contd.

Deutsche Normen
(German (test) Standards)

DIN Entwurf 91 52623	Prüfung von Holzschutzmitteln Bestimmung von Giftwerten gegenüber holzzerstörenden Insekten. (Testing of Wood Preservatives, Determination of Degree of Toxicity Against Wood Destroying Insects).	Juni 1944 June 1944
DIN Einheitsheft 92 52175	Holzschutz. Begriffsbestimmungen. (Wood Preservation, Definition of the Conception).	Nov. 1944

The publication here marked will be available at the Official Depository of the TIIC Sub-Committee on Forest Products, Forest Products Laboratory, Madison, Wisconsin.

APPENDIX C

List of photographs on file at the Official Depository of the Forest Products Sub-Committee, Forest Products Laboratory, Madison, Wisconsin.

The R. Avenarius & Co. Plant, Gau Algsheim.

The R. Avenarius & Co. Office, Stuttgart.

The First Bombed-Out Office of Allgemeine Holzimpregnierung, Berlin.

The Second Bombed-Out Office of Allgemeine Holzimpregnierung, Berlin.

The Factory of Chemische Fabrik Florsheim, Florsheim/Main.

The Office and Factory of E. Merck, Darmstadt.

The I.G. Farbenindustrie Plant, Uerdingen.

The Wood Preservation Laboratory of I.G. Farbenindustrie, Uerdingen.

The Office of Rutgerswerke, Berlin.

The Former Office of Cellonwerke, Fire-Retardant Manufacturers, Berlin.

Fire-Test Equipment of the Staatlichen Materialprüfungsamt, Berlin.

Special Fire-Test Equipment for Load-Bearing Walls at the Staatlichen Materialprüfungsamt, Berlin.

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FIAT FINAL REPORT NO. 90

L.F. & L.

UNCLASSIFIED

I N T E R R O G A T I O N O F

P R O F E S S O R F R A N Z F I S C H E R

Horne, W.A.

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

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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. 90 — 24 September 1945

INTERROGATION OF PROFESSOR FRANZ FISCHER

BY

Dr. W. A. HORNE

Technical Industrial Intelligence Committee

FIELD INFORMATION AGENCY, TECHNICAL

3p.

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Personnel of Team:-

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

Mr. B. L. MacKusick, U.S.

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

INTERROGATION OF PROFESSOR FRANZ FISCHER AT MUNICH, GERMANY 8 AUGUST 1945.

Introduction.

Professor Franz Fischer, former director of the Kaiser Wilhelm Institute, Mülheim, was located and interrogated at the home of his daughter at Possartstrasse 27, Munich. He was only generally familiar with the recent work of the Institute, having been inactive since March 1943. The following information was given from memory, since his reports, reprints and library were destroyed in the bombing raid of 11 July 1944 which demolished his home.

Isosynthesis.

The production of predominantly isobutane and isopentane from carbon monoxide and hydrogen is known as "isosynthesis". The process is carried out at 300-600 atm. and 400-500°C. in the presence of a thoria catalyst, preferably activated with 10-20% Al_2O_3. The isobutane can be dehydrogenated readily to isobutylene and used for polymerization or alkylation, yielding isooctanes. This latter is considered the product of isosynthesis and had led to the erroneous conclusion that isooctanes are prepared directly by the process.

The product contains higher -boiling products consisting of naphthenes, aromatics, ethers and alcohols. The proportionate amounts of low-boiling isoparaffins, and naphthenes and aromatics can be varied by changing operating conditions and by proper promotion of the thoria. The addition of zinc oxide favors the formation of naphthenes and aromatics; the addition of alumina favors the formation of isoparaffins.

The pressure is normally 300-600 atm. At lower pressures, the reaction of CO with hydrogen is too slow, and at higher pressures, the formation of methane and dimethyl ether becomes excessive. The temperature is maintained between 400 and 500°C., varying to some extent, inversely with the pressure. Further operating details were not known.

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The method of preparing the thoria catalyst is critical; for example, a thoria-zinc oxide catalyst prepared by pouring the nitrate into the soda solution (the reverse of normal precipitation) resulted in a catalyst of almost double the activity of a normally precipitated catalyst with respect to liquid hydrocarbons. No further details were known. Dr. Pichler and Dr. Ziesecke, at the Kaiser Wilhelm Institute, have carried out numerous experiments in an attempt to replace the thoria with other elements, but without success. A part of the thoria, at most 25%, can be replaced by either alumina, zinc oxide or a mixture of both.

Experimental investigations are still being carried out in small laboratory-scale equipment at the Institute. A pilot-plant was planned for construction at Ruhrchemie, Sterkrade, but Prof. Fischer did not know whether the construction had been carried out, due to the war.

It was pointed out that there is no marked distinction between "isosynthesis" and "naphthene" synthesis. The two processes are concurrent, the products being influenced by the method of operation and the nature of the catalyst.

Iron Synthesis.

The middle-pressure synthesis of hydrocarbons from carbon monoxide and hydrogen over an iron catalyst was initiated at the Institute by Dr. Pichler and Prof.Fischer but was taken over by industry which considered it highly important, largely due to the cost and scarcity of cobalt.

The comparative experiments conducted at Ruhland demonstrated that iron catalysts at medium pressures and 220°C. were satisfactory. The hydrocarbons obtained were more unsaturated than those obtained by cobalt normal-pressure synthesis, and have a better anti-knock rating. There is also produced an appreciable amount of alcohol. Further results and developments were unknown.

Nickel Catalysts.

Nickel catalysts are unsuitable for middle pressure synthesis, due to formation of nickel-carbonyl. At normal pressure, nickel can be used but is not very satisfactory since its strong hydrogenation activity leads to the undesirable formation of methane.

Suspended Catalysts.

No further experiments have been conducted on oil or water suspensions since publication about ten years ago. Synthesis can be carried out in this way, but there is no technical advantage.

Isomerization.

With Dr. Herbert Koch and other co-workers, Prof. Fischer initiated experiments on the isomerization of Fischer-Tropsch products. The best results were obtained with aluminum chloride for pure isomerization and for so-called cracking isomerization. Hydrogen chloride was used as a promoter in both types, hydrogen being used as well for cracking isomerization. Details were not known.

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FIAT FINAL REPORT NO. 426

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INTERROGATION OF DR. PIER AND STAFF I. G. FARBENINDUSTRIE, A. G. LUDWIGSHAFEN/ OPPAU

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

MAY 1946
REC'D.....
TIIC L.F. & L. S-C.

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

FIAT FINAL REPORT NO. 426

14 November 1945

INTERROGATION OF DR. PIER AND STAFF
I. G. FARBENINDUSTRIE, A.G.
LUDWIGSHAFEN/OPPAU

BY

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

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

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Personnel of Team:
Dr. W. F. Faragher
Dr. W. A. Horne.

I. INTRODUCTION

Previous interrogation of German scientific personnel by numerous investigators and the examination of evacuated documents indicated that further information was desirable on a miscellany of products and processes of interest to the Petroleum Industry. Accordingly, Dr.Pier and a large number of other men of the I.G.Farbenindustrie, A.G. plant at Ludwigshafen/Oppau were further interrogated in July 1945.

The information contained in this report supplements that previously reported in the CIOS report of 16 August, 1945: "Report on Investigations by Fuels and Lubricants Teams at the I.G.Farbenindustrie A.G. works at Ludwigshafen and Oppau", edited by Lt. Col. R. Holroyd (MFP).

II. SYNTHESIS OF HYDROCARBONS FROM WATER GAS MICHAEL PROCESS.

The following information concerning the synthesis of hydrocarbons from water gas was obtained by the interrogation of Dr. Wilhelm Michael who was conducting the research and development on the so-called "Michael Process". Two methods of operation had been studied that were outlined briefly in the earlier report on Ludwigshafen.

Both methods employed an iron catalyst which was stated to have the following advantages over the cobalt catalyst:

a. The gasoline is better.

b. A higher concentration of olefins is formed

c. The process is cheaper.

Dr. Michael had also investigated the use of iron catalysts in a tubular reactor at reduced temperatures.

Special precautions are required with the iron catalyst, which more than the cobalt catalyst, is subject to "run-away" reaction and the formation of carbon on the catalyst. The methods investigated were designed to prevent the conditions which lead to carbon formation.

A. Fixed-Bed Circulating-Gas Process

In this process gas is recirculated over the catalyst and through a cooler at such a rate that the temperature rise in the catalyst bed is limited to a maximum of 10°C. The reaction is

carried out at a pressure 20 atmospheres. At lower pressures the reaction velocity is too small. The gas recycle ratio is 100 volumes of recycle to one volume of fresh gas. Contact time in the catalyst bed is approximately one half to one second per pass, with a gas velocity of about 1 m. per second. The flow sketch (Fig. 1) illustrates the process. An important limitation is that the gas must flow through the catalyst bed without turbulence, otherwise static zones form and lead to a dangerous temperature rise resulting in the formation of methane and carbon. This necessary flow condition has been obtained in small-scale experiments (as shown in Fig I), using a 5 liter catalyst bed which were conducted successfully for as long as 10 months. Experiments of shorter duration have been successful in the same type of system with a 400 liter catalyst bed. Dr. Michael believes this single-bed design could be built to still greater diameter; channeling is the limitation.

With larger scale experiments (4-cubic meter catalyst bed), space restriction required the bed construction shown in Fig. 2. The operation of this unit was unsuccessful, because the gas undergoes a change of direction simultaneously with a velocity change (owing to change in diameter), which results in turbulent flow and stagnant spots develope in the catalyst bed. This unit was shut down after 2 months of operation because of the formation of carbon pockets. A further large-scale experiment utilizing cylindrical construction was proposed but the equipment was not built, due to the war. This unit was to have alternating sections of catalyst and condensers, in one container, as shown in Fig. 3.

Reaction Data.

Gas	CO: H_2 about 1:1 or 4:5
Pressure	20 atm.
Gas purity	Sulphur - under 2 mg. per cu.m., CO_2 free.
Gas recirculation	100 times.
Temperature change of gas	10° C.
Working temperature	300-325°C. (mainly 325°C.)
Catalyst	Sintered iron catalyst. Pellets about 1 cm.
CO_2 in exit gas	40-45%

Output per cu.m. of catalyst: 700-800 kg./day.

Catalyst

The best gasoline is obtained with iron catalysts when the synthesis is conducted above 300°C. Therefore it is necessary that the catalyst be insensitive to such temperatures and a good conductor

of heat. This type of catalyst is obtained by high-temperature sintering of iron powder pasted with about 1% of alkali during the reduction with hydrogen. An example of the catalyst preparation is as follows: Fine iron powder prepared by thermal decomposition of iron carbonyl is pasted with a concentrated solution of borax (1 gram of borax per 100 grams of iron) and formed into approximately 1 cm. cubes. In order to insure loose packing, the cubes are made with slightly irregular edge lengths. The cubes are sintered and reduced with hydrogen at 800-850°C. for 4 hours. The catalyst is cooled in a hydrogen atmosphere, which is replaced by carbon dioxide before charging to the reactor. In place of iron powder, Fe_2O_3 may be used in the preparation but it yields a catalyst which is very porous and of relatively low stability.

Reaction:

In contrast to the cobalt catalyst which yields, besides hydrocarbons, mainly water, the iron catalyst forms predominantly carbon dioxide. Under the conditions given above, 80-85% gas conversion is obtained with 40-45% of carbon dioxide in the exit gas. If a two-stage process is employed, this carbon dioxide must be removed. Condensation takes place in 3 cooling stages as follows:

1) Cooling to 120°C to condense the paraffin and some of the water;

2) Cooling to 20°C to condense the gas oil, heavy naphtha and additional water;

3) Cooling to minus 40°C to condense light gasoline and part of the liquefiable hydrocarbon gases. Prior to this stage the gas must be intensively dried with calcium chloride or silica gel.

The exit gas from this third cooling stage is washed free from carbon dioxide with water or alkazid solution and is further converted in a smaller second system, whereby an overall conversion of 92 to 95% is obtained. The products from this second system are separated in a manner similar to that described above.

Composition of Product.

When operating with a hydrogen to carbon monoxide ratio in the charge gas of 5:4, the exit gas from the first stage is as follows:

CO_2	40-45%
H_2	25-30%
CH_4	5-10%
CO	15-20%

The so-called "useful" products are as follows:

$C_2 - C_4$ (excluding ethane)	30%	
Ethylene	8%	
Propylene	9%	
Propane	3%	
Butylene	8%	3/4 of iso-structure
Butane	2%	3/4 of iso-structure
Gasoline (to 200°C.)	48%	(7% alcohol content)
Gas oil	14%	(4% " ")
Paraffin	1%	
Alcohol (in aqueous layer)	7%	(mainly C_2)

Only straight-chain and alpha methyl primary alcohols are produced. For every 100 kg. of these useful products, 25 kg. of methane and ethane are formed. From the liquefied hydrocarbon gases, additional gasoline can be prepared by polymerization and alkylation.

The crude gasoline product has an octane number of 68 to 70 (research method). By passing this crude product over alumina at 400-450°C, for the removal of oxygen and then refining over fuller's earch at 180-200°C, the octane number is increased to 84 (research method) and to 75-78 by motor method. The refining loss is about 5%. The gasoline, which has an olefin content of about 70%, must be inhibited for storage. The gas oil has a cetane number of 45 to 50.

Oxygenated Products in the Water.

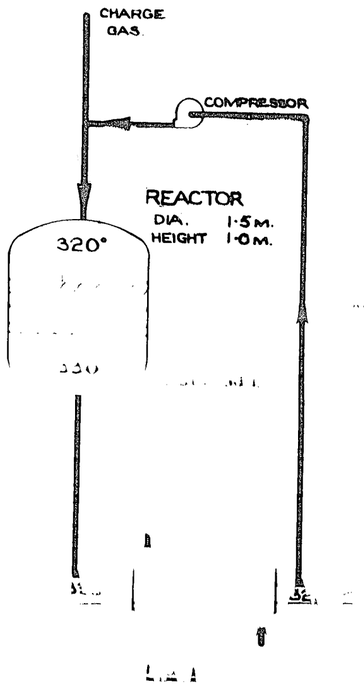
Acetaldehyde	5%
Acetone	10%
Ethenol	55%
Propanol	20%
Butanol and over	10%

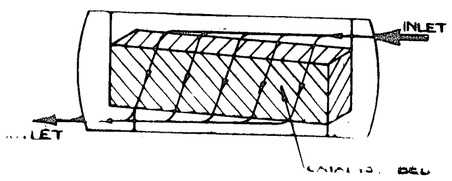
B. The Foam Process.

If the object of the operation is not to produce a gasoline, but rather chemical products, olefins of greater chain length, such as occur in the gas-oil fraction, are the more desirable compounds. To increase the gas-oil yield, the operating temperature must be lowered (250° or below). Therefore, to obtain a reaction, a more active catalyst than the sintered catalyst is required. The following process was developed to work with the highly active catalyst in a liquid phase in which the reaction gases are only slightly soluble and in which the catalyst is suspended in a finely divided state. Fig. 4 shows the flows.

Apparatus.

The gas distribution is best effected by ceramic plates (0.15 mm. pore size). The finely divided catalyst is kept in suspension in the





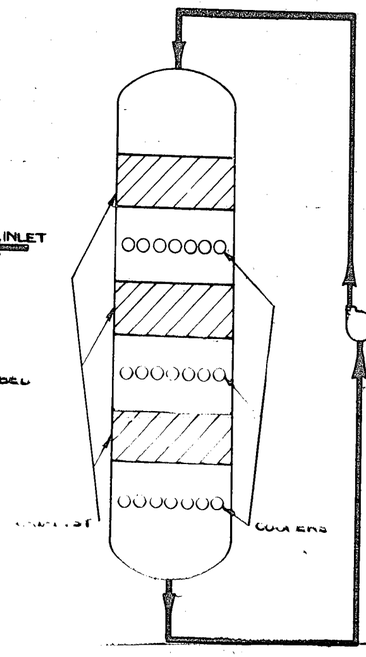


FIG. 3.

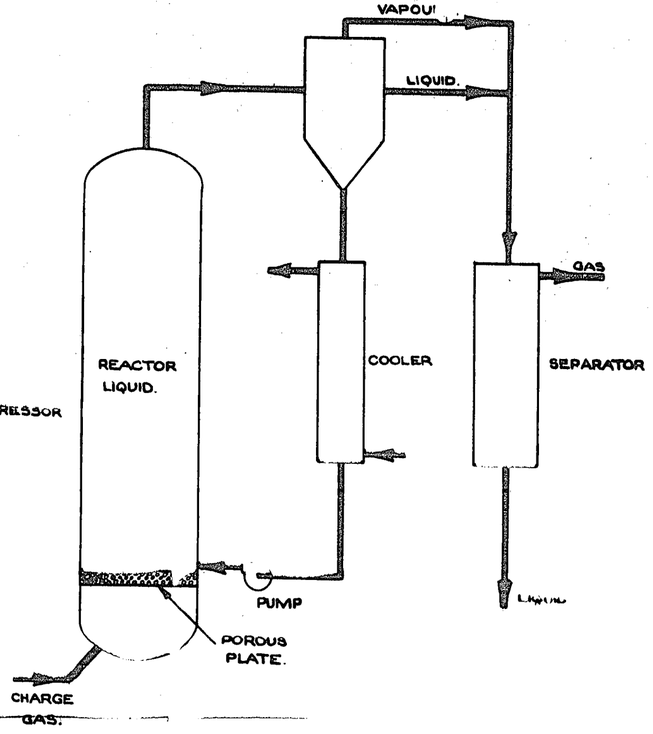


FIG. 4.

SKETCHES FROM Dr. MICHAEL

I.G. LUDWIGSHAFEN / OPPAU.

31ST. JULY. 1945.

oil in the reactor by the ascending gas stream. The high-boiling part of the reaction product serves as the suspending medium (250-300 kg. of iron per cu.m. of oil). The gas passes out overhead through a separator. The liquid is slowly carried upward and flows overhead into the separator. The spent gas and the admixed vaporised product pass to the condensers. From the separator, only the excess liquid is removed. The recycle suspension passes into a cooler, and thence to a pump, which returns it to the reactor. At a circulation temperature of 250°C, the suspension temperature increases 10°C over the period of 3 minutes in the reactor.

After the separation of the product as described in section A. further conversion of the gas is possible by recirculation (after removal of CO_2). Several stages are preferred, since in a second stage 85% conversion is reached and in a third, 90%.

Reaction Data.

Gas	-	$CO:H_2$ about 1:1 or 4:5
Pressure	-	20 atm.
Temperature	-	about 250°C
Reaction duration	-	about 3 minutes/cycle
Temperature rise	-	10°C.
Conversion	-	70%
CO_2 in exit gas	-	40-45%
Yield	-	1 cu.m.reaction volume yields 350-450 kg./day.

Catalyst.

In contrast to the sintered catalyst, the reduction of the catalyst for the "Foam" process is effected at lower temperature (350-450°C) with a very high hydrogen throughput. Iron oxide is obtained in the finely divided state either by precipitation or by the decomposition of iron carbonyl. The oxide is stirred into a paste with Alkali solution (K_2CO_3 or potassium borate) and formed into small granules which are dried, reduced and ground fine in a ball mill in admixture with gas oil.

The iron carbonyl can also be decomposed in the suspension oil, in which case, a smaller amount of iron suffices.

Product

Liquefiable gas	(C_3 and C_4)	10%
Gasoline <200°C		40-50% with 70% olefins.
Gas oil <350°C.		30% with 40-50% olefins.
Paraffin.		20-25%, of which 2/3 boil over 450°C.

For 100 Kg. of utilisable product, there are 5-10 kg. of CH_4.

Utilization of Product.

The olefins are readily polymerised to lubricating oil or converted to sulphonates (detergents) with sulphuric acid. By reaction with $CO-H_2$, the olefins may be converted into higher alcohols, aldehydes or acids.

Large-Scale Experiment.

The largest unit, tried out was a 1½ cu.m. system (including the separator). It produced 450-500 kg. of product per day. After two months a catalyst deposit was observed in the upper portion of the reactor. A stirrer was added to prevent this occurrence, but so much deposit formed around the stirrer and then fell off that the foam-plate was covered.

The final solution of these problems was prevented by the war.

C. Iron Catalyst in Tubular Reactors.

Dr. Michael also gave the following information on iron Fischer-Tropsch catalysts.

Synthesis iron catalysts produced by precipitation in the same manner as the cobalt catalyst, is unsatisfactory because a "run-away" reaction developes: a sudden temperature rise occurs, in which the formation of methane and carbon predominates. The catalyst preparation was changed, therefore, in order to obtain a solid catalyst with good heat conductivity and high activity. In this method the sintering was carried out before the reduction and the reduction itself performed at as low a temperature as possible while maintaining a high hydrogen velocity.

In order to attain high activity, 5-25% of alkali-earth metal in the form of oxide or carbonate, (MgO or $MgCO_3$ preferably) is incorporated into the catalyst. The iron oxide or hydroxide is mixed with the alkali earth and 1-2% of K_2CO_3 or $K_2B_4O_7$, pressed into pellets, heated to 850°C, and then reduced with hydrogen after cooling to 350-450°C. The catalyst has a very high activity at 240°C and lower temperatures, and excellent therm al stability in the tube reactor. The catalyst was used in a 20-liter tube-reactor for several months under the following conditions:

Pressure, atm.	20
Temperature, °C	230-250
Charge-gas composition	$CO:H_2$ = 4:5 to 5:4
Conversion	70-80%

Under the above conditions the yield was 0.35 - 0.45 kg. per liter of catalyst per day of the following products:

Liquefiable gas (C_3, C_4)	10%	with 70% olefins
gasoline (<200°C:)	35-50%	" 70% "
gas oil (<350°C:)	25-35%	" 40-50% "
Paraffin wax:	15-25%,	(60% boiling above 450°C.)

The oxygen content of the gasoline was 4-6%
The oxygen content of the gas oil was 3-5%

The methane yield was about 10 kg. per 100 kg. of the above products.

The oxygen-containing products are mainly alcohols, with aldehydes, ketones and esters, as well as a small quantity of free acids, as the other compounds.

D. Iron Catalysts in the Fixed Bed, Oil Circulation Process.

The following information was given by Dr.Duftschmid on the fixed-bed, oil-circulation process which he had developed for iron catalysts.

The object of this development was to remove the heat of reaction by circulating product-oil of fixed boiling range over the catalyst. The heat is removed by raising the temperature of the oil as well as by partial evaporation. This procedure eliminates local overheating and prevents the formation of excess methane and carbon.

Dr. Duftschmid believes that the capacity of a reactor would be limited only by the economics of construction. The process has been tested for a long time in a pilot unit of 8-10 tons per month capacity.

The process operates at a pressure of 20-25 atm. and at temperatures of 260-300°C in the first stage and 280-330°C. in the second stage. Synthesis gas with a high ratio of CO to H_2 is required, for example, $CO:H_2$ = 55:45. The throughput is controlled to yield 20-25 gms. of total product per liter of catalyst per hour. The catalyst employed is the same as that used by Dr.Michael in his fixed bed process.

The yield from 1 cu.m.of CO plus H_2 in the synthesis gas is about 150 gms. of product of the following composition:

16% C_3 plus C_4 hydrocarbons, 85% unsaturated
40% gasoline (<200°C) , 50% "
20% gas oil , 25% "
20% paraffin wax.
4% alcohols. (largely methanol and ethanol)

The gasoline contains about 1% of oxygen and the gas oil, about 0.5%.

The crude gasoline has a research-octane number of 62-65, and must be further refined. The gas oil has a cetane number above 70.

Further details of this process may be found in English Patents Nos 468,434 and 465,668

III. TOLUENE PRODUCTION

Nearly all the toluene produced in Germany was a by-product of the coke ovens. At the beginning of the war, production amounted to about 7,000 tons per month: and during the course of the war, the quantity was increased to about 12,000 tons per month by the building of precision-fractionation plants. In 1944 the synthetic plant at Waldenburg came into production, adding 4,000 tons per month. (This synthesis of toluene from benzene and methanol by means of a phosphoric-acid catalyst is described in the Leuna report.)

Two other processes were considered for the production of toluene but neither had been carried out commercially.

A. Double DHD Process.

One of most important research projects at Ludwigshafen was the development of the double DHD process. This process consists in treating heavy naphtha by the DHD process, fractionating the product to remove a toluene concentrate (100-115°C Boiling range), and re-treating this fraction in the DHD unit. Close fractionation of this product yields nitration-grade toluene (99+%) without further treatment. The flow scheme for this process is shown in Figure I.

This process gives a good yield of toluene, and at the same time, aviation gasoline of excellent quality.

In 1943 an expansion of the DHD plant at Ludwigshafen was begun for the production of 10,000 tons per year of toluene by this process. Also, projects were discussed for units at Leuna and Bröx, as well as at a Brabag plant.

B. Sulfur Dioxide - Propane Extraction of DHD Naphtha.

In 1939 a project was worked up for Pölitz for the production of about 15,000 tons per year of toluene by extraction of DHD naphtha with SO_2 - propane. A similar project was also discussed for Scholven. Neither plant was built.

The DHD naphtha was fractionated to yield an aromatic cut

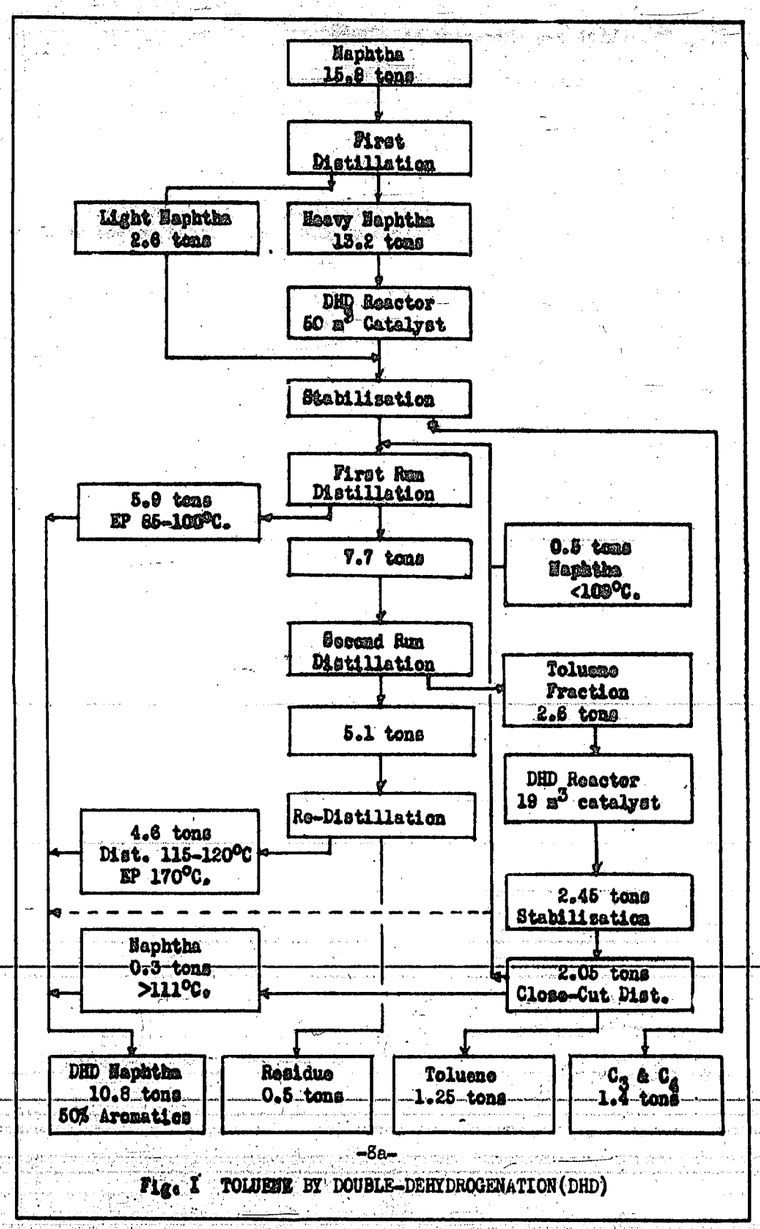


Fig. I TOLUENE BY DOUBLE-DEHYDROGENATION(DHD)

(70-120°C) which was extracted at - 76°C.

The quantities used were as follows:

100 volumes of naphtha
100 " " propane
100-150 " " sulfur dioxide.

The aromatic extract was then fractionated closely to yield nitration-grade toluene in practically 100% yield (based on the toluene in the naphtha charge).

The flow is illustrated in Figures II and III. The fractions other than toluene are blended back to produce gasoline, which is of inferior quality. The process costs are about the same as for the double-DHD process.

This information was obtained from Dr.Donath.

IV. OXIDATION PROCESS.

A. Fatty-Acid Production.

The following information was obtained from Dr.Schiller and Dr.Kürzinger.

The paraffin wax used for the production of fatty acids by oxidation with air should consist of straight-chain hydrocarbons as largely as possible; that is, it should not contain large amounts of branched chain or cyclic hydrocarbons. The preferred chain length is between 16 and 30 carbon atoms. Sulfur compounds and phenols should not be present because they inhibit oxidation. The density of the paraffin wax should not be appreciably higher than that of the corresponding pure paraffin hydrocarbon. The specifications for the paraffin wax are as follows:

Paraffin for Oxidation.

1) Sulfur<0,1%
2) Melting point 40°C Sp.gr./70° 0.765
   50°C " " /70° 0.770
   55°C " " /70° 0.775
3) Boiling Range @ 15 mm 180-350°C.
   760 mm 320°C.
4) Melting Point 35-60°C.*
5) Anilins point 100°C.

* If the melting point is above 60°C, the wax can be cracked until it meets the specification.

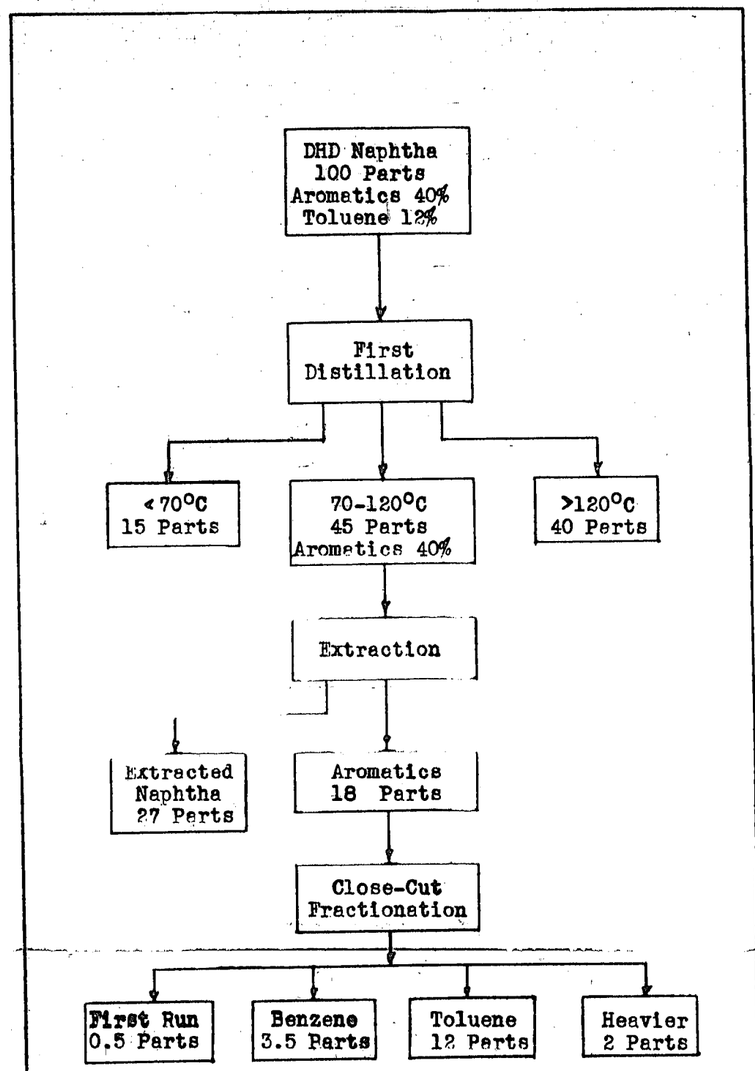


Fig. II TOLUENE EXTRACTION FROM DHD-NAPHTHA USING PROPANE-SO_2

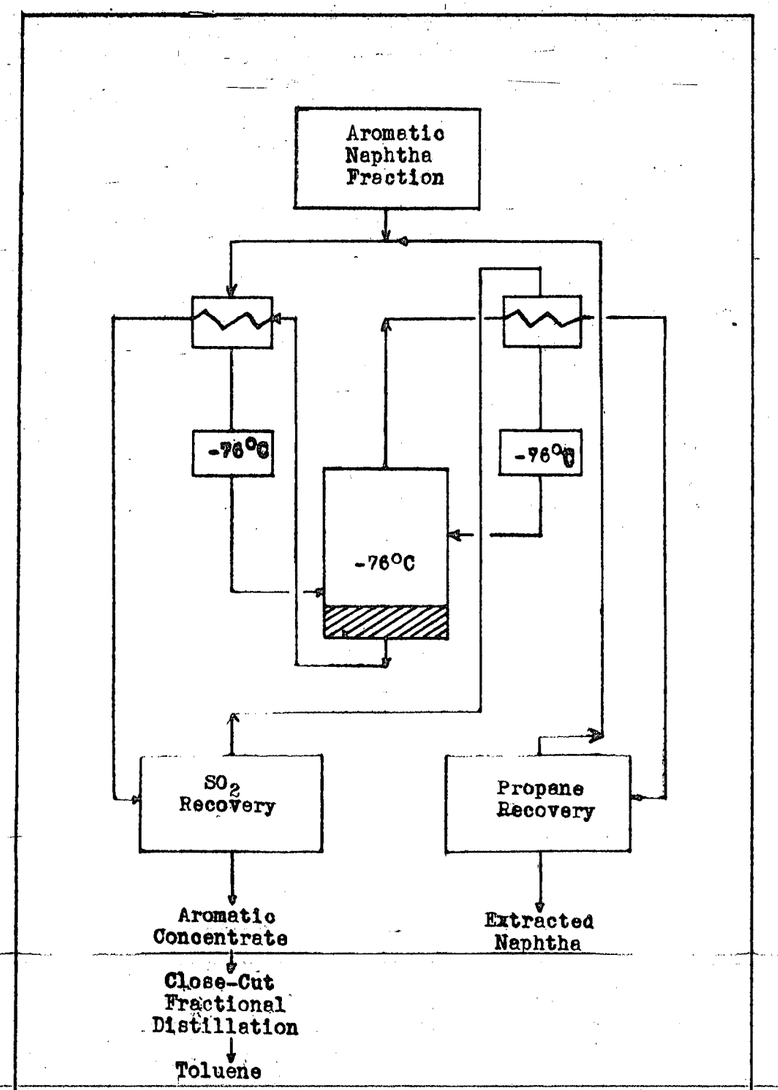


Fig. III FLOW SHEET FOR TOLUENE EXTRACTION PLANT

A trial run will determine if the purity of the paraffin wax is sufficient. Paraffins that can be oxidized only with difficulty must be purified; for example, by heating with 1-3% of aluminum chloride, by hydrogenating, or by prior oxidation with air until a small amount of fatty acid is formed which is then removed as soap.

Paraffin wax produced by the hydrogenation (TTH) of brown coal, from crude petroleum oils and from the Fischer Tropsch synthesis, have been oxidised successfully to fatty acids.

Oxidation.

The molten paraffin wax is blown with air in pure aluminum towers in the presence of manganese compounds, such as 0.1 - 0.2% of potassium permanganate or manganese soaps. There is also added 0.08 - 0.15% of sodium, or potassium carbonate which greatly improves the quality of the oxidation products. The temperature is maintained at 130 to 160°C. until oxidation begins and is then lowered to 100 to 120°C. The lower the oxidation temperature, the smaller is the formation of peroxides, but the longer the time of reaction. The air flow is continued until approximately 30% of the paraffin is converted to acid (10-30 hours). The product from the oxidizer has an acid number of 75 and a saponification number of 130-150.

Saponification.

The oxidation product is saponified with aqueous sodium hydroxide (20-25% at 80°C. The mixture is then pumped into an autoclave where it is heated to 130-150°C under pressure, the greater part of the unsaponifiable product separating in an upper layer (paraffins, alcohols, ketones.) This upper layer is recycled to the oxidation tower. The lower layer (soap solution) is heated (in a pipestill) to 280-350°C at a pressure of 80-100 atmospheres. On release of the pressure, water vapor and the remaining unsaponifiable material are flash. The unsaponifiable material is recycled to the oxidation stage.

Hydrolysis and Distillation.

The molten soap obtained as a residue from the flash tower, is dissolved in water and hydrolysed with sulfuric acid. The wax fatty acid is washed with water and distilled under a vacuum of 3-5 mm. The distillation yields three overhead fractions. The properties of the fractions depend on the molecular size and quality of the paraffin.

Based on 100 parts of paraffin. The following quantities are obtained:

1. Acids, C_3 to C_{10}, boiling point to 150°C. at 3 mm. 7-15%.
2. Soap acids, C_{10}-C_{18}, boiling point 150°C. to 240°C. at 3 mm, 45-55%.
3. Higher acids, C_{18}-C_{25} boiling point 240-300°C, at 3 mm, 2-5%.
4. Residue - 5-20%.

The quantities shown on the drawing (Figure IV) are for a typical plant run at Oppau with TTH paraffin. The plant at Oppau has a capacity of 20,000 tons of paraffin wax per year.

B. Methane-Oxygen Process.

The following information on the methane-oxygen process was obtained from Dr.Schiller and Dr.Bartholomé. The information on materials of construction was obtained from Dr.Koch.

The conversion of methane with oxygen according to the equation:

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 + 8 \text{ Kcals},$$

has been carried out during the last several years for the production of hydrogen for the ammonia and methanol synthesis. In most cases, coke-oven gas has been used as the raw material. Plants were operating at Linz, Waldenburg and Oppau, and a plant was under construction at Auschwitz.

The conversion does not take place exactly according to the equation above, part of the methane remaining unconverted, and part being oxidized to carbon dioxide and water. Besides, some carbon black is formed from methane cracking. Most of the methane and some of the carbon can be eliminated by conversion with water at elevated temperatures. Therefore, there are two stages in the conversion. The first stage, the combustion with oxygen, is carried out without a catalyst, and the second stage, the conversion of the hydrocarbons with steam is carried out over one of the standard nickel catalysts.

This process was investigated in 1927/30 in experimental plants at Oppau and Leuna for about 100 m^3. of gas per hour. Raw materials were pure methane, coke-oven gas or waste gases from coal hydrogenation containing higher hydrocarbons. The gas was mixed with oxygen as rapidly as possible in several burners and passed over a layer of active nickel catalyst (20% nickel). It was found suitable to add

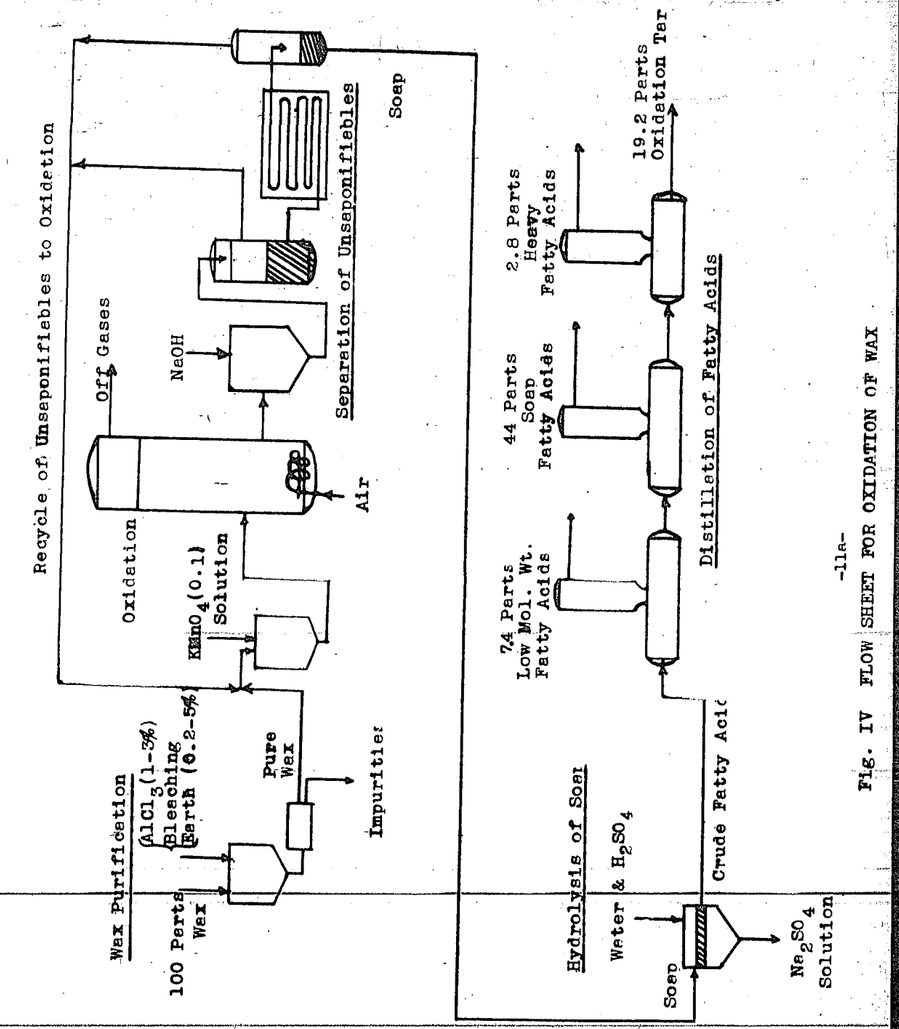


Fig. IV FLOW SHEET FOR OXIDATION OF WAX

steam and to use a temperature of about 1200°C. in the first stage. The gas produced was practically free from carbon black and contained about 1% of methane.

The following examples illustrate the conversion of methane:

1) Conversion with oxygen and steam:

120 m^3 CH_4 + 62 m^3 O_2 + 70 kg. H_2O = 350 m^3 of gas.

	Charge Gas. %	Product Gas. %
CH_4	91.6	0.7
CO_2	1.0	8.5
H_2	1.0	64.1
N_2	6.4	5.3
CO	-	21.0
O_2	-	0.4

2) Conversion with air, oxygen and steam:

133 m^3 CH_4 + 50 m^3 O_2 + 92 m^3 air + 70 kg. H_2O = 437 m^3 gas.

	Charge Gas. %	Product Gas. %
CH_4	91.6	0.9
CO_2	1.0	6.5
H_2	1.0	51.7
N_2	6.4	22.3
CO	-	18.4
O_2	-	0.2

In the first example, the methane was preheated to 200°C. and in the second to 300°C.

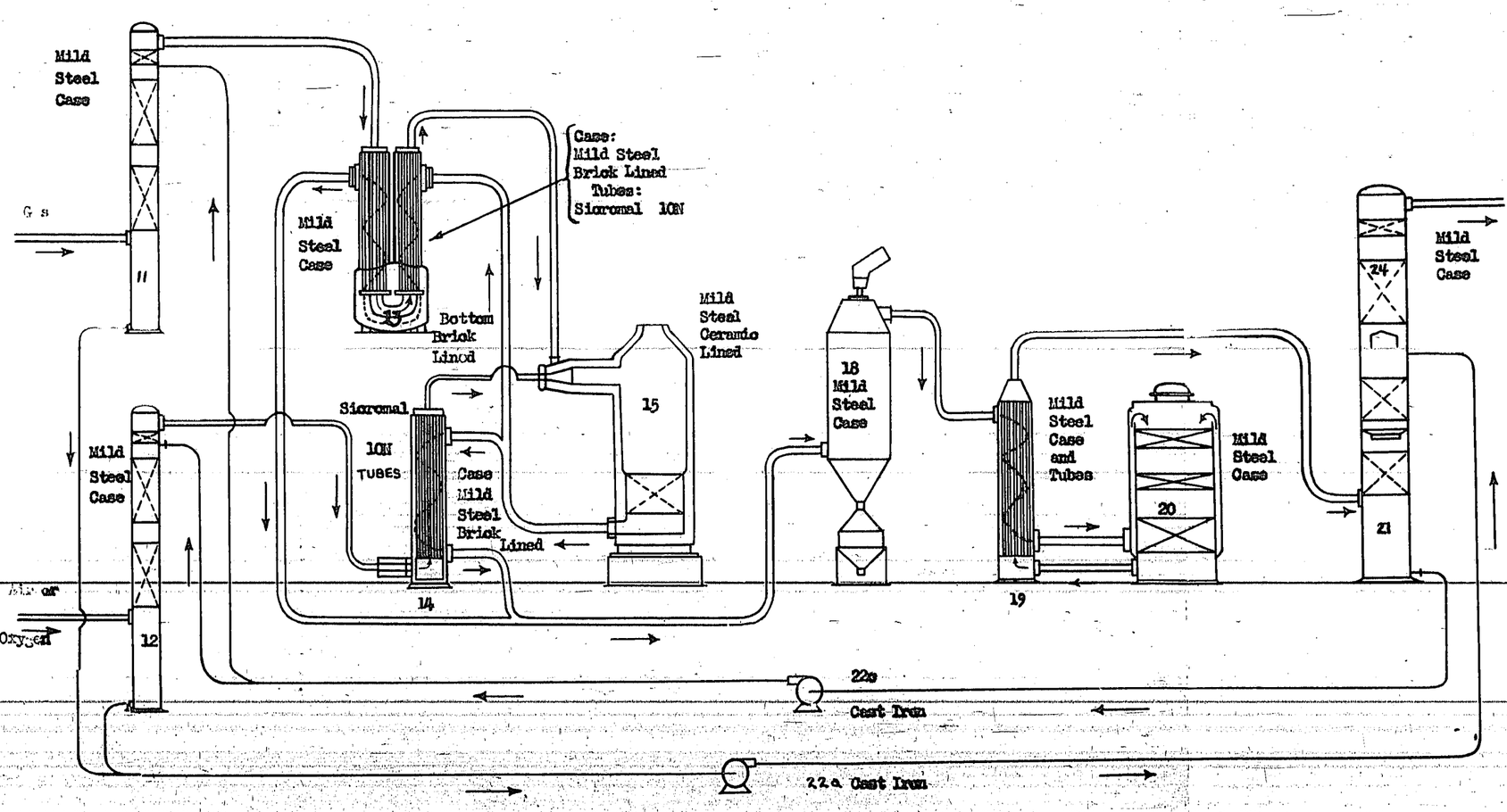
The reaction vessel contained 400 liters of catalyst in each experiment.

At first, no technical application resulted from this work, but the process was taken up again. It was tried to lower the quantity of oxygen by using less steam and allowing more carbon black to form. For separating the carbon black, special filters were designed,

FIGURE No. V

FLOW SCHEME FOR METHANE CONVERSION

11 Gas Saturator
12 Air Saturator
13 Gas Heat Exchanger
14 Air Heat Exchanger
15 Methane Converter
18 Filter
19 CS Heat Exchanger
20 CO Converter
21 Recycle Cooler
24 Final Cooler
22a Pump for Recycle water
22b " " " "



consisting of towers filled with coke or pumice. These filters were constructed to allow continuous removal of part of the packing for regeneration.

The operation of the commercial plants is as follows (see Fig. V).

The coke-oven gas and an air-oxygen mixture are saturated with water vapor in separate towers and preheated separately in the heat exchangers. These exchangers are subjected to very high temperatures and the slightest permeability of the tubes will lead to combustion and melting of the metals. The actual alloy used for the tubes is Sicromal 10 (13% Cr, 1% Si, 1% Al). This alloy is not the final answer but was a war necessity. Seamless tubes of higher alloying metal content would probably be more satisfactory. Due to the high temperature differences in the exchangers, the alloy must have a high tensile strength. The gases are mixed and burn in the upper portion of the converter. As considerable carbon is formed in the conversion, a small quantity of nickel nitrate solution is injected into the combustion space to decrease the carbon formation. The gases then pass through a catalyst bed of 5% nickel on refractory (such as MgO). The throughput of the oven is 2000 m^3 of gas per sq. m. of reactor cross-section per hour.

The converted gas heats the fresh gas and air and is then cooled to the dew point by the injection of water. The soot is removed in the shaft filters filled with coke. In the second part of the plant, the gas passes through a heat exchanger, a reactor to convert the CO and steam into CO_2 and hydrogen, and is then cooled to air temperature in a spray tower.

At full production, the Oppau plant charges 8300 m^3 of coke oven gas with 4100 m^3 of oxygen to produce 18,300 m^3 of synthesis gas of the following composition:

CO_2	16%
CO	3%
H_2	60.4%
CH_4	0.3%
N_2	20.3%

For 8300 m^3 per hour of gas, the following utilities are required:-

Electricity, high voltage,	150 KW
low voltage,	35 KW
River Water	70 tons
Steam, low pressure	0.5 ton

The catalyst has a life of more than three years.

Three men per shift are required to operate the plant.

The same plant can operate on other gases containing up to 50% hydrocarbons, figured as CH_4. If the feed gas contains more hydrocarbons, part of the synthesis gas is recycled as a diluent.

This process has the advantage that it can be carried out with gases containing sulfur, since the conversion temperature can be raised easily so high that the nickel catalysts are not poisoned.

The formation of carbon is troublesome, but this difficulty can be overcome, probably by changing the design of the combustion chamber.

When gas is manufactured for the methanol synthesis, only oxygen is used and the feed gas must be low in nitrogen.

C. Production of Hydrogen Peroxide by Propane Oxidation.

The following brief description of this process was obtained from Dr.Bartholome.

Propane is preheated to a temperature of 350 to 450°C. and admixed with 5 to 10% by volume of oxygen. This mixture flows into an empty reaction chamber where it remains for about 10 seconds, 90% of the oxygen reacting in this interval. The reaction gases are cooled to give an aqueous product containing 30-37% of peroxides. Approximately 50% of these peroxides are organic and the remainder is hydrogen peroxide, which is equivalent to a conversion of about 25% of the oxygen. The dry gas analyzes about 90% propane and 10% propylene.

The reaction vessel consists of apparatus glass "Duran" or of quartz.

These experiments were carried out on a scale of 300 liters of propane per hour.

D. Production of Acetylene by Oxidation of Ethane.

The following information was obtained from Dr.Sachsse. Additional details were not obtained due to the similarity of these experiments to the process of converting methane to acetylene. (See Ludwigshafen CIOS Report of 16 August 1945).

Ethane and oxygen are preheated separately and mixed, whereby an incomplete combustion occurs, resulting in a flame. No catalyst is used. The reaction takes place at 1-2 m. of water pressure and a reaction temperature of 1300-1600°C. The exit gas contains about 8% of acetylene besides carbon oxides, hydrogen and unconverted hydrocarbon. The yield of acetylene is about 0.33 kg. per kg. of ethane.

V. POLYMERIZATION AND CONDENSATION PROCESSES.

A. Oppanol.B.

The following information on the preparation and properties of Oppanol was given by Dr.Güterbock and on applications, by Dr.Schwarz.

Oppanol is polyisobutylene, prepared by polymerizing isobutylene in the presence of ethylene to control the temperature at -100°C. and of about 0.05% of boron fluoride as catalyst. The isobutylene and ethylene (liquid ratio 1:2) with the boron fluoride are charged in liquid phase onto a concave endless belt. The ethylene evaporates as the polymerization progresses, maintaining the temperature at -100°C. The belt is inclosed in a case from which the vaporized ethylene is recovered for recycling. The boron trifluoride (prepared from CaF_2, B_2O_3 and H_2SO_4) leaves the reactor with the ethylene and is removed from it by contacting with CaO. The polymerized product is scraped from the belt into a heated kneader, where the last traces of ethylene are evaporated.

The belt is made of V2A steel; the case and other equipment, of iron.

The ethylene and isobutylene must be of the highest purity obtainable (99.5 %). The isobutylene is prepared by the dehydration of isobutanol at 400°C under atmospheric pressure with an aluminagel catalyst.

Products of various molecular weights are obtained by adding a polymerization "poison"; the best results were obtained with diisobutylene. The commercial grades were as follows:-

B3	3,000	mol. wt.
B15	15,000	"
B50	50,000	"
B100	100,000	"
B200	200,000	"

Properties of B-15 are:

Sp.gr.	0.9
Ignition Point	Very high
M.P.	Not definite, thermoplastic.
Neutralization No.	Neutral.

The applications of these products were as follows:

a) Oppanol B3

Cable oil, lubricating oil, softeners for resins and waxes, etc.

b) Oppanol B15

Viscosity improver for lube oil and cable oil. Additive to bitumens, waxes, paraffin, etc. Softener for polyethylene, gutta percha, and similar resins.

c) Oppanol B50, B100 and B200.

Foils for electrical insulation and protection against corrosion. Gaskets for chemical containers and grooved-can joints. Combination with polystyrene and polyethylene for electrical insulation for high-frequency cable casing and packing. Combination with polyethylene for submarine cable. Adhesive plasters and adhesive tape. Combination with wax,paraffin etc. for doubled steam-impermeable paper. Covering materials of all kinds in liquid form, with special stability against aging and chemicals. Blending with bitumens to increase viscosity and "dripping point". Mixed with natural and synthetic rubber for special applications.

B. Isobutylene Dimerization.

The following information was obtained from Dr.Kuhn:

Isobutylene is passed in the liquid phase at a space velocity of 3 to 5 liters per liter catalyst per hour over phosphoric acid on activated charcoal as catalyst. Conditions: 180-200°C., 25 atm. gage pressure. Thirty to fifty percent of this isobutylene polymerizes per pass, the remainer, after distillation, is recycled. Diisobutylene is the desired product but triisobutylene cannot be avoided. One liter of catalyst can produce one to two cubic meters of product. Isobutylene as pure as possible is used to avoid losses in (pressure ?) vent-release in the recycle system. Construction material is iron. The yield is practically 100 percent if the equipment is gas tight. There are no byproducts, excepting 0,1-0.5 percent of tetraisobutylene which is separated by distillation. The product is a mixture of diisobutylene and triisobutylene, which is hydrogenated to "Tannol". The product is tested for octane number and distillation range.

C. Lupolen H.

The following information on the preparation of Lupolen was obtained from Dr.Heinrich Hopff, and on the properties, from Dr.Schwarz.

The process is carried out at a pressure at 1500-2000 atm., using 0.05-0.10 percent of oxygen as catalyst. The reaction starts at 220°C. and temperature is controlled between 180 and 220°C. by cooling. The

apparatus, as shown in Fig. VI, consists of (a) a first-stage compressor to 300 atm., (b) a high pressure compressor to 1500-2000 atm., (c) a pipe coil 24 mm. diameter and 80 m. long, 40-50 l. volume, (d) a separator, and (e) a caustic washer. Heating and cooling are done by water under pressure at 200-220°C. in the first section of the coil, and 100-120°C. in the second section. The conversion to polymerization products is 8 to 10 percent per pass. Monthly production is 5 tons.

The ethylene feed is 98-99% ethylene, about 1% ethane, about 0.5% nitrogen and a trace of acetylene.

The viscous Lupolen H is drained into a tub and after cooling it becomes a snow-white mass. The product contains 0.2 to 0.3 percent of oxygen. Testing is done by milling a thin sheet on heated rolls and determining the stress, crease number (Knitterzahl) and dielectric-loss angle. In addition, the molecular weight which should be between 15,000 and 25,000 is determined in boiling tetralin by the method of Staudinger.

Lupolen H is a horny, tough material of paraffin-like charater, tasteless and odorless, waterproof, heat-proof up to about 100°C., stable against chemicals, and with good dielectric properties. It is used alone or with Oppanol B as electrical insulating material, including use in submarine cable, as a low-loss insulation in high-frequency work, also as a cable-covering material.

It is also used alone or with Oppanol B. for acid-proof covers, packing etc., and for taste- and odor-free wrappings of all kinds.

D. Paraflow.

The following information concerning the preparation of Paraflow was obtained from Dr.Fritz Christmann.

Hard paraffin, 1000 kg., 50-52°C M.P., is chlorinated to 12-14 percent chlorine by the addition of gaseous chlorine at a temperature of 80°C. It is then diluted in a stirred vessel with about 1000 kg. of ethylene chloride. After cooling to 20°C., 150 kg. of naphthalene, 10 kg. of polystyrene and 35 kg. of zinc oxide are added. Gradually, over 12 hours, 70 kg. of $AlCl_3$ is added, with stirring. In this period, the reaction temperature rises slowly to 30 to 35°C. After an additional 24 hours, the reaction temperature reaches 60°C., after which the

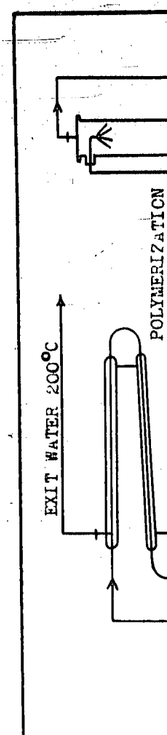


FIGURE VI
LUPOLEN H PLANT
2000 ATM

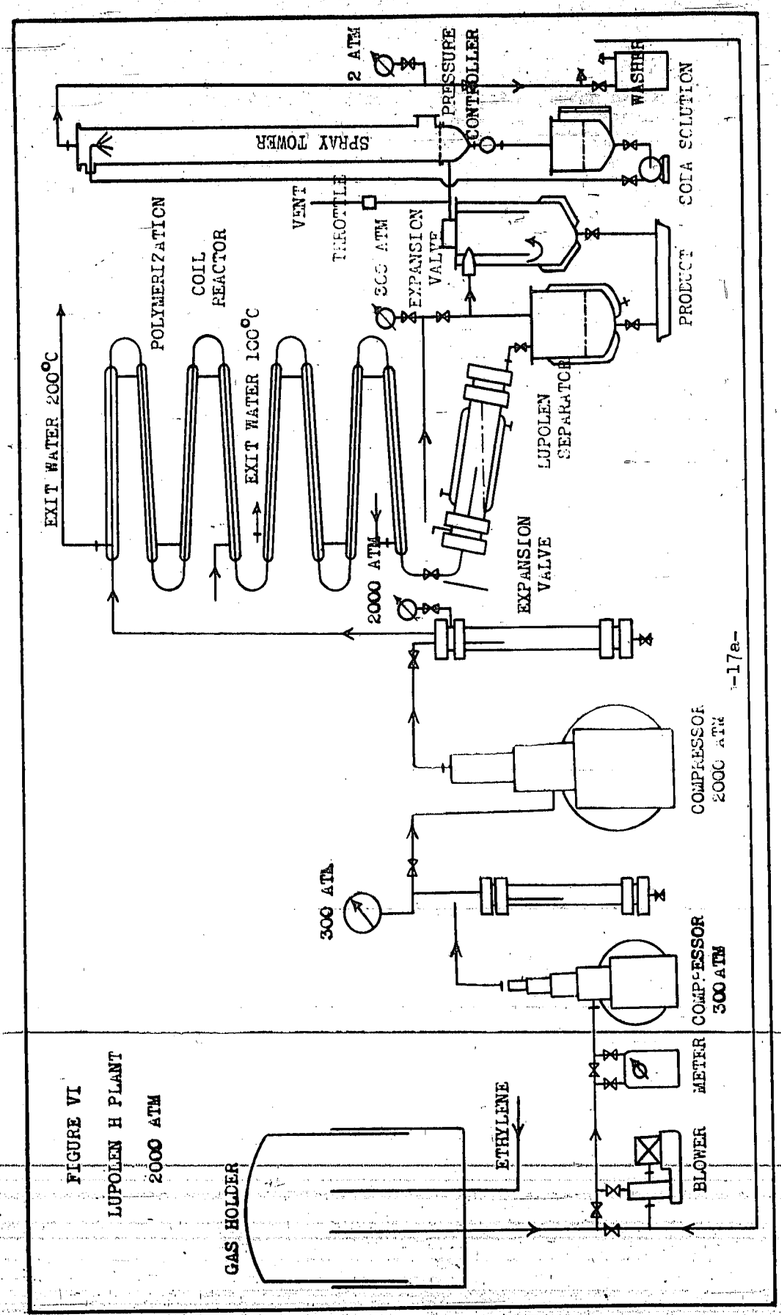


FIGURE VI
LUPOLEN H PLANT
2000 ATM

-17a-

reaction product is centrifuged to remove insoluble salts.

The centrifuged product is then treated with 30 kg. of fuller's earth (Terrana) in a gas-heated agitator, during which time (12 hours) the temperature is raised to 240-270°C. The ethylene chloride is distilled off in the process and is replaced with kerosene. The product is cooled to 100°C. and filtered. The filter cake is twice extracted with kerosene. The filtrates are combined and vacuum-steam distilled in a pipe still, where kerosene and a paraffin-containing spindle oil are recovered as overhead products. The residue of 650 kg. (65% of original paraffin) is Paraflow fluid with a viscosity of 50-80°E. at 100°C, which is mixed with other oils (motor oils, spindle oils) in a ratio of 10:90 and sold as Paraflow.

The Ludwigshafen Paraflow plant has a capacity of about 20 T/Month Paraflow Fluid (= 200 T/Mo commercial Paraflow). The plant is practically intact and can reach this capacity in a few months.

E. Bunol.

The following information was obtained from Dr.Steinhofer on the preparation of Bunol, which is a butadiene polymer, claimed to be a suitable substitute for drying oil, such as linseed oil.

Butadiene is introduced with stirring into a suspension of two parts of potassium sodium alloy in 400 parts of toluene at 90°C. The reaction takes place violently, the temperature rising to 170°C. so that the toluene boils under reflux. After 8 to 10 hours, the reaction subsides. About 8000 parts of oil are formed; half is taken off and filtered. The other half, remaining in the kettle, is mixed anew with 200 parts of toluene and can be used again for the reaction without the addition of catalyst.

Details could not be furnished since the process was carried out at Schkopau, and due to lack of communications, the information was not available.

F. Buna D.

The following statement concerning Buna D was obtained from Dr. Herbeck.

Buna D is a co-polymer of butadiene and Dimol. Dimol is ethylidene dimethylvinylcarbonol, and is made by the addition of vinyl acetylene to acetone.

The product is polymerized in emulsion by customary methods and its qualities are about the same as those of Buna S.

G. Production of Koresin.

The following brief information was obtained from Dr.Christ on Koresin preparation:

Koresin is prepared by treating a mixture of p-tert butylphenol (distilled product) and 8% zinc naphthenate ("Solingenzink") in a stirred autoclave with a mixture of acetylene and nitrogen until 1.3 to 1.5 mols of acetylene have reacted with 1 mol of the butylphenol. Operating conditions are 200-240°C, 20 atm. total pressure, 3 atm. partial pressure of nitrogen. The reaction product is forced by pressure to another agitator at 200°C., and from this vessel is emptied at 180-200°C. into wooden barrels or paper bags. It sets to a brittle brown resin of 120-130°C. melting point, corresponding to a dripping point of 130-140°C. by the method of Kramer and Sarnow.

Report No. 241, Dr.Hecht, May 25, 1940, "Koresin" is available through CIOS, CAFT III.

VI. CHLORINATION PROCESSES.

A. Preparation of Alkyl Dichlorides.

The following information was obtained from Dr.Leutner:

The chlorination of propane to dichlorides is carried out by mixing liquid propane and liquid chlorine in equimolar amounts in the presence of propylchloride, ten times the equivalent of the chlorine. This mixture is precooled and exposed to a mercury-arc lamp, in several stages. Intermediate cooling takes place between the stages so that the temperature does not exceed 70°C. The pressure has to be sufficient to maintain the liquid phase and insure solution of the hydrogen chloride formed. The process may be carried out batchwise or continuously by recycling the products through the coolers and exposure stages, removing product equivalent to the fresh feed.

The products are separated, by distillation, into hydrogen chloride, propane, propyl chloride, propyl dichloride (50% of 1,3 dichloropropane) and a small residue of higher chlorinated products. The propane is mixed with fresh propane and returns to the process with the propyl chloride. The yield of propane dichloride is about 99% of theory.

Butane dichloride can be produced in a similar manner. In this process, the temperature must not exceed 40-50°C. A pressure of 15 atm. is required. A yield of almost 100% is realized, including some trichlorobutane.

B. Preparation of Butadiene from Butylene.

This information on the production of butadiene from butylene was obtained from Dr.Leutner:

The chlorination of butylene is carried out in a high-speed centrifugal pump by introducing gaseous chlorine into a mixture of liquid butylene and an excess of dichlorobutane. In order to obtain an immediate reaction with the butylene, the chlorine is introduced axially into the pump through a nozzle. At a pressure of 4-6 atm. the circulating mixture is maintained in the liquid phase at 40-60°C. In order to be certain that the chlorine enters in the vapor phase, the supply line is steam jacketed. The liquid is circulated through a cooler and product corresponding to the feed is removed continuously. Distillation yields the dichlorobutane, the unreacted butylene being returned to the system.

The production of butadiene by splitting off of hydrogen chloride is carried out in empty tubes heated to 600-610°C. The best results are obtained with a 1:1 mixture of dichlorobutane to monochlorobutane, the monochlorobutane being obtained by splitting hydrogen chloride from dichlorobutane. The mixture is vaporized and passes into the reaction tubes; almost quantitive yields of butadiene are obtained.

The monochlorobutene and unreacted dichlorobutane are recycled to the decomposer.

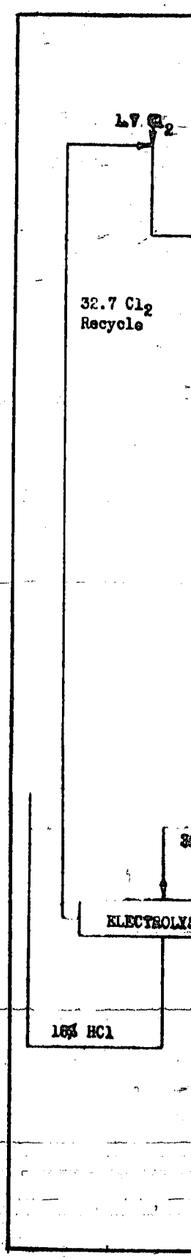
In principle, the chlorination of propylene can be carried out in the same manner, but due to the higher boiling point, lower temperatures and higher pressures are required to maintain the liquid state.

C. Preparation of Butadiene from Butane.

The following information on the vapor-phase chlorination of butane was obtained from Dr.Waldmann.

With reference to Figure VII, butane and chlorine are mixed at atmospheric pressure in the proportion of 1 to 1 and brought to a temperature of 300-350°C. The reaction takes place very rapidly in the absence of a catalyst and produces more heat than is necessary to maintain the temperature. The products are cooled to condense the chlorides and are washed with dilute hydrochloric acid to wash out the HCl. The chlorinated butanes are caustic washed and distilled to separate the higher chlorides ("Poly"). The monochloride and dichlorides are decomposed without a catalyst at 550-600°C., and the products are worked up in the same system and together with the chlorination product.

The gaseous product, Butane, butylene and butadiene, passes to an absorber where it is contacted with a copper solution. The butane-butylene stream is conducted back to the chlorinator. The butadiene is liberated from the rich absorber solution by decomposition with heat and the lean copper solution recycled.



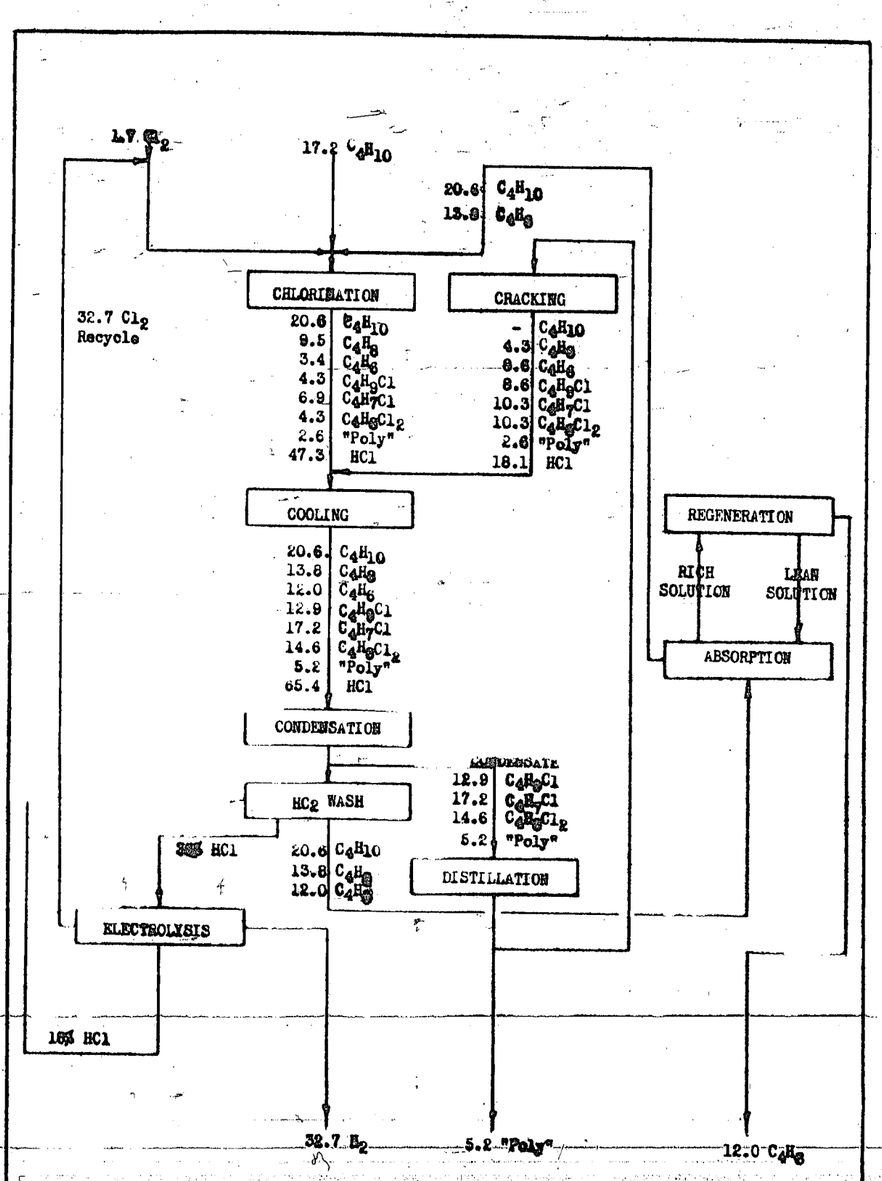


Fig. VII FLOW SCHEME FOR BUTADIENE PRODUCTION.

The concentrated hydrochloric acid is electrolyzed, yielding chlorine, which is recycled, and hydrogen. The chlorine is recovered to the extent of about 90%; the remaining 10% being present in the polychlorobutane produced.

From 1000 kg. of butane and 120 kg. of chlorine, the following yields are obtained:

C_4H_6	650 kg.
H_2	65 kg.
Polychlorobutane (25-30% Cl)	400 kg.

The process has thus far been carried out only on a small scale (10 kg. per hour). It is believed it can be successfully applied to the production of butylene or to butylene and butadiene, as well as for the production of propylene from propane.

VII. MISCELLANEOUS PROCESSES AND PRODUCTS.

A. Hydrogenation of Butadiene to Butylene.

The following information on the investigation of catalysts for the hydrogenation of butadiene to butylene was obtained from Dr.Conrad.

In the catalytic dehydrogenation of normal butane, a certain percentage of the butylene is dehydrogenated to butadiene. A small percentage of butadiene is detrimental in the alkylation of butylene to iso-octane, since the consumption of sulfuric acid is greatly increased.

In the experimental plant, Op.339, in which normal butane is dehydrogenated on a semicommercial scale by a multistage process, experiments were made to hydrogenate the butadiene with the hydrogen contained in the gas. A hydrogenating catalyst was tried which had been developed for the removal of small quantities of acetylene in the gas stream of an ethane cracking plant. It was possible to reduce the butadiene content from about 1-1.5% to 0.1% without changing the total olefin content of the gas. Since the dehydrogenation of butane as well as alkylation was interrupted by changed requirements, the investigation could not be pursued further on a commercial scale, especially the determination of the sulfuric acid consumption in the alkylation step. Further laboratory experiments, however, were made with a series of catalysts, the preliminary results of which follow:

The method of experimentation was as follows. The gas produced in a butane dehydrogenation plant was collected in a gas holder and the butadiene content brought to 1-2% by the addition of butadiene.

The mixed gas had, on the average, the following composition:-

Olefins	20-25%
Butadiene	1-2%
Hydrogen	23-28%
Butane	remainder

The gas was drawn from the gas holder at the rate of 25 liters per hour through a gas meter and a drying section, then into the catalyst chamber, which was a vertical tube of 30 mm. diameter, heated electrically. The different space velocities were obtained by altering the quantity of catalyst. The freedom of the gas from butadiene was determined by the failure of a portion of the stream to discolor 87% sulfuric acid. The butylene content was determined in the usual way by absorption in 87% sulfuric acid. The following observations were made in the series of experiments.

If the temperature of the catalyst is raised at a given space velocity of the charge gas, hydrogenation of butadiene to butylene begins at a definite minimum temperature, and with further increase of temperature, all the butadiene disappears without any hydrogenation of butylene, that is, the olefins remain unchanged. This result holds over a definite limited temperature range which is different for each catalyst. Further increase of temperature generally causes a decrease in the olefin content of the gas, since butylene is then hydrogenated to butane. The temperature range of selective hydrogenation is different for each catalyst and can change for a given catalyst in the course of continued use, an effect which can, of course, be ascribed to a change of catalyst activity. All catalysts investigated showed this behavior, with the exception of copper chromite on silica gel. With this catalyst only, selective hydrogenation was observed over a wide temperature range. Further increase of temperature resulted only in the reappearance of butadiene and no butylene was hydrogenated. A further investigation of this catalyst and other chromite catalysts is planned.

In the course of the experiments it was found necessary to remove from the gas stream the polymerization products which are always present in such dehydrogenated gases as vapor or entrained as mist. The removal is necessary to protect the catalyst from fouling. The removal was easily effected by a mist filter and an activated carbon filter. The lack of such purification was the reason that the butadiene content was not completely reduced to zero in the commercial experiment.

The principal results are summarized in the following table.

The second column shows the space velocity employed, stated in liters per hour per liter of catalyst. The third column gives the

temperature range within which the catalyst hydrogenates selectively at the space velocity shown.

Catalyst	Space Velocity	Temperature range °C
Cr_2O_3+NiO (Dr.Häuber)	1000 2000	85-130° 80-138°
8376/High Pressure expts Sulfide catalyst,clay support	250 1000 4000	110-260° 130-240° 160-270°
CuO Cr_2O_3 on silica gel	1000 2000 4000	140-320° 220° and higher 260° and higher
Cu On clay	1800 4500	105-150° 130-200°
Ni on clay	500	225-300°

These experiments show that the selective hydrogenation of butadiene in the presence of butylene is possible with each catalyst tried, and it is only necessary to find by experiment the particular conditions that a given catalyst requires.

In order to determine accurately the hydrogenation product, pure butadiene was hydrogenated over copper supported on clay. In this experiment, the catalyst was fully active at 75°C. The products were removed as solids by carbon dioxide. The Raman analysis gave the following results:

Trans-butene - 2	80%
Cis-butene-2	15%
Butene-1	5%

No butane and no butadiene were present. These results show that the addition of hydrogen is principally 1,4-addition.

B. Kybol.

The following information concerning the manufacture of Kybol was obtained from Dr.Waldman.

Kybol (diethyl benzene) is manufactured from benzene by alkylation with ethylene, using aluminum chloride as catalyst. Ethylene and benzene (mol ratio 2:1) are reacted in a tower containing aluminum chloride at the boiling point of benzene at atmospheric pressure, vaporization removing the exothermic heat of reaction. The ethylene is nearly completely absorbed in one pass. The product is washed and distilled.

The first fraction containing benzene, as well as the third fraction containing triethyl benzene, is recycled to the alkylation towers. The middle fraction (about 30% of the mixture) represents the final product, "Kybol". There is also a residue of the higher alkylated benzenes.

From 1000 kg. of benzene and 720 kg. of ethylene, 1450 kg. of Kybol are produced with a consumption of 5-7% of aluminum chloride (based on the benzene).

Kybol was chiefly obtained as a by-product of the manufacture of ethyl benzene for styrene.

In the same manner, isopropyl benzene can be prepared from benzene and propylene.

C. Tannol.

The following brief statement on Tannol was obtained from Dr.Kuhn.

Diisobutylene and triisobutylene from polymerization are hydro-genated in the liquid phase at 200 atm. pressure and 250°C. over a tungsten-sulfide catalyst. A space velocity of 3 liters of liquid charge per liter of catalyst per hour was employed. Yield is practically 100% of Tannol (isooctane and isododecane), which is used for a gasoline blending agent.

At first, nickel on a carrier such as pumice or kieselguhr was used, but was later replaced by tungsten-sulfide pellets.

D. Vanol H.S.

The following description of the preparation of Vanol was obtained from Dr.Lorenz.

A mixture of 1 mol of formaldehyde and 2 mols of methanol with 2% H_2SO_4 as catalyst is introduced into a distillation

column (see Fig. VIII). Methylal (dimethoxymethane) in an azeotrope with 8% of methanol is taken overhead. The azeotrope is mixed with 0.1% cobalt acetate (dissolved in methanol) and reacted with $CO:H_2$ in the ratio of 1:2 at 170°C. and 300 atm. The product is stabilized to remove dimethyl ether and methane. Methylal is taken overhead in distillation I, methanol in distillation II, and both are recycled. After adding sufficient water to form the 82% water azeotrope of vanol acetal (1,1,2 trimethoxyethane), the mixture is distilled off at 92°C. and hydrolized in the presence of H_2 at 300 atm. and 250°C. The products, methanol, water, and methyl glycol are charged to distillation II.

The main product, methyl glycol (2 methoxyethanol) is obtained by distillation IV, and finally in a vacuum distillation, Vanol HS is recovered, leaving a viscous residue. The vanol HS is a mixture of polyoxy compounds, partly ethers, containing acetal groups which can be hydrolyzed by hydrogenation over nickel.

The technical experimental plant for this investigation was working only partly. It was built for 50 tons per month of methyl glycol in continuous operation. The methyl glycol was to be hydrolized to glycol but this stage had not been satisfactorily developed.

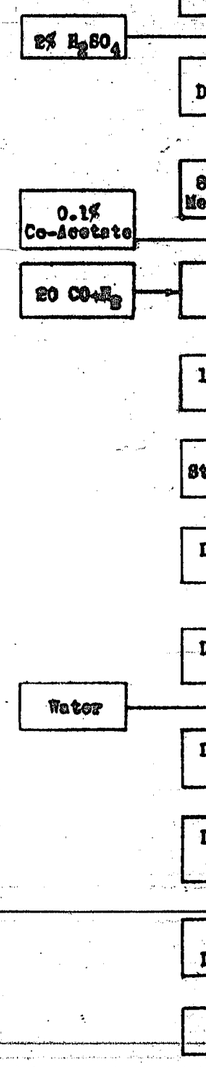
From 100 parts of reactor product, the following materials are obtained:

Dimethyl ether	5 parts
Methylal	45
Methane	14
Vanol acetal	12
Methyl glycol	13
Vanol HS	9
Residue	2

E. Diolefins from Olefins and Formaldehyde.

The following brief information on the preparation of isoprene was obtained from Dr.Bueren.

The preparation of diolefins is carried out by first reacting the olefin with formaldehyde in the liquid phase at ordinary temperature in the presence of hydrogen chloride, to form a 1,3 dioxane. The dioxane is then decomposed to the diolefin by contacting with phosphoric acid catalyst at about 220°C.



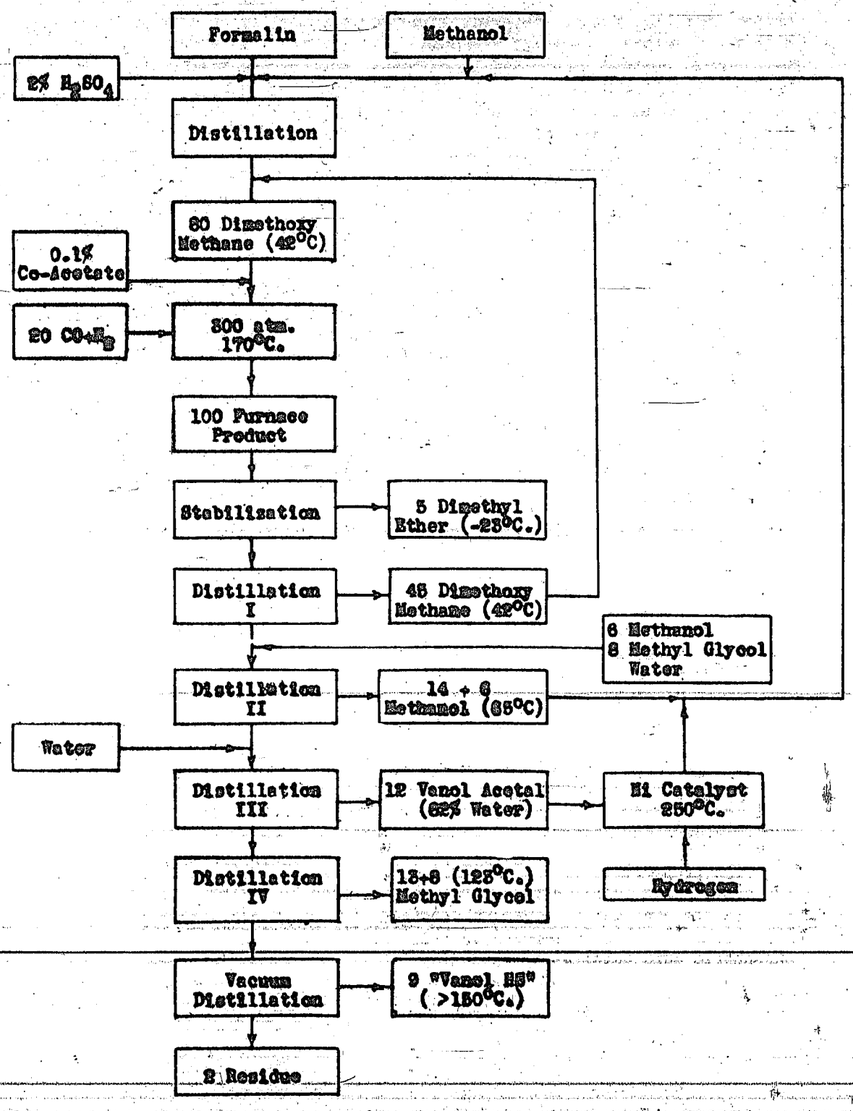
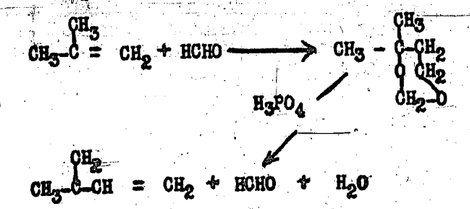


Fig. VIII FLOW SHEET FOR PRODUCTION OF VANOL

This is illustrated in the following reaction:



When trimethyl ethylene is used, besides dimethyl butadiene, pinacolin is obtained.

Further details may be obtained in DRP. IG. No.663/43 and DRP. 610,371

F. Preparation of Allyl Alcohol.

The following information on the preparation of allyl alcohol from allyl chloride was obtained from Dr.Klein.

Soda solution (1.25 m^3/h. of 2.5 normal) is preheated to 130-140° C. and mixed with 250 liters per hour of allyl chloride. The allyl chloride contains 3-4% of isomers of lower molecular weight.

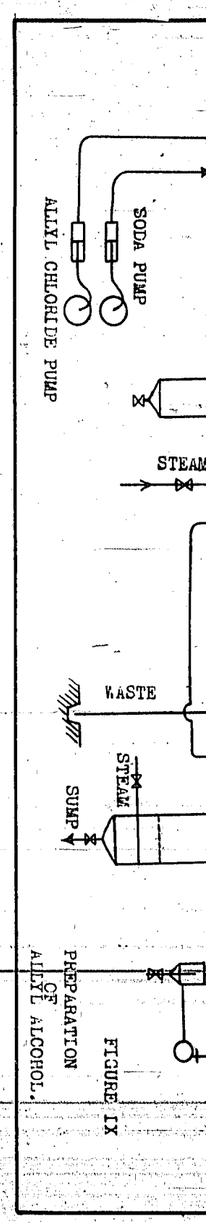
The mixture passes into a steam-jacketed reactor (see Fig.(IX) where it is maintained at 150°C, afterwards flowing into a secondary reactor. As it is unknown in which stage of the reactor the major portion of the CO_2 is liberated, the contact time cannot be calculated exactly, but it is estimated to be 20-30 minutes. Pressure in the reactor is maintained at 10-11 atm.

The reaction mixture is expanded to 8 atm. into a spray tower, in which the liquid phase separates from the CO_2. The gases pass through a cooler to a separator and are then vented.

The liquid phase from the spray tower is charged to a distillation column heated by direct injection of steam where an azeotrope (250 liters per hour) containing 30% water and 70% allyl alcohol is taken overhead. The allyl alcohol frequently contains small quantities (0.5-1.5%) of diallyl ether. The salt solution leaving the column should have a slightly alkaline reaction and contain no traces of allyl alcohol (by bromine test).

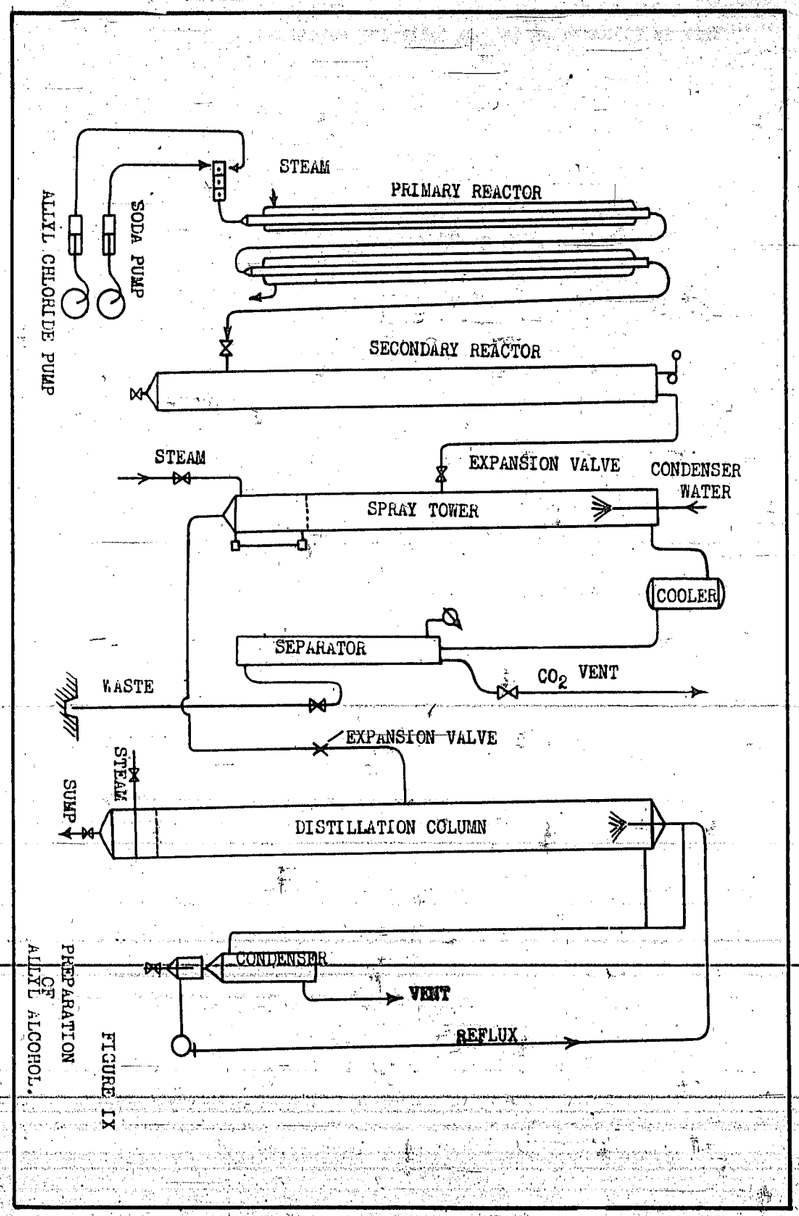
G. Methacryl Nitrile.

The following information on the preparation of methacryl nitrile was obtained from Dr.Lorenz.



PREPARATION OF ALLYL ALCOHOL.

FIGURE IX



PREPARATION OF ALLYL ALCOHOL.

FIGURE IX

Isobutyl alcohol is oxidized, through the aldehyde, to isobutyric acid. This acid with ammonia is contacted over beauxite at 500°C. to obtain isobutyronitrile in 95% yield. The isobutyronitrile is chlorinated at 65-70°C. in a quarz tube by exposure to a mercury vapor lamp, the chlorine being added in such amounts that the chlorination does not exceed 40%. The product is distilled, and the first fraction containing unconverted isobutyronitrile and so-called "alpha-chloroisobutyronitrile" (BP 119°C) is recycled to the chlorinator. A second fraction (160-170°C), containing the so-called "beta-chloroisobutyronitrile" and an unknown "dichloroisobutyronitrile", is treated with 10% KOH. Approximately 5% of an unsaponifiable, highly chlorinated product is obtained as a residue.

By the KOH hydrolysis, the beta-chloroisobutyronitrile splits off HCl yielding methacrylnitrile I which is separated by distillation. The dichloride residue is passed over TiO_2 at 420°C., yielding methacrylnitrile II, which is less pure. The yield of methacrylnitrile is about 75% based on the butyric acid.

This investigation had not proceeded beyond the experimental stage, and the preparation for pilot-plant construction.

VIII. SPECTROGRAPHIC STUDIES.

A. Research.

The following information was obtained from Dr.Fromherz. As other investigators were covering this subject thoroughly, only a brief summary of the conclusions was obtained.

Experiments were performed by Dr.Fromherz together with Dr. Luft (of Oppau Manufacturing Control Dept.) on the use of the infrared spectrum of hydrocarbons for qualitative and quantitative analysis of hydrocarbon mixtures, and to prove the advantages and disadvantages of infrared analysis as compared with Raman analysis. The studies led to the following conclusions:

1. The infrared fundamental oscillations between 3 mu and 12 mu are very characteristic for the individual hydrocarbons; they give sufficiently intensive absorption bands and permit a good qualitative analysis of mixtures with not more than three components, and a quantitative analysis with a precision up to 0.5 per cent.

2. A comparison of infrared analysis with the Raman analysis shows that the Raman analysis is in general preferable for qualitative investigations, because the characteristic Raman lines of different

hydrocarbons can be observed lying adjacent to each other, while infrared absorption bands for different hydrocarbons are overlapping. Therefore, the individual hydrocarbon in a mixture can be identified more easily by the Raman spectrum, and mixtures of more than three components can be qualitatively analyzed satisfactorily.

3. For quantitative analysis, the infrared method is generally better, because the intensity of absorbed light can be measured easily with great accuracy. In quantitative Raman analysis, it is necessary to measure photometrically the blackness of photographic places, which is difficult, not too accurate and subject to many errors. If special precautions are not taken, the accuracy may not exceed 5%. Further, the results are not expressed in absolute concentration, but only in relative ratios.

4. The latter fact leads to a further advantage of infrared analysis. If, in Raman analysis, one component is missed because of its very weak Raman line, the remaining components (by ratios) will still add up to give a total of 100 per cent for the analysis. If the same mixture is analyzed by infrared rays, it can be determined if the sum is actually 100 per cent, or if it is less than 100 per cent (beyond the limits of errors). If the latter condition is found, some component has escaped Raman analysis, and the infrared analysis will give the quantity of this component by difference from 100%, and possibly from some disagreement in the infrared spectra, a clue to the identity of the missing component may be gained.

B. Equipment.

The information given below was obtained from Dr.Luft.

In Oppau, two infrared spectrographs were developed; one registers the course of the energy, the other gives directly the spectral course of the absorption relation (ratio ?) of the substance being examined. The spectral range of the first apparatus extends from 1 to 8; that of the second from 1 to 14. Both instruments have rock-salt prisms. In the last few years, these apparatus have been used to investigate the infrared absorption of a number of substances (including paraffinic and aromatic hydrocarbons).

Both of these apparatus were described in the "Zeitscrift für technische Physik". In addition, a recording apparatus was developed for plant analysis using a summing up (integrating) method of infrared absorption. This apparatus serves to record continually the analysis of CO, methane, etc. (Infrared absorption recorder).

Both spectrographs are in the Lenard Institute at Heidelberg. Spectra, calibrating curves, etc. are partly in the Lenard Institute and partly in the salt mine at Heilbronn. Both places are under control of the American authorities.

The standard samples had mostly remained in Oppau, Building Op. 567, where they were partly destroyed in the air raid in December, 1944. The others were stored in the basement of building Op.567. A few samples were stored in the Lenard Institute in Heidelberg. Infrared absorption recorders are in place in various parts of the Oppau and Ludwigshafen plants.

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U.S. GROUP CONTROL COUNCIL

GERMANY

OFFICE OF THE DIRECTOR OF INTELLIGENCE

Butadiene from Hydroaromatics

Reported by:-

IRVIN H. JONES (U.S.)

REPORT ON INVESTIGATION BY THE

TECHNICAL INDUSTRIAL INTELLIGENCE COMMITTEE

Prepared by Direction of

FIELD INFORMATION AGENCY, TECHNICAL (U.S.)

USFET (Main)

APO 757

NEW YORK, N. Y.

Date of Trip: - October 9 - 10, 1945

BUTADIENE FROM HYDROAROMATICS.

Dr. George Niemann of the I. G. Farbenindustrie, A. G. was interrogated at Ludwigshafen, Germany, on October 4, 1945, by the reporter relative to the production of butadiene by the catalytic cracking of hydro-aromatics and particularly cyclohexane and cyclohexene, Dr. Niemann having, according to a previously siezed document, stated at an I.G. colloquiun on May 12, 1944 that, "We have in our work in the I.G. originally worked out a catalytic cracking process involving the cracking of hydrogenated benzene. Tetrahydrobenzene is converted into ethylene and butadiene. Hexahydrobenzene behaves similarly. However, since benzene is not available in Germany in adequate amounts, this process was not further pursued". Dr. Niemann was therefore interrogated in order to learn how far the process had been developed before it was abandoned. He spoke entirely from memory and had no documents immediately available but promised to forward to F.I.A.T. at Hoechst, Germany, a copy of the final report on this work which he felt assured could be located.

Dr. Niemann indicated that the above method of preparing butadiene had been carried through both the laboratory and pilot-plant stages before it was finally given-up in 1928 amongst other reasons because of Germany's relatively limited resources in aromatics to meet other demands. This situation required that other methods be developed to produce butadiene with the result that the now well-known processes for preparing 1, 3 and 1, 4 butanediol were developed employing acetylene as a starting product.

The research and development work on the cracking of hydro-genated benzene was initiated by Dr. Schmidt and continued by Dr. Grossinsky who is no longer employed by I. G. Farben but directs research work of the Gesellschaft fuer Kohlentechnik at Dortmund-Ewing. Dr. Niemann functioned as Dr. Grossinsky's assistant during this development work; Dr. Grossinsky was the author of all the reports.

As developed in the pilot-plant, cyclohexane was cracked, in so far as Dr. Niemann could recollect, at 550° - 600°C. in the vapor phase at about atmospheric pressure in admixture with an equal weight of water-vapor over CaO as the catalyst. MgO was also employed as the catalyst but the results were always about the same when either one or the other of said oxides was employed. In fact, Dr. Niemann said that probably any difficulty-reducible oxide could be used and give substantially identical results because the employed oxide soon became covered with a coating of graphite (glanzkohle) and this was probably the active catalytic agent, the employed oxide thus serving

as a supporting element for the graphite. He further indicated that it was definitely advantageous to assure that a satisfactory coating of graphite had been deposited before drawing any operating conclusions or obtaining optimum results. Any hydrocarbon that is thermally easily decomposible can be employed for the purpose including the products of cracking of hydrogenated benzene themselves.

In the pilot-plant only ordinary iron was used as the material of the shell of the cracking chamber, the surface of the same eventually becoming covered with the required coating of graphite.

The employed hourly liquid space velocity was said by Dr. Niemann to be about 0.2; that is, $\frac{\text{Vol of liquid cyclohexane treated per hr}}{\text{Vol.of Catalyst.}}$

Liquid and vapor reaction-products represent about 95% by wt. of the employed cyclohexane and of this amount approximately 50% by weight is butadiene, the remainder being principally hydrogen, ethylene, and considerable propylene. The butadiene yield was said to be about 75 - 80% of theoretical.

Dr. Niemann indicated that in an economy having an adequate supply of benzene costing not more than about 0.3 RM per kilogram (about 1.0 RM per U.S. gallon) and with advantageous use of the above by-products, production of butadiene by catalytic cracking of hydrogenated benzene, as above, is economically feasible. (In this connection, it is interesting to note that in a relatively recent economic set-up seized at the Buna Works at Hüls, Germany, 84 RM was employed as the equivalent of $56 $\frac{00}{}$ instead of the then current 140 RM, this relationship being stated as representing more nearly their relative values as based on the relative hourly wages of trained workmen in Germany and the United States. This then means that, during the immediate pre-war period, 1.0 RM in Germany had about the same relative purchasing power as $0.66 2/3 in the U.S.A.) Thus, Dr. Niemann says in effect that in an economy where benzene can be procured for $0.66 per U.S. gallon, butadiene production, with utilization of by-products, by catalytic cracking of hydrogenatad benzene is economically practical.

When this method of butadiene manufacture was originally undertaken by the I.G.Farben it was planned to isolate the hydrocarbons and hydrogen by distillation under pressure of about 10 to 15 atmospheres.

Assuming a nominal value for the by-products, it was estimated that the cost of the butadiene by weight is about 1.4 times the cost of the weight of benzene that is required to produce it.

The residual gases after the separation of butadiene from the reaction-products are adopted for conversion to carbon-black of high quality.

Dr. Niemann said that he knew of no process for directly hydrogenating benzene to cyclohexane, said that all such material which the I.G.Farben had used in these investigations was prepared by removal of water from cyclohexanol.

It is requested that any copy of Dr. Grossinsky's report that is received at F.I.A.T. Hoechst, be forwarded to the U.S. Bureau of Mines, Washington 25, D. C.

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U. S. GROUP CONTROL COUNCIL

GERMANY.

OFFICE OF THE DIRECTOR OF INTELLIGENCE

Gasification of Brown-Coal Briquettes in Pintsch-Hillebrand Water-Gas Generators at Wesseling, Germany.

Reported by:-

IRVIN H. JONES (U.S.)

REPORT ON INVESTIGATION BY THE
TECHNICAL INDUSTRIAL INTELLIGENCE COMMITTEE

Prepared by Direction of

FIELD INFORMATION AGENCY, TECHNICAL (FIAT)

OSFET (Main)

APO 757

NEW YORK, N. Y.

Date of Trip:- October 9 - 10, 1945.

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Personnel of Team:-

IRVIN H. JONES (U.S.)

GASIFICATION OF BROWN-COAL BRIQUETTES IN PINTSCH-HILLEBRAND WATER-GAS GENERATORS AT WESSELING, GERMANY

GENERAL

The first large installation of Pintsch-Hillebrand Water-Gas Generators was made at the plant of the Union Rheinische Braunkohlen Kraftstoff A.G., at Wesseling, Germany. This plant was visited between March 10 - 12, 1945, inclusive, by a Team of the Combined Intelligence Objectives Sub-committee and the present reporter was a member of that Team. Reference is here made to CIOS Report XXVIII - 40 describing operations at the Wesseling plant.

For the purpose of obtaining more detailed information relative to the general construction of the Pintsch-Hillebrand generators and especially the type of refractories employed at divers points in their construction, the reporter again visited the Wesseling installation on October 9 - 10, at which time Dr. Ernst Peukert and more particularly Dipl. Ing. Erwin Rose were interrogated, the latter having years' long experience in the operation and development of this novel type of water-gas generator; he had been formerly employed by Julius Pintsch of Berlin, and was in charge of construction of the Wesseling installation and remained there as Superintendent of their gasification operations.

PROPERTIES OF SOLID FUELS ADAPTED FOR USE IN PINTSCH-HILLEBRAND GENERATORS.

During the course of the interrogation, Rose emphasized that these water-gas generators were developed especially for employing brown-coal briquettes formed from such brown coals as have an ash which will not exhibit incipient fusion below about 1290° - 1300°C. This was stressed as a most important criterion for determining whether to choose the Pintsch-Hillebrand type of water-gas generators for operation on a specific brown-coal. Also the lump size or shape of the employed briquettes must be relatively uniform to avoid channeling of the employed Wälzgas. In addition, the briquettes must exhibit a good resistance to rupture; their "Druckfeatigkeit" must be not less than about 140 kg and preferably 180 kg/cm^2. In form, they should preferably be cylindrical in shape, their diameters being about 1.5 times their height which is about 1.75 inches. Successfully employed has been that briquette-product having the shape known in Germany as "Industrie Form". All these requirements must be rigidly observed otherwise this type of water-gas generator is uneconomical of use doubtless in consequence of the features around which it is constructed.

TECHNICAL FEATURES OF THE GENERATOR, ETC.

Inside the generator, there are no moving parts and the gasification process depends for its necessary heat entirely on the sensible heat that is carried by a Wälzgas. In the event of such channeling therefore as can develope when the fuel is of heterogenous sizes, by creating zones of unequal resistance to gas-flow through different fuel-bed portions, there are no mechanical means for agitation to alleviate the condition and charged fuel could pass through the gasification zone of the water-gas set without being gasified. Obviously, a coking or caking coal could not be employed. In consequence of the fact that the sole source of gasification heat resides in the sensible-heat carried by a Wälzgas too low a fusion point of the coal-ash would limit the effective heat carried by a given volume of the Wälzgas. It was stated that if the ash of a given coal cannot withstand a temperature of about 1300°C without becoming tacky, such coal is uneconomical of use in this type of generator and another design of apparatus and type of process should be chosen for its use. This will be more clearly appreciated when it is realized that in the method of gasification employed in these generators, the highly-preheated Wälzgas is first introduced into the generator fuel-bed through a peripheral ring-grate which also accomodates passage of the coal-ash as it flows downwardly into the ash-discharging means; if the coal-ash therefore exhibits a tendency to fuse or to adhere to the ceramics forming the grate-openings and to restrict them, not only is the down-flow of coal impeded but also the inflow of Wälzgas into the gasification section of the generator.

Dipl.Ing.Rose said that the fusion-point of the coal-ash is normally determined by the well-known Baum Test but that an empirical control-test was used at Wesseling and found satisfactory for plant work. This test comprised igniting a quantity of the ash in an open crucible in a muffle-oven wherein the temperature is periodically increased by small amounts and held constant for a time. If the ash remains relatively powdery at about 1300°C, the briquettes from which it is derived, if they are adequately resistant to breakage, are considered satisfactory for use. Although this test does not provide the reducing atmosphere encountered in actual practice, the results obtained by its use are close enough to be determinative for operational purposes.

The composition of the ash of the Rhineland brown-coals employed at Wesseling is given as follows in a volume entitled "Braunkohlen Anhaltszahlen", 4-Ausgabe (1934) published by the Rhenische Braunkohle Syndikat, Köln:-

Ash of the Rhineland Brown Coals.

a) Composition in Percent.

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Sulfate
6	15	5	50	4	20

b) Fusion Point of the Ash - 1300°C.

Resistance to Rupture of the Brown-Coal Briquettes - 140-180 Kg/cm^2.

The briquettes are formed by drying the raw coal to a moisture content between 13-14% by wt., and then compressing the dried coal without added binder at a pressure of about 1500 atm. They are then sufficiently strong for use in the Pintsch-Hillebrand generators.

CONSTRUCTIONAL FEATURES OF THE GENERATOR

As is shown in drawings of the herein-above-mentioned CIOS report, the Pintsch-Hillebrand water-gas generators comprise:-

a. - A low-temperature distillation zone for the charged briquettes;

b. - A gasification zone (generator) for the residual briquettes of the above distillation;

c. - A combustion zone for burning producer-gas and pre-heating regenerators;

d. - A regenerator structure divided into two alternately-operative halves;

all said structural features being disposed the one above the other in the stated sequence. The zones (a) and (b) have separate off-takes for the make-gas and tar.

The distillation zone (a) is about 9.25 feet in diameter exclusive of brickwork; its lower walls are formed of Sicromal shaped as a tube that extends downwardly into the gasification zone (the actual water-gas generator) for a distance about one-third the latter's height. This tube, or insert, serves both to support charged briquettes in the distillation zone at a considerable height above the gasification zone during their distillation and so to direct their flow from the former into the latter as to restrict them to a relatively thin bed providing a relatively high and large gas-space thereabove in said gasification zone.

The gasification zone (b), that is, the water-gas generator itself, is nearly 20 feet in diameter exclusive of brick-work. From the ring-grate, that is formed as a peripheral annulus, to the start of its crown, the gasification zone is about 12.6 feet high. The greater part of the bottom-surface of the gasification - zone is

shaped as a stationary truncated cone that is formed of masonry; its top is about 8.4 feet above the level of the ring-grate and has a diameter of substantially 5 feet. The diameter of the base of said cone is 14.7 feet. The sides of the cone thus direct the briquettes being gasified, in their downward flow-path, outwardly toward the ring-grate through which the Walzgas is introduced into the gasification zone and also through which the ashy residues is withdrawn into a stationary water-sealed annular ash-receiver that is equipped with a rotatable shovel which continuously lifts it over the receiver's outer edge to disposal means.

The ring-grate that is as aforesaid, located at the lower outer periphery of the gasification zone has openings formed by spaced refractory members; the Walzgas is delivered into said zone through said openings from a circular conduit directly therebeneath which communicates by a plurality of horizontal ducts with the combustion zone (c) which in turn is in direct communication with the regenerators (d); these horizontal ducts so communicate with the combustion-zone that they can all be supplied simultaneously with regeneratively-preheated Walzgas.

The so-called combustion-zone (c) is formed as a vertically-disposed cylinder and it communicably connects the regenerators beneath with the gas generator. Its over-all diameter, which is considerably less than that of the gasification - or the regenerator-zone, is about $9\frac{1}{4}$ feet and it is 18.4 feet in height to the base of its crown-arch which also forms a part of the support for the above said truncated refractory cone located in the gas-generator section. A division wall disposed along a diameter of this combustion shaft extends upwardly about three-quarters of its height, thereby dividing it into two substantially semi-circular shafts that are interconnected at their tops in hair-pin fashion and they are each thus in communication with all the ducts supplying the entire ring-grate, so that the same can be supplied optionally with Walzgas preheated in either of those regenerator-sets that individually communicate with one or the other of the semi-circular combustion shafts. This division wall is in effect structurally a vertical extension of a similar wall that also divides the regenerator-space therebeneath also into two-semi-circular halves. This combustion-zone is employed for the combustion of producer-gas whereby the regenerator brick-work and checker-bricks are alternately preheated. Its combustion-products always flow downwardly through the combustion-zone and through the associated regenerators during the latter's preheating period and are not allowed to enter the gasification-zone, otherwise they would introduce nitrogen into the produced water-gas. This is prevented by always carrying a slightly higher pressure in the up-flow (Walzgas) regenerators than in the down-flow ones. Producer-gas and adjacent air-nozzles are supplied in the walls of each semi-circular combustion-shaft, and valve means supply these gases simultaneously from a source therefore to each said shaft in alternation.

The regenerator structure is circular. It has an over-all diameter of about 23¼ feet and a height of 24 3/4 feet including the sole-flues. It is operatively divided, as above indicated, into two halves or semi-circular regenerators each of which is further divided into three equal sections by radially-disposed walls, and all three of these sections of a regenerator-half communicate with the lower part of one of said semi-circular combustion-shafts by individual ports. The two so-formed semi-circular regenerators are operatively disposed by means of appropriate supply-pipes and outlet-pipes, and valves alternately to function as down-flow regenerators when they are preheated by combustion-products flowing from the combustion zone and as up-flow regenerators for preheating Wälzgas when the same is flowing into the gasification zone. Usually the gaseous flow is reversed every 15 minutes. As previously indicated, there are no valve means for separating the two semi-circular combustion-shafts from each other during their alternate operations of carrying combustion-products to the regenerators and Wälzgas to the gasification zone, both operations being continuously in progress simultaneously. By means of an appropriate pressure maintained in the upper part of the hair-pin portion of the combustion-shaft a small amount of Wälzgas is continuously bled into the down-flow combustion-products thereby preventing their entering the gasification zone.

The ring shaped piping that serves both for introducing Wälzgas into the regenerator sole-flues and for carrying away combustion-products therefrom is divided into two half-rings by means of two mechanically-operated Wälzgas valves and of two combustion-products valves whereby, according to their positions, one ring-half can be placed in communication with that pipe containing Wälzgas under pressure while the other ring-half is connected with the combustion-products stack.

The masonry of the gasification zone of the Pintsch-Hillebrand generator is contained in a metallic shell that is suspended at its upper part at points immediately below its cover by bracket members. The stationary ash-receiver is supported on a separate platform therebelow and its inner-wall is in gas-tight contact with the metallic shell also provided for the combustion-zone. The total expansion of the shell for both the regenerators and the combustion-zone is compensated for by an expansion member positioned adjacent the lower part of the latter and just above the annular cover-plate for the regenerators. An expansion member in the piping between the gasification chamber and its waste-heat boiler is also provided and the piping is resiliently supported. Expansion joints permit the masonry walls of the combustion-zone and the regenerators to expand vertically independently of the masonry of the gasification zone and of the crown-arch of the former, said crown-arch being structurally integral with the masonry of the bottom of the gasification space.

REFRACTORIES EMPLOYED AT DIVERS POINTS IN THE
PINTSCH-HILLEBRAND WATER-GAS GENERATORS

REFRACTORIES EMPLOYED AT DIVERS POINTS IN THE PINTSCH-HILLEBRAND WATER-GAS GENERATORS AND THEIR PROPERTIES.

Location	Name of Refractory	Composition	Seger Cone	Resistance to Load. At °C	Resistance to Load. Amount
1. Regenerator Sole Flues	Chamotte B4	Less than 30% Al_2O_3	28/29	1200-1250	2 kg/cm^2
2. Lower Half Regenerator Walls	Chamotte A5	About 30% Al_2O_3	30/31	1300-1520	2 kg/cm^2
3. Upper Half of Regenerator Walls & Lining of Combustion Zone	Silica	About 94.5% SiO_2	32/33	1630	2 kg/cm^2
4. Crown-Arch of Combustion Zone & Inner part of ducts therefrom to Ring-Grate	P.T.22	About 90% SiO_2	33	1450-1500	2 Kg/cm^2
5. Exterior Brick Tiers of Combustion Zone	Porous Silica Bricks.	-	32	1550	1 kg/cm^2

REFRACTORIES EMPLOYED AT DIVERS POINTS IN THE

REFRACTORIES EMPLOYED AT DIVERS POINTS IN THE PINTSCH-HILLERBRAND WATER-GAS GENERATORS AND THEIR PROPERTIES. (Contd)

	Location	Name of Refractory	Composition	Seger Cone	Resistance to Load At °C	Resistance to Load Amount
6.	Intermediate Brick Tiers of Ring-Grate	Alumanit	80% Al_2O_3	40	1550	2 kg/cm²
7.	Top & Bottom Brick Tiers of Ring-Grate & Fuel Gas & Air Nozzle-Bricks of Combustion Zone	Sillimanite	About 60% Al_2O_3	38	1650-1700	2 kg/cm²
8.	Interior of Central Cone of Gasification Zone.	Porous Chamotte	Under 30% Al_2O_3	30	1250-1470	2 kg/cm²
9.	Outer Brick Tiers of Central Cone and Lower Portion of Walls of gasification Chamber	Chamotte a5	A bout 30% Al_2O_3	30/31	1360-1520	2 kg/cm²
10.	Upper Brick Tiers & crown of Gasification Chamber	Chamotte B4	Under 30% Al_2O_3	28/29	1250	2 kg/cm²

OPERATING RESULTS

A. Quantities per Generator

1. - Briquette Through-put:- 71,180 kg/24 hrs = 2966 kg/hr.

2. - Produced Water-Gas:- 5,500 Nm^3hr (0°C; 760 mm Hg) = 1.85 Nm^3 /kg.Briquettes

3. - Wälzgas :- 3850 Nm^3h = 1.30 Nm^3/kg. Briquettes.

4. - Underfiring:-

   a. - Producer Gas - 3,100 Nm^3/h = 1.04 Nm^3kg. Briquettes

   b. - Air :- 6,800 Nm^3/h = 2.29 Nm^3/kg "

5. - Saturation Steam:-
   Contained in Wälzgas from evaporation of Water in the Saturator:-
   1,475 Kg/h = 0.5 kg/kg Briquettes

6. - Steam Additions:-
   To Wälzgas

   a. - From Waste-Heat Boiler at 2 atm - 75%
   b. - " Power Plant 25%

   Total :- 3,100 Kg/h = 1.04 kg/kg Briquettes

7. - Total added Steam to Wälzgas at inlet to Regenerators = 4,575 kg/hr or 1,54 kg/kg Briquettes

ANALYSES OF GASES

	CO_2	CmHn	CO	H_2	CH_4	N_2	Net Heating Value
1. - Watergas	13.7	0.0	28.2	55.9	1.4	0.8	2408
2. - Wälzgas	16.4	0.6	26.8	50.4	5.0	0.8	2634
3. - Schwelgas	17.3	0.8	26.4	48.5	6.2	0.8	2710
4. - Producer Gas	5.9	0.3	38.9	7.1	1.6	46.2	1544

OPERATING TEMPERATURES

1. - Wälzgas:-	Inlet Generator	1270°C
2. - Klargas:-	Outlet "	705°C
3. - "	" Waste-Heat Boiler	240°C
4. - "	" Saturator	72°C
5. - "	" Dust Separator	68°C
6. - Schwelgas	" Schwel Zone	92°C
7. - "	" Tar Separator	84°C
8. - Wälzgas	" Blower	72°C
9. - "	Inlet to Regenerator after addition of 2 atü steam, about	100°C

The propertion of Schwelgas and Klargas in Wälzgas is

a. - Klargas 25% and
b. - Schwelgas 75% ;

Therefore, since the Total Wälzgas employed per kg. Briquettes is 1.30 Nm^3, there enters the generator per kg treated briquettes,

a. - 0.325 Nm^3 Klargas and
b. - 0.975 " Schwelgas.

Since in the low-temperature distillation zone of the generator at a temperature of 650°C, the total gas yield is 0.174 Nm^3/kg briquettes, there consequently enters the low-temperature distillation zone from the gasification zone 0.975 - 0.174 = 0.801 Nm^3 Klargas/kg Briquettes treated. This functions in effect as a Spülgas. The total quantity of Klargas leaving the generator's gasification zone is therefore

1.85 Nm^3	Watergas
0.325 "	Klar and Wälzgas
0.801 "	Spülgas
2.976 Nm^3/ Kg. Briquettes Treated.	

In order to effect adequate distillation of the briquettes, a temperature of about 90°C must be maintained at the outlet of the low-temperature distillation zone. The amount of Spülgas directed therethrough depends on the water-content of the briquettes, which is normally 15% and the volume of Schwelgas varies accordingly. Since for a desired through-put the quantity of Wälzgas must remain constant,

the proportion of Klargas and Schwelgas in the "Walzgas varies

for Klargas between 40% to 15%, and
" Schwelgas " 60% to 85%.

In the producer-gas plant employed to furnish the fuel-gas for preheating the regenerators of the water-gas generators, the through-put of briquettes per producer is 30 tons/24 hours when adding steam to the air-blast and is 38 tons/24 hours when adding CO_2 to the blast. The producer-gas yield is 2.3 Nm^3/kg briquettes.

Engineering Drawings:-

In series G, reel 13, of Microfilms taken by the Liquid Fuels and Lubricants Group there will be found copies of the following drawings:-

Item 57, Partial Elevational View and Partial Vertical Section through the Pintsch-Hillebrand Water-Gas Generators at Wesseling, Germany, showing Construction and Support of the Generator Shell and the Arrangement of the Brick-Work; and

Item 58, Partial Plan View of Top of Regenerators and Gas-Piping and Partial Horizontal Sections through the Regenerator Brick-Work of the above Pintsch-Hillebrand Water-Gas Generators.

These Microfilms have been deposited with the Secretary of Interior, Interior Building, Washington 25, D. C. and also with the Ministry of Fuel andPower, London, England.

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FIAT FINAL REPORT NO. 488

POLYMERIZATION OF ETHYLENE

APR 1946
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TIIC L. I. & L. S-C.

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

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

FIAT FINAL REPORT NO. 488

8 November 1945

POLYMERIZATION OF ETHYLENE

BY

NORMAN W. KRASE

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

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PERSONNEL OF TEAM

Norman W. Krase, Civ.,TIIC

POLYMERIZATION OF ETHYLENE

Earlier reports have given information on German developments on the polymerization of ethylene to solid polymers. In the report "Investigation of German plastics plants, Item No. 9 and 22, File No. XXIX - 62, CIOS, by Kline, Rooney, Crawford, Love, and Curtis, a description of the Gendorf plant is given. A flow-sheet for production of Lupolen H is included. In the report "Miscellaneous Chemicals, I. G. Farbenindustrie A. G., Ludwigshafen and Oppau", Item No. 22, File No. XXVII-85, CIOS, by Kern, Murray, and Sudhoff, a description of the development work on a semi-works scale is given. A third location for Lupolen production was Zweckel where a 10-15 ton per month plant for production of Lupolen N was operated, following methods developed at Ludwigshafen.

Additional material presented in this report is mainly a progress report prepared by Dr. Hopff and Dr. Goebel on "Ethylene Polymerization", I. High Pressure Polymerization" dated February 15, 1943. A translation and the original German follows.

I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, LUDWIGSHAFEN

INTERMEDIATE PRODUCTS GROUP

26th MEETING OF SYNTHETIC COMMITTEE

REFERAT LUDWIGSHAFEN

Dr. Hopff and Dr. Goebel

Z. K. - Laboratory Z

On

Ethylene Polymerization

I. High Pressure Polymerization

February 15, 1943

Ludwigshafen/Rhine, February 15, 1943

ETHYLENE POLYMERIZATION

1. High Pressure Polymerization: As was stated in our report of the 24 "Kuko-Sitzung" of November 20, 1940, "On the High Pressure Polymerization of Ethylene", polythenes have a series of properties that deserve the strongest consideration. In addition to the outstanding electrical properties which permit extensive application in the cable field, there are the resistances to acids, alkalies and solvents and the compatibility with Oppanol to be mentioned. In addition, ethylene is the cheapest polymerizable compound which in normal times can be obtained in unlimited amounts.

The properties of polyethylene depend markedly on the degree of polymerization. The low molecular weight products are known to be valuable lubricating oils (ss öle). Other products are hard, waxy bodies, the high molecular weight pfoducts are white, paraffin-like masses which permit themselves to be drawn into elastic sheets with good fatigue value.

ICI, whom we have to thank for discovering the solid polyethylenes, has produced the types shown in the following table:

Our own work was therefore directed toward production of ICI products. Because the ICI patents gave no description of the equipment employed it was necessary to develope this from the ground up. It was clear to us from the beginning that only a continuous process could be considered because only a relatively small fraction of the ethylene polymerized and the majority of the gas must be recirculated.

Following this our efforts were directed toward developing procedures which were not dependent on ICI. Because the foreign patents covered conditions over 500 atm., the necessary directions were guided accordingly.

Experimentally it was possible to polymerize ethylene to solid products in the presence of organic solvents. The background of the experimental equipment installed at Zweckel (10 tons per month) extends over almost two years. The product is a waxlike, low molecular weight body manufactured under the name "I. G. Wax A", by the plant and by section K as "Lupolen N".

I. G. WAX A (Lupolen N)

PURITY OF ETHYLENE

The early batch autoclave experiments with ethylene containing acetylene led to the conclusion that a small contamination with acetylene lowers the yield. During the further development of the experiments, before the completion of the 10 ton/month plant, it was found that small amounts of acetylene, between 0.1% and 0.3%, had no noteworthy effect on the polymerization.

Different ethylenes, recovered from coke oven gas at Holten (near Zweckel), from Saargas at Oppau, and the acetylene-free ethylene at Schofen, gave practically the same results in yield.

The average compostion of the gas is:

98%	C_2H_4
1-2%	C_2H_6
0.5-1%	N_2
0.1-0.3%	C_2H_2

IMPROVEMENT OF THE CONTINUOUS TECHNIQUE - EXPERIMENTS AT 200 ATM.

The process depended on a method of operation that required pumping a catalyst suspension of benzoyl peroxide in methanol with a special pump or intensifier at 200-300 atm. into a solution of ethylene in methanol and carrying out the reaction at 110°-120° in a tube coil. Following the reaction, the bulk of polyethylene was removed in a separator. The unconverted ethylene was purified from aldehydes by an alkali scrubber and used again; the methanol was recirculated after distillation. With more experience it was found that pumping a concentrated suspension of benzoyl peroxide in an ethylene-methanol solution was unsuitable for long continued operation; the fine crystals permitted only a short life for the pump valves.

Equally unsuitable were modified intensifiers. The catalyst was finally powdered in methanol and this dispersion brought to the suction side of the methanol pump with a circulating pump. The methanol injector pumped the dispersion without difficulty to 200 atm. In this way the catalyst was introduced into the polymerization system and a long life of valves attained.

PLANT FOR THE PRODUCTION OF 10 TONS PER MONTH OF I. G. WAX A (Lupolen N) AT ZWECKEL (Fig. 1).

The plant works according to the following scheme (Fig.2): Ethylene is conducted, by means of a blower, from a gasometer via a washing vessel filled with caustic soda solution and a drying tower to a compressor. This compressor compresses the gas over a buffer flask to 200 atm. Simultaneously a dispersion of 1% strength of benzoylsuperoxide in methanol is conveyed from the catalyst preparation vessel, past the suction side of a high pressure pump, by means of a centrifulgal pump. The dispersion is comprised to 200 atm. by the pump and reaches the polymerization system through a mixing nozzle, together with the compressed ethylene.

A hot water circulation heating serves as heating for the polymerization system from110°-120° and for good heat exchange (1000 Kcal./kg of wax are set free). The hot water circulation heating works according to the reflux system. By introducing the polymerization tube into the lower third of the vertical separator (Fig. 3), good separation of the wax from the specific lighter mixture of ethylene-methanol is obtained. The wax is removed at the bottom of the separator. The non-reacted ethylene, the methanol, and the wax still dissolved in this mixture are tangentially expanded through an expansion valve into a vessel. Here methanol and wax particles are precipitated. Owing to the cooling to 40-50° caused by expansion, the wax is obtained in the form of a fine suspension in methanol. This suspension runs via a siphon into the column where the methanol is distilled off and returned by a condenser into the catalyst preparation vessel. The benzoic acid still dissolved in the wax of the column is blown off with nitrogen after drawing it off. The ethylene returns to the circulation after mixing with fresh gas. The apparatus works without difficulties. Occasional troubles during the starting period, especially in recycling, showed a brownish color of the products and a heavy decrease of the yield. These drawbacks were caused by leakage of the centrifugal pump for the alkali which sucked minor quantities of air into the apparatus.

Those parts of the apparatus coming into contact with benzoylsuperoxide and, after reaction, with benzoic acid, are made of V_2A-steel or aluminium. The capacity of the plant is at 200 atm. working pressure: 615 kg of wax/day; at 250 atm. working pressure: 10-15% higher.

The circulation-methanol is composed of:

Methanol	87%
Water	10.9% +)
Acids (benzoic)	0.7 milliequivalent per liter
Water-insoluble oil	0.5 vol.%
Dry Residue	0.14 g per liter
Oxygen of peroxide	not detectable

The m.p. of the wax is 105-110°. The oxygen content lies between 0.7-1.3%. The active oxygen introduced by benzoylsuperoxide, calculated as to the yield of wax, is, however, only 0.4-0.5%. Further experiments must show, in how far the benzoic acid is connected with the higher oxygen content of the polyethylene. I. G. wax A turned out to be very good in practice both as addition to Oppenol B 200 as well as a high quality wax for the production of polishing wax and show cream.

+) The benzoylsuperoxide contains 25% of water for safety reasons.

MAXIMAL PRESSURE POLYMERIZATION.

For the use as plastics, especially for insulating cables, only high polymeric polyethylenes come into question. For the time being, these must be produced with high pressure (over 600 atm. excess pressure). This method depends on patents of the I.C.I. The corresponding product of the I.C.I. has been found as insulating materiel of wireless transmitting devices of shot-down Wellington bombers of the R.A.F.

IMPROVEMENT OF THE CONTINUOUS SEMI-TECHNICAL TESTS AT 100 ATM.

The method of polymerization is based upon the fact that ethylene with an oxygen content of 0.05-0.1% as catalyst is pressed to 1000-2000 atm. and polymerized to polyethylene in a tube coil between 180-220°. The residual gases, after introducing fresh oxygen, are purified from chiefly formaldehyde and oil fogs in a caustic soda solution wash and reconducted to polymerization after compensating the loss of gas by fresh gas.

The first experiments carried out in horizontal tubes with an inside diameter of 3 or 6 mm. respectively, yielded very good products with K-values of 70-80 and folding numbers (Faltzzahlen) up to 1000, as corresponding to a molecular weight of 15000-20,000. Continuous running, however, could not be obtained since the tubes were too narrow and were blocked after some time. On the suggestion by Dr. Hopff, we started to arrange the tubes vertically and to fit each descending leg with a wax separator. This has the advantage that the tough polyethylene is easily separated in the descending tubes and that the particular reaction zones can be detected. In order to prevent blocking in the rising tubes, a smaller cross section of the tubes was chosen on suggestion of Dipl. ing. Reichert (3-6 mm), thus allowing a higher velocity of flow. But even with this method, the tubes were blocked after some time. In spite of this we believe the vertical arrangement to have a good chance on account of space considerations and improved separation.

It was further tried, with the seme negative result, to introduce the gas to be polymerized into a vertical double tube. Polymerization was carried on in the outer tube of 16 mm. diameter, while after separation of the polymerizate the hot residual gases were supposed to pre-heat the inflowing gas to which it went upwards in counter-current in the inner 8 mm. tube.

Only intubes with a constant inner diameter of 10 mm. continuous running without blocking and pressure differences within the tubes could be obtained. In a 5 m long vertically rising tube, preliminary polymerization is effected with a hot water circular heating at 180-190°. Final polymerization is done by cooling a similarly long descending tube to 90-100°. Cooling with circulating water is necessary in order to quickly remove the great reaction heat and to prevent decomposition of the products into carbon and hydrogen. After polymerizationone can either expand directly from 1000-0 atm., or gradually from 1000-200 atm. and then from 200-0 atm. If expanded directly, the polyethylene is obtained in form of a powder, because the polymerizate solidifies at once by cooling, which occurs when the non-polymerizied ethylene is expanded. In the case of gradual expansion to 200 atm., the polymerizate separates as a liquid in a heated 10-liter separator, except for 0.1% of lower polymeric polyethylenes, which are drawn off by residual gases and collected in another light vessel.

Here we shall say something about the machines for compressing ethylene and about the lubricant problems involved.

COMPRESSORS AND LIQUID PUMPS FOR ETHYLENE.

For the experiments of half technical scale, a compressor aggregate (Fig. 4) with a capacity of 20 n-cu.m. per hour was established. It consists of a preliminary compressor of 0-350 atm., and additional compressor of 350-1000 atm. and another additional compressor of 1000-2000 atm. (Fig.5) of the firm Hofer. These compressors were built for nitrogen. In order to be able to run them likewise for compressing ethylene, whose compressibility differe from that of nitrogen, they were fitted with adjustable drives. Furthermore a liquid pump (Fig. 6) was built in for pumping the same amount of liquefied ethylene (crit. pressure 51 atm., crit. temp. 10°) to 1000-2000 atm. and fitted with an adjustable drive.

For the plant of 10 tons per month 2 preliminary compressors with a total capacity of 265 n-cum./h of 0-300 atm. were established, an additional 2-stage compressor (Fig. 7) of the Maschinenfabrik Esslingen of 300-4000 atm. and 3 liquid pumps (Fig. 8) of the Dept. for High Pressure Tests, Ludwigshafen to 2000 or 4000 atm., respectively. Since the additional compressor was constructed for nitrogen, only pressures up to 1100 atm. could be obtained with ethylene owing to its different compressibility. With the liquid pumps, however, liquified ethylene could be pumped without difficulty to 2000-4000 atm. How far this method will prove to be effective in practice on the long run is under examination at present.

LUBRICATING PROBLEMS OF THE COMPRESSORS AND LIQUID PUMPS.

It can be said in general as to the experiences with lubricating ethylene compressors and liquid pumps, that normal mineral oil is not good as a lubricant under high pressure, because a great part of the oil is not separated but remains dissolved in the ethylene.

On account of these oil-dissolving qualities of highly compressed ethylene the packings of the pistons leak very soon, thus causing the compressors to blow off.

For this reason 1,3 - butyleneglycol was utilized with good success as a lubricant for the smaller compressor aggregates

(3 cu.m. or 8 cu.m./h to 200 atm.). Its lubricating property, however, did not suffice for the larger Hofer compressors (20 cu.m./h). Instead of that, experiments were made with ABG-oil (i.e. adipic acid butylene glycol). Use of this slightly acid oil could not be recommended for continuous running of the compressors, because the acid number steadily increased on account of the high compression temperatures during operation and the compressors were likely to be corroded. Very soon the use of a new synthetic lubricant from trimethylolpropane and ethylene oxide was started. This oil, delivered under the name of Öl LK 2200, was a great success for medium compressor aggregates.

Only in the tests with larger machines (250 n-cu.m./h) it was found that, especially with pressures over 1000 atm., in spite of various installations in the 8-liters separators, a good separation of oil could not be warranted anymore. That is why glycerol or methylglycerol (= butanetriol) had to be used as lubricants. Both of them are separated without difficulty owing to their insolubility in ethylene and their high density:

The liquid pump for compressing liquefied ethylene was built as selflubricating device. Since this construction did not stand the test, the lubricant was added to the liquid ethylene at the suction side of the pump (Fig. 6) by means of a Bosch-oiler and, (together with it) brought to 1000 sufficient to render the packings tight.

A 10-TONS-MONTH PLANT FOR THE PRODUCTION OF LUPOLEN H (Fig.9)

Ethylene is conducted from a gasometer by means of a blast to the suction side of a compressor. The compressor compresses the gas over a buffer-flask to 300 atm. The ethylene at 300 atm. is compressed by an additional compressor to 1100 atm. and conducted to a polymerization coil (Fig. 10). It can also be liquified in a refrigeration apparatus and pumped to 4000 atm. with a liquid pump. In the first part of the polymerization coil consisting of 10 mm tubes, the reaction is started with a hot-water circulation heating of 200° and completed in 16 mm. tubes while cooling at 100°. 10 mm. tubes as polymerization tubes get blocked after some time. After the reaction has finished the Lupolen-ethylene mixture is expanded to

200 atm. over a gradual expending valve into a separator. The Lupolen still containing dissolved gases at this pressure is expanded into a degasifying vessel and drawn off here in liquid state. The non-reacted gas runs continuously over an expanding valve into another separator, in which wax particles still carried along are deposited. The oxygen used during the reaction is conducted into these non-reacted gases via a throttle and mixed well ina lye wash with the remaining gases. Simultaneously the lye wash purifies the gas from aldehydes, especially formaldehyde and traces of oily products. An overflow valve keeps the lye wash at a constant pressure of 1.5 atm. to save a drying tower, for preventing a too far reaching saturation of the residual gases with water. The residual gases are conducted to the suction side of the blast and, together with fresh gas, returned to the polymerization. The plant runs without difficulties. Its output amounts to 550 kg per day at an effective yield of ethylene of 93-96%, while a single use of the gases yields 8-15%.

PROPERTIES OF THE LUPOLENS DEPENDENT OF PRESSURE, TEMPERATURE, OXYGEN CONTENT OF ETHYLENE, AND OF THE VELOCITY OF FLOW.

The quality of the products expressed by molecular weight and elasticity (folding number, "Falzzahl") rises to the disadvantage of the yield with higher pressure, a polymerization temperature lying as low as possible, and a low oxygen content of the ethylene. The oxygen content, however, shall not go below a certain degree, as otherwise so-called netted polyethylenes are obtained showing no definite m.p. between 110-115°, but a softening point of more than 115°. These netted polyethylenes may likewise be obtained in polymerizing ethylene without oxygen.

The velocity of flow within the tubes may, according to the experiences made hitherto, not lie below 20 cm/sec., since the highly polymeric products decompose by local accumulations of heat. Such products with bad elasticity (folding number 2 - 5) were delivered under the name of Lupolen S. Completely unelastic, hard, and brittle polyethelenes are formed at 700-800 atm., temperatures of 250-300° and an oxygen content of 0.5%. These products differ from I. G. Wax A (Lupolen N) insofar that I. G. wax A contains still smaller amounts of soft waxes and is contaminated with traces of benzoic acid.

Tentative experiments at 500-600 atm. and polymerization temperatures higher than 300° with ethylene showing an oxygen content of 1 - 2% yielded vaseline-like substances.

The oxygen content of the Lupolenes fluctuates between 0.2 - 0.4%, according to the degree of polymerization.

The folding number of the products obtained hitherto in the 10-tons monthly plant is 45, corresponding to an average mol. weight of 9000. According to preliminary experiments it is easily possible to considerably raise the mol. weight as soon as the pumps and compressors can run continuously at 1500-2000 atm.

Lupolen H is almost insoluble in all solvents. Only at 70° a noticeable solubility is to be seen in e.g. benzene, xylene, and carbontetrachloride. It is not attached by acids, alkalies, and ultraviolet light. Owing to its excellent electric properties (tg:0.0005 at 50 cycles) it is used with preference in the cable industry.

By adding Lupolen to Oppanol B 200 a substance is obtained which can easily be drawn on the roll into foils. The resistence to tearing is double as compared with Oppanol B 200.

SAFETY DEVICES AND MEASURING INSTRUMENTS

1. Safety valves up to 4000 atm., blowing off at excess pressure.

2. Contact manometers up to 3000 atm. turning off the compressors at excess pressure.

3. Safety against explosion accidents. Between the buffer flasks for 2000 atm. and the polymerization system a safety device against explosion accidents was fitted (suggested by Dr. Weissweiler) which shall check an eventual backing of the explosion wave into the compressors. The safety device consists of a tube of 1 m. length and 30 mm diameter, which is packed with V_2A steel cuttings as much as possible. The large surface of the cuttings cause a momentary carrying off of the high explosion temperature and stops the decomposition of the ethylene.

4. Device for continuous measuring of the oxygen content in ethelene. The device which was constructed by Dr. Weidner is based upon the easy oxidation of NO to NO_2. The coloration of the gases occurring according to the oxygen content of the ethylene is recorded by 2 selenium cells in a tube and serves as measure for the oxygen content in the ethylene.

5. Thermoelements for 4000 atm. fitted in the polymerization tubes control the course of the polymerization reaction.

SUMMARY

1. The half technical method for continuous polymerization of ethylene in methanol at 200 atm. was improved and a plant with a capacity of 10 tons per month for the production of I. G. wax A (Lupolen N) was established at Zweckel. The plant runs without difficulties and yields 615 kg/day. I. G. wax A proved very successful in practice as filling (casting) substance for the cable industry, as addition to Oppanol B 200 and as polishing or shoe cream.

2. The method of continuous polymerization of ethylene in half-technical-scale at 1000-2000 atm. was further improved and a plant yielding 10 tons per month was erected at Ludwigshafen. This plant works well and yields 550 kg/day. Lupolen H was a success for the cable industry on account of its excellent electric properties and its elasticity.

3. Moreover, a less elastic Lupolen was obtained at 900 atm., which was delivered under the name of Luplen S.

4. For polymerization, ethylene of 98% strength, such as produced at the various I. G. plants, can be utilized without further purification. The effective yield of ethylene amounts to 93-96%.

Abschrift/Sch.

I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, LUDWIGSHAFEN

Zwischenprodukten - Gruppe

26. Sitzung der Kunststoff-Kommission

Referat Ludwigshafen

Dr. Hopff und Dr. Goebel

Z.K.-Laboratorium Z

über

Äthylen-Polymerisation

I. HOCHDRUCKPOLYMERISATION

15.Februar 1943

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I.G.Farbenindustrie A.G.
Z.K.-Laboratorium Z

Ludwigshafen/Rhein, 15.2.43

ÄTHYLEN-POLYMERISATION.

I. Hochdruckpolymerisation.

Wie bereits in unserem Bericht zur 24. Kulo-Sitzung vom 20.11.40 "Über die Hochdruck-Polymerisation von Äthylen" berichtet wurde, haben die Polyäthylene eine Reihe von Eigenschaften, die stärkste Beachtung verdienen. Neben den ausgezeichneten elektrischen Daten, die einen grossen Einsatz auf dem Kabelgebiet ermöglichen, sind vor allem die Beständigkeit gegen Säuren, Alkalien und Lösungsmittel, sowie die gute Verträglichkeit mit Oppanol hervorzuheben. Ausserdem stellt das Äthylen die billigste polymerisationsfähige Verbindung dar, die in normalen Zeiten in fast unbegrenzten Mangen zugänglich ist.

Die Eigenschaften der Polyäthylene sind stark vom Polymerisationsgrad abhängig. Die niedrig-molekularen Produkte sind bekanntlich hochwertige Schmieröle (SS-Öle), die mesokolloiden Produkte harte, wachsartige Körper, die hochmolekularen Produkte weisse, paraffinähnliche Massen, die sich zu elastischen Folien mit guten Falzzahlen durchziehen lassen.

Die I.C.I., der wir die Erfindung der festen Polyäthylene verdanken, hat bisher folgende, in nachstehender Tabelle aufgeführten Typen entwickelt.

Unsere eigenen Arbeiten waren zunächst darauf gerichtet, die Produkte der I.C.I. nachzustellen. Da in den Patenten der I.C.I. keinerlei Angaben über die verwendete Apparatur enthalten sind, war es notwendig, diese von Grund auf zu entwickeln. Es war uns von Anfang an klar, dass nur ein kontinuierliches Verfahren in Frage Kommen kann, da nur ein verhältnismässig kleiner Anteil des Äthylens polymerisiert und daher die Haptmenge des Gases im Kreislauf geführt werden muss.

Darüberhinaus war unser Bestreben darauf gerichtet, Verfahren zu entwickeln, die von der I.C.I. unabhängig waren. Da die fremden

Schutzrechte sämtlich auf Drucke über 500 atü angestellt sind, so war die Arbeitsrichtung gegeben. Tatsächlich gelang es, Äthylen in Gegenwart organischer Lösungsmittel zu festen Produkten zu polymerisieren. Die aufgrund dieser Arbeiten in Zweckel erstellte Versuchsanlage für 10 Moto läuft nun schon fast 2 Jahre. Das Produkt ist ein wachsähnlicher, niedrigmolekularer Korper, der unter dem Namen "I.G.-Wachs A" von der Farbensparte und als "Lupolen N" von der Abteilung K vertrieben wird. Im folgenden soll zunächst die Entwicklung dieses Produktes beschreiben werden.

I.G.-WACHS A (Lupolen N).

Reinheitsgrad des Äthylens.

Die früheren diskontinuierlichen Autoklavenversuche mit Acetylenhaltigem Äthylen führten zu dem Ergebnis, dass kleine Verunreinigungen an Acetylen die Ausbeute herabsetzien. Während der weiteren Ausarbeitung der Verfahren, vor allem bei der Inbetriebnahme der kontinuierlichen 10 moto- Anlage, stellte sich heraus, dass geringe Mengen an Acetylen 0,1 bis 0,3% keinen nennenswerten Einfluss auf die Polymersiation haben.

Die verschiedenen Äthylene, gewonnen aus dem Zechengas in Holten bezw. Zwecke, aus dem Saargas in Oppau und das acetylenfreie Hydrieräthylen vonSchkopau zeigten in der Ausbeute praktisch dieselben Resultate.

Die durchsahnittliche Zusammensetzung der Gase ist:

98% Äthylen
1 - 2% Äthyn
0,5 - 1% Stickstoff
0,1 - 0,3% Acetylen

VERBESSERUNGEN DER KONTINUIERLICHEN TECHNIKUMS-VERSUCHE BEI 200 ATM.

Das Verfahren beruth nach dem eingangs erwähnten Bericht darauf, dass man einen Kontaktbrei aus Methanol-Benzoylsuperoxyd mit

einer geeigneten Pumpe oder einem Drucksteigerer bei 200-300 Atm. in eine Lösung von Äthylen in Methanol pumpt und in einer Rohrschlange bei 110-120° zur Reaktion bringt. Nach der Reaktion setzt sich das entstandene Polyäthylen zum grössten Teil in einem Abscheider ab. Das nicht umgesetzte Äthylen wird in einer Natronlaugewäsche von den Aldehyden gereinigt und wieder eingesetzt, während das Methanol erst nach der Destillation in den Kreislauf zurückgeht.

Bei der weiteren Ausarbeitung dieses Verfahrens zeigte sich, dass das Pumpen eine konzentreirten Benzoylsuperoxyd-breiss in die Äthylen-Methanol-Lösung für einen Dauerbetrieb ungeeingnet war, da abgesehen von den damit verbundenen Gefahren der feinkristalline Brei nur eine kurze Lebensdauer der Pumpenventile zuliess.

Ebensowenig waren alternierend arbeitende Drucksteigerer, deren Kolben jeweils mittels einer kleinen Bosch-Pumpe mit Methanol gegen einen Druck von 200 Atm. arbeiten müssen zur Förderung des Kontaktbreies geeignet. Ein grosser Teil der Kontakt-Kriställchen setzte sich nach kurzer Zeit in den Drucksteigerern ab und liess keine gleichmässige Förderung des Kontaktbreies zu.

Nun wurde der Kontakt in dem gesamten, zum Einsatz kommenden Methanol fein verteilt und diese Dispersion mit einer Kreiselpumpe an der Saugseite der Methanolpumpe vorbeigeführt. Die Methanolpumpe pumpt die Dispersion ohne Schwierigkeiten auf 200 Atm. Damit gelang es, den Kontakt gleichmässig verteilt in das Polymerizations system einzuführen und eine grosse Lebendauer der Ventile zu erreichen.

10 MOTO- ANLAGE ZUR HERSTELLUNG VON I.G.-WACHS A (Luvolen N) IN ZWECKL (Abb.1).

Die Anlage arbeitet nach folgendem Schema (Abb.2): Aus einem Gasometer wird Äthylen mit einem Gebläse durch eine Natronlaugewäsche und einen Trockenturm einem Kompressor zugeführt. Der Kompressor komprimiert das Gas über eine Pufferflasche auf 200 Atm. Gleichzeitg wird eine 1%ige Dispersion von Benzoylsuperoxyd in Methanol aus dem Kontaktenrührtopf mit einer Kreiselpumpe an der Saugseite einer Hochdruckpumpe vorbeigeführt. Die Dispersion wird von der Pumpe auf 200 Atm. gedrückt und gelangt über eine Mischdüse mit dem komprimierten Äthylen in das Polymerisationssystem.

Als Heizung des Polymerisionssystems auf 11-120° und zur Erzielung eines guten Wärmeaustausches (es werden 1000 Kcal./kg Wachs frei) dient eine Heisswasserumlaufheitzung. Sie arbeite nach dem Gegenstromprinzip. Durch Einführung des Polymerisationsrohres in das untere Drittel des stehenden Abscheiders (Abb.3) wird eine gute Trennung des Wachses von dem spezifisch leichteren Äthylen-Methanol-Gemisch erreicht. Das Wachs wird am Boden des Abscheiders abgelassen. Das nicht ungesetzte Äthylen, das Methanol und in diesem Gemisch noch gelöste Wachse werden über ein Entspannungsventil tangential in ein Gefäss entspannt. In diesem Gefäss werden Methanol und Wachsanteile niedergeschlagen. Infolge der bei der Entspanung auftretenden Abkühlung des Gemisches auf 40-50o fällt das Wachs fein suspendiert in Methanol an. Diese Suspension geht über einen Syphon in die Kolonne, in der das Methanol ausgetrieben und über einen Kühler in den Kontaktanruhrtopf zurückgeführt wird. Die in dem Kolonnenwachs noch gelöste Benzoesäure wird nach dem Ablassen mit Stickstoff ausgeblasen. Das Äthylen geht nach Aufnahme von Frischgas in den Kreislauf zurück.

Die Apparatur arbeitet ohne Schwierigkeiten. Gelegentliche Störungen während der Anfahrperiode, vor allem beim Kreisfahren der Anlage, traten durch Braunfärbung der Produkte bei starkem Absinken der Ausbeute ein. Diese Mängel waren auf Undichtigkeiten der Laugekreiselpumpe zurückzuführen, die kleine Luftmengen in die Anlage einsaugten.

Die teile der Anlage, die mit Bezoylsuperoxyd und nach der Reaktion mit Benzoesäure in Berührung kommen, sind in V2A-Stahl bezw. Aluminium ausgeführt.

Die Leistung der Anlage ist bei 200 Atm. Betriebsdruck 615 kg. Wachs pro Tag, bei 250 Atm. 10-15% höher.

Das Kreislaufmethanol setzt sich zusammen aus:

Methanol	87%
Wasser	10,9% 1)
Säuren (Benzoesäure)	0,7 Milliäquivalent i.Ltr.
Wasserunlösliches Öl	0,5 Vol.%
Trockenrückstand	0,14 g i.Ltr.
Peroxydsauerstoff nicht nachweisbar	

Der Schmelzpunkt des Wachses ist 105-110°.

---

1. Das Benzoylsuperoxyd enthält aus Sicherheitsgrunden 25% Wasser.

Der Sauerstoffgehalt liegt zwischen 0,7 und 1,3%. Der durch das Benzoylsuperoxyd eingeführte aktive Sauerstoff, benzogen auf die Wachsausbeute, ist aber nur 0,4-0,5%. Inwieweit hier die Benzoesäure an dem höheren Sauerstoffgehalt des Polyäthylens beteiligt ist, müssen weitere Untersuchungen ergeben.

I.G.Wachs A hat sich in der Praxis ausser als Zusatzmittel zu Oppanol B 200 als hochwertiges Wachs zur Herstellung von Bohnermassen und Schuhcreme sehr gut eingeführt.

Höchstdruck-Polymerisation.

Für die Verwendung als Kunststoff, insbesondered für die Isolation von Kabeln, kommen nur hochmolekulare Polyäthylene, die vorläufig bei hohen Drucken (über 600 atü) hergestellt werden müssen, in Frage. Diese Arbeitsweise ist von den Schutzrechten der I.C.I. abhängig. Das entsprechende Material der I.C.I. ist in abgeschossenen Wellington-Bombern der R.A.F. als Isoliermaterial der Funksendeeinrichtung nachgewiesen worden.

Verbesserung der kontinuierlichen Technikums-Versuche bei 1000 Atm.

Das Verfahren der Polymerisation beruht darauf, dass man Äthylen mit einem Sauerstoffgehalt von 0,05 - 0,1% als Kontakt auf einen Druck von 1000-2000 Atm. bringt und in einer Rohrschlange zwischen 180-220° zu Polyäthylen polymerisiert. Die Restgase werden nach Zuführung frischen Sauerstoffes in einer Natronlaugewäsche hauptsächlich von Formaldehyd und Ölnebel befreit und nach Ergänzung des Gasverlustes durch Frischgas der Polymerisation wieder zugeführt.

Die zunächst durchgeführten Polymerisationsversuche in liegend angeordneten Rohren mit einer lichten Weite von 3 bezw. 6 mm brachten

zwar bei 1000 Atm. bereits sehr gute Produkte mit K-Werten von 70-80 und Falzzahlen bis zu 1000, entsprechend einem Molekulargewicht von 15,000-20,000; aber ein kontinuierlicher Betrieb liess sich nicht erreichen, da die Rohre zu eng waren und sich nach einiger Zeit zusetzten.

Auf Vorschlag von Herrn Dr. Hopff gingen wir dazu über, die Rohre senkrecht anzuordnen undjeden absteigenden Schenkel mit einem Wachsabscheider zu versehen. Dies hat den Vorteil, dass das zähe Polyäthylen in den absteigenden Rohren leicht abgeschieden wirk und die einzelnen Reaktionszonen gut feststellbar sind. Zur Verhinderung von Verstopfungen in den aufsteigenden Rohren wurde auf Vorschlag von Herrn Dipl. Ing. Reichert hier ein kleinerer Rohrquerschnitt (3-6 mm) gewählt, um eine erhöhte Strömungsgeschwindigkeit zu erzielen. Doch auch bei diesser Fahrweise setzten sich die Rohre nach einiger Zeit zu. Trotzdem halten wir die senkrechte Anordnung aus Gründen des Platzbedarfes und der besseren Abscheidung für aussichtsreich.

Weiter wurde mit demselben negativen Erfolg versucht, das zu polymerisierende Gas in ein senkrechtes Doppelrohr einzuführen. In dem ausseren 16 mm - Rohr wurde polymerisiert, während nach der Abscheidung des Polymerisates die heissen Restgase in dem inneren 8 mm Rohr im Gegenstrom aufwärts geführt als Vorheizung der einströmenden Gase gedacht weren.

Erst in Rohren mit einer durchgehenden lichten Weite von 10 mm konnte ein kontinuierlicher Betrieb ohne Verstopfung und ohne Durchunterscheid in den Rohren erzielt werden. Dabei wird in einem 5 m langen senkrecht aufsteigendem Rohr mit einer Heisswasser-Umlaufheizung bei 180-190° anpolymerisiert und unter Kühlung eines ebenso langen absteigenden Rohres auf 90-100° auspolymerisiert. Die Kühlung mit umlaufendem Wasser ist notwendig, um die grosse Reaktionswärme schnell abzuführen und um eine Zersetzung der Produkte in Kohlenstoff und Wasserstoff zu verhindern.

Nach der Polymerisation kann entweder stufenlos von 1000 auf 0 Atm. entspannt werden oder stufenweise von 1000 auf 200 Atm. und dann von 200 auf 0 Atm. Bei der stufenlosen Entspannung fällt Polyäthylen in Pulverform an, da das Polymerisat durch die Abkühlung, die beim Entspannen des nicht polymerisierten Äthylens eintritt, augenblicklich erstarrt. Durch die stufenweise Entspannung auf

200 Atm. scheidet sich das Polymerisat in einem geheizten 10 Ltr.-Abscheider bis auf 1,1% niedriger polymerer Polyäthylene, die von den Restgasen mitgerissen und in einem weiteren drucklosen Gefäss aufgefangen werden, flüssig ab.

In diesem Zusammenhang soll einiges über die aufgestellten Maschinen zur Kompression von Äthylen und über die dabei aufgetauchten Schmierprobleme gesagt werden.

Kompressoren und Flüssigkeitspumpen für Äthylen.

Für die Technikums-Versuche ist ein Kompressorenaggregat (Abb.4) mit einer stündlichen Leistung von 20 n-cbm aufgestellt worden. Es besteht aus einem Vorkompressor von 0-350 Atm., einem Zusatzkompressor von 350-1000 Atm. und einem weiteren Zusatzkompressor von 1000-2000 Atm. (Abb.5) der Firma Hofer. Die Kompressoren waren für Stickstoff gebaut worden. Um sie in gleicher Weise zur Kompression von Äthylen, dessen Kompressibilität stark von der des Stickstoffs abweicht, fahren zu können, wurden sie mit regelbarem. Antrieb versehen.

Ausserdem wurde eine Flüssigkeitspumpe (Abb.6) zum Pumpen der gleichen Menge verflüssigten Äthylens (krit.Druck 51 Atm., krit. Temp- 10°) auf 1000-2000 Atm. mit regelbarem Antrieb eingebaut.

Für die 10 moto - Anlage wurden zwei Vorkompressoren mit einer Gesamtleistung von 265 n-cbm/Std. von 0 - 300 Atm. aufgestellt, ein zweistufiger Zusatzkompressor (Abb.7) der Maschinenfabrik Esslingen von 300-400 Atm. und drei Flüssigkeitspumpen (Abb.8) der Abteilung für Hochdruckversuche Ludwigshafen auf 2000 bezw. 4000 Atm. Da der Zusatzkompressor für Stickstoff gebaut worden war, konnten mit Äthylen infolge der anderen Kompressibilitäts-Verhältnisse nur Drucke bis 1100 Atm. gefahren werden. Dagegen wurde mit den Flüssigkeitspumpen verflussigtes Äthylen ohne Schwierigkeiten auf 2000 bis 4000 Atm. gepumpt. Wie weit sich dieses Verfahren in der Praxis für einen Dauerbetrieb eignet, wird zur Zeit noch geprüft.

Schmierprobleme der Kompressoren und Flüssigkeitspumpen.

Über die bisherigen Erfahrung zur Schmierung der Äthylen-Kompressoren und Flüssigkeitspumpen ist allgemein zu sagen, dass normales Mineralöl als Schmiermittel unter hohen Drucken nicht geeignet ist, da ein grosser Teil des Oles nicht abgeschieden wird,

sondern im Äthylen gelöst bleibt. Infolge dieser ölösenden Eigenschaften von hochkomprimiertem Äthylen werden sehr bald die Packungen der Kolben undicht, sodass die Kompressoren abblasen.

Es wurde daher für die kleineren Kompressorenaggregate (3 cbm bezw. 8 cbm/Std. auf 200 Atm.) mit gutem Erfolg 1,3-Butylenglykol zur Schmierung angewandt. Seine Schmierfähigkeit reichte aber für die grösseren Hofer-Kompressoren (20 cbm/Std.) nicht aus. An seiner Stelle wurden zunächst Versuche mit dem Öl A.B.G, (Adipinsäure-Butylenglykol) gefahren. Ein Einsatz dieses schwach sauren Öles war aber für einen Dauerbetrieb der Kompressoren nicht ratsam, da sich die Säurezahl infolge der hohen Kompressions-Temperaturen während des Betriebes ständig steigerte und die Gefahr bestand, dass die Kompressoren angegriffen werden. Es wurde nun sher bald dazu übergegangen, ein neues synthetisches Schmieröl aus Trimethylolpropan und Äthylenocyd zu verwenden. Dieses Öl, das unter der Bezeichnung Öl LK 2200 ausgegeben wird, hat sich bei den mittleren Kompressoren-aggregaten sehr gut bewährt.

Erst bei den Versuchen mit grösseren Maschinen (250 ncbm/Std.) stellte sich heraus, dass vor allem bei Drucken über 1000 Atm., trotz verschiedener Einbauten in die 8 Ltr. - Abscheider, eine einwandfreie Ölabscheidung nicht mehr gewährleistet war. Es musste deshalb mit Glycerin oder Methylglycerin(= Butantriol) geschmiert werden. Beide Schmiermittel werden infolge ihrer Unlöslichkeit in Äthylen und ihrer hohen Dichte ohne weiteres abgeschieden.

Die Flüssigkeitspumpe zur Komprimierung von verflüssigtem Äthylen war selbst-schmierend gebaut worden. Da sich diese Konstruktion nicht bewährte, wurde das fehlende Schmieröl an der Saugseite der Pumpe (Abb.6) durch einen Boscholer dem flüssigen Äthylen zugegeben und mit diesem auf 1000-2000 Atm. gebracht. Die hierdurch erreichte Benetzung des Plunschers mit Schmieröl reichte zur Abdichtung der Packungen aus.

10 MOTO - Anlage zur Herstellung von Lupolen H (Abb.9).

Äthylen wird aus einem Gasometer mit einem Gebläse auf die Saugseite eines Kompressors gebracht. Der Kompressor komprimiert das Gas über eine Pufferflasche auf 300 Atm. Das Äthylen von 300 Atm. wird mit einem Zusatzkompressor auf 1100 Atm. komprimiert und in eine Polymerisationsschlange (Abb.10) geleitet. Es kann aber auch in

einer Kälteanlage verflüssigt und mit einer Flüssigkeitspumpe auf 4000 Atm. gepumpt werden. In dem ersten Teil der Polymerisationsschlange, die aus 10 mm - Rohren besteht, wird die Reaktion mit einer Heisswasserumlaufheizung von 200° eigeleitet und dann in 16 mm - Rohren unter Kühlung bei 100° zu Ende geführt. 10 mm - Rohre als Polymerisationsrohe verstopfen sich nach einiger Zeit. Nach der Reaktion wird das Lupolen-Äthylen-Gemisch über ein Stufen-Entspannungsventil in einen Abscheider auf 200 Atm. entspannt. Das Lupolen, das unter diesem Druck noch gelöste Gase enthält wird in einen Entgasungstopf entspannt und hier flüssig abgelassen. Das nicht umgesetzte Gas geht kontinuierlich über ein Entspannungs ventil in einen weiteren Abscheider, in dem noch mitgerissene Wachsteilchen haften bleiben. In diese nicht umgesetzten Gase wird der während der Reaktion verbrauchte Sauerstoff über eine Drossel zugegeben und in eiber Laugewäsche mit den Restgasen gut vermischt. Gleichzeitig reinigt die Laugewäsche das Gas von entstandenen Aldehyden, vorzugsweise Formaldehyd und von Spuren öliartiger Produkte. Ein Überströmventil hält die Laugewäsche zur Einsparung eines Trockenturmes konstant unter einem Druck von 1,5 Atm., um eine zu grosse Sättigung der Restgase mit Wasser zu verhindern. Die Restgase werden auf die Saugseite des Gebläses geführt und erneut mit Frischgas der Polymerisation zugeleitet. Die Anlage arbeitet ohne Störungen. Ihre Leistung ist 550 kg/Tag bei einer effektiven Äthylenausbeute von 93 - 96%. Während bei einem einmaligen Durchsatz der Gase mit einer Ausbeute von 8 - 15% gefahren werden kann.

Eigenschaften der Lupolene in Abhängigkeit von Druck, Temperatur, Sauerstoffgehalt des Äthylens und Strömungsgeschwindigkeit.

Die Güte der Produkte, die durch das Molekulargewicht und durch die Elastizität (Falzzahl) ausgedrückt wird, steigt auf Kosten der Ausbeute mit höherem Betriebsdruck bei möglichst niedriger Polymerisationstemperautr und geringem Sauerstoffgehalt des Äthylens. Dabei soll der Sauerstoffgehalt ein bestimmtes Masz nicht unterschreiten, da andernfalls sog. vernetzte Polyäthylene erhalten werden, die keinen definierbaren Schmelzpunkt von 110-115°, sondern einen Erweichungspunkt über 115° zeigen. Diese vernetzten Polyäthylene können ebenso bei der Polymerisation von Äthylen ohne Sauerstofferhalten werden.

Die Strömungsgeschwindigkeit innerhalb der Rohre darf nach den bisherigen Erfahrungen nicht unter 20 cm/sec. liegen, da durch

örtliche Wärmestauungen die hochmolekularen Produkte zerfallen. Solche Produkte mit schlechter Elastizität (Falzzahl 2 - 5) wurden unter der Bezeichnung Lupolen S ausgegeben.

Vollkommen unelastische, harte und spröde Polyäthylene bilden sich bei 700-800 Atm., Temperaturen von 250-300° und einem Sauerstoffgehalt von 0,5%. Diese Produkte unterscheiden sich von I.G.-Wachs A (Lupolen N) dadurch, dass I.G.Wachs A noch kleinere Mengen Weichwachse enthält und mit Spuren Benzoesäure verunreinigt ist.

Testversuche bei 500-600 Atm. und Polymerisationstemperaturen über 300° mit Äthylen von einem Sauerstoffgehalt von 1 - 2% ergaben Vaselin-artige Produkte.

Der Sauerstoffgehalt der Lupolene schwankt je nach dem Polymerisationsgrad zwischen 0,2 und 0,4%.

Die Falzzahl der bisher in der 10 Moto- Anlage erhaltenen Produkte ist 45, entsprechend einem mittleren Molekulargewicht von 9000. Nach den Vorversuchen ist es ohne weiteres möglich, das Molekulargewicht noch wesentlich zu steigern, sobald die Pumpen und Kompressoren im Dauerbetrieb bei 1500 - 2000 Atm. arbeiten können.

Lupolen H ist in sämtlichen Lösungsmitteln fast unlöslich. Erst bei 70° tritt beispielsweise in Benzol, Xylol, Tetrachlorkohlenstoff merkliche Löslichkeit auf. Es wird von Säuren, Alkalien und ultraviolettem Licht nicht angegriffen. Infolge seiner hervorragenden elektrischen Eigenschaften (tg. 0,0005 bei 50 Perioden) wird es vorzugsweise in der Kabelindustrie eingesetzt.

Durch Zusatz von Lupolen zu Oppanol B 200 erhält man ein Material, das sich auf der Walze einwandfrei zu Folien ziehen lässt und dessen Reissfestigkeit doppelt so gross ist wie bei Oppanol B 200.

Sicherheitsvorrichtungen und Meszinstruments.

1. Sicherheitsventile bis 4000 Atm., die bei Überdruck abblasen.

2. Kontakt-Manometer bis 3000 Atm., die die Kompressoren bei Überdruck abstellen.

3. Explosionsschutz. Zwischen der Pufferflasche für 2000 Atm. und dem Polymerisations-System ist auf Vorschlag von Herrn Dr. Weissweiler ein Explosionsschutz eingebaut, der bei etwaigen Zersetzungen ein Zurückschnellen der Explosionswelle in die Kompressoren verhindern soll. Der Schutz besteht aus einem 1 m langen und 30 mm weiten Rohr, das möglichst dicht mit V2A-Spänen bepackt ist. Die grosse Oberfläche der Späne bewirkt eine momentane Ableitung der hohen Explosionstemperatur und bringt die Zerseztung des Äthylens zum Stillstand.

4. Gerät zur kontinuierlichen Sauerstoffmessung im Äthylen. Das Gerät, das von Herrn Dr. Weidner entwickelt wurde, beruht auf der leichten Oxydation von NO zu NO_2. Die dabei je nach dem Sauerstoffgehalt des Äthylens auftretende Trübung der Gase wird in einem Rohr von zwei Selenzellen festgestellt und dient als Masz für den Sauerstoffgehalt im Äthylen.

5. Thermoelemente für 4000 Atm., die in die Polymerisationsrohre eingebaut sind und den Verlauf der Polymerisationsreaktion überwachen.

Zusammenfassung:

1. Das Technikumsverfahren zur kontinuierlichen Polymerisation von Äthylen in Methanol bei 200 Atm. wurde verbessert und eine 10 Moto Anlage zur Herstellung von I.G.-Wachs A (= Lupolen N) in Zweckel erstellt. Die Anlage arbeitet ohne Schwierigkeiten und leistet 615 kg/Tag. I.S.- Wachs A hat sich in der Praxis als Vergussmasse für die Kabelindustrie, als Zusatz zu Oppanol B 200 und als Bohnermasse bezw. Schuhcreme sehr gut bewährt.

2. Das Verfahren zur kontinuierlichen Polymerisation von Äthylen im Technikumsmaszstab bei 1000-2000 Atm. wurde weiter vervollständigt und eine 10 Moto - Anlage in Ludwigshafen erstellt. Die Anlage arbeitet einwandfrei und leistet 550 kg/Tag. Lupolen H hat sich wegen seiner hervorragenden elektrischen Eigenschaften und wegen seiner Elastizität in der Kabelindustrie sehr gut eingeführt.

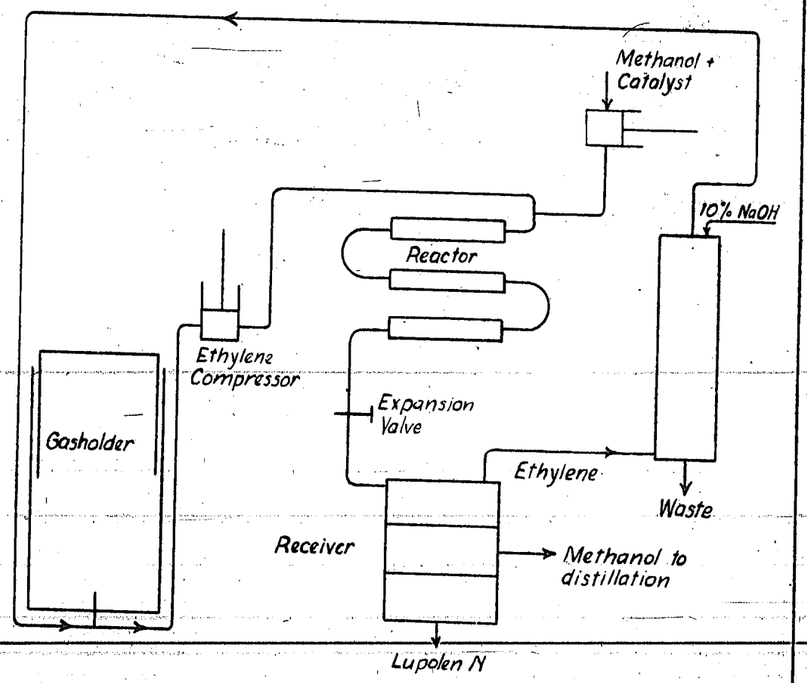
3. Darüber hinaus wurde bei 900 Atm. ein weniger elastisches Lupolen erhalten, das unter der Bezeignung Lupolen S ausgegeben wurde.

4. Zur Polymerisation kann 98% iges Äthylen, so wie es an den verschiedenen Stellen der I. G. erzeugt wird, ohne weitere Reinigung eingesetzt werden.

Die effektive Äthylenausbeute beträgt 93-96%.

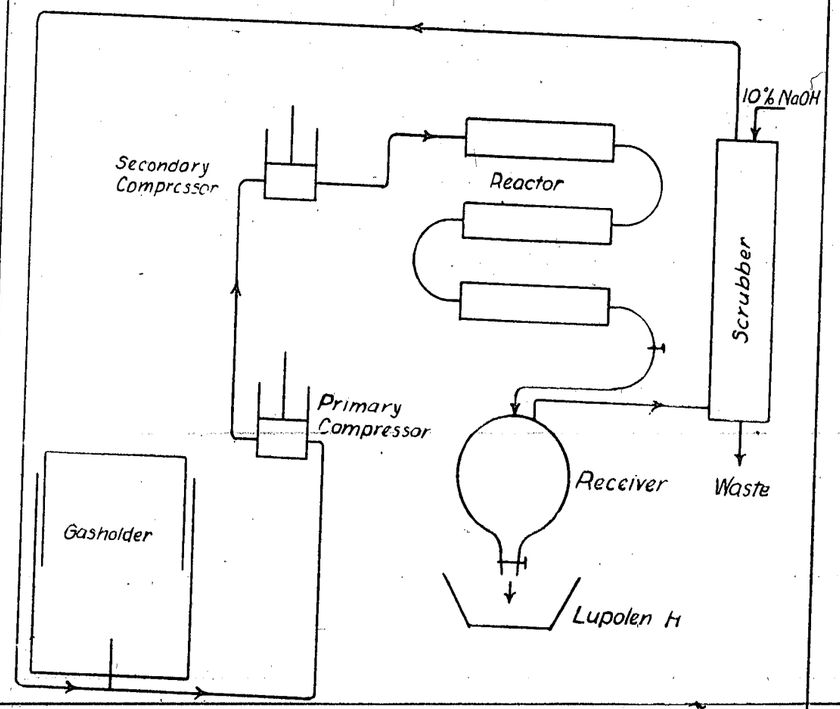
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LUPOLEN N

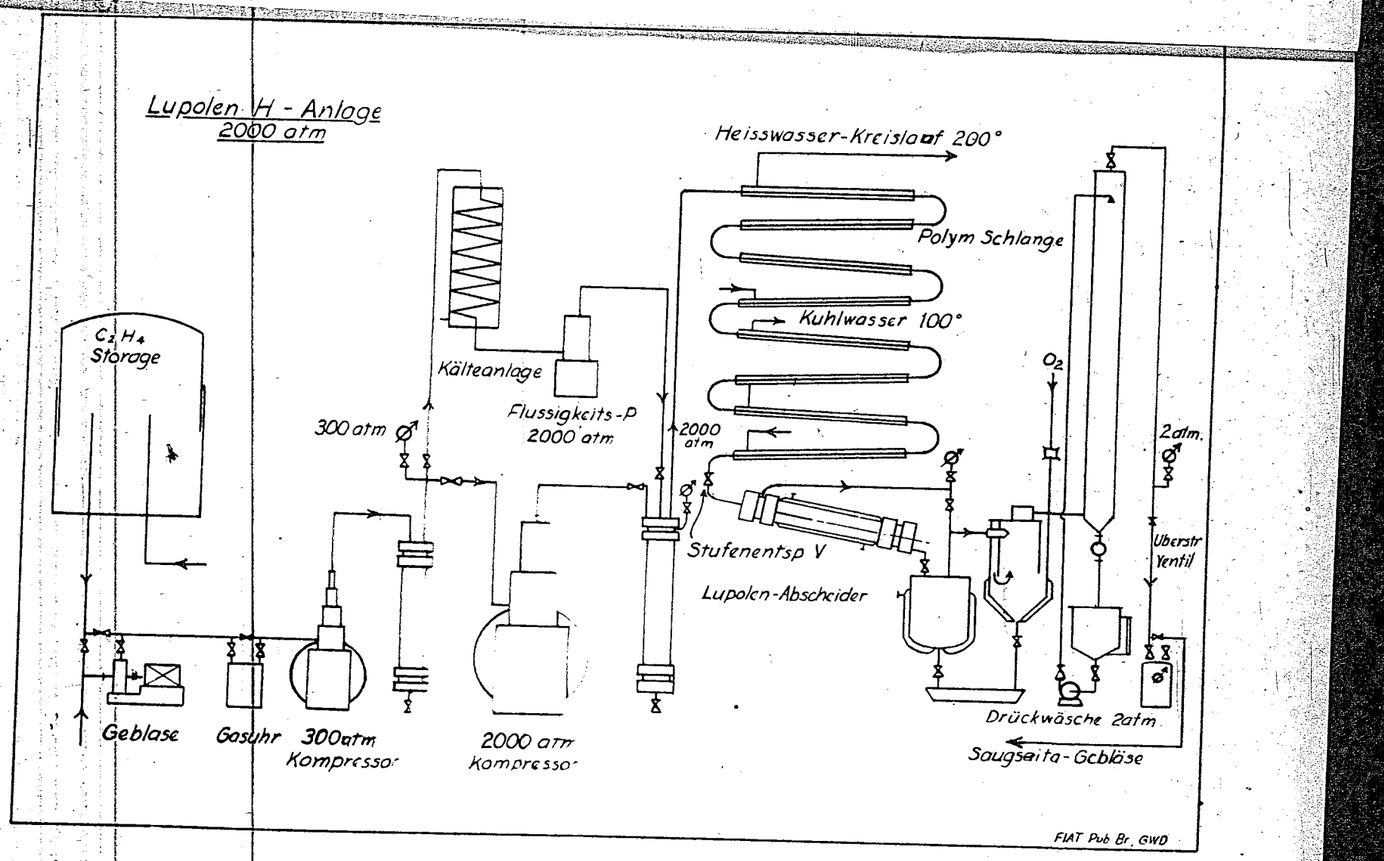


FIAT Pub. Br., GWD.

LUPOLEN H



FIAT Pub. Br., GWD.


Lupolen H - Anlage
2000 atm
Heisswasser-Kreislauf 200°
Polym Schlange
Kuhlwasser 100°
C_2H_4 Storage
Kälteanlage
Flussigkeits-P 2000 atm
300 atm
2000 atm
O_2
2atm.
Uberstr Ventil
Stufenentsp V
Lupolen-Abscheider
Geblase
Gasuhr
300atm Kompressor
2000 atm Kompressor
Drückwäsche 2atm
Saugseite-Gebläse
FIAT Pub Br. GWD

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FIAT FINAL REPORT NO. 606

UNCLASSIFIED

OPPANOL (POLYISOBUTYLENE) MANUFACTURE AT THE OPPAU FARBEN WORKS

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

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JOINT INTELLIGENCE OBJECTIVES AGENCY

WASHINGTON, D. C.

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

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

FIAT FINAL REPORT NO. 606 — 12 December 1945

OPPANOL (POLYISOBUTYLENE) MANUFACTURE AT THE OPPAU FARBEN WORKS

BY

J. W. LIVINGSTON

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY TECHNICAL

7 p.

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Target: Oppanol plant of I.G.Farben at Oppau
Date of Visit: June 21, 1945
Personnel Interviewed: Dr. Mannhart, chemist formerly in charge of operations, visited at Heidelberg June 28.
Dr. Haarer, who knew some of the operations.
Meister Schmidt, who knew the plant intimately.

Summary

1. Oppanol B, or polyisobutylene production was started in 1939 at the Oppau plant at the rate of 50 tons per month and reached 400 tons per month in 1945. Expansions planned would have pushed production to 1200 tons per month.

2. Oppanol was used as a natural rubber substitute, and was superior to rubber in being unaffected by light.

3. Manufacture begins with isobutyl alcohol produced from hydrogen and carbon monoxide in high pressure autoclaves.

4. Purified isobutyl alcohol is converted to isobutylene in the presence of a catalyst, under four atmospheres pressure, and controlled to 365°C by mercury vapor.

5. Liquid ethylene is produced for use in maintaining a very low temperature later in the process. Its production is by dehydration of alcohol in equipment similar to that used to produce isobutylene.

6. The isobutylene is polymerized in liquid ethylene using boron trifluoride as catalyst, at a reaction temperature of -80 to -100°C. The reaction is strongly exothermic.

7. The reaction takes place as the boiling mixture moves along a continuous metal band in a long cylinder. At the end of the 4-5 meter band the isobutylene is 98-99% polymerized and is removed by a wiper.

8. The spongy material is kneaded to remove ethylene and then extruded as finished Oppanol.

9. Various grades or molecular weights of Oppanols are produced by poisoning the catalyst with diisobutylene in varying amounts, along with isobutyl alcohol and methanol.

10. One of the most troublesome problems in the process is keeping the transparent plastic windows in the enclosing cylinder clean enough to allow observing and controlling the reaction. When visibility through these windows gets too low from the splashing of the boiling liquid the unit has to be shut down for 30 minutes to allow flushing out with nitrogen, and cleaning.

Introduction

The manufacture of Oppanol B, or polyisobutylene, was first started in 1939 at the Oppau plant under the supervision of Dr. Gutterock, with capacity operations limited to 50 tons per month. Dr. Mannhart credits the late Dr. Otto of Standard Oil (New Jersey) as the discoverer of the isobutylene polymer called Vistanex in America.

Oppanol was used in Germany as a natural rubber substitute for many purposes: for manufacturing cable, for the impregnation of fabrics in gas masks against poisonous gases, for adhesives and for waterproofing railroad tunnels. Oppanol was superior to natural rubber for many of these applications because it is not affected by light.

After inquiry concerning vulcanizable polymers, it was learned that the men at the Oppanol plant knew nothing about this work. Dr. Mannhart did say however that some Oppanol vulcanizable polymer in 100 kilo lots had been made in the technical laboratory by a Dr. Theobald, using 1-2% of isoprene based on the isobutylene. The research did not apparently get far enough along to try the polymer containing isoprene on a continuous band unit as used in the plant.

Production Rate and Planned Expansions

The Oppanol plant at Oppau adjoins the Ludwigshafen plant so closely that the two form practically a continuous unit. The present installation has a maximum capacity of 400 tons per month when sufficient isobutyl alcohol is available. The gas compressors used for isobutylene and ethylene are said to be the limiting factor in output. Because of this limitation, all four of the polyisobutylene reactors in the plant cannot be operated at their rated capacity of 150 tons a month each.

To meet the large war uses demand for polyisobutylene, a second Oppanol plant was built at Frosa in Anhalt, 80 km. from Magdeburg. This plant was to provide its own isobutylene but to get isobutyl alcohol from the Leuna works. Its capacity was 300 tons of Oppanol per month. A third plant, the most modern of the three and based upon latest Oppanol operating experience, was

to be built in Heydebreck near Obersohlesien. This plant was to provide its own isobutyl alcohol and isobutylene and would have a monthly capacity of 500 tons. The plant was not erected although the isooctane part (from isobutylene over isobutyl alcohol) was said to be in operation. Both Frosa and Heydebreck were in the Russian zone of occupation and were not visited.

The total scheduled production from the three plants was 1200 tons of Oppanol per month.

Manufacturing Processes

(1) Isobutylene from Isobutyl Alcohol

The Oppanol plant produces isobutylene for the polymerization starting from isobutyl alcohol. Isobutyl alcohol is produced at Oppau by the reaction of hydrogen and carbon monoxide in high pressure autoclaves.

The isobutyl alcohol is vaporized in a steam-heated unit at 120 to 130°C. and the vapor is then passed over a catalyst in a steel tubular converter (tubes 25 to 30 mm. in diameter 2½ meters long) maintained at a temperature of 365°C. and a pressure of four atmospheres. The converter is heated by means of mercury vapor supplied from a mercury boiler at a lower level;-the condensed mercury refluxes to the boiler. Catalyst is inside the tubes and the mercury vapor outside. The catalyst in the tubes is in the form of broken pieces 4 to 5 mm. in diameter. There are four dehydration converters, each with a separate mercury heating unit. Only about 7 liters (or 90 kg) is used in each system.

The gas leaving the reactor goes to a cooler, then to a separator, and then to a storage tank (at 3 atmospheres pressure). From the storage tank the liquid isobutylene is pumped through a vaporizer to a column 1.1 meters in diameter and 20-24 meters high, containing about 60 to 70 plates, the feed entering at the fifth or seventh plate from the bottom of the tower. The tower operates at 5 atmospheres pressure and the temperature at the top of the column is about 66°C. The isobutylene goes overhead and the bottoms from the column go to a second fractionating column. The overhead from this column is called "gasolene" and goes into gasolene products not used at Oppau. The bottoms are also sent away for oil uses. The isobutylene obtained is 98-100% pure. Impurities may be traces of isobutyl alcohol.

(2) Ethylene from Alcohol

Liquid ethylene for maintaining the very low temperature in isobutylene polymerization is produced by dehydration of alcohol, using the type of equipment described for the production of isobutylene. The temperature in the ethylene reactor is 380°C. The ethylene gas goes directly to a gasometer, then to the compressor, and then is dried and purified by distillation.

It was stated that ethylene was prepared from alcohol instead of other sources to produce the purer material essential for the isobutylene polymerization. However, at Ludwigshafen, the purest ethylene for ethylbenzene use was supplied from Oppau and derived from Saar illuminating gas. This ethylene required much less aluminum chloride in the ethylbenzene reactions. Perhaps the alcohol dehydration ethylene purified by distillation results in a better material for use in the Oppanol reaction. This ethylene was said to be practically 100% pure.

The operation of the mercury heating system was fairly satisfactory but Oppau had had some trouble with dirt in the mercury. Dirt is recovered about every 3 months by removing all mercury from the system, letting it settle and skimming the iron oxide and other impurities off the top.

There are four compressors in the plant, two for ammonia refrigeration, two for ethylene liquifaction and purification. Each ethylene compressor has a capacity of 1600 cubic meters per hour.

(3) Polyisobutylene

Isobutylene is polymerized in liquid ethylene solution using boron trifluoride (BF_3) as catalyst. The reaction is conducted at -80 to -100°C., the boiling point of the mixture of isobutylene and ethylene. The reaction is continuous and is conducted on a moving metal band enclosed in a long cylinder. The band in passing over rollers is formed into a trough onto which the liquid materials are run. Much trouble was experienced with the steel band in the first Oppanol work due to the bending over the rollers at the very low temperature. These difficulties have now been entirely overcome.

The first liquid mixture added to the band trough is isobutylene and ethylene. The second liquid added is a mixture of ethylene and boron trifluoride. These two streams are mixed on the band which is kept stirred by the gas evolution from the boiling liquid heated by the polymerization reaction which is strongly exothermic. The band moves at the pace of a slow walk and the total travel is 4 - 5 meters. By the time the mixture on the band has reached the end of horizontal travel, where it is removed by a wiper, the isobutylene is 98-99% polymerized.

The last of the ethylene is removed by a kneader which works the "sponge" of polyisobutylene. The polymer is then extruded continuously from the end of the reactor into open containers, in the form of finished Oppanol.

The gas evolved from the boiling liquid by the polymerization reaction heat is a mixture of ethylene, isobutylene and boron trifluoride. The BF_3 is removed by contacting the gas with calcium oxide (CaO). The mixture of ethylene and isobutylene remaining is compressed, cooled and fractionated to separate the ethylene and isobutylene which are both returned to the reactor.

The four polymerization units installed at the Oppau plant each take a feed of 300 kg. isobutylene per hour. Ninety-eight percent of this weight is obtained as Oppanol polymer. The output averages 150 tons per month per unit, if not limited by compressor capacity and including outage for repair time and servicing. The length of the run obtained before the polymerizer has to be shut down depends on the isobutylene purity. If the product is very good, the run length obtained is 15 to 20 hours. Average production runs are 12 to 15 hours long. When spots are formed on the transparent plastic windows in the enclosing cylinder above the moving band, the unit must be shut down for cleaning because the progress of the polymerization can no longer be observed. It is from this visual control that the amount of catalyst used and the band speed is regulated. When the unit is stopped it is flushed out with nitrogen, the windows are cleaned and any other needed adjustments made. The whole operation from shutdown to startup can be done in 30 minutes.

It seems rather extraordinary that some device to clean the windows cannot be devised or the opening in the cylinder be raised high enough above the band so

that the splashing of boiling liquid does not throw polymer on the windows. However, Dr. Mannhart stated that all efforts to solve the problem along these and other lines have so far failed.

(4) Controlling Grades of Oppanol Produced

Oppanols with a number of different ranges of molecular weight are made. The highest molecular weight is 200,000 and others are 150,000, 100,000 and 50,000. The plant operators stated that the molecular weight can be controlled to plus or minus 5,000, but Dr. Mannhart stated that when aiming at a 200,000 molecular weight polymer the resulting material varies from 180,000 to 230,000. When a 150,000 molecular weight polymer is desired, the actual material runs from 130,000 to 180,000. The molecular weight can be reduced as low as 3,000 and at this point the material is a liquid. The molecular weight is measured from the viscosity in isooctane. For this purpose 20 mg. of polymer is dissolved in 20 cc of isooctane at 50°C.

The different grades of Oppanol with lower molecular weights are produced by poisoning the catalyst. For this purpose, diisobutylene is added to the isobutylene feed tank along with 0.01% isobutyl alcohol and 0.005% methanol. To make 150,000 molecular weight material 150 cc. of diisobutylene is added to each cubic meter of isobutylene and proportionately increased amounts are used for lower molecular weight polymers. To obtain Oppanol with a molecular weight of 200,000, 0.005% methanol and 0.01% isobutyl alcohol is added but no diisobutylene is used.

The boron trifluoride used averages 0.3% based on the isobutylene. The amount of BF_3 material to be added is graduated so that the reaction is finished at the end of the moving band. One looks through the window to see if the polymerization is finished and if not, one can still see liquid on the band. In order to obtain a satisfactory reaction a pure ethylene must be used. If propylene is used in place of ethylene, a liquid polymer is formed.

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FIAT FINAL REPORT NO. 388

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COUNTING DEVICES GERMANY

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MAY 1946
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OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 388

October 9, 1945

COUNTING DEVICES,

GERMANY,

BY

G. L. MANKE

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

10p.

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Personnel of Investigating Team

G. L. Manke

FOREWARD

CLASSIFICATION OF FIELD

Since the field of counting devices embraces a great variety of types and designs and each group has its own peculiar type of construction, it is advisable to divide it into separate classes. The investigator deemed it fitting to set up the following classification:

Group A - General Purpose Counters
Group B - Small Instrument Counters
Group C - Gasoline & Oil Dispensing Counters

Group A embraces the general line of counters most commonly used on production machinery to indicate the number of pieces produced on a machine or the work, revolutions for example, that the machine is doing. In this group belong such counters that have a predetermining feature whereby the machine is stopped, a signal or alarm is given, etc., and printing attachments for counters.

Group B includes the small counters that are used on watt-hour meters, gas meters, speedometers, etc., where due to their size and functional characteristics, for example, low operating torque, they are manufactured differently than those in Group A.

Group C includes a specialized line of counters such as dial type with or without totalizer, computing type, etc. Here again the designs, method of manufacture and applications differ from the other two groups.

SUMMARY OF FINDINGS

The investigations have very definitely established that the German counter manufacturing industry has brought forth nothing novel and has actually been dormant during the war period. During the war period their productions of counters were low, making only such counters as actually were needed for the war. In some cases some of these manufacturers made closely related items such as air-log counter for V-1 bomb (Exhibits 34 & 35), or those with die casting and molding facilities simply made other die cast or plastic parts. The two most prominent manufacturers with casting and molding equipment

also continued to make figure wheels and pinions only which were purchased by concerns that made a complete apparatus into which they built a counter assembly.

In the general purpose line the salient item of interest is the preponderance of quick reset for reset counters whereby the figure wheels are reset to zero by moving a reset lever through an angle of about 45°. The extensive use of thermo-plastic material (Trolitul) for figure wheels and pinions for use in small instrument counters is outstanding in that group. Counters for gasoline and oil dispensing apparatus are still of the old dial type for over 75% of the pumps made in Germany. Consequently, this field revealed nothing new.

One target, Scheidt & Backmann, did manufacture a pump having a figure wheel type counter in which the figures were 10 cm. high. This same target also made a limited quantity of pumps with a computer that they purchased from Kienzle Apparate, Villingen Schwaizwald. This was purely on a trial basis and future manufacturing of same was not encouraged since such a unit cost considerable more than the old dial type.

TARGET NOTES

In addition to the targets referred to in this report other targets were called on which were listed in the Reichsamt Industrial Directory as counter manufacturers. This included the following:

Carl Liehe, Drontheimerstr 21, BERLIN
Mierisch & Co., Baumschulen Weg, Kiefholzstr 177/78, BERLIN
Frieda Kallmann, Chausseeste 54, BERLIN
Alfred Raestel, Amsterdamerstr 25, BERLIN
Zaehler, Klosterstr 69, BERLIN

These targets did not manufacture counters except in a very limited way. They were predominantly counter repair businesses and occasionally made special counting apparatus by buying the counter proper from one of the leading counter manufacturers and making the necessary attachments and assembly required for the application. This may be considered to have been done on a model making basis only.

In the course of getting all targets that made counter assemblies the concern Sueddeutsche Nummerier (Dr. HERMANN DOLD) Tuttlingen/Wurtt came forth. This target was investigated and they simply made stamping and printing devices. They purchased all their figure wheel castings from L. Loewe (See Exhibit 21 & 22).

GENERAL PURPOSE COUNTERS

The following targets manufactured this line of counters:

Irion and Vosseler, Schwenningen a. Neckar/Wurtt. (Exhibit I)
Schlenker Grusen, Schwenningen a. Neckar/Wurtt. (Exhibit II)
J. Hengstler, Aldingen bei Spaichingen/Wurtt. (Exhibit III)
Fritz Keller, Hagelburgerstr 52, BERLIN. (Exhibit 4)

Of these Irion and Vosseler was definitely the largest manufacturer. Fritz Keller was principally a distributor for Irion and Vosseler but also made some special attachments for such counters, principally for film measuring. The small counters shown in the Irion and Vosseler catalog were purchased from either L. Loewe, BERLIN, or E. Hardtmann, BERLIN.

The counters that they manufactured were the customary ratchet, revolution, electro-magnetic, hand speed indicators and predetermining types. The only features embodied in their counters that are deserving of comment are the following:

1. Extensive use of quick reset for reset counters.
2. Use of watch as part of hand speed indicators.
3. Variety of printing attachments for counters.

The quick reset means in all cases embodied the use of a heart shaped cam assembled to each figure wheel. By means of a set of actuating fingers actuating these cams the figure wheels were brought to zero. In all cases the figure wheels were solid (20 T. gear was integral part of figure drum) and transfer pinions had to be disengaged from the figure wheels to permit them to independently rotate freely when being reset. (Exhibit 36, 37, 38, 39 and 40).

The incorporation of a watch in a hand speed indicator

is rather unique. The counter and watch always work simultaneously upon slight pressure of the tip against the shaft being checked for speed. One turn of the reset knob resets the counter and watch to zero and also winds up the spring in the watch ready for the next check. (See exhibit 23).

While never made in quantities over a 100 or so per year, they did manufacture counters with printing attachments so cards or continuous tapes could be used. These constructions embodied the use of a typewriter ribbon which is advanced slightly after each printing. Most of these counters with printing attachments were developed for use in the textile industry. (See exhibit 38).

MANUFACTURE OF FIGURE WHEELS

Each of these targets making the general purpose counters made their figure wheels out of bar stock. Brass or zinc alloy were used for the standard items while steel (S.A.E. 1113) was used for the high speed types (excess of 1,000 R.P.M.).

The wheel blank was turned on the automatic screw machine and the 20 tooth gear on one side and 2 T or more segment on the other side were hollow milled. The most common form of tooth was the pin type but for greater strength needed at high speed operation they used a compromise involute form that still permitted them to hollow mill them.

The depressed figures were then sunk in by a type roll under pressure and the periphery carrying the figures was turned. For the steel wheels the figures were engraved. The periphery was then coated with white enamel, baked and again turned. This left the white enamel in the figure depressions. The entire wheel was then plated black to get the black background. (See exhibit 24).

The printing wheels used in their printing attachments were zinc or tin alloy and were purchased as die castings from either L. Loewe, BERLIN, or Otto Hardtmann, BERLIN. (See exhibits 5 and 6).

NEW APPLICATIONS AND DEVELOPMENTS

Irion and Vosseler was the only one that developed a new counter application in the last 7 years. This was the running weight counter for a table balance. (See exhibit 25).

They had great hopes to build this in relatively large quantities (500 - 1,000 per year) when the war broke. As a matter of fact they were seriously thinking of making the complete balance.

The predetermining counter with shears for a thread winding machine is not a recent development, but it is a novel idea that due to relatively high cost was not made in large quantities. (See exhibit 26).

SMALL INSTRUMENT COUNTERS

The following targets manufactured this line of counters:

L. Loewe&Co. A.G., Huttenstr 17 -20, BERLIN (Exhibit 5)
Otto Hardtmann) Markusstr 2, BERLIN (Exhibit 6)
Ernst Hardtmann)
Bernhard Thormann, Wassmannstr 25/26, BERLIN (Exhibit 7)
L. Hoffmann, Marsiliusstr 23, BERLIN

Of these L. Loewe & Co. was the largest manufacturer while E. Hardtmann made a greater variety.

Practically all of their counters used case figure wheels and pinions made as die castings using tin alloy. This alloy contained 75% tin, 17% antimony, 5% copper and 3% lead (DIN - 1742). (Exhibit 8). Most of it was purchased from Georg von Giesche's Erben, BRESLAU. As tin became scarce in Germany, they used alloys with lower tin content until finally they could not obtain tin alloy at all.

Zinc alloy coatings were then used to some extent but due to difficulty encountered with dies previously used for the tin alloy castings they confined the manufacture to the larger types of counters. The zinc alloy used contained 4% alum, 0.5% copper, balance zinc (DIN -1743)(Exhibit 8). This was obtained from Georg von Giesche's Erben, BRESLAU and metalgesellschaft A.G., FRANKFURT a.M.

The figure wheels and pinions that they made for concerns building the counter into their units were eventually made of plastic. They used Trolit (cellulose-acetate and plasticizer such as dimethyl phthalate) and Trolitul (polystyrol) purchased from Jenditor, Troisdorf near Cologne. Of these two Trolitul was the most popular primarily for its low H_2O absorption property. (Exhibit 9).

The die castings were made on automatic casting machines or small hand machines (Exhibit 10) that they built themselves or on a larger machine purchased from Pollack, PRAGUE, Czech.

The moldings were made on machines purchased from Franz Braun, Zerbst (Desseau) and Eckert and Ziegler G.m.b.H., 124 Eupenerstr, COLOGNE.

In both die cast and molded figure wheels the figures were depressed. The periphery carrying the numerals was coated with white enamel, baked and then turned to remove the while enamel except in the depressed figures. The die cast wheels were then treated by hand with a solution consisting of antimony trichloride mixed with $HClO_3$ and entire mixture diluted in alcohol. This provided the black background for the die cast wheels (Exhibit 27) while the molded wheels were already made of black material. For white material wheels the same procedure was followed except black enamel was used instead of white.(See exhibits 28, 29 & 30).

Most of the counters, figure wheels and pinions which these targets made were used in watt-hour, ampere-hour, gas and water meters, elapsed time recorders, speedometers, tachometers, etc. The following list of targets which used such products were visited but there are others that were covered by another group of investigators and the work was identical to that found at these:

A.E.G., Ackerstr 71, BERLIN
Siemens-Halske, Werner Werk, BERLIN
Schlenker-Grusen, Schwenningen a Neckar(Exhibit II)
J. C. Eckardt, Pragstr 72/82, STUTTGART - Constatt (Exhibit XI)
Scheidt & Backmann, Breitstr 132, RHEYDT (RHLD) (Exhibit XII)
Deutsche Geraete Bau, Salzkotten i.W. (Exhibit XIII)
Heliowatt Werke Elektris, Wilmersdorferstr 39, BERLIN
Paul Firchow, Bell - Alliancestr 3, BERLIN (Exhibit XIV)
Kienzle Apparate A.G. Villingen-Schwartzwald (Exhibit XV)

While these small counter manufacturers were the principal source of supply several of their customers understood

to make the wheels themselves or purchase them from other sources who made them differently. Thus, for example, Siemens-Halske used figure wheels made of aluminum sheet metal by Siemens-Schuckert NURNBERG (Exhibit 31) and also of steatite made by Steatite-Magnesia A.G., BERLIN (Exhibit 32).

U.D.O. Tackometer A.G., FRANKFURT a.M. made their own die cast and molded wheels (Exhibit 33). They used their own type of machine which was built along the lines of the Eckert and Ziegler G.m.b.H. machine.

GASOLINE AND OIL DISPENSING COUNTERS

DIAL TYPE

The pumps that used this type of counter were made by Deutsche Geraete Bau, Salzkotten i.W. and Scheidt and Backmann, Rheyat,(Rhld). These were the two outstanding manufacturers with the former getting about 75% (5,000 pumps per year) of the German business. (See exhibits 12 & 13).

The most common type of counter used was the dial type with totalizer. Most of these were built by themselves although Irion and Vosseler (Exhibit 1) and Kienzle Apparate, Villingen/Schwarzwald (Exhibit 15) also made such a register. The figure wheels for the totalizer were either purchased from L. Loewe or Otto Hardtmann or made by the pump manufacturer out of bar stock in the manner used by Irion and Vosseler.

Most of the gasoline pumps were equipped with counter having a predetermining attachment so delivery would automatically cease when a predetermined quantity had been dispensed. These were either made by pump manufacturers or purchased from Irion and Vosseler. (See exhibitis 12, 13 & 17). Deutsche-Geraete Bau also made a few pumps with dial type counter having a printing attachment for issuing receipts for sales. (See exhibit 16).

FIGURE WHEEL TYPE

Scheidt and Backmann made a pump-model KMO/RA36 (See exhibit 18) that had a figure wheel counter with figures 10 cm. high. This pump was made with a pre-selector mechanism to stop delivery when predetermined quantity was

delivered. This pre-selector mechanism could be disconnected by simply rotating a handle through 180°.

The figure wheels were large sand cast spiders which carried the figure bands. These bands were sheet aluminum and the figures etched on in the flat strip stock.

COMPUTERS

To compute the cost of gasoline dispensed Deutsche Geraete Bau had a computed scale ring which was assembled around the periphery of the quantity dial. (See exhibit 19). When the price of gasoline changed a different ring had to be put on the pump.

The figure wheel counter in the Scheidt and Backmann pump had a wheel which carried a similar band. This wheel rotated as the quantity figure wheels were driven. Here, too, a different band had to be assembled to the computing wheel each time the price of gasoline changed.

Scheidt and Backmann also made a few pumps for Shell, HAMBURG, using a computing counter made by Kienzle Apparate. (See exhibit 20). This was never made in large quantity since cost of pump would increase considerably because of the more costly computing counter.

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FIAT FINAL REPORT NO. 239

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FISCHER TROPSCH PLANT OF
HOESCH BENZIN, A. G. AT
DORTMUND, GERMANY

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

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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. 239 2 October 194

FISCHER-TROPSCH PLANT of HOESCH BENZIN, A.G. at DORTMUND, GERMANY

BY

W. C. SCHROEDER
R. NEUMANN, BR.

Technical Industrial Intelligence Committee

FIELD INFORMATION AGENCY, TECHNICAL

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Personnel of Inspection Team.

W. C. Schroeder, U.S. Department of the Interior, Bureau of Mines.

H. H. Bates, R. Neumann } British Ministry of Fuel and Power.

FISCHER TROPSCH PLANT OF HOESCH BENZIN A.G.AT DORTMUND, GERMANY

General Description of Plant.

This plant employed the medium-pressure Fischer-Tropsch process using cobalt catalyst. Synthesis gas was made by the usual procedure of manufacturing blue water gas from coke, followed by conversion of part of the carbon monoxide to hydrogen by a shift-catalyst in order to obtain the 2/1 ratio of hydrogen to carbon monoxide required for medium-pressure Fischer-Tropsch operation.

Synthesis gas production was at the rate of 900,000 to 1,000,000 m^3 per day, and the average yield of primary product was 150 g. per m^3. This means a total annual production rate of 50,000 metric tons of primary product, which is considerably less than the 90,000 at which this plant was rated before the plant inspection was made on April 22nd 1945.

The water-gas plant, gas purification units, shift-catalyst conversion unit, and other equipment connected with production of the synthesis gas were all of the usual types encountered in Fischer-Tropsch plants and require no further description here.

The catalyst chamber house contained 68 catalyst chambers of the usual concentric double-tube design used in other medium-pressure Fischer-Tropsch plants. These chambers were operated in three stages with indirect coolers after each stage. Following the final stage, gas pressure was reduced and the gas passed through the usual active carbon chambers to remove C_3 and C_4 hydrocarbons. This plant did not have facilities for recirculation of the gas through any stage.

Method of Plant Operation.

Of the 68 catalyst chambers, normally only 64 were in operation at any one time, the remaining four being out of operation for replacement of catalyst, etc. The following table summarizes the more important operating data for each stage:

Stage.	First.	Second.	Third.
Number chambers operating	40	16-20	4-8
Gas pressure, atmospheres	10	<10	<10
Temperature, °C	180-205	180-205	180-205
Gas contraction, %	50-60	35-40	30

The rate of feed of synthesis gas to the first stage was 1000 m^3 per hour per chamber, which was the normal rate claimed for other Fischer-Tropsch operations.

Catalyst Procedure.

The catalyst used in this plant was secured from the central catalyst manufacturing plant of Ruhrchemie A.G. at Sterkrade-Holten. According to plant personnel interrogated, it contained cobalt, thoria, magnesia, and kieselguhr in the normal proportions. Since the manufacture of this catalyst has been described in considerable detail in other reports, no further data are given here.

The Hoesch Benzin procedure in adding fresh catalyst to the plant differs from normal practice as recommended by Ruhrchemie. Fresh catalyst is put into operation in any stage at this plant instead of the recommended practice of starting its operation in the third stage only.

Hoesch Benzin also claimed that regeneration of the catalyst with hydrogen does no good, despite the fact that this is a regular procedure at other plants. Periodically the catalyst is extracted with some middle oil from the process and then dried with heat, but, other than this, no attempt is made at regeneration in the plant. After service of 1500-2000 hours, the catalyst is removed and shipped back to Ruhrchemie as spent catalyst.

Products.

As stated earlier, average yield of primary product from this plant was 150 g. per m^3 of synthesis gas. At times, under good operating conditions, the yield would be as high as 160-165 g. per m^3.

The products obtained from the primary product, aside from the gasol (C_3-C_4) fraction, are approximately as follows:

Benzin	20-25%
Diesel Oil	30%
Heavy Oil	25%
Paraffin	20-25%

The benzin shows an octane number of 40-45, the Diesel oil has a cetane number of 100, and the paraffin wax is quite hard, having a melting point of 60-70°C. and an initial boiling point of approximately 350°C. At one time, this plant attempted to crack the benzin in order to obtain motor fuel with a higher octane number, but losses were too high, so this was abandoned.

Research and Special Products.

Interrogation revealed that little research had ever been carried out at this plant. Some research work had been done on motor lubricants, cutting oils, etc. with no particularly significant results. Although some work had been planned for tests of iron catalysts and a pilot plant built, the actual work had not been commenced.

Fatty acids amounting to one ton per day were recovered from the Fischer-Tropsch condensate water. This was worked up for the manufacture of soap and ethyl, propyl and butyl alcohols.

R. NEUMANN
W. C. SCHROEDER

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FIAT FINAL REPORT NO. 401

WIFO BERLIN EVACUATED PERSONNEL AT MUNICH

REC'D APR 1946
TIIC L.F. & L. S-C.

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

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

FIAT FINAL REPORT NO. 401 3 October 1945

W I F O BERLIN - EVACUATED PERSONNEL AT MUNICH

Target of Opportunity

Report by

[redacted]
Capt. C. Grafton [redacted]

12 p.

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[illegible]

[illegible]mas, Br., Ministr
Capt [illegible] Chaffee, U. S. Army [illegible]
1st Lt. R. J. Ozol, U. S. Army Ord.

I. INTRODUCTION

General, operational and technical information were given to a CIOS investigating party by Herr. F. H. Wehling, formerly General Manager and part-owner of the WIFO system and other key personnel, on 1-8 August 1945, during an investigation of the Munich "WIFO" located at Freiham. Herr Wehling had previously been located in Berlin, then Neuber-Donau and finally was moved to Munich. The contents of this report, supplement and supersede any information presented in Ordnance Progress Report No. 37 entitled "Distribution of Fuels and Lubricants to the German Military Forces".

II. SUMMARY

A. The contract establishing the "WIFO" was signed on 24 August 1934 and registered with the German Board of Commerce on 11 Septemper 1934. The undertaking was to establish and maintain industries, trades and crafts devoted to tests and research work for the benefit of the German State. The working capital of RM 20,000 was obtained from the Board of Commerce. The first board consisted of 8 members, including the president, the representative of the president, a member of the Board of Commerce representing the iron manufacturing industry, the head of the Chemical Department of the Board of Commerce, a member of the Reich Ministry of Economics, and three members from the Reich Ministry of Finance. By decree of 18 September 1942 the board was increased to ten members. The board had control over income and expenses, they passed on the appointment of directors and secretaries, and each member had at one time, cooperated in the future planning of the organization in the capacity of a "Technical Consultant". Later, when the turnover of goods became excessively high, special commissions were appointed, one to handle the mineral oil section and another to handle the chemical section. The commissions were charged with the settlement of any questions regarding building of facilities, and their decisions were forwarded to the "WIFO" in the nature of an order on the financial department for the necessary funds. All orders were filed in a so called "Hauptauftragsliste" (main register for orders).

B. At the beginning of the war, consumer storages consisted of:

1. Fifty to sixty economic storages to cover the requirements of the economical and military section.
2. Ten Army Tank storages.
3. Seven Air Force Tank Storages.

and were well provided. Later on, due to destruction of storage facilities open to air attack, the whole turnover was more and more transferred to underground "WIFO" storages. Apart from transportation by tank cars, 20-25% was accomplished by tankers which belonged to private ship owner firms. On the average 35-40 tankers were employed by the "WIFO".

By the end of 1944, the company had 37,347 tank cars in use with a capacity of 1,062,000 M^3. Additional information concerning storage sites and their capacities is contained in the discussion.

C. At the start of the war only 20% of the "WIFO's" activity was devoted to army requirements which was increased to 80% as the war progressed. The increasing destruction of storages mainly affected the turnover plants (railroad stations and road facilities), therefore, other facilities for the transfer of fuel to and from tank cars and trucks had to be created. Portable quick-coupling pipe lines were resorted to in order to alleviate the above problem.

D. Due to the increasing shortage of fuel, the so-called OKW Reserve (a reserve of the Supreme Command) was formed. This reserve consisted of 40,000 tons aviation gasoline and 60,000 tons motor gasoline. In the last years of the war, the right of disposal of the contents of this reserve was transferred to the Fuhrer's staff and the reserve got the name of 'Fuhrer Reserve'.

III DISCUSSION

Information concerning the WIFO system was obtained from Herr F. H. Wehling, formerly General Manager and part-owner, during a CIOS investigation of Oil and Petroleum targets in the Munich Area, 1-8 August 1945. Comments on the operational and financial aspects of the WIFO were supplemented by technical information given by Dr. H. Bubel, Assistant Chief Chemist for the WIFO system. The salient features of the WIFO are discussed in the following order: general picture, operational aspects, storage facilities, and technical information. It is intended that the information contained herein supplement and supersede any conflicting information contained in Progress Report No. 37, entitled "Distribution of Fuels and Lubricants to the German Military Forces"

A. [illegible]

1. The refinery and the production [illegible]

[illegible] completed in the thirties, it was necessary to build up [illegible] of fuel distribution and transportation. Formerly the supply of fuels and lubricants to Central Europe had been accomplished by the importation of fuels by sea going tankers to Hamburg, Rotterdam and Antwerp. Each of these harbors had a storage capacity of approximately 500 000 cu.m. each. Most of the new synthetic plants were located inland, near sources of coal such as the Ruhr, Saxony, Bohemia and Silesia and they were not permitted to build large storage facilities for fear of air force bombing by foreign countries. Since each plant produced several fuel components, the total being in the neighborhood of 25-30, it was necessary that appropriate blending and storage be accomplished. The WIFO was ordered to build such a new system of storage tanks for the

collecting, mixing and distribution of oil products to replace the harbor storage facilities.

2. The WIFO system was undertaken on 24 August 1934 when the company contract was signed. On 11 September 1934 the new organization was registered with the Board of Commerce. The principle duty of the "WIFO" was to establish and maintain industries, trades and crafts devoted to the furtherance of tests and research work for the benefit of the German State. A fund of RM 20,000 was set aside to finance the organization. The working capital was made up by government subsidies and entrusted to the company, which in turn had to render an account of its transactions. By a decree of the partners, a board of 8 members was established on 25 April 1939 to administer the affairs of the expanding organization. The members of the board were appointed by the Reich Economic Minister, who was and remained general office manager. The first Board consisted of the following:

a. Ministerial Director Illgner als Vorsitzender (President)
b. Ministerialdirigent Godlowski als Stellvertretemder Vorsitzender (Representative of the President)
c. Ministerialdirigent Ruelberg, Abteilungsleiter im Reichswirtschaft ministerium fur die Abt Eisen und Eisenverarbeitende Industrie (Board of Commerce member from iron industry)
d. Ministerialdirgent Mubert, Abteilungsleiter der Abt Chemie (Board of Commerce member from Chemical Industry)
e. Ministerialdirigent Michel aus der Allgemeinen Verwaltung des Reichswirtschaftministeriums (Member from the Reich Ministry of Economics)
f. Ministerialdirgent Kender (Appointed from Ministry of Finance)
g. General Major Becht, aus dem Oberkommando der Wehrmacht (Representative of Army)
h. Ministerialdirigent von [illegible], aus dem Reichsluftfahrtministerium (Representative of Air Ministry)

By decree of 18 September 1942 the number of members was [illegible]. In the course of time the above named board of control [illegible] following members in consequence of death or withdrawal:

a. Mr. Mubert, Mr. Ruelberg and Mr. Michel from the Reichswirtschaftsministerium
b. Mr. von Heemskerk from the Reichsluftfahrtministerium and Generalmajor Becht from the Oberkommando der Wehrmacht (supreme command of the armed forces)

They were replaced by the following:

a. Dr. Fischer, Leiter der Mineralolabteilung

b. Dr. Drexl, Referent in der allgemeinen Verwaltung (both in the Reichswirtschaftsministerium)
c. Kapitan zur See Griebel, OKW
d. Mr. Dr. Nocker and Mr. Ahrens from the mineral oil department of the Ministry of Air, and
e. Mr. Doye from the finance department of the Ministry of Air.

3. The essential task of the board of Company Control (Aufsichtsrat) was to handle income and expenses. They further had to give their consent to the appointment of directors and secretaries (Clerks entitled to sign for the firm). As a rule this board met annually for two or three full conferences. Questions relating to personnel were dealt with by correspondence. Already before their appointment as members of the board of Company Control (Aufsichsrat) the greater part of the gentlemen named above had cooperated in the future planning of the company, as technical consultants. During the initial period, the period of building, these commissions as embled once a month for the settlement of all building issues. The commissions were combined according to the tasks required, thus enabling all parts interested in the problem, to make their wishes understood. During the construction period, the division into a commission for the mineral-oil section on one hand and the chemical section of the other was a matter of course. Later on, when the turnover of goods became greater, special commissions were appointed for this section. These commissions were retained, regardless to the establishment of the board of Company Control or Aufsichtsrat. As a rule one member of the board presided during all conferences of the commissions. The commissions were charged with the settlement of all questions during discussions as a preliminary to conclusions written later on. These conclusions finally lead to an order, given to the company, by the financing party, mainly the Reichswirtschaftsministe. The company kept a register containing all such orders, the so called "Hauptauftragsbuch" (main register for orders) The essential activity of the commissions remained limited however to building. In the course of time, some clearly defined principles were worked out for the execution of management, and were put into practice. These were:

a. The title remained in the possession of the company. The main consumer had to conduct the contract negotiations with the producing works as regards quality, quantity and price agreements. The contract when signed, was transferred to WIFO for the purpose of execution of order, i.e. collection of material from suppliers and storing of these in the WIFO storage system. During this storage stage a new settlement on quantity, price and mixtures was made. The overall charges of WIFO were made up by expenses of transportation, of mixing, of storage rents and of storage turnover; that is a fixed price attached to every weight unit.

b. The component fuels were brought to the WIFO by means of tank-cars, in the possession of the WIFO. The finished product was sent to the consumers' storage facilities by the same cars. When the war broke out, the consumers' storage consisted of:

a) 50-60 economic storages to cover the requirements of the economical and military sector.
b) 10 army tank storages for economy and army requirements.
c) 7 air force tank storages (later on some more) for aviation requirements and 30-40 Hilfslufttanklager (Storage of commercial sector to help out).

At the beginning of the war these consumers' storage facilities were well provided, later on, due to the increasing destruction of all storages facilities, open to air-raids, the whole turnover was more and more transferred to the underground WIFO system. Apart from the transportation by tank cars, that by tankers in inland waters about 1/4-1/5 of the total amount of transportation. For the accomplishment of this task the cargo space of private ship-owner firms was made use of. On the average, 35-40 tankers were in the employment of the WIFO.

c. During the initial stages, the WIFO-bulk storage system provided only for a ship and tank car turnover, to be transferred by ship and tank car again. It was not before some time, that auxiliary devices were established at some places mainly for breakdown into small containers for distribution. Building projects of the last years provided for the establishment of permanent equipment for can and barrel filling.

4. By the beginning of the war the building of 820 000m^3 tank fuel and 110 000m^3 tank space for lubrication was finished and the storage facilities were filled with about 640 000 tons of the above named material. The possible monthly turnover of all plants was estimated to be about 175 000 tons on a 10 hour work day. Up to spring 1942 the bulk storage facilities could balance supply and demand. After that period, however, the available material was reduced to 150 000 tons. This manipulation stock had to remain untouched, for it was made up by a great number of single ingredients, of half finished products and finished products, and because it was distributed to all WIFO. Turnover now became the main task of WIFO on an increasing scale. The products of hydrogenation plants were promptly collected. Danger of bombardment made it necessary that no large stocks be stored up and that daily delivery control be intensified. The WIFO storing facilities had to keep step with the increase in supply from hydrogenation plants. The enlargement of bulk storage had to be continued with the final aim of a monthly turnover of about 350 000 tons. The increase in turnover was partly due to

a doubling of railway installations and to the building of new storage blocks. Before the war the total enlargement program had been fixed at a storage capacity of about 2.2 millions m^3. In the beginning of 1941 the building program was stopped, and only buildings on the point of completion were finished. Thus an enlargement of about 1.5 millions m^3 of storage capacity was effected. Though further enlargement of storage capacity was not required at the moment, because of the quick turnover, it was nevertheless continued. From the end of May 1944 onwards suplies from producing works were constantly reduced and the lowest level was reached during Oct/Nov 1944. During the following months an essential improvement could not be realized.

B. WIFO STORAGE FACILITIES

1. The building of the first storage facilities was started by WIFO in October 1934 at Derben (Elbe) Nienburg (Weser) and Stassfurt (Elbe). The following year building was started at Munchen (or Munich), Neuburg (Donau), Hitzacher (Elbe), and Dragehnen (north of Konigsberg). The storage facilities in Strassfurt were located underground on two floors in a salt mine and consisted of 250-300 cu.meter tanks. The tanks for the other locations were cylindrical with a capacity of 3,300 cu. meters, and were located underground in a concrete building, the roof of which was about 6 feet below the earths surface. These tanks were combined in groups, each containing ten tanks, having a distance of 50 meters between single tanks and 250-300 meters between groups. The tanks were supplied and emptied by pumps capable of transferring 65 cu. meters hour during a 16 hour working day approximately 25,000 tons of fuel could be handled per month. The storage system at first had a capacity of 82,000 cu. meters of which 20,000 cu. meters was in Stassfurt.

In 1938 the development of storage facilities was changed. The system of tanks was altered and consisted of five tanks of 3,000 cu. meter capacity, in a block in a concrete building. The total capacity of a block was therefore 80,000 cu.meters. The roof of each so-called block was at least 18-20 feet below the earth's surface. The new system of storage increased the capacity at Derben (Elbe) by 80,000 cu.meters. New installations of the above type were installed as follows:

Farge (Weser)	5 Blocks or 80,000 cu. meter capacity.
Bohmdarf	
Wien (Donau)	8 Blocks or 160,000 cu.meter capacity

The following table shows the fuel storage capacity of the installations after 1938.

LOCATION	NUMBER OF TANKS	CAPACITY-CU.METERS
Derben (Elbe)	50	180,000
Nienburg (Weser)	30	100,000
Stassfurt (Elbe)	70	220,000
Muchen	30	100,000
Neuberg (Donau)	30	100,000
Hitzacker (Elbe)	30	100,000
Dragehnen	30	100,000
Farge (Weser)	80	320,000
Raudnitz (Elbe)	50	100,000
Wien (Donau)	40	160,000
TOTAL	440	1,480,000

The building of one block in Munchen and two blocks in Hitzacker were under way but not completed.

3. Lubricating oil storage was underground in heated tanks and also above ground. Heated storage facilities were located at:

LOCATION	CAPACITY-CU.METERS
Derben	18,500
Neinburg	10,200
Hitzacker	46,800
Munchen	5,700
Neuberg	5,700
Dragehnen	6,000
TOTAL	92,900

These tanks had a capacity of 1,200 to 200 cu.meters. They were generally used for bulk transfer. Additional storage facilities for barrel, drum and small container filling, consisting of twelve tanks of 600 cu.meter capacity located above ground were at Ruthen, Neuenheerse, Eickelah, Zarrentin, Munchenbernsdorf, Vorderheide, Ebrach, Amstethen and Heiligenstadt. At Mahrisch-Schonberg there were facilities for handling 5,000 cu.meters. The total amount handled by this type of installation amounted to 69,800 cu.meters. An additional storage facility for barrelled lubes of 100,000 barrel capacity, was located in Nidersachswerfen in the Harz Mountains.

4. In order to accomplish the transfer of fuel and lubricants the WIFO system used RR Tank cars. At one time the capacity of cars used by the WIFO system amounted to 1,062,000 cu.meters. By the end of December 1944 the company owned 18,369 cars, had 8,115 in trusteeship and had 10,863 on hire, making a total of 37,345 cars.

C. TECHNICAL INFORMATION

During the inspection of the Munich WIFO some valuable technical information was also obtained. Dr. Bubel, assistant chief chemist and Herr. F. H. Wehling revealed the following:

1. It was company policy to maintain a six months lead reserve at each of the WIFO's and an additional six months TEL reserve in the underground Stassfurt WIFO. The large stock of ethylenedibromide found at Stassfurt was used by the TEL plants in making ethyl fluid and was not used by the WIFO system for the purpose of adding more evacuants to highly leaded fuels. Previously it had been reported erroneously that ethylene dibromide stored at Stassfurt had probably been used for this purpose.

No deterioration of TEL in storage had been experienced and normally, leaded fuel was in storage only 2-3 months with an inhibitor addition of 0.01% of Z V 1 (Cresol).

2. The use of alcohol in fuels was rather limited since its use was never approved by the HWA due to danger from separation. It was assumed however that civilians were familiar with such problems and therefore its use in civilian transport equipment was prescribed. For student flyer training the fuel A_3 was prescribed. It had the following characteristics: 30% alcohol, 30% benzol, 40% gasoline, 10 mg. gum max. While the 10mg. gum limit was considered normal, in the field they used up to 25mg. gasoline, recognizing that most of the gum was from oil contamination introduced by the blending components. To determine the true gum they used fullers earth to absorb the oil, followed by extraction of gum with benzol and finally the gum was weighed after evaporation of the benzol.

[illegible] and this data was used in the valuation of depreciation which had been in storage for a long time. The German Air Force [illegible] laboratories were better equipped than those of the Ground Force. The WIFO system was never permitted to have mobile laboratories.

As a general practice toluene and xylene were removed from the fuel because it could be spared from such fuels and was needed in explosives. The toluene had to be left in benzol used in G A 1 fuels, otherwise the octane of that component was not sufficient.

Early in the war the army had two gasolines, ie RAMBOTEL of 74 O.N. containing TEL but no benzol for transport use, and GEMBOTEL of 76 O.N., containing both TEL and Benzol for use in tanks.

Dr. Bubel stated that most of the WIFO technicians did [illegible] highly in the lube oil or gasoline additives they used, but admitted their test and service information was meagre. He did venture

that it was necessary to develop a protective lining for the concrete storage tanks which would be better than the I.G. IGLET materials. The material "LITORIN" which is magnesia silica fluoride was stated to be entirely satisfactory for this purpose.

6. Some interesting information was given on the effects of bombing on military and civilian supply of motor and aviation fuels:

a) Only the WIFO's at Farge and Drugehnen were entirely knocked out by enemy action and in general bombing did not do great damage, except to sidings and lube oil storage in barrels. An example of the bombing of Nienberg was cited which had resulted in a loss of 2,300 M^3 of fuels, one tank was damaged heavily, eight were damaged somewhat and fire resulted in only two of the damaged tanks.

b) By the end of the war civilian distribution of Fuels and Lubricants had become so critical that the WIFO's at Stassfurt and Derben were used entirely for Zentral Buro Supply, and they only remained under WIFO management operationally.

7. Estonian Shale Gasoline

The WIFO only had about 500 tons of this material, which had been captured from the Russians. It contained 2-5% sulphur and its disposition was to be decided by the Zentral Buro. Towards the end of the war experiments were run to determine its suitability in "Flying Bombs", but it could not be used because it would not pass a 3 hr. copper strip test. They therefore used reject gasoline having better corrosion characteristics, but containing up to 50 mg. of gum, for this purpose.

8. The Speer ministry had decreed that producer and other fluid gases were to be used as far as possible in Germany for both civilian and military transportation purposes. Dr. Bubel was not familiar with many of the problems resulting from these practices, except that damage to engines was excessive due to corrosion.

9. It was stated that the following additional technical personnel were expected to arrive at the Munich WIFO shortly.

Dr. Klemstedt	Chief Chemist.
Dr. Rohrmann	Lube oil expert from the WIFO [illegible] er.
Dr. Sommers	Plant chemist at Neuburg.

A list of technical questions were left with Herr Wehling and Dr. Bubel, for specific answers when the above additional technicians were available. It was also requested that the research or development projects worked on by or known to the WIFO personnel be fully discussed as to purpose, results and application. It was specifically requested

that a complete story be written covering the rather extensive Rust Preventive Tests, which were conducted at Stassfurt.

The above report was to be promptly prepared and delivered to Capt. Rush, OQMG, officer in charge of the WIFO for transmittal to Ord. Serv., Res. and Intell. Br., APO 413.

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FIAT FINAL REPORT NO. 273

TOM-12

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INTERVIEW WITH DR. J.W. REPPE

I.G. FARBENINDUSTRIE, A.G.

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

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JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D.C.

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

FIAT FINAL REPORT NO. 273

2 October 1945

INTERVIEW WITH DR. J. W. REPPE
I.G. FARBENINDUSTRIE, A.G.

— BY

Dr. E. B. PECK
Irvin H. JONES

Technical Industrial Intelligence Committee

L vgnau Farbe

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FIELD INFORMATION AGENCY, TECHNICAL

25 p. diagrs.

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Personnel of Team:

Dr. E.B.Peck - U.S. Petr.Admin.for War.
Irvin H.Jones - U.S. Bureau of Mines.

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Dr. J. W. Reppe, director of I.G.Farbenindustrie and head of the Hauptlaboratorium at Ludwigshafen, was interviewed with respect to his contribution to the German war effort. He played an important part in the last war (1914-1918) in developing the German process for making mustard gas but has had nothing to do with war gases in this war.

His principal contributions to this war were stated to be:

a. Synthesis of a substitute for blood plasma called Periston;
b. An adhesive that makes Buna adhere to fabric and is called Korosin - it formed an essential part of the German synthetic rubber program;
c. New reactions in the synthesis of butadiene.

Dr. Reppe and his co-workers have developed new processes that involve novel reactions of the acetylenes, olefines and reactions of metallic carbonyls; these developments will probably be of future industrial importance and are discussed below along with other reactions described by Dr. Reppe.

The industrial success of the above acetylene chemistry depended first on the development of safe method and means of handling acetylene (C_2H_2) under pressure, and for some of its reactions, and the safe use of large quantities of metallic acetylides - more especially that of copper. Reppe's laboratory has C_2H_2 piped at 30 atm.pressure and plans are made to use it at pressures of 150 atm. Basic

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investigations of explosions in compressed acetylene in the absence of oxygen in small bombs showed that the pressures developed to 10 times its initial partial pressure in a mixture and that the large scale application depended (1) on the provision of equipment to withstand such possible pressure increases and (2) restricting possible explosions to rather small volumes. This latter requirement was met in small-scale apparatus by using for a required delivery of acetylene instead of a single pipe a plurality of smaller pipes about one inch in diameter through which more than a given output of acetylene was continuously circulated by looping the lines back to the suction-side of the large capacity compressor and by using one-way bicycle-tire valves at spaced intervals in the lines. In larger installations, the 4-6 inch pipelines were completely filled throughout their length with pipes of small diameter (about 5-10 mm.) to form a sort of honeycomb structure throughout their extent. The latter has worked so well that, in the large plant for manufacturing about 4500 tons per month of butindiol from acetylene and formaldehyde at Ludwigshafen, of the three explosions experienced, only the lines were burnt through in a very small area without further trouble. After these explosions, the tubes were carefully cleaned and reassembled.

Explosions are prevented in large masses of metal-acetylide catalysts by keeping them wet. They are formed in situ by depositing a salt of the required metal, for example the nitrate, on silica-gel pellets and heating the same for conversion of the nitrate to the oxide and thereafter treating them with acetylene under pressure. The only acetylide catalyst in commercial plants is made by reacting copper oxide with acetylene in situ (see butindiol process).

Acetylene Chemistry.

Reactions of Alcohols and Acetylenes.

Dr. Reppe discussed the well-known reaction between acetylene and alcohols and stated that the reaction was quite general for both aliphatic and aromatic alcohols including primary and secondary alcohols, mercaptans and phenols. Potassium hydroxide is employed as the catalyst. Ethers and esters and secondary amines also react with acetylene under pressure. For example, the reaction

between methyl alcohol and acetylene goes very smoothly at about 200°C. to give methyl vinyl ether in the presence of KOH:

$$CH_3OH + HC \equiv CH \longrightarrow CH_3O - C = CH_2$$

Methyl vinyl ether is hydrolyzable at 180°C. with water to give acetaldehyde and methyl alcohol and the latter can be returned to the process.

This production of acetaldehyde without a mercury catalyst was considered important for German industry because 2 kgs of mercury are lost in the production of a ton of Buna; however, a plant was never built.

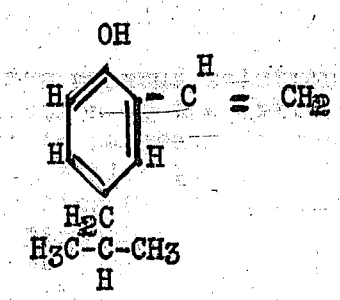
Another important reaction of acetylene and an alcohol is that with phenol, also employing KOH as the catalyst, which gives first phenyl vinyl ether that can convert to vinyl phenol. Depending upon the amount of acetylene substituted on the benzene nucleus, will depend the characteristics of the polymer made from the resultant oxystyrenes wherein the vinyl groups are normally in the ortho and para position to the hydroxy group. To make a resin of the Bakelite type, phenol is reacted with acetylene at a pressure of 10 atm.

Organic zinc salts, for example the naphthenate, are good catalysts for the phenol-acetylene reaction and they can give substituted oxy-styrenes that are solids.

Although the mercaptans, as above mentioned, react with acetylene to give products analogous to those derived from the oxygen alcohols, the products are malodorous and are not of particularly practical value.

Korosin, the adhesive for synthetic rubber, is made by reacting isobutylphenol with acetylene. This was considered an indispensable development in the German synthetic rubber program as this material bound the synthetic rubber to the fabric. It also assists in producing a tire that does not get hot in use. In this case, the acetylene does not form an ether but substitutes for hydrogen on the benzene ring under the influence of zinc naphthenate as the catalyst. The reaction takes place in the liquid phase (Rieselverfahren) forming the hypothetical monomer shown below which, however, polymerizes as formed;

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At Ludwigshafen, the I.G.Farbenindustrie has a small plant for the production of vinyl ether especially from methyl alcohol and acetylene. The reaction was carried on in liquid phase at 15 to 20 atm. pressure of acetylene which was delivered to the reaction vessel as a 50-50 mixture with nitrogen; the total pressure in the system was thus about 30-40 atm. The compressors were of the vertically-reciprocating piston type and the connecting rods were enclosed in a transparent case to prevent ingress of dust as a precaution against friction and possible explosion that the presence of dust in the cylinder would cause. The compressors were of the usual type and were capable of delivering 100 and 180 m^3 per hour.

Reactions of Aldehydes with Acetylene.

Such aldehydes as formaldehyde, acetaldehyde, propion-aldehyde etc. can be reacted with acetylene under pressure in the presence of metallic acetylides to form unsaturated alcohols. Either one or two molecules of the employed aldehyde can react with the acetylene and the so-formed alcohols have as many carbon atoms as are present in the reacted reagents, for example with acetylene and formaldehyde, there can be prepared both

(1) Propargyl Alcohol $HC \equiv C\text{-}CH_2OH$
(2) Butine 3 diol 1,4
$HOCH_2 - C \equiv C - CH_2OH$

The reaction is one of the most promising developments of Dr. Reppe and his co-workers. The above alcohols are made by introducing a mixture of reaction products with

sufficient of a 35% aqueous solution of formaldehyde to provide a 10% solution of the latter in concurrent flow into a tower that is packed with copper acetylide (10-12%) deposited on baked silica gel pellets. The catalyst is prepared by depositing CuO ($Cu(NO_3)_2$ and roasting - it may contain some Bismuth also - and treating with acetylene in situ in the contact vessels in the presence of water at 60-70°C. The reaction may be controlled to make up to 70-80% of the product as propargyl alcohol, but the usual procedure makes 92% of said butinediol and 4% propargyl alcohol. The latter is recycled when only the diol is wanted. The reaction conditions employed are 5 atm. pressure and 100°C. The acetylene is employed in excess and is dry upon entering the process; it therefore evaporates water sufficiently to remove the exothermic heat of reaction. The outlet gaseous mixture from the reactor should be water-vapor and acetylene in the ratio of respectively about 4 to 1.

A plant has been running at Ludwigshafen for two years at a capacity of 4500 metric tons per month of butinediol. In this plant the acetylene is compressed in 2 stages to 5-6 atm. with water-ring centrifugal compressors and the compressed gas (without dilution by N_2) is piped to the honeycomb pipes described above. There are 6 reactors (1.5x 18 m.) designed for 50 atm. pressure which however operate at the above 5 atm. only. They are lined with stainless steel (V_4A) and have each a volumetric capacity of 20 m^3 of catalyst containing 2000 kg. of copper acetylide. The inlet solution of formaldehyde is dripped (Riesel verfahren) through the tower at the rate of 10 m^3 per hour concurrent to a stream of acetylene of 1 m^3 per hour. The reaction being highly exothermic, the only heating employed is heat exchange in the formaldehyde feed lines. The Leistung is 1 ton of butinediol per cubic meter catalyst per day. The outlet solution from the reactor is distilled to recover 10% unreacted formaldehyde and produced propargyl alcohol which are recycled. Based on formaldehyde, the yield of butinediol is about 98%. There were some difficulties at the beginning of the top of the reactor which were overcome by diluting the formaldehyde solutions, as above described. There have been acetylene explosions in the pipes near the control valve to the reactor, but the only damage was to burn a small hole in the pipe.

The reaction solution contains about 30% butinediol. By evaporation and crystallization from ethyl acetate, the butinediol can be recovered in crystalline form; the butinediol as prepared above in aqueous solution can be hydrogenated while still in such solution to butenediol 1,4 and also to butanediol 1,4 by means of a nickel or copper catalyst at 200-300 atm. by means of circulated hydrogen. The conversion of butinediol 1,4 to butanediol 1,4 by hydrogenation is 96%.

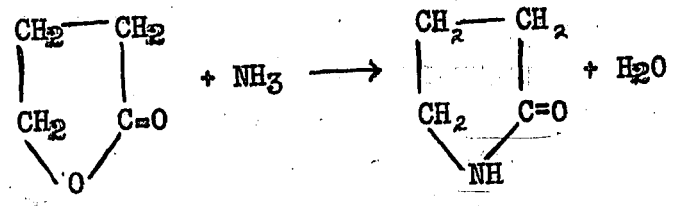
The butanediol 1,4 (n-butylene glycol) can be recovered from the aqueous solution and can be dehydrated in one step to butadiene over a phosphate catalyst as developed by I.G.Farben in 1926. The butanediol is now made at Ludwigshafen for 60 pfg. per kilo and it is expected to reduce this to 40-50 pfg. per kilo.

However, it is preferable because of higher yields and for other reasons according to Dr. Reppe, to dehydrate the butanediol to butadiene in two steps: that is, first to tetrahydrofurane and then the latter to butadiene.

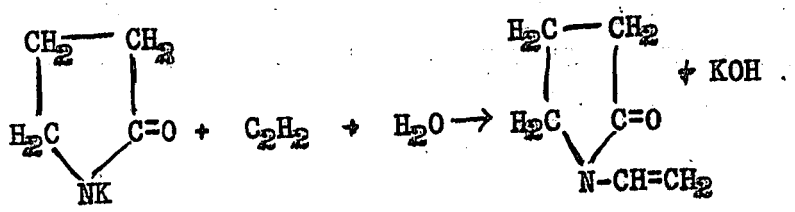
Tetrahydrofurane appears to be an important new building block in synthetic chemistry. It is a good solvent for many types of compounds including also such high polymers as polyvinylchloride, polyvinyl carbazol, natural rubber and Buna. It enters many reactions. Adipic acid can be made therefrom (see below) In the above aqueous solution of 30-35% butanediol 1,4, obtained by hydrogenation of the reaction product of formaldehyde and acetylene, the formol can be dehydrated to tetrahydrofurane in said solution by the addition of a small amount of H_3PO_4 and maintaining the pH at at least 2 and distilling the mixture at a temperature of about 260-300°C. and a pressure of 60-100 atm; the THF (tetrahydrofurane) is easily volatilized under these conditions and is quantitatively produced. The Na and Ca ions in the solution added for control of the pH value are substituted by H ions and by ion-exchange media (Wolfatite).

The THF can then be converted at 260-280°C. to butadiene by means of a phosphate catalyst; it can also be treated with metallic carbonyls and converted to adipic acid.

Butanediol 1,4 is also the starting product for the new blood plasma substitute. By oxidation of its hydroxy-groups to aldehydes, by simple spraying over a Cu catalyst at 200°C., by the well-known Cannizarro reaction, there is produced gamma hydroxybutyric acid and butyrolactone which is the end-product of the reaction, and gamma butyrolactone by reaction with liquid ammonia at 250°C. gives alpha pyrrolidone, as described by Prof. Späth of Vienna, and in accordance with the following equation:



Conversion of pyrrolidone to its potassium salt and the latter's reaction with acetylene, similarly to the known preparation of vinyl carbazole, gives a N-vinyl-pyrrolidone which is the monomer of Periston.

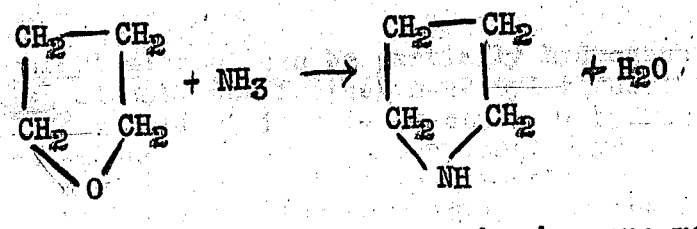


Vinyl Pyrrolidone can be polymerized to Periston by aqueous solution of $NaHSO_3$ or by oxidation with H_2O_2 at a temperature of 70-80°C.; the H_2O_2 is the catalyst and is employed in amounts of 0.05 to 1% plus NH_3 to the extent of $\frac{1}{4}$ to $\frac{1}{2}$ of the employed H_2O_2 which determines the degree of polymerization. Periston is neutral, has a high viscosity and is broken down in and eliminated by the human body. It has been used in thousands of German soldiers, but the Allied medical experts have not accepted its use.

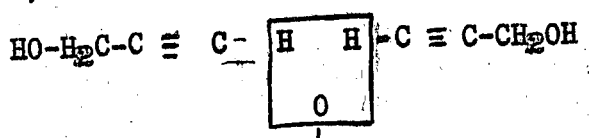
By reaction of NH_3 or amines with THF, it is converted to Pyrrollidine and its N- substituted products; these products are valuable in insecticides and in vulcanization acceleration. The dehydration of pyrrollidine gives pyrrol. The reaction between THF and NH_3 is:

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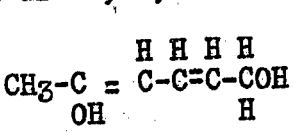
Propargyl alcohol which is made when one mole of formaldehyde adds to acetylene has promising uses. When oxidized with air at 30°C. in the presence of copper chloride, it forms the following:



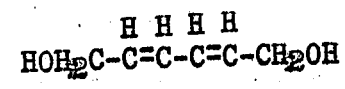
Hexadiindiol, 2,4 diin, - 1,6 diol.

This latter compound, on incomplete hydrogenation, yields two isomers of hexdienol -

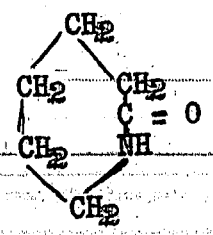
a) Hexadienediol, 2,4 diene, 1,5 diol -



b) Hexadienediol, 2,4 diene, 1,6 diol -



No use is known for the compound (a), but the compound (b) can be converted to either of two Nylon building blocks. It is hydrogenated to hexanediol 1,6 and it then can be oxidized with nitric acid to adipic acid on the one hand, or said diol can be partially oxidized to give epsilon hydroxy caproic acid that easily dehydrates to caprolactone; reaction of the latter with NH_3 gives epsilon caprolactam which has the following structural formula:



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Propargyl alcohol can be partially hydrogenated to give allyl alcohol and further n-propyl alcohol in neutral or alkaline solution; in acid solution by hydrogenation the propargyl alcohol converts to propionaldehyde. Allyl alcohol can be converted to glycerine either by treatment with hydrogen peroxide (or persalts) or by the conventional method with chlorine and water. For the hydrogenation step Fe can serve as the catalyst and for the H_2O_2 oxidation to glycerine selenic acid is employed.

Carbonylation.

Carbonylation is the name given to reactions wherein carbon monoxide is added to another compound, for example to acetylene, olefine, cyclic oxide, and the like, along with such a hydrogen-containing compound as H_2, H_2O, ROH, NH_3, RSH, etc. These reactions include the OXO reaction (olefines + CO + H_2) as a special case. In this reaction, olefines in liquid phase are reacted with CO + H_2 in the presence of the Fischer-Tropsch cobalt catalyst to give a mixture of aldehydes, having more carbon atoms than the employed olefines; the aldehydes are thereafter hydrogenated to alcohols for separation by distillation. A characteristic of this process resides in the fact that, due to the shift of olefinic double bond along the hydrocarbon chain during the reaction (isomerization), a multiplicity of isomers of the produced branched and normal alcohols is formed. Separation of a single compound in pure form is difficult if not impossible even when a single olefine is that starting material. This result seems to be a property of the cobalt catalyst.

Dr. Reppe prefers to use as the catalysts Nickel Carbonyl ($Ni(CO)_4$) or Iron Carbonyl ($Fe(CO)_5$) and H_2O instead of H_2 when the desired end-product is alcohols; by means of this advance, Reppe produces from a given olefine, or the like, a mixture of two isomeric carboxy acids having each one more carbon atom then the employed starting material, the acids can then be reduced to corresponding alcohols or aldehydes if they are the desired products. The said acid isomers are usually straight chain and alpha substituted acids if the employed olefine is straight-chained compound.

The nickel carbonyl can be formed outside the reaction vessel and be added to this reaction mixture or it can be formed in situ from a nickel salt, for example $NiCl_2$, that forms $Ni(CO)_4$ but in any event it must be present in a stoichiometric relationship to the product formed. $NiCl_2$ in the presence of excess NH_3, reacts readily with CO at 150-180°C to give the Nickel Carbonyl, as follows:

$$NiCl_2 + 2\,NH_3 + H_2O + 5CO \longrightarrow Ni(CO)_4 + 2NH_4Cl + CO_2$$

The NH_4Cl is regenerated with CaO.

As an example of the above reaction, the following synthesis of acrylic acid from acetylene was given, the reaction taking place at 40-42°C;

$$Ni(CO)_4 + 4\,C_2H_2 + 4\,H_2O + 2\,Hcl \rightarrow H_2 + NiCl_2 + 4\,CH_2 = \underset{H}{C}\text{-}COOH$$

Cobalt and iron catalysts do not react as well in the above reaction.

Similarly also to acetylene, the olefines react with CO and H_2O and form saturated acids in the present of $Ni(CO)_4$; for instance, ethylene yields propionic acid at 270°C. and 200 atm. pressure, as follows:-

$$C_2H_4 + CO + H_2O \longrightarrow CH_3\text{-}CH_2\text{—}COOH$$

and if an acid is used instead of water in the above reaction, it is possible to go directly from ethylene to propionic anhydride in the reaction -

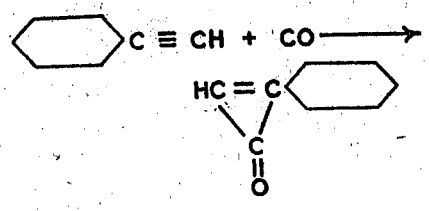
$$C_2H_4 + CO + CH_3CH_2COOH \longrightarrow (CH_3CH_2CO)_2O$$

If alcohol, ammonia, or amine is used instead of water, the corresponding ester or amide of the corresponding acid is obtained.

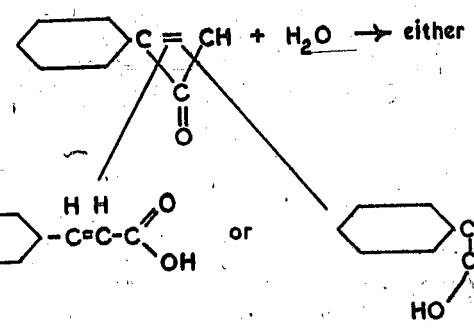
If the employed acetylene or olefine lacks symmetry in respect of the unsaturated bond, two isomers of the formed acid, or the like, are formed; this is consonant with Dr. Reppe's theory that during the reaction CO unites at the

unsaturated bond of the hydrocarbon to form the propenone ring because there thus exists the possibility of severing the ring at either carbon valence of its CO-group; for example, when reacting phenyl acetylene with CO - H_2O, the reaction may progress as follows:

(1)



(2)



Cinnamic Acid Atropic Acid

Oleic olefine reacts as above to give corresponding fatty acids.

As aforementioned, these carbonylations can be carried out with $Ni(CO)_4$ added to the reactor or it may be formed in situ from such soluble nickel salt as nickel chloride activated with sodium iodide - said carbonyl being formed under the pressure conditions of reaction.

In the preparation of propionic acid from C_2H_4, CO and H_2O, said acid is formed as follows: into a reactor maintained at about 235°C-280°C. and at a pressure of 250-300 atm., CO, C_2H_4 and H_2O are introduced at the bottom thereof, said reactor also containing elemental nickel or nickel acetate. $Ni(CO)_4$ is formed from said nickel or its compound by reactions with the inflowing CO. In the case of ethylene, as the unsaturated hydrocarbon, no solvent or liquid phase is necessarily present in the

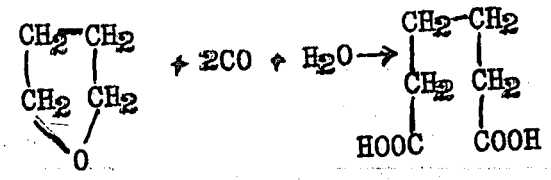
reactor although it is of advantage. The reactor can be made with a lining of absolutely pure copper; iodine or other halogens are not necessary but they have an advantage if apparatus resistant to them are developed - which copper is not. The use of the halogens has the disadvantage that they must be eliminated from the product.

The propionic acid formed in the reactor upon removal therefore contains some $Ni(CO)_4$ which can be removed therefrom by volatilization - it is very poisonous and boils at 45°C. and decomposes in the air. Fractional condensation has been found effective in performing the separation - the separated $Ni(CO)_4$ can be returned to the process.

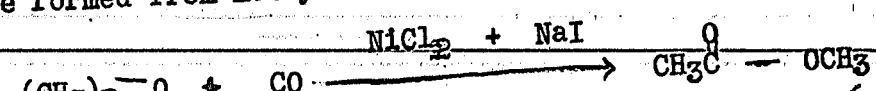
When the employed unsaturated hydrocarbon is propylene or butylene, it is necessary to employ a solvent, such as the formed acid in the reactor; in the case of the higher olefines (such as produce fatty acids) the use of a solvent is not necessary probably because of their high boiling points.

From ethylene up to 95% yield of propionic acid is obtained.

Not only can monocarboxylic acids be made from olefines but also from alcohols, and polycarboxylic acids are preparable from CO and the glycols as well as from cyclic ethers of the latter. For example, Hexandiol 1,6 smoothly reacts to Suberic acid; and Tetrahydrofuran with CO + H_2O converts to Adipic acid in the presence of the above metal carbonyls as follows:-



Although not specifically so-stated by Dr. Reppe, it may be assumed, from his above statement, that methyl acetate can be formed from methyl ether -

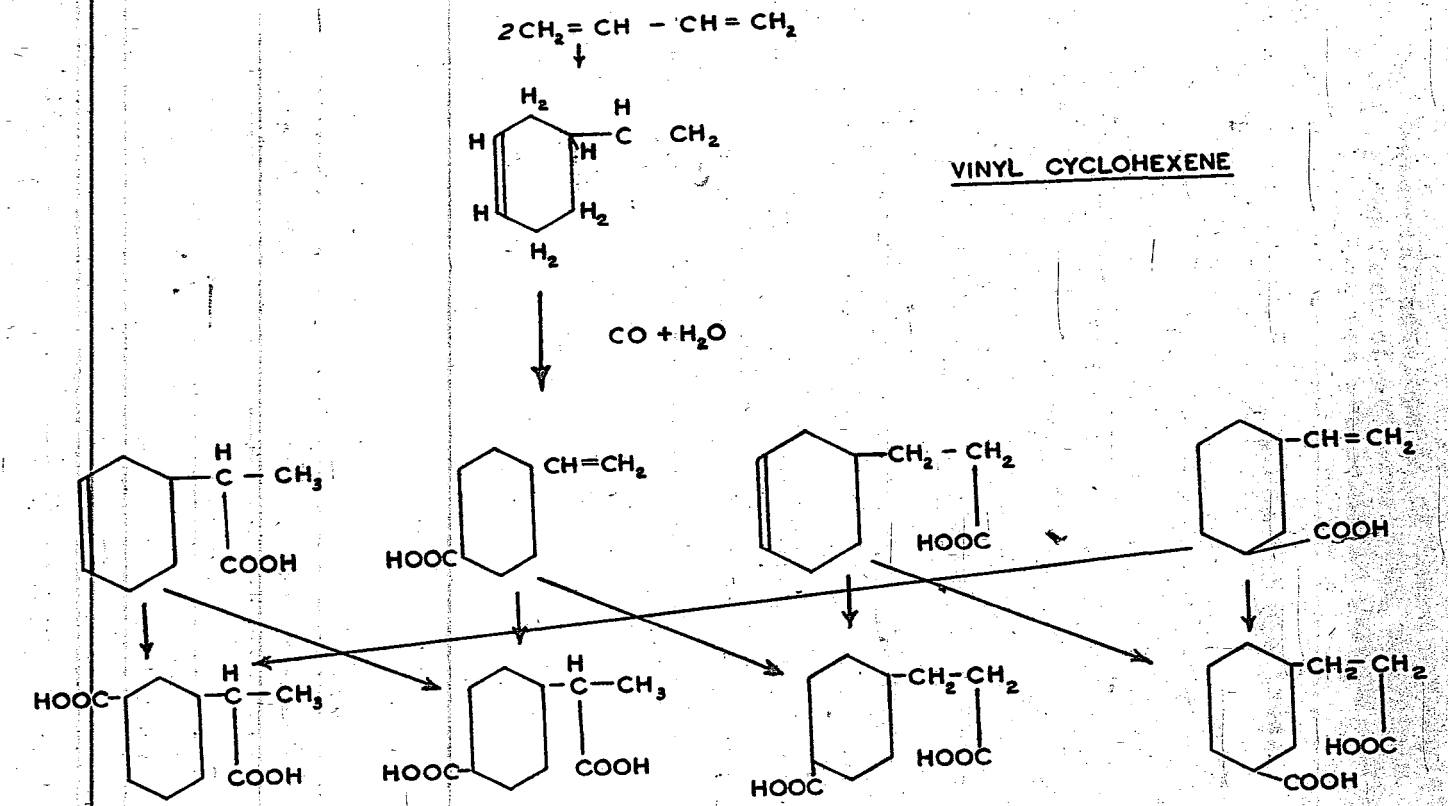


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The above carbonylation of the THF is carried out in continuous operation in the liquid phase with $NiCl_2$ and NaI as catalyst at 200 atm. and 270°C. In an 8-liter reactor, 40 liters/hour of CO, measured at 200 atm., is passed counter-current to a downward flow of 300-600 cc/hour of a 10% aqueous solution of THF containing 1% of NaI, the CO being recycled; the conversion of THF to adipic acid is better than 90%.

The diolefin, butadiene, reacts with CO and H_2O in the presence of $Ni(CO)_4$, giving a 70%-90% yield of fatty acids at 200 atm. pressure and about 270°C. The reaction is good for the manufacture of poly-amides to make high polymers of the Nylon-type. The reaction proceeds along rather complicated courses giving a multiplicity of closely-related products. Firstly, under the conditions of reaction, butadiene condenses with itself to form vinyl cyclohexene which then carbonylates at the unsaturated bonds to give carboxy-acids, as shown on the next page.

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VINYL CYCLOHEXENE

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The commercial development of these carbonylations was held up for lack of acid-resisting materials of construction that were not available in Germany during the war.

Synthesis of Alcohols from Water and Olefines.

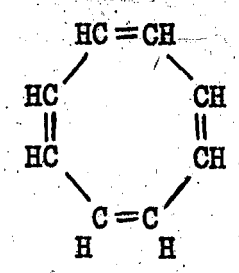
At a pressure from 200-300 atm. and a temperature of 300°C. for ethylene and about 250°C. for propylene, these unsaturateds can be converted directly to alcohols by reaction with water in the presence of tungsten oxide supported on silica gel. The tungsten oxide forms about 20% of the catalyst by weight. The higher the pressure employed, the better. Tungsten Trioxide (WO_3) is inoperative but must be reduced at 600°C. to W_2O_5 before starting; about 5% ZnO in methylamine solution promotes the catalyst.

In practising the above process, C_2H_4, for example, and H_2O are introduced at the above pressure into the top of a reactor tower containing the catalyst which is maintained at the above required temperature. From the bottom of the reactor tower, there is withdrawn into an expansion vessel, about a 20% aqueous solution of the formed alcohol. Molybdenum is also operative for the same purpose, but is not as good as the tungsten.

When propylene or butylene are used in the above reactions, the secondary alcohols are produced.

Cyclopolyolefines.

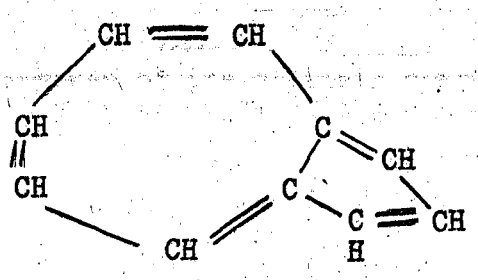
Dr. Reppe discussed his recent developments in the field of cyclopolyolefines, a development that may have only scientific interest, but may have wide future application. He has done extensive research to establish the structural formula of especially C_8H_8 - cyclooctatetraen, which is the counterpart of C_6H_6 in the benzene series of compounds. It is now indisputably established that this compound has the structure -



In the preparation of these compounds, acetylene, at a pressure of 10 to 20 atm. using nitrogen as a diluent and such neutral solvent as especially tetrahydrofurane, is coverted at temperature of from 60-70°C. and up to 130-140°C. in the presence of such nickel compounds as its cyanide, thiocyanate, or halide into the cyclopolyolefines by condensation with itself. The yield of product from acetylene is about 90%. The formed cyclopolyolefines are predominantly C_8H_8 with minor amounts of $C_{10}H_{10}$, $C_{12}H_{12}$, and some soluble resins, and azulene. The $C_{10}H_{10}$ and $C_{12}H_{12}$ are monocyclic compounds where as the azulene is dicyclic; the latter is an isomer of naphthalene and is formed by the dehydrogenation and rearrangement of cyclododecapentaen.

The inert solvent used is preferably tetrahydro furan (THF). The actual catalyst is assumed to be a very labile nickel - acetylene compound that is just made from the nickel halide, or the like, by reaction of C_2H_2 under pressure. The formation of nickel acetylide can be promoted by the addition of a cyclic oxide such as ethylene oxide.

The portion of the condensed acetylene that converts to $C_{10}H_{10}$ and $C_{12}H_{12}$ can be considerably increased by variation of the temperature of reaction. At 60-70°C., there is a preponderance of cyclooctatetraen formed. The optimum temperature for $C_{10}H_{10}$ is 80-90°C. whereas that for $C_{12}H_{12}$ is 130-140°C. The most azulen (intense blue color) is formed by a by-product of reaction at 120°C. Azulen is a dicyclic hydrocarbon having a C_7 and a C_5 ring with 5 olefine bonds as follows:



Azulen has a m.p. of 99.5° in the abolutely pure form in which Dr. Reppe has prepared it.

Physical Properties of the Cyclopolyolefines.

	Name.	B.P.	Color.
1)	Cyclooctatetraene	142-3°C. at 760 mm.	Golden Yellow
2)	Cyclodecapentaene	190-195°C. " " at 2 mm. 48-50°C.	Orange
3)	Cycloduodecahexaene	230-235°C. at 760 mm. 60-65°C at 0.5 mm.	Bright Yellow

The constitution of the latter two compounds has not been definitely established.

These compounds have no practical value; they have been investigated pharmacologically and no essential action established by their use. However, Prof. Kuhn at Heidelberg in the case of the $C_{12}H_{12}$ fraction (b.p.230°C. to 235°C. and colored deep-blue with some azulen - about 3%) determined that the increases of certain pathological bacteria were completely suppressed in dilution of said fraction of 1:100,000.

Dr. Reppe said that the $C_{10}H_{10}$ fraction called cyclodecapentaene did not yield an oxidation sebacic acid and he believes that the compound may be instead vinyl cyclooctatetraene.

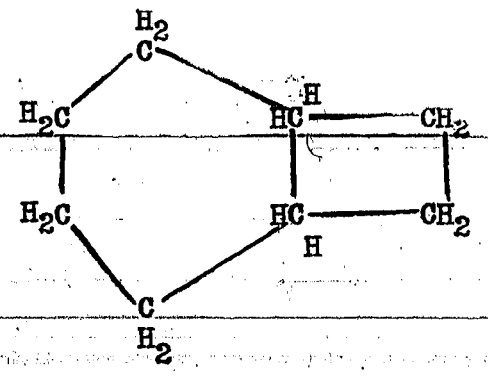
Samples of the above three fractions and of the refined azulen prepared by Dr. Reppe were obtained by members of CIOS Trip No. 215 - Ministry of Supply.

In consequence of its olefinic character, cyclo-octatetraene is very reactive in the presence of various reagents. It --

1. Easily oxidizes even in the air.
2. Absorbs Halogens quickly.
3. Polymerizes to a dimer and hard resins even with standing.
4. Forms crystalline addition products with aqueous $AgNO_3$ and cupric-ammonia, chloride solution.
5. Hydrogenates to cyclooctane.

In certain of its reactions, cyclooctatetraene: -

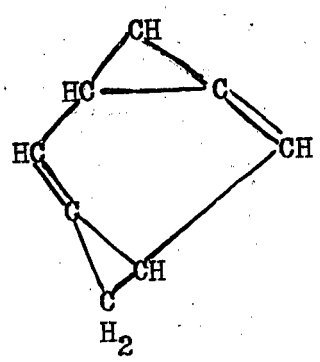
1. Retains its 8-carbon ring structure.
2. Converts to aromatic series forming derivatives of ethylbenzene and p-xylene; phenylacetaldehyde is formed by water suspension of C_8H_8 with, for example, $HgSO_4$; dehydrogenation of C_8H_8 with Se yields p-xylene.
3. Converts to compounds having both a 6- and a 4-carbon ring; for example, upon halogenation (complete) the highest chlorinated compound is formed in $C_8H_8Cl_6$, m.p. 126°C., and thus shows there has been an extensive change in structure to a derivative of C_8H_{14}. Dr. Reppe showed C_8H_{14} to be -



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Bicyclo - [0.2.4] - octane m.p. - 136°C.

4. By treatment of C_8H_8 with hypochlorite there is produced terephthalic aldehyde which must be derived from a compound having the basic structure -



Recent Advances in Carbonylation Chemistry

The latest development in the carbonylation chemistry is the use of the metallic hydro-carbonyls which are strong acids and react quite differently than do the above simple carbonyls. Dr. Reppe has worked with both the nickel and cobalt hydrocarbonyls.

Dr. Reppe developed new methods of preparing the compounds, $H\,Co\,(CO)_4$ and $H_2Fe\,(CO)_4$, in large quantities and studied their physical constants and chemical behavior. This work showed that $H\,Co(CO)_4$ belonged to the group of strongest acids (about like HCl) and that $H_2\,Fe(CO)_4$ behaved like an average mono-basic acid. These compounds were reacted with acetylene and olefine in the presence of water and the reaction-products in the case of the olefines proved to be aliphatic alcohols, and in the case of the acetylene to be hydroquinone, or the like. The empirical equation for the reaction with the iron compound can be the following:

$H_2Fe(CO)_4$ + 2 H_2O → CH_2 + 2 H_2O

2 $CH_2CH_2OH_2OH$ + [illegible]

that is, 2 C_2H_4 + [illegible] C + 2 H_2O → [illegible]
2 CO_2

The reaction progresses at about 100-110°C. and [illegible] no Iodine, but there should be present an organic base that does not react with CO (amines), to form the

6 6

$H_2Fe(CO)_4$, as follows:

$$2\ Fe(CO)_5 + base + 2\ H_2O \longrightarrow$$

$$2\ H_2Fe(CO)_4 + base + 2CO_2$$

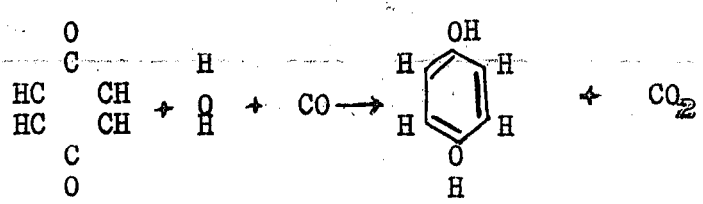
In contrast to $Ni(CO)_4$, the iron hydrocarbonyl can react at ordinary pressure but has the disadvantage that for each CO taken up to form product, two CO_2 molecules are lost. The relation between this reaction and that with $Ni(CO)_4$ as catalyst in the reaction between ethylene, carbon monoxide, and water to give ether propionic acid or its anhydride is recognizable.

If a portion of the water in the above empirical equation is substituted by NH_3, propylamine is produced, as well as the di- and tri- propylamine.

$$CH_2 = CH_2 + 3CO + H_2O + NH_3 \longrightarrow$$

$$H_2N - CH_2 - CH_2 - CH_3 + 2CO_2 .$$

By extension of this olefinic reaction with metallic hydrocarbonyls, Dr. Reppe thought to arrive at unsaturated alcohols but, instead, with substituted acetylene arrived at hydroquinone derivatives in a yield of about 30% as far as his investigations have been conducted: empirically it seems to progress about as follows:



Stoichiometrically, the reagents react in the following ratio:

$$H_2Fe(CO)_4 + 4C_2H_2 + 2H_2O \longrightarrow$$

$$2\ C_6H_6O_2 + Fe(OH)_2$$

When/employed substituted acetylenes and $H_2Fe(CO)_4$, benzene derivatives are formed; for example $CH_3 - C \equiv CH$

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yields trimethylbenzene.

The success of this new carbon-monoxide chemistry is attributable to this first use of these hitherto unusable catalysts or their substitution products, i.e. metal carbonyls or metal hydrocarbonyls, as is also the similar situation in the use of the heavy metal acetylides and their first employment as catalysts in the ethylenation reactions.

(The metallic hydrocarbonyls are not new chemical compounds. They have been extensively investigated by W. Hieber and his colleagues. In 1932, he and others published method of preparation and certain reactions of $Fe(CO_4)H_2$ in the Z. anorg. allgem. chemie, Vol. 204, pages 145-64. Hieber therein describes the preparation of $Fe(CO)_4\ H_2$ according to the following reaction:

$$Fe(CO)_5 + CH_3ONa + H_2O \longrightarrow$$

$$Fe(CO)_4\ H_2 + CH_3OCO_2Na$$

Hieber also states that alkaline solutions of iron hydrocarbonyl have a strongly reducing action on organic substances such as nitrobenzene, quinone and dyes - for example indigo. Although stable in alkaline solution, the hydrocarbonyl easily decomposes in the free state or in the presence of acids because of the initial reaction $2\ Fe(CO)_4H_2 \longrightarrow Fe(CO)_5 + Fe(CO)_3 + H_2$ which proceeds further leading to indefinite results).

APPENDIX A.

A LIST OF IMPORTANT PATENTS, BOTH GERMAN AND FOREIGN ISSUED ON INVENTIONS OF DR. REPPE

DRP 489 537	DRP 510 712	DRP 511 517	DRP 550 403
DRP 550 425	DRP 552 987	DRP 566 033	DRP 578 994
DRP 584 840	DRP 588 352	DRP 589 970	DRP 591 774
DRP 591 845	DRP 593 399	DRP 610 371	DRP 617 543
DRP 618 120	DRP 621 963	DRP 624 622	DRP 625 017
DRP 625 660	DRP 631 016	DRP 636 077	DRP 639 843
DRP 624 886	DRP 643 220	DRP 645 112	DRP 646 995
DRP 647 036	DRP 662 156	DRP 662 936	DRP 663 779
DRP 664 231	DRP 679 607	DRP 684 820	DRP 695 218
DRP 695 219	DRP 696 774	DRP 696 779	DRP 697 802
DRP 698 273	DRP 699 430	DRP 699 945	DRP 700 036
DRP 701 825	DRP 703 956	DRP 704 235	DRP 704 237
DRP 705 273	DRP 706 108	DRP 706 694	DRP 708 262
DRP 709 370	DRP 711 709	DRP 713 565	DRP 714 359
DRP 714 490	DRP 715 268	DRP 715 815	DRP 721 004
DRP 724 759	DRP 725 326	DRP 725 532	DRP 726 714
DRP 727 476	DRP 728 466	DRP 730 648	DRP 734 241
DRP 624 845			
AP 1827 285	AP 1998 413	EP 466 316	EP 497 939
EP 504 957	EP 508 543	EP 510 876	EP 510 902
EP 512 182	FP 50208/Zspat.	FP 806 715	FP 814 349
FP 842 577	FP 844 533	FP 845 600	FP 851 178
FP 853 148	FP 853 606	FP 858 185	FP 865 354
PP 865 428	Schweiz. 220 204	Schweiz P 220 208	

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DOCUMENTS

Three type-written and bound documents relating to the herein-discussed subject-matters have been deposited with the MIRS in CIOS Document Bag No.3518 for safe-keeping. They have been duplicated in the B Series of microfilms which will be filed in Washington, D.C., in the custody of the Petroleum Administrator for War. The documents consist of:-

(1) Report on Cyclopolyolefines;
33 Pages and Appendix 24 Pages.

(2) Dr.J.W.Reppe: Personal History and Contributions in the Field of Acetylene Chemistry;
39 Pages and 2 Tables.

(3) Dr.J.W.Reppe; Further Details of his Work including Activities in Divers Fields of Organic Chemistry; 10 Pages.

25-60665-450

B.) BLAST FURNACE LININGS

While at the MANNESMANNROHREN plant at DUISBURG-HUCKINGEN in connection with electric steel furnaces, the technical organization were also questioned about the performance of their carbon-lined blast furnaces. These linings are of the pre-baked, large machined block (single pieces up to about 23"x29"x80") type. The general results with this type of lining have been so satisfactory that MANNESMANNROHREN have completely standardized on them.

At the time of the shut-down at the end of the war, the following campaign figures had already been realized for these carbon-lined furnaces. It is believed that even Furnace No. 1 is capable of being restarted.

Blast Furnace Number	Date Lining Installed	Long Tons Produced to April, 1945	No. of Run-Outs
1	May 1929	3,150,000	1
2	May 1929	2,480,000	3
3	June 1937	1,400,000	0
4	May 1939	1,000,000	0

The run-outs were at the iron notch and were caused by failures not connected with the carbon linings.

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PART V

SUMMARY OF PLANTS

A.) ELECTRODE MANUFACTURERS

Firm: C. CONRADTY
Location: NÜRNBERG 2 - RÖTHENBACH
Target Number: 1/121
Plant Condition: Only slightly damaged; laboratory building burned down; one graphitizing transformer in need of repairs.
Personnel Interviewed: EUGEN CONRADTY, OTTMAR CONRADTY, MR. ZÖLLNER, MR. KRETSCHMAR
Date Visited: August 25-27, 1945
Research and Development: This firm has no separately organized and equipped research and development facilities, all of its experimental work being done in its regular production departments by the regular operating staff.
General Comments:

This is a very old plant founded in 1855. The graphite electrode department was installed in about 1942-3 and is well-equipped with modern machinery.

This company also owns a graphitizing plant in AFFOLTERN, SWITZERLAND. The basic stock for processing by the Swiss plant was supplied from the NÜRNBERG plant.

Firm: C. CONRADTY
Location: KOLBERMOOR (near ROSENHEIM)
Plant Condition: Undamaged
Personnel Interviewed: MR. J. HECKEL
Date Visited: August 21, 1945
General Comments:

This is a small branch factory of the NÜRNBERG company, and is equipped only for graphitizing the basic stock supplied from NÜRNBERG. The original small graphitizing unit is not in good operating condition, but the two relatively new, medium size units are in good condition.

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Firm: I.G.F.
Location: GRIESHEIM (near Höchst am Main)
Target Number: 8/59a
Plant Condition: Only slightly damaged
Personnel Interviewed: DRS. ENGELBRETZ, PETER
Date Visited: August 17, 1945
Research and Development: This plant has no facilities for research and development on carbon products, except as can be carried out with operating facilities and organization.
General Comments:
This plant is equipped only for the manufacture of basic baked stock for either carbon or graphite electrodes. Graphitizing was formerly done by their BITTERFELD plant, but now would have to be performed by either the SIEMENS or CONRADTY plants.

Firm: SIEMENS PLANIAWERKE
Location: BERLIN-LICHTENBERG
Target Number: C31/110
Plant Condition: Reportedly only the brush department was damaged, but the entire plant equipment is now boxed for shipment to RUSSIA.
Personnel Interviewed: DRS. ADAM, RAGOSS, CONRATH, WARTBURG, OBERING, RHEE
Date Visited: September 20, 1945
Research and Development: This plant was well organized for research and development, and was the leader in this industry in GERMANY.
General Comments:
This plant produced the basic baked stock for graphitization at the MEITINGEN branch plant.

Firm: SIEMENS PLANIAWERKE
Location: MEITINGEN (near AUGSBURG)
Plant Condition: Undamaged
Personnel Interviewed: DR. H. MENSCHING, ING. H. HUBMANN
Date Visited: August 22-23, 1945
General Comments:
This is a branch factory of the BERLIN company, and is equipped only for graphitizing. The basic baked stock was originally furnished from the BERLIN factory. In order to use the graphitizing capacity of this plant,

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the basic stock would have to be supplied from some other plant, such as the I.G.F. plant at GRIESHEIM.

This is the largest and most efficient graphitizing plant in GERMANY.

Firm: AUGUST THYSSEN HÜTTE
Location: HAMBORN
Target Number: C31/478
Plant Condition: Badly damaged
Personnel Interviewed: DR. BRANDI
Date Visited: September 1, 1945
General Comments:
Reviewed their experiences with electric steel furnaces. Electrode usage about 8-10 kg. per ton with cold charges.

Firm: BOCHUMER VEREIN
Location: BOCHUM
Plant Condition: Damaged
Personnel Interviewed: DIR. BREMER
Date Visited: August 30, 1945
General Comments:
Discussed their experiences with 40 ton electric steel furnaces with 20" graphite electrodes. Usage about 8½ kg. per ton.

Firm: DEMAG ELEKTROSTAHL
Location: DUISBURG, Fuldastrasse 4
Target Number: C31/89
Plant Condition: Not inspected
Personnel Interviewed: ING. GENVO
Date Visited: September 3, 1945
General Comments:
Discussed general design features and trends in electric furnaces.

Firm: DEUTSCHE EDELSTAHLWERKE
Location: KREFELD
Plant Condition: Slightly damaged
Personnel Interviewed: DR. MARTIN, ING. VOIGT
Date Visited: September 3, 1945

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General Comments:
Reviewed their experiences with electric steel furnaces. Graphite electrode usage about 10 kg. per ton; carbon electrode usage about 13 to 16 kg. per ton.

Firm: FRIED. KRUPP
Location: ESSEN-BORBECK
Target Number: C31/284
Plant Condition: Badly damaged
Personnel Interviewed: DIR. HEISCHKEIL
Date Visited: August 31, 1945
General Comments:
Reviewed their experiences with electric steel furnaces of 50 ton capacity. Graphite electrode usage about 8.5 to 9.5 kg. per ton.

Firm: LUDWIG RIEDHAMMER
Location: NURNBERG, Burgschmiedstrasse 42
Plant Condition: Office damaged
Personnel Interviewed: ING. RIEDHAMMER
Date Visited: August 26, 1945
General Comments:
This man is a consulting engineer, specializing in the design of furnaces, kilns, etc. for the carbon and ceramic industries. He has designed and supervised the installation of carbon electrode plants in JAPAN, RUSSIA, ITALY, FRANCE, etc.

Firm: MANNESMANNROHREN
Location: DUISBURG-HUCKINGEN
Plant Condition: Slightly damaged
Personnel Interviewed: DR. KNAPP, ING. KAHLHOFER
Date Visited: September 1, 1945
General Comments:
Discussed their experiences with electric steel furnaces and carbon linings for blast furnaces.

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