Heavy gas oil is taken overhead in the vacuum tower. The light and heavy gas oil is mixed and then dewaxed to produce diesel oil.

Lubricating oil cuts are taken off the three side stream draw-offs on the vacuum tower. Asphalt is made as a bottoms product.

The yields were as follows:

| | |
|---|---|
| Straight Run Gasoline | 4.0% by vol. |
| Kerosene | 21.0% |
| Atmos. Gas Oil | 12.6% |
| Vacuum Gas Oil | 8.4% |
| Light Lube Oil | 21.0% |
| Med. Lube Oil | 21.0% |
| Heavy Lube Oil | 3.0% |
| Asphalt | 9.0% |

Proper proportions of the three lube cuts are mixed to produce three grades of lubricating oils. The oil, after mixing for the proper viscosity, is first treated with sulphuric acid, using a centrifuge to separate the sludge, and then with clay. The clay is filtered out in a filter press and the oil passed to a solvent dewaxing plant.

The dewaxing plant is a "Barisol" type plant employing centrifuges for the separation of the wax. Ethylene dichloride is used as the solvent, but it was reported that butyl alcohol was to be used.

Following the dewaxing step, the oil is again treated with clay, the clay being removed in a filter press.

The wax from the dewaxing plant is treated with aluminium chloride in an agitator, filtered and moulded into cakes.

Three grades of lubricating oil were produced. The viscosities of the three oils were 6°E, 8°E, and 16°E.

## VII. FISCHER TROPSCH SYNTHESIS.

The I.G. have continued research on this process during the war, partly in the hope of achieving some important improvement which might give them an entry into this side of the synthetic fuel business and partly because of the interest in certain Fischer products as chemical raw materials, e.g. Kogasin fractions for carboxylic acids and synthetic soaps.

At Ludwigshafen one senior man - Dr. Michael and two or three juniors were engaged on this work. Up to 1940 the main objective was an improved quality of petrol, using medium pressure and high space velocity of reactants over an iron catalyst. Carbon formation on the catalyst was the chief trouble. Periodic revivification with air was not entirely satisfactory because this had no effect on carbon combined with the catalyst as iron carbide. Revivification with oxygen introduced the danger of melting the iron. The best catalyst life achieved in a

500 mm. diam. pilot converter was 2 months. In these pilot plant experiments the catalyst was removed from the converter for revivification and it was intended that any large scale plant would work on some sort of moving catalyst bed principle. The best quality petrol product obtained with this process had an octane number of 75-78 motor method.

Michael failed to have his ideas accepted for any large scale project and, after 1940, shifted his attention to higher molecular weight products particularly olefines. Liquid phase reaction conditions were employed using a finely divided iron catalyst in suspension in the reactants. The catalyst was made by suspending finely ground iron oxide in recycle Fischer Tropsch product and reducing it with hydrogen. Potash was also added to the suspension to the extent of 1-2% on the iron. The catalyst input was said to be 250 mgs.Iron/$M^3$ of oil product leaving the reaction. A 500 mm. diameter hydrogenation converter was converted for trial of this process at Ludwigshafen. With a reaction volume of $1\frac{1}{2}$ $M^3$, 520 Kgs/day of crude product were made. Reaction temperature was kept as low as possible but it was not found feasible to get below 450°C. The crude product consisted of:

10% $C_2$-$C_4$ hydrocarbons

30 - 40% gasoline.

30 - 45% Diesel oil.

15 - 20% wax.

Two thirds of the wax boiled above 450°C under a high vacuum, and one third of it had a melting point above 100°C. The wax contained 2-4% $O_2$. It was suitable for shoe polish etc., but for most purposes it had to be hydrogenated before it was of satisfactory quality. The Diesel oil contained 30-35% unsats and had a Cetane number of 70.

The above sketchy information was obtained hurriedly from Dr. Pier and Dr. Donath. Dr. Michael himself was interrogated by the U.S. Navy team (Messrs. Spaght and Reichl) who may have a much more complete story.

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Additional information was obtained at Heidelberg during a later visit by W.A. Horne, in early July. According to the information then received, the process differs in several essentials from that described above. No attempt has therefore been made to reconcile the two versions and the information obtained on the later visit is given in its entirety below:-

Michael Process.

This process involves the conversion of carbon monoxide and hydrogen to a mixture of hydrocarbons and alcohols. It has been carried out in two types of equipment: fixed bed catalyst and suspended catalyst.

The first method is similar to that used in the Synol process at Leuna. The catalyst bed in the largest reactor studied, was 2 metres in diam. and 1 metre high, containing a solid bed (no internal cooling tubes) of fused-iron ammonia catalyst in the form of 1 cm. cubes or lumps. The temperature was controlled to a 2-3°C rise by extremely high gas recycle rates and low conversions per pass.

The temperature of operation is 280 to 320°C, with a gas recycle of approximately 100 volumes per vol. of fresh carbon monoxide and hydrogen. The linear velocity of the gas through the reactor should be at least 1 metre per second for proper operation. The fresh charge gas ratio is 4 CO to 5 $H_2$. The ratio of hydrogen to carbon monoxide in the recycle gas is quite high, and this provision accounts for the low carbonyl formation. The gas composition corresponds to approximately 10 to 12 atmospheres partial pressure of hydrogen, 2 to 3 atmospheres partial pressure of carbon monoxide, and 5 to 7 atmospheres partial pressure of residual gas, consisting of carbon dioxide, nitrogen, methane and uncondensed higher hydrocarbons.

The process is operated in two stages, each with recycle, and with intermediate condensation and a carbon dioxide scrubbing tower between the stages. The conversion cited in an example of the operation was 91.5%, based on the pure gas. The yield of products based on one N cubic metre of 4CO : $5H_2$ was as follows:

35 gms. of methane and ethane
160 gms. of useful product.

The useful product consists of the following:

14 gms. of alcohols
105 gms. of oil
41 gms. of ethylene, propane-propene and butane-butene.

On distillation the oil yielded:

2 gms. of wax
21 gms. of Diesel oil
82 gms. of gasoline.

The gasoline fraction was stabilised and cut to 195°C end-point to yield 77 gms. of refined gasolines of 84 to 88 research-octane number, 50 - 60% boiling up to 100°C and 70 - 80% of unsaturated substances.

The second method of operation, the so-called "Schaum" or foam process, was carried out with the same catalyst suspended in a liquid phase with the gas blown through the suspension.

Very few data were available on this type of operation because experiments had not been satisfactory. The principal difficulty was the formation of high molecular weight products on the catalyst particles,

which caused them to agglomerate and to settle from the reaction zone. Also the concentration of catalyst when suspended in the liquid medium was considerably less than for a corresponding fixed-bed gas phase operation.

In a comparison of the two methods of operation, the conversion per weight of catalyst was the same. Thus, the increased surface of the powdered catalyst was apparently balanced by the slower diffusion through the liquid phase and did not compensate for the higher concentration of catalyst in the large pieces which were used in the fixed-bed gas phase operation.

## VIII. MISCELLANEOUS CHEMICAL PROCESSES

### Introduction

Incidental to the study of processes related directly to the synthetic fuels, some information was obtained at Ludwigshafen on a number of miscellaneous chemical processes which may be of interest to the oil industry. These processes are listed and described below. No attempt was made, in view of the very limited amount of time and the secondary interest of these processes, to get complete details.

(1) Condensation of acetylene with formaldehyde.
(2) Hydrogenation of 2,3-butinediol-1,4 to 1,4-butane-diol.
(3) Dehydration of 1,4-butanediol to tetrahydrofuran and butadiene.
(4) Ethylbenzene and styrene.
(5) Polyisobutylene (Oppanol).
(6) Polyethylene.
(7) Nitroparaffins.
(8) Nylon and Koresin.
(9) Catalyst preparations for miscellaneous processes.

### (1) Condensation of Acetylene with Formaldehyde.

The reaction is that of adding formaldehyde to acetylene to produce 2,3-butinediol-1,4 according to the equation:

$$2\ HCHO + C_2H_2 \longrightarrow HOH_2C-C \equiv C-CH_2OH$$

The reaction is the first step of the so-called Reppe process, and is carried out in the presence of one of two catalysts. According to the first operation, the catalyst is copper acetylide in water suspension. Approximately 1% of copper acetylide is present. The reaction takes place at 100-120°C. and 4-5 atms. pressure. The total catalyst volume is 30 cc.m. and 30 tons of butinediol is produced per day. The catalyst is prepared by passing acetylene over copper oxide in aqueous suspension at 70°C. According to the second method of operation, the catalyst employed consists of 1-3% bismuth and 10% copper on silica gel. The bismuth and copper are impregnated on the silica gel in the form of nitrates followed by drying and decomposition.

(2) Hydrogenation of 2,3-butinediol-1,4 to 1,4-butanediol.

This reaction is the second step of the Reppe process:

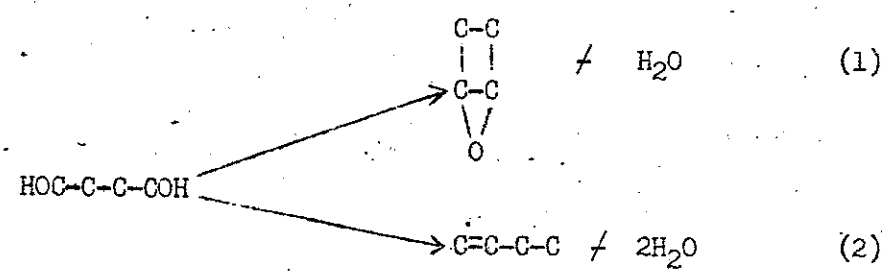
$$HOH_2C-C \equiv C-CH_2OH + 2H_2 \longrightarrow HOH_2C-CH_2-CH_2-CH_2OH$$

and is carried out at 200 atms. pressure and "low" temperatures, in the presence of a catalyst which is prepared as follows:

Silica gel, 4 mm. granules, is impregnated twice with a nickel-copper-manganese nitrates solution. The total concentration of the nitrates in the impregnating solution is 12-14% based on the metals. The ratio of the various nitrates is such as to give, in the final catalyst, 15% Ni, 5% Cu and 1% Mn. After each impregnation the catalyst is dried at 100°C. Finally, the catalyst is dried in a muffle furnace at 450°C until there is no further evolution of nitrogen oxides.

(3) Dehydration of 1,4-butanediol to tetrahydrofuran and butadiene.

The dehydration of 1,4-butanediol can be carried out according to the following equations:




To effect reaction (1), the diol in 30% water solution is treated at 300°C and 100 atms. pressure with a liquid phosphoric acid catalyst. To make butadiene, according to reaction (2), the diol is passed over a sodium acid phosphate catalyst at 280°C, and atmospheric pressure (vapour phase reaction). The catalyst is actually a mixture of sodium acid phosphates, the major constituent being $NaH_2PO_4$. This is deposited on carbon, so that the sodium acid phosphate concentration on the catalyst is 40%. The catalyst life is approximately 4 weeks, the changeover requiring 1-2 days. The yield of butadiene is 94% of the theoretical. In some cases, tetrahydrofuran has been added to the diol and the mixture then dehydrated to butadiene. It is said that tetrahydrofuran, being a heat-stable compound, can be used as a heat carrying medium for the less stable diol.

(4) Production of ethylbenzene and styrene.

Ethylbenzene is manufactured from ethylene and benzene using aluminium chloride as a catalyst. There are two reactors, their dimensions are 1 metre ID and 6 metres high. The production of ethylbenzene is 500 tons per month. The reaction is carried out at 80°C, fresh aluminium chloride, recycle sludge and benzene being introduced at the top of the reactor while ethylene is pumped in at the base of the reactor.

The product is removed from the bottom, the sludge is separated from the hydrocarbon layer and the latter is fractionated. The reaction product contains 60% unreacted benzene and 40% alkylbenzenes. The ratio of ethylbenzene to higher ethylbenzenes in the converted material is 4 to 1. The higher ethylbenzenes fraction is recirculated together with fresh benzene to produce more ethylbenzene by the disproportionation reaction. The conversion efficiency to ethylbenzene is 90%. The consumption of aluminium chloride is 5-10% by wt. of the ethylbenzene produced.

The ethylbenzene produced is dehydrogenated to styrene at 600°C. and atmospheric pressure in the presence of steam. The weight ratio of ethylbenzene to steam is 5 to 1. Each reactor contains 20 tubes. The catalyst is prepared as follows:

The following components -

(1) 204 kg. of ZnO
(2) 12.5 kg. of CaO
(3) 24.6 kg. of $Al(OH)_3$
(4) 7.5 kg. of $K_2Cr\ O_4$
(5) 7.5 kg. of $K_2SO_4$
(6) 64 kg. of $H_2O$

are mixed together in the form of a homogeneous paste and extruded. The extruded material is dried at 100°C. for 12-24 hours followed by heating to 450°C. in air for 8 hours. The finished catalyst is screened to 4-5 mm. particle size. The zinc oxide used in the preparation is made from zinc sulphate and sodium carbonate, the precipitate is washed free of electrolytes and calcined at 450°C. The aluminum hydroxide is prepared from sodium aluminate solution (8-10% $Al_2O_3$ in solution) to which is added nitric acid (30-40%), followed by washing of the precipitate free of electrolytes. The catalyst is regenerated every few months.

(5) Production of polyisobutylene (Oppanol) and isooctane.

The source of isobutylene at Ludwigshafen was the dehydration of isobutyl alcohol. This was done by passing isobutyl alcohol over alumina at 330-360°C. and atmospheric pressure. The yield of isobutylene was 95% of theoretical; the catalyst life was 3-4 months. The dehydration was apparently carried out in two stages; the first stage, where the reaction conditions were less severe, produced purer isobutylene than the second stage. The polyisobutylene process required very pure isobutylene and, therefore, the first stage was used for the polyisobutylene production. The total production of isobutylene was 35 tons per day.

The Oppanol process is carried out using boron trifluoride as a catalyst. The reaction takes place at low temperatures using ethylene as the temperature controlling medium. The ethylene is mixed with the isobutylene, but the former does not enter into the reaction. By maintaining a constant pressure in the reactor, the ethylene is refluxed at

a constant temperature. The molecular weight of the Oppanol is 100,000-200,000 and it is used for insulating equipment etc. The cost of the finished oppanol is 3-5 RM. per kilogram. No further details of the process have been obtained.

The manufacture of isooctane, which was then converted to isooctane, was formerly carried out on a minor scale at Ludwigshafen, but has been completely suspended during the last 12 months. The process is described in section VB(i).

(6) Production of polyethylene.

Two types of polyethylene were made at Ludwigshafen: Lupolen A, having a molecular weight of 2,000-3,000 and a melting point of 110°C, and Lupolen H with a molecular weight of 15-20,000. Lupolen A is a hard wax and has been made to the extent of 20 tons per month, while the production of Lupolen H was 5-7 tons/month. The process for the manufacture of Lupolen A has been developed at Ludwigshafen and later used on a larger scale at Zweckel. The following is the method of manufacture of Lupolen A:

The apparatus consists of a preheater, reaction coils immersed in an oil bath, a separator, a distilling column and a silica gel tower. A mixture of methanol and benzoyl peroxide goes through the preheater and is mixed with a stream of ethylene before it reaches the reaction coils. The weight ratio of methanol to ethylene is 4 to 1, the benzoyl peroxide concentration being 3-5% based on the total mixture. The entire mixture passes through the oil-heated coils at 120-150°C and 200 atms. pressure using a residence time in the coils of 30 minutes. The conversion to wax in the coils is 20% per pass. The product from the coils enters a separator where the methanol-insoluble wax is removed as a lower layer and the methanol/benzoic acid layer goes to a distilling column where methanol is flashed off and then pumped back to the preheater. The ethylene which flashes off in the separator is purified by silica gel, then recompressed and recycled to the reaction coils. As indicated above, an operating pressure of 200 atms. is employed; however, it has been stated that it is possible to use 60 atms.

The use of other solvents, such as benzol, produces polyethylene of a different molecular weight. With benzol, the molecular weight of the product is 3000, as compared to 15-20,000 with methanol. Lupolen A is used in combination with Oppanol for preventing cold flow of insulators and also finds applications as a wax and floor polish.

Lupolen H is made at 1500-2000 atms. pressure in the presence of oxygen.

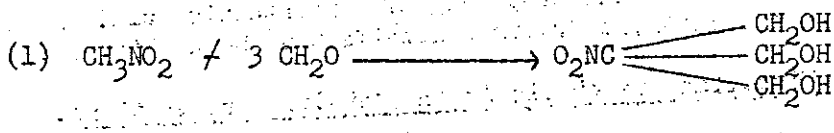
(7) Production of Nitroparaffins.

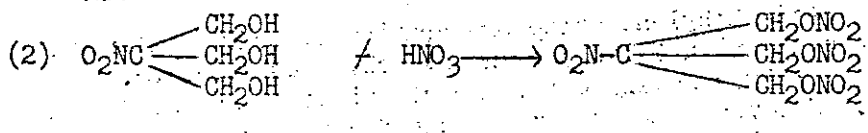
The production of nitroparaffins at Ludwigshafen was directed toward their utilization as starting materials for explosives. Thus, nitromethane, nitroethane and nitropropane were condensed with formaldehyde

in the presence of lime to give the corresponding polyalcohols. These were in turn esterified with nitric acid and the resulting nitrocompounds were used in anti-aircraft ammunition.

The nitration is carried out as follows:

A mixture of ethane and propane enters through a nozzle into a stainless steel mixing chamber. 60% conc. nitric acid is also supplied through a nozzle into the mixer, the latter being maintained at 200°C. From the mixer the gases enter a stainless steel coil which is maintained at a temperature of 400°C. The coil contains no catalyst and the reaction time in the coil is 2 minutes. After leaving the coil, the reaction products are cooled and pass to a separator. The unconverted gas is recycled to the mixer. The conversion to nitroparaffins per pass is 20-25% and a 20-25% loss is incurred by oxidation. The nitroparaffins produced are distilled in glass columns. The products obtained were then reacted according to the following equations:





(8) Production of Nylon and Koresin.

The production of "Igamid A" (hexamethylene adipate polycondensation product-nylon) at Ludwigshafen amounted to 50 tons a month; Igamid B (aminocaproic acid) was produced to the extent of 200 tons per month. Both Igamids A and B are insoluble in alcohol, while a mixture of 60% A and 40% B is soluble.

Igamid B is produced by hydrogenation of phenol to cyclohexanol using a nickel-on-kieselguhr catalyst at 200°C. The cyclohexanol is dehydrogenated to cyclohexanone over copper spirals at 250°C. Cyclohexanone is converted by the use of hydroxylamine to cyclohexanone oxime, the latter upon treatment with sulfuric acid undergoes a Beckmann rearrangement to the lactam. The latter, in 70% water solution, is heated to 270°C. in a large autoclave under 16 atms. pressure until all the water is evaporated. It is important to maintain an atmosphere of pure nitrogen (0.003% impurities) above the melt during the heating, otherwise the product darkens in colour. The heating is done by steam at 100 atms. for 5 hours, the charge in the autoclave being 2 tons. The melt is then extruded under water and the solid is ground in the wet state to chips (5 mm. size) and then dried.

Igamid A is prepared by hydrogenating phenol to cyclohexanol followed by oxidation of the latter to adipic acid. The oxidation is carried out by means of 65-70% nitric acid using a water-cooled reactor. The yield of adipic acid is 60-70% of the theoretical. The adipic acid separates out on cooling and is crystallized from water. Adipic

acid is then reacted with ammonia at 300°C, using a boron phosphate catalyst, to give pure adiponitrile in a 70% yield of the theoretical. The adiponitrile is then hydrogenated to hexamethylene diamine at 120-150°C., 200 atms. pressure in the presence of Raney cobalt catalyst. A three ton charge was hydrogenated within 5 hours in the presence of 3% Raney cobalt catalyst and 10-12% $NH_3$. The yield of hexamethylene diamine is 85% of the theoretical. Finally, adipic acid in methanol solution is added to a 20% hexamethylene diamine solution in methanol.

Koresin, a condensation product of para tertiary butyl phenol and acetylene was manufactured at Ludwigshafen to the extent of 100 tons/month. The reaction is carried out at 15-20 atms. pressure and 150-180°C. in the presence of the zinc salt of a naphthenic acid. No further particulars on the catalyst or other details have been obtained.

(9) Miscellaneous chemicals and catalyst preparations.

(a) Ethylene oxide preparation at Ludwigshafen was carried out along conventional lines using hypochlorous acid etc.; the newer method using a silver catalyst for direct oxidation was studied in the laboratory. However, a large scale unit for the production of 500 tons of ethylene oxide per month was to be built at Zweckau. This plant was to employ the direct catalytic oxidation method.

(b) Catalyst preparations:

(1) Catalyst for the production of butylamine from butyrylaldehyde:

$$C_3H_7CHO + NH_3 \longrightarrow [C_3H_7CH = NH] \xrightarrow{H_2} C_4H_9NH_2$$

The catalyst is prepared as follows:

825 kg. of finely powdered Italian pumice is suspended in 8660 kg. of app. 8% solution of sodium carbonate. This suspension is mixed with a solution of 1275 kg. of nickel sulphate (cryst.) in 2500 litres of water. The mixing is done in a vessel which is previously filled with approximately 7 cu.m. of water at 50°C. The precipitation is carried out at 60°C. The addition requires about 12 hours and this is followed by stirring for 24 hours at the same temperature. The precipitate is then washed by decantation until the wash water is free of electrolytes. This is followed by filtration, using a filter press. The cake thus obtained weighs 3100-3200 kg. and contains 75% water. (This amount of water appears to be somewhat high considering the original input of pumice and the amount of basic nickel carbonate produced on precipitation). 100 kg. of the paste are used to incorporate the desired amount of chromia by treating it in a rotating drum with a solution made up as follows: 1 kg. of water, 1 kg. of chromium trioxide and 1 kg. of 25% ammonium hydroxide. The impregnated mass is dried at 100°C. and ground to dust on a mill.

(2) Catalyst PH-86 for the preparation of fatty alcohols from fats.

Preparation:-

5200 kg. of a copper nitrate solution containing about 12% copper is added, at room temperature, to about 2000 kg. of a 6% sodium carbonate. After the precipitation has been completed, the precipitate is washed by decantation until the wash water is free of electrolytes. This requires about 10-15 washings with 15 cu.m. of water per each washing. This is followed by the addition of 44 kg. of barium nitrate, 42 kg. of zinc nitrate and 62 kg. of chromium nitrate to the suspended basic copper carbonate. The precipitation is carried out using a solution of 176 kg. of sodium carbonate in 1760 litres of water. Upon the completion of the precipitation, the precipitate is washed by decantation until the wash water is free of electrolytes. This requires about the same number of washes as the washing of the basic copper carbonate. The precipitate then goes to a filter press and the cake is dried at 100°C. The dried catalyst is powdered.

(3) Catalyst 4711 for the hydrogenation of aldol to 1,3-butylene glycol.

$$CH_3CHOHCH_2CHO \xrightarrow{H_2} CH_3CHOHCH_2CH_2OH$$

The catalyst is prepared by impregnating silica gel, 3-6 mm. particle size, with a copper nitrate-chromic acid solution. The impregnation is carried out twice and after each impregnation the catalyst is dried at about 100°C. The impregnating solution contains about 35% copper nitrate and a correspondingly smaller amount of chromic acid, so that the final catalyst contains 20% copper and approximately 1% Cr. After the second impregnation and drying, the catalyst is heated in a muffle furnace at 450°C. until there is no further evolution of nitrogen oxides. The resulting catalyst is screened to 1.5-3 mm. size.

It should be noted that this is one of a number of catalysts used for hydrogenation of acetaldol. In another preparation, silica gel is impregnated twice with a solution containing the calculated amount of nickel-copper-nitrate-chromic acid solution, the concentration of nitrates in the solution being about 35%. After each impregnation, the granules are dried at 100°C. and finally heated at 450°C. in a muffle furnace until there is no further evolution of nitrogen oxides. The resultant catalyst is screened to 1.5-3 mm. size. The final catalyst composition is 15% Ni, 5% Cu and 1% Cr, the rest being silica gel.

## IX. INFORMATION CONCERNING OTHER GERMAN FACTORIES

### A. HEYDEBRECK

Heydebreck, referred to in black target lists as Blechhammer South, is a tremendously large new factory built and operated by the I.G.