, Freiham
2. Nienburg Fuel Storage Depot, Nienburg
3. Farge Fuel Storage Depot, Farge

2. INTERESTED AGENCIES

(a) Office, Chief of Engineers, Washington 25, D. C.
(b) The Engineer Board, Fort Belvoir, Virginia

3. TARGETS VISITED AND PERSONNEL INTERROGATED

(a) Aboveground Installations

1. Ebenhausen Bulk Storage Plant, Ebenhausen

A German civilian, formerly employed as a plant operator, was the only person found on the premises. He apparently operated some of the equipment as he was thoroughly familiar with the location of all tanks, valves and fire control apparatus.

2. Ebrach Bulk Storage Plant, Ebrach

There were two German civilians in the wrecked Administration Building. They were of the office type, well-dressed; but knew little about the actual operation of the Plant.

(b) Underground Installations

1. Freiham Fuel Storage Depot, Freiham

The Freiham Fuel Storage Depot was in charge of Captain C. M. Rusk, 53rd QM Base Depot, Sub-Depot 5315. Captain Rusk had a German Chief Engineer by the name of Herr Franz Heinrich Wehling

in custody and had the "Wifo" Organisation employees under his control. The "Wifo" employees unlocked and ventilated the various underground compartments and were able to give factual answers to questions pertaining to the equipment.

2. Nienburg Fuel Storage Depot, Nienburg

A chief chemist by the name of Rudolph Diegle and a German electrician acted as guides and furnished information to the investigators.

3. Farge Fuel Storage Depot, Farge

A U.S.A. QM Company is operating the Plant handling U.S. fuels. They had German chemists and operators show the investigators representative installations of each type.

4. NAMES OF INVESTIGATORS

(a) Mr. R. E. Ost, Tech Rep., C.I.O.S. Section, Int. Div., O.C.E.

(b) Lt. Arnold Malzer, M.I.S. USFET

5. RESULTS OF INVESTIGATIONS

(a) Aboveground Installations

1. Ebenhausen Bulk Storage Plant

The Ebenhausen Bulk Storage Plant formerly under control of the "Luftwaffe" is located out in the country along side of a wooded hill. A railroad spur follows the contour at the base of the hill and is enlarged to several ladder tracks at the bulk storage site. Wood framed sheds camouflaged with tree branches and nets spanned the tracks at two loading points. Camouflage was elaborate but not complete as it was impossible to cover all of the railroad tracks. Tank cars were framed in with wood false work to make them appear like boxcars.

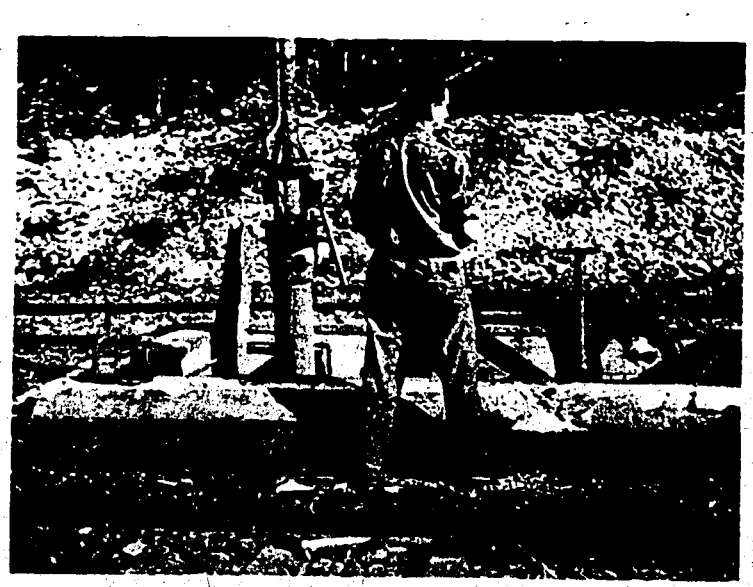
All storage was in aboveground tanks and all equipment was installed in relatively shallow underground rooms. The underground rooms served to hide the equipment and as fragmentation protection. Eleven 600,000 l. (158,500 gallons) tanks approximately 30 ft. diameter by 30 ft. high were located in dispersed positions in the woods. In addition there were three 300,000 l. (79,250 gallons) mixing tanks. All tanks were aboveground and were inclosed in brick fragmentation walls 21 in. thick with extra pilasters. The majority of the tanks were destroyed either by Allied bombing or by sabotage at the hands of the Germans. One of the operators remained at the plant and talked freely of the Allied bombing. He made no mention of sabotage by German Forces possibly himself included. One cone bottom tank was blown clear of its protective masonry wall in a vertical direction. The tank metal was severed neatly at the junction between the cone and cylindrical

walls while the surrounding masonry structure was untouched. It is believed that the tank was filled with hydrocarbon vapors and exploded by Germans.

This plant was apparently designed principally for the storage and trans-shipment of liquid fuels in carload lots. Overhead loading stems rotated by a hand lever about a vertical center line were provided. Photograph No. 1, below, shows a railroad fueling pit with vertical loading stem. Loading stems were 5 in. outside diameter reduced to 4 in. at the outlet. It is claimed that a 200 hectaliter car (5290 gallons) could be loaded in one hour. Tank cars were unloaded through the bottom at the same fill box shown in Photograph No. 1. Tank cars were equipped with a horizontal side connection having a shut-off cock. 4-in. I.D. wire wrapped hoses were used but they were so heavy that winches were provided to handle them. Sufficient fill boxes and valve pits were provided at the railroad sidings for unloading sixteen 200 hectaliter (5290 gallons) cars simultaneously in 90 minutes.

Fire protection was controlled from a central underground foam house using a single powder. There were sixteen 4-in. O.D. foam pipes leading to tanks and tank inclosures; one pipe for each space. One 3½ in. O.D. water heater at 8 Atü (137.6 psi) pressure furnished the water supply. Two foam generators were used. Valve pits at the railroad siding as well as pump rooms were protected by CO_2 which was piped from a battery of twelve 30 Kg storage cylinders.

The storage plant is badly damaged and should never be repaired as it is strictly a military project.



Railroad Fueling Pit Photo. I