

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 21**  
**Prepared by**  
**SHELL DEVELOPMENT COMPANY**

Shell Development Co.  
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Report on Roll 21 (Series A) of  
U.S. Technical Oil Mission Microfilm

The material in Roll 21 represents technical papers seized at the Leuna plant of Ammoniakwerk Merseburg, GmbH (an I. G. Farbenindustrie subsidiary). A variety of subjects are included. Those judged to be of greatest interest are:

- 1) Compressibility of pure and mixed gases.
- 2) Minutes and papers from a conference on heat transfer.
- 3) Tests of fractionating columns, and novel tray designs.
- 4) Experimental work on hydroforming.
- 5) A summary of Leuna work on hydrocarbon synthesis from CO, February 1939.
- 6) Sulfochlorination of alkyl chlorides; preparation of sulfonyl chlorides, "sultones", "sultams", and sulfonamides. Use of these for laundering agents, plasticizers, etc

Other subjects included that may be of interest are:

- 1) Novel pressure regulators.
- 2) Method of computing the design of pressure vessels.
- 3) Brief description of hydroforming plant.
- 4) Toluene, methods of recovering and purifying.
- 5) Miscellaneous chemical studies.
- 6) Wax production from tar from brown coal.
- 7) Nitroparaffin sulfates.

Abstracts covering all the items in Roll 21 follow. The abstracts are intended only to furnish an idea of the material in the roll, and do not present more than a small fraction of the information.

Roll 21 - Abstracts  
Bag 3042 (continued)  
Target 80/4.02, Ammoniakwerk Merseburg, GmbH, Leuna

- p. 2931-2936 Report on a Pressure Regulator for very viscous solutions.  
Description of a regulator in a service where the flowing liquid cannot be left stagnant in the tubing system and where the corrosiveness of the liquid does not prevent the use of rubber diaphragms and a transmitting fluid. The new regulator is inserted directly into the line.  
Wolfen, December 7, 1938.
- p. 2937-2942 Draft of patent application: Electro-pneumatic Regulator, where a photo-electrically regulated compensation current flows through the field winding of the electro-pneumatic relay and where the demand as well as the slope of the characteristic can be set by a resistor for each.  
Leuna, July 24, 1940
- p. 2943-2948 Report on a simple remote indicating pressure and level meter, pneumatically operated, and automatically compensated. The upward force of a float is transmitted via bellows and diaphragms to a valve which permits air pressure to build up on the opposite side of a diaphragm on which the float exerts a force. Equilibrium is stabilized at a definite air pressure for each level in the vessel.  
Wolfen, January 8, 1940
- p. 2949-3014 Compressibility of plant gases, important pure gases and mixtures. Report includes graphs of experimental data on gases of Fischer-Tropsch, methanol, and coal hydrogenation plants, generally covering the temperature range of 10-50°C and 10 up to 200 atmospheres. Published data on pure gases and mixtures are also included.  
Leuna, January 13, 1941
- p. 3015-3100 Conference on heat technology and technical thermodynamics at Oppau, March 25, 1941. Dated Oppau, May 14, 1941. At this meeting the publication of certain data was discussed and several papers were presented. These are: Similarity between heat and material transfer. For the countercurrent heat exchanger, temperature curves for both fluids  $T = f(x)$  are developed and their exponential nature proven. From the temperature differences a measure of reversibility is derived. The exponent of  $e$  is given in the form of similarity values. Concentration and partial pressure differences are treated in a similar way. From entropy changes it is found that the exponential curves correspond to the Laplace vector field. The general differential equation is investigated. Considerations of thermodynamic probability show that the "integrating numerator" of the general exponential equation is related in a simple manner to the most probable value of the Maxwell-Boltzmann distribution.

Special heat exchanger, particularly made of plastics.

This is primarily a discussion of flat plate heat exchangers where the plates are supported by grids and their wall thickness is very low, in the order of 1/10 mm. It is used primarily for vapor exchangers where complete separation of the exchanging gases is not essential. Aluminum foil of 0.06 to 0.08 mm. thickness was used commercially. A cubic unit has a surface area of 17 m<sup>2</sup> and weighs 6.5 kg. The price is about 4-6 RM/m<sup>2</sup>. The space requirements are about a tenth of other types. Because the foils are very thin, their heat conductivity is not important and it was therefore thought that cost could be reduced by substituting plastics. It appears that sealing will be easier with plastics and therefore application to liquids may become possible.

The industrial use of diphenyl mixture I: Experience with the use of diphenyl as a substitute for glycerine as a heat medium is discussed.

Approximate methods for calculating concentration changes on partial condensation of multicomponent hydrocarbon mixtures: This report deals with a method for calculating recoveries in partial condensation and feed vaporization.

Experiments on the cooling of moist air in packed towers: Various packing materials were investigated. Rings gave the highest transfer, but the ratio of heat transfer to pressure drop was the lowest of all packing materials (it was highest for solid cylinder); increasing rate does not affect the pressure drop very much but increases heat transfer greatly;

$$Q/F\Delta i_m = C(WL) \frac{0.25 WL}{W + L}$$

Q = cal./hour transferred

F = m<sup>2</sup> packing surface

$\Delta i_m$  = Kcal/kg. log-mean heat content difference

C = constant

W = tons/hour water rate

L = tons/hour air rate (dry)

p. 3101-3108 Investigation of a 1 meter diameter perforated plate column with flat bubble caps of steatite (talc). (Drawing showing tray layout and downspout arrangement with overflow guard is attached, but bubblecap detail is missing).

A 43 tray column built for the distillation of gasoline, cyclohexanol and cyclohexanone, was tested with ethanol-water and with crude methanol. Tests with ethanol-water were at total reflux. At 3500 l/h total reflux an average tray efficiency of 94% was found for the fourth to the fifteenth trays.

The load was varied between 1.1 and 5.0 m<sup>3</sup>/h total reflux (0.17-0.79 m/sec. vapor velocity at a vapor density of 1.49 kg./m<sup>3</sup>). The upper load limit was determined by the downspout capacity. Between 1.1 and 2.2 m<sup>3</sup>/h total reflux the tray efficiency increased from 71 to 87% which may be caused by insufficient submergence at the lower velocity. Above 2.2 m<sup>3</sup>/h the efficiency was constant at about 90%.

The pressure drop was low, ranging from 17 mm. water at 1.1 m<sup>3</sup>/h to 51 mm. at 5.0 m<sup>3</sup>/hr.

Distillation of crude methanol at a 1:1 reflux ratio yielded methanol with a boiling range of 0.2°C. At a total overhead of 4500 l/h the tray efficiency was 100% and the pressure drop at 1.05 m/sec. was 45.5 mm. Leverkusen, August 11, 1942.

p. 3109-3107 Experience with flat bubblecap perforated trays. (Drawing of the bubble cap is shown; it consists of a flat plate 7 mm. thick on which 15 mm. long teeth are arranged in the usual circle, three of which are 1 mm. longer and rest on the tray. The riser has no chimney.)

After a general discussion of the characteristic properties of fractionating columns (such as capacity, efficiency, pressure drop, etc.) these properties are discussed for the flat bubble cap trays. Discussion is based on experience with columns of 20 to 100 cm. diameter and 6 to 43 trays.

Allowable vapor velocity was generally 50% above the value indicated by Kirschbaum (velocity (m/sec.) =

$$0.055 \sqrt{H \text{ (mm. tray spacing)} \cdot D \text{ (vap. dens. m}^3\text{/kg.)}}$$

Tray efficiencies were between 90 and 100%.

Load range is about 1:2.3 but many other factors enter, such as rhythmic motions of the liquid and non-uniform vapor distribution.

Pressure drop can be varied easily if one is willing to increase the lower load limit.

Cost is about 30% less than for ordinary construction.

Tray spacing was 18 cm. (top to bottom of plate) for the 100 cm. diameter column though 15 cm. would have been adequate. In general, it appears that spacing can be decreased between  $1/3$  and  $1/2$ .

Some faulty applications are discussed which indicate the necessity for very careful design work.

Leverkusen, July 20,  
1944

p. 3118-3151 On the effect of flow direction and liquid separation on bubble trays.

The effect of directional baffles to balance the load on a bubble tray is first discussed. Improvements of 50% and more were achieved. Kirschbaum's work on prevention of liquid carryover is then discussed. A new type of disc and doughnut tray is then discussed in which the liquid moves in baffled circular flow (alternately on an annular ring and on a circular tray) while the vapor, by passing through the disc and doughnut arrangement, is freed of most liquid. This type of design is recommended for diameters up to 1.25 meters. Because this construction permits high vapor velocity it is particularly desirable for perforated trays.

Kirschbaum's published photographs of operating bubble caps are then discussed and a new "umbrella cap" is described which operates like a venturi. Vapor coming up the riser sucks liquid in through slit openings in the bottom of the riser. The vapor-liquid mixture has its direction reversed by an "umbrella" baffle above the riser which separates the liquid and returns it to the tray while the vapor passes to the next tray. The tray rim can also be used as a riser. A complete tray layout is shown which has been used in commercial columns. (With 2 meter diameter columns, 15 cm. tray spacing is adequate and even with the largest trays (4-5 meters) 20-25 cm. spacing is adequate while formerly at least 50 cm. was required. Bitterfeld, April 1941

p. 3152-3164 Experiments with a new type of flowmeter: A rotameter for metering liquid adipic acid where the liquid enters a vertical pipe at right angles. The liquid first flows up in an annular space around the concentric metering pipe and then down around the float which is mechanically connected to a spring balance. Standardization curves are attached. Leuna, July 11, 1941.

p. 3165-3200 Development of a bubble tray for high liquid loads. This report describes, in detail, the development of a bubble tray for high liquid loads at normal vapor loads. It consists, in principle, of parallel pipes spaced about 2 mm. apart. Vapor rises through the slits thus produced and liquid is prevented from flowing down at low loads by placing 4 mm. diameter rods in the space between the pipes which are lifted by vapor and whose upward travel is limited. Designs for large trays are also developed.

Leuna, January 19, 1942

p. 3201-3227 Consideration on the calculation of hollow cylinders for high internal pressure at high temperature and recommendations for a more realistic method of calculation.

The problem arose in connection with pressure increases in hairpin tubes at Gelsenberg and for the design of other high pressure-processes. This is a mathematical stress analysis under conditions of plastic flow. A new method of calculation is developed and compared with older ones. Experimental work is planned including the effect of hydrogen.

Leuna, November 5, 1942

p. 3228-3235 Patent Application: Valve system for moving bed catalyst. The valve consists of two parts both attached to the stem. The first is a cylindrical slide which closes first by forming a high enough weir that the catalyst will not overflow. When the space below the weir is free of catalyst, the stem is lifted further, thus closing a conical globe valve at the bottom of the stem whose sealing surfaces may be freed of catalyst by a liquid spray prior to sealing.

Ludwigshafen, August 18, 1943

p. 3236-3255 Plant experiments to improve the performance of a fractionating column. The capacity of a 10 ft. diameter column was increased by a change in tray layout and by increasing the feed preheat. Photographs of plants, diagrams, etc.

Leuna, February 27, 1938

Bag 3045

Target 30/4.02, Ammoniakwerk Merseburg, GmbH, Leuna

p. 1-4 Table of contents of bag.

A.) H. F. Process

p. 5-13 Short descriptive report of the hydroforming plant at Ifoosbierbaum.

The plant produced gasoline of 80 octane number (50-55% aromatics) from a S.R. charge of 58-60 octane number (10%-15% aromatics). Pressure is 15 atmospheres, the gas: oil ratio 650:1, temperature 500-530°C, space velocity 0.5 kg./liter/hr., cycle time 10 hours reaction, 10 hours regeneration. The gasoline yield is 70-75% hydroformed gasoline on a charge basis.

A comparison of hydroforming at present, hydroforming with heated reactors, and DHD (high pressure dehydrogenation) is attached as are schematic flowsheets for the proposed second hydroforming unit at Moosbierbaum. August 7, 1942

p. 14-21

On the use for hydroforming charge of the total gasoline produced by hydrogenation of brown coal over 5058 catalyst.

~~Experimental work indicates that this hydrogenation~~ product behaves like a mixed base straight run gasoline and should therefore be hydroformed at 15 atmospheres. An increase in aromatic content from 2 to 50% can be accomplished with a yield of 77-78%, which is 7-8% lower than for the more naphthenic gasoline from the preliminary hydrogenation step. However, the rich mixture rating is a little higher.

August 28, 1941

p. 22-140

Progress reports on hydroforming experimental work, December, 1939, to February, 1943. (These reports are in reverse order on film, but are abstracted chronologically here.) Place of origin is not given.

December, 1939:

Vapor phase cracking over alumina-silica. Heating up to 800°C does not affect catalyst activity. Gas oil above 165°C, from the cracking of Austrian gas oil, was hydrogenated over tungsten nickel sulfide and yielded oil whose crackability was equal to that of the original charge.

Hydroforming. Investigation of charge stocks was continued including American naphthas, other S.R. naphthas, and gasoline from coal hydrogenation. Catalyst studies using Cr<sub>2</sub>O<sub>3</sub> on alumina and MoO<sub>3</sub> on alumina. The latter appears to be superior, with water-soluble alumina as the best carrier. Catalyst 1879 (94% alumina, 1% Kaolin, 4% MoO<sub>3</sub>) was considered best.

Hydrocracking. Catalyst is a cracking catalyst (1726) to which MoO<sub>3</sub> is added. MoO<sub>3</sub> contents from 1 to 20% were investigated and contents from 5 to 20% range were found to be equally good.



June, 1940:

Catalyst studies: It appeared more practical to activate alumina by heating (800°C) rather than by peptization with nitric acid. Such a catalyst is 5396. Tests with the most active catalysts developed so far in a large reactor with gas recycle indicate that catalyst 2425 (Stoewen activated alumina plus 10% MoO<sub>3</sub>) is the best.

Gasoline from liquid phase coal hydrogenation can be hydroformed satisfactorily when diluted with gasoline from preliminary hydrogenation.

Pilot Plant: A plant resembling the commercial one and including three 50 liter adiabatic reactors was put in operation.

August, 1940:

Catalyst studies: Several precipitated catalysts were prepared and tested, of which one precipitated from Al(NO<sub>3</sub>)<sub>3</sub> with NH<sub>3</sub> and subsequently peptized with nitric or formic acid appeared particularly active. The most active catalyst was prepared by partial denitration of Al(NO<sub>3</sub>)<sub>3</sub> at 200°C, grinding with ammonia and subsequent heating to 450°C. The reaction temperature with this catalyst was 460-470°C. Active catalysts have also been prepared from Bauxite but these appear to have a short life.

Studies with pure hydrocarbons and their mixtures: Cyclohexane, methylcyclopentane plus cyclohexane (2:1), n-heptane, isooctane, and a 100-200° fraction of Fischer Kogasin were used.

Testing of active catalysts: The favorable results with 2425 reported in June did not continue. The catalyst activity declined rapidly. Other catalysts tested were 5396 (precipitated alumina activated by heating to 900°C), 5436 (precipitated alumina from nitrate, activated with nitric acid), and 2663 (technical alumina) activated with HNO<sub>3</sub>. 5436 was found to be sensitive to steam.

Product studies: Gasoline from coal hydrogenation was treated over catalyst 2425, as were several naphthas from different crude oils. Olefinic gasolines were studied and it was found that pretreatment over the same catalyst at 400-415°C for hydrogenation of olefins permits subsequent hydroforming at 475-485°C. Such olefinic gasolines were also treated successfully with 2368 (alumina from oxycetate), but the higher cracking activity of the catalyst gave more C<sub>3</sub> and C<sub>4</sub> yield.

Mechanical stability of catalysts. Several catalysts were tested for stability at atmospheric pressure.

Maintenance of reactor temperature. Experiments are reported in which part of the reaction mixture is recycled as a heat carrier gas. This appears to be a desirable move in the case of adiabatic reactors. The addition of CO, which is hydrogenated to methane thus releasing heat, is also promising.

Discussion of the adiabatic reactor. This reactor appears very undesirable because only a small section of catalyst is used since the reaction is endothermic and the reaction rate decreases very rapidly with temperature.

October, 1940:

Catalyst studies. The effect of varying MoO<sub>3</sub> content was tested thoroughly on 5425 (Al(NO<sub>3</sub>)<sub>3</sub> precipitated with NH<sub>3</sub> and peptized with HNO<sub>3</sub>) for concentrations from 3 to 20%. Activity increases up to 10% and then levels out. Product distribution is about the same throughout, but catalysts with 20% MoO<sub>3</sub> appear to have a more rapid decline.

Similar to denitration, an active catalyst can be prepared by partially dechlorinating AlCl<sub>3</sub>·6H<sub>2</sub>O at 200°C, peptizing the product with NH<sub>3</sub> and heating to 600°C.auxite catalysts were stabilized by repeated treatment with HCl, steam, and NH<sub>3</sub>, alternately.

The effect of an additional component in the catalyst was investigated. It was found that Na<sub>2</sub>O increased the required temperature, while 2% ZnO appeared to reduce coke formation slightly.

Product studies. A larger scale experiment with 100-200°C Kogasin was made over 5436 at 470°C, 15 atmospheres and 0.5 v./v./h. Considerable cracking was observed.

Maintenance of reaction temperature. The addition of air was tried and considered feasible.

Pilot plant study of temperatures. It was found that by adjusting temperatures in and out of the three reactors and during the run, reaction periods could be increased. It was also found that using catalysts of increasing activity in the series reactors resulted in improvements.

Pilot plant experiments with isothermal reactors. The system is described. Preliminary experiments indicate a considerable improvement, particularly in the time required for regeneration.

December, 1940:

Catalyst studies. Work on the addition of a third component was unsuccessful. A catalyst prepared by coprecipitation of  $Al_2O_3$  and  $MoO_3$  was tested. Stability of catalyst 5436 was tested in the absence of steam. The activity decline was slower but was still quite noticeable and may have been caused by steam formed during the regeneration process.

Maximum tube diameter for isothermal reaction. Experiments with a 150 mm. diameter externally electrically heated tube indicate that it is too large, causing excessively hot tube walls,  $35^\circ C$  difference between the outside and center of the reactor and  $35^\circ C$  difference between entrance and center. The yields were correspondingly poor.

February, 1941:

Catalyst studies. Two methods for preparing very active alumina have been developed: a) heating  $AlCl_3 \cdot 6H_2O$  at  $150^\circ C$  for 12 hours, then at  $200^\circ C$  for 12 hours, grinding with aqueous  $NH_3$ , washing free of  $Cl$ , drying, and peptizing with  $HNO_3$ . b) Precipitation from aluminate with  $HNO_3$  at pH 6, washing, drying and peptizing as usual.

Stability of hydroformed gasoline. In order to obtain a passing bombtest for leaded gasoline, treatment with 0.22% 98%  $H_2SO_4$  was sufficient. Larger acid quantities had a detrimental effect.

Use of different activity catalysts. Pilot plant experiments with different catalysts of gradually increasing activity are described.

April, 1941:

Catalyst studies. Catalyst 3063 (dechlorination of  $AlCl_3 \cdot 6H_2O$ ), which did not have to be peptized for maximum activity, was further investigated in a 4 liter reactor. It gave the longest reaction periods (lowest coke formation) of any catalyst tested so far. However, higher gas and  $C_3$  plus  $C_4$  yields resulted in a lower gasoline yield than with 5436.

Hydrogen concentration. Experiments are reported with different hydrogen concentrations in the recycle gas at pressures from 15-50 atm.

June, 1941.

Catalyst studies. A mechanically stronger catalyst could be produced by grinding part of the  $Al(OH)_3$  in a colloidal mill. The aluminate catalyst thus prepared was the strongest.

The use of several catalysts of different activities is discussed further as are results with isothermal tubular reactors.

August, 1941:

Catalyst studies. Nitrate and chloride aluminas treated during processing with potassium hydroxide which is subsequently removed by washing do not suffer in activity.

Activity decline tests with 5436 have been continued. The catalyst has been operated for 2400 hours so far, being at  $440^\circ$  for 6 months.

Further work on the chloride catalyst indicates that because of its high cracking activity it may not be applicable in spite of its otherwise excellent properties including simple production methods.

October, 1941:

Catalyst studies. Reinvestigation of  $Cr_2O_3$  substitution for  $MoO_3$  did not yield any favorable results.

The subject of catalyst pills versus granules was also being studied further.

Different commercially produced catalysts for the Moosbierbaum plant were being studied in the pilot plant.

Some experiments were made with a catalyst from aluminum oxy-chloride.

December, 1941:

Catalyst studies. Further experiments on the addition of KOH during processing of alumina, and subsequently washing it free of potassium, gave very favorable results. In the case of one alumina from chloride, a 72 hour reaction period was observed.

The deactivation run with 5436 catalyst was temporarily discontinued because the reactor was needed for other work. The catalyst had been at temperature for 6780 hours of which 4115 hours was reaction time. The reaction period, which was 22-24 hours at first, sank quickly to 18-19 hours where it remained for several months.

Pilled catalyst appeared to be superior to granules.

Catalyst studies. An alumina from sulfate yielded a catalyst equal to aluminate catalyst.

Conclusions on the superiority of pillared catalyst in the December report were reversed when it was found that the size of the granules was the critical factor. 3-6 mm. granules were superior to 9 mm. pills.

April, 1942:

Catalyst studies. The relationship between activity and grain size was definitely established.

Catalyst 5931 has not shown any activity decline after 1870 hours of hydroforming reaction time (3140 hours at temperature).

Addition of SiO<sub>2</sub> gives catalyst of unusually high mechanical strength. Such a catalyst, 5809 (90% of 95% Al<sub>2</sub>O<sub>3</sub> plus 5% SiO<sub>2</sub> and 10% MoO<sub>3</sub>), was investigated in spherical form. Reaction periods and yields were low. The SiO<sub>2</sub> content appeared to give the catalyst cracking properties.

Operating variables. With a Romanian gasoline and 5931 catalyst, changes in pressure, space velocity, and recycle gas rate (temperature adjusted to give 62-63% aromatics) were studied. Increasing pressure decreased the yield. Reaction period increased with increasing pressure but decreased with increasing space velocity. The recycle gas rate had no appreciable effect on product distribution.

June,

Catalyst studies. All spherical catalysts prepared so far were poor, because of a poor batch of alumina.

October, 1942:

Experiments on a unit consisting of an isothermal and an adiabatic reactor in series. The desirability of this system seems to depend on the charge used.

Attempts to rehydroform a 100-115° cut containing 82% aromatics in order to increase the toluene content was unsuccessful. No aromatics were formed from the nonaromatic portion of the charge.

February, 1943:

Continuation of experiments with isothermal and adiabatic reaction in series. Because of high tube temperatures, particularly at the inlet, the durability of the commercial tubes was to be studied.

It was found that an active catalyst could be prepared by precipitating alumina with ammonium nitrate instead of ammonia. Other ammonium salts did not yield active catalyst.

B. Toluene from DHD Gasoline

- p. 142-148 Changes required at Leuna to recover nitration grade toluene from DHD gasoline. In each scheme the recovery process consists of several distillations, extraction, and an azeotropic distillation with methanol. Leuna, September 18, 1942
- p. 149-151 Revisions required at the Leuna DHD plant to make it possible to convert to the production of 30,000 tons per year of toluene. In this scheme one of the DHD reactors is used for retreating a 100-115°C fraction which decreases the nonaromatic content enough to make extraction and azeotropic distillation superfluous. Leuna, March 22, 1943
- p. 152-158 Letter concerning the various possibilities for changing the Leuna DHD plant to toluene production by rehydroforming. A cost comparison between this scheme (several cases) and extraction is attached. Leuna, February 25, 1943
- p. 159-166 Experimental work and discussion of a process for producing toluene from DHD gasoline by distillation which consists of preparing a toluene cut, azeotropic distillation with methanol, removal of methanol by extraction with water, redistillation of the toluene. Leuna, December 5, 1942
- p. 167-170 Cost comparison between toluene production by rehydroforming and by extraction. Leuna, January 30, 1943 and January 16, 1943
- p. 171 Report on discussion of toluene production with the government. The government preferred the Ruhrchemie process from heptane to the I.G. process by rehydroforming or extraction since by the Ruhrchemie process only motor gasoline is lost and because it seemed undesirable to enlarge Leuna because of vulnerability to air attacks. The Ruhrchemie process yields 60%w toluene on a heptane basis. Leuna, January 11, 1943
- p. 172-178 Cost comparison of toluene by extraction from DHD gasoline or by re-DHD treatment Ludwigshafen, January 5 and 6, 1943
- p. 179-182 Construction maturity declaration for a toluene plant by extraction at Leuna. This discussion includes yields, process description, analyses, etc. Leuna, January 4, 1943
- p. 183-184 Discussions on the problems of fitting toluene production into the Leuna plant. Equipment requirements for the various steps. Leuna, December 4, 1942

p. 186-189 Report on the Leverkusen plant for purifying toluene by distillation.  
Leuna, October 12, 1942

p. 190-198 Recovery of toluene from DHD gasoline by a Duo-Sol type of extraction with propane and SO<sub>2</sub> in a single column. Experiments at Ludwigshafen. The object was quantitative recovery of toluene in place of the 60% proposed by Leuna. At an operating temperature of -80°C complete recovery of 100% toluene is achieved. At -45°C the recovery is complete but the purity is only 96%. On the basis of charge, 100% propane and 120% SO<sub>2</sub> was used. ~~The charge used had a boiling range of 70-120°C. It is felt that with a narrower cut of higher aromatic content a higher temperature (-45°C) may be permissible.~~

A second method for toluene purification would be the removal of non-aromatics by cracking (rehydroforming).

The two processes were then compared. The possibility of single solvent extraction (SO<sub>2</sub>) was taken up but it was thought that nitration grade material could not be produced in this manner.

The removal of adsorbed sulfur from DHD catalyst during regeneration was discussed. Leuna, September 7, 1942

C. Miscellaneous.

p. 200-206 Investigation on the applicability of organic lead-iron carbonyls as anti-knock agents.

Two compounds were prepared and tested: diethyllead-iron tetracarbonyl and diphenyllead-tetrairon carbonyl. Because of their sensitivity to oxidation and their poor anti-knock properties, further work on such compounds did not appear promising.

Leuna, December 28, 1943

p. 207-208 Commercial scale experiments on the discontinuous hydrogenation of adipic-dinitrile to hexamethylenediamine.

Reaction was carried out in an autoclave equipped with mixer and external hot water heater. Operating conditions were 90°C and 200 atm. hydrogen in the presence of ammonia. Yields were 60-90%. The catalyst is a cobalt alloy paste which can be improved by the addition of nickel (16%). Ludwigshafen, June 9, 1939



p. 209-213 Conversion of chlorhydrins into oxides and carbonyls.

Chlorhydrins are converted to oxides by distillation over KOH and  $K_2CO_3$  with a release of HCl. The oxides can be converted to carbonyl compounds by isomerization over zinc chloride. Such carbonyls can be produced in one step by distillation of chlorhydrins over slightly soluble oxides of the first and second group of the periodic system. 40% Yield was obtained in a once-through operation.

January 5, 1932

p. 214-339 Hydrocarbon synthesis experiments at Leuna (summary) including laboratory and pilot plant work, technological and theoretical investigation on heat transfer, plans for two projects, and construction of an experimental reactor.

After a description of laboratory equipment, water gas analysis, etc., experiments on catalysts are discussed. Cobalt-uranium and cobalt-magnesia catalysts were among the more desirable ones. Iron catalysts were not further investigated at that time. Details of catalyst preparation and reactivation are given and product distribution is discussed. The effect of temperature variations and their control is then taken up. One technique is to run heavy liquid reaction products over the catalyst which not only reduces the temperature gradient between the center and the outside of the tube but also removes waxes which form on the catalyst. The theoretical basis of the reaction is described and in this connection the effect of some operating variables is discussed and supported by experimental work.

Pilot plant experiments are next taken up. The catalysts used were primarily Co-ThO<sub>2</sub> on kieselguhr and Co-ThO<sub>2</sub>-MgO on kieselguhr. ZnO, MgO, Al<sub>2</sub>O<sub>3</sub> were also tested as activators with Co. Preparation and reduction methods are discussed, as is the technique for filling and emptying the reactors. Control methods are described. Gas purification methods are taken up. From experimental work, curves were established for conversion and total yield versus space velocity. The effects of pressure, two stage treatment, bulk density of the catalyst, height of catalyst bed, and use of recycle gas, were then investigated. Next, different types of reactors were studied. The wax synthesis is described briefly.

The report continues with a theoretical discussion of heat transfer in different types of reactors. Methods for reducing temperature differences are then taken up. These include special construction, increasing the heat conductivity, increasing the gas rate, and vaporizing liquids in the catalyst bed. The effect of pressure on the rate of heat removal is taken up, as is gas velocity.



The choice of the number of stages is then discussed. In general, 4-6 stages is optimum.

Designs have been prepared (but are not given in detail) for two commercial plants, each producing 180,000 tons/year of primary product Kogasin, one using coke and the other natural gas.

Different reactor designs are described such as low pressure parallel plate reactor, same under pressure, single tube reactor for pressure to 25 atm. and to 200 atm., same for 100 atm. with oil injection. Experimental tubular reactors are described, as are reactors in which the catalyst is placed in layers.

Leuna, February, 1939.

p. 340-396 Calculations of the probable cost for producing wax from brown coal tars.

This report is a detailed cost analysis for a plant to extract and purify 37,000 tons/year of wax from tar. Flowsheets showing material balances and detailed flow are attached.

Oppau, February 22, 1936

p. 398-408 Preparation and testing (for soap substitutes) of nitroalkyl sulfates.

In the Rodleben research laboratory of Henkel A.G. (soap) a process was developed by which higher molecular weight paraffins could be nitrated in the liquid phase at 150-200°C by injecting super-heated, finely-divided nitric acid vapors. Under these conditions little breakdown to fatty acid was noted. It was stated that in the case of straight chain paraffins, nitration took place preferentially in the 2 position. It was thought that a second nitro group could be introduced in the remaining 2' position which would permit the preparation of other bifunctional derivatives. (n-decane would yield 2,8-dinitrodecane).

Since on chlorination and sulfochlorination no such selectivity was noted, the results of the Henkel laboratories were tested and found to be in error. Equimolar mixtures of the all possible products were formed. Thus this process did not endanger the I. G.'s position in the plastics field.

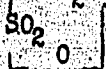
The preparation of mixed amines and amides from the nitro-paraffins was under consideration.

Henkel converted the nitroparaffins to nitroalcohols by adding formaldehyde in the presence of KOH (French Patent 874,902), and these were then converted with chlorosulfonic acid into water soluble sulfates (French Patent 876,422). The latter compounds were prepared for hydrocarbons of the C<sub>12</sub> to C<sub>18</sub> range ("mepasin" fraction) and compared with "oxo" alcohol sulfates and "Mersolat" 30 as soap substitutes. Problems in carrying out the synthesis are described. The chemical requirements were higher than for the preparation of the "Mersolats" and the properties were not as good.

Leuna, December 11, 1943

p. 409-431 Preparations of "sultones" and "sultams" from lower alkyl chlorides.

This is a description of experimental work on the sulfochlorination of lower alkyl chlorides, and different methods for preparing sultones, "sultams", and of sulfur compounds related to the "sultones". It was found that sulfochlorination of the lower alkyl chlorides could be improved by the use of lower temperatures. "Sultones" were prepared most satisfactorily from chlorosulfonyl chlorides via the hydroxysulfonic acids. "Sultams" were prepared from sulfonyl chlorides by way of sulfonamides and hydroxy-sulfonamides. Attempts to prepare the analogous compounds in which the ring forming oxygen is replaced by sulfur were not successful. (Note: One of the possible butane "sultones" has the structure  $\text{CH}_3\text{-CH-CH}_2\text{-CH}_2$ ,



In the case of "sultams" the O atom in the ring is replaced by NH.)  
Leuna, January 22, 1943

p. 432-436 On the effect of sulfochlorination rate and temperature on the yield and quality of the disulfonyl chlorides produced.

It was found that the proportions of the undesirable (for soap) disulfonyl chlorides increased with increasing temperature and rate of reaction.  
Leuna, November 26, 1942

p. 437-450 On the composition of "Mepasin" sulfonates. (Products from the sulfochlorination of largely straight chain paraffins in the C<sub>12</sub> to C<sub>18</sub> range.)

Dodecane and hexadecane were investigated. It was found that the monosulfonyl chlorides formed included all the possible isomers in about equimolar quantities, except that substitution in the end CH<sub>3</sub> groups was not so frequent. The same thing appears to be true in the direct chlorination of these hydrocarbons.

The Hass rule, which says that the substitution rate for primary, secondary and tertiary hydrogen is 1:3:25:4.43 respectively, holds except that on sulfochlorination, tertiary hydrogen does not react because of steric hindrance.

Leuna, October 29, 1941

p. 451-484 The conversion of sulfonyl chlorides with ammonia and amines.

The lower as well as the "Mepasin" (C<sub>12</sub>-C<sub>18</sub>) sulfonyl chlorides were studied with ammonia, alkylamines, anilines, and cyclohexylamine. The main reaction is:



In side reactions sulfonamides are converted to disulfonimides.

The reaction can be carried out in liquid ammonia or amine as solvent. Other possible solvents are isobutyl alcohol, chloroform (for low molecular weights) and carbon tetrachloride (for "mepasin"), benzene and petroleum ether (for "mepasin").

Analytical methods for the reactants, products and solvents are described.

"Mepasin" sulfonamide ("mesulfam") can be used as a plasticizer in viscose manufacturing in the extrusion step. When reacted with ethylene oxide, it forms polyglycol ethers which can be used for laundry soaps.

Experimental work is described in detail, as is pilot plant work for which flowsheets are included.

Leuna, January 1941

p. 485-504 Preparation, properties and comparative investigation of capillary properties of eight sulfonates and sulfates derived from hexadecane.

The purpose of this investigation was to determine if esterification with sulfuric acid of the primary alcohols derived from the "oxo" process would yield products more capillary-active than those obtained by direct sulfonation of olefins and sulfochlorination of paraffins of the same number of carbon atoms.

The alcohol sulfates, olefin sulfonation products, and cetane sulfonates have about the same wetting and foaming properties. In the laundering of white goods in distilled water the sulfates are superior but in the presence of soda there is no difference. In the case of wool in the presence of soda, the sulfates are far superior.

Leuna, January 1941

p. 505-539 "Mesamoll", its preparation, properties, and development up to the summer of 1940.

In the reaction of sulfonyl chlorides with phenols, phenyl esters of aliphatic sulfonic acids are formed which are excellent plasticizers for Igelit (a plastic).

Two processes were developed. In the "wet" process, the sulfonyl chloride is added to a phenolate solution (phenol + NaOH) at about 60°C. Two layers are formed. The lower, aqueous, layer is acidified and returned to the phenol recovery unit, while the upper layer is freed of phenol and neutral oil by a vacuum steam distillation. The recovered ester is treated with bleaching clay at 70°C.

In the dry process a mixture of sulfonyl chloride and phenol is mixed with dry ammonia vapor. The desired ester and ammonium chloride are formed. The latter, being insoluble in the ester, precipitates out and can be removed by filtration. The rest of the process is the same as above. The dry process was considered better because it was simpler and could be more easily converted to a continuous process.

Operating conditions were investigated and different derivatives of the reactants used. The equipment is described as are attempts to improve some properties of esters such as color, pH value, viscosity, and water resistance.

Leuna, January 1941

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