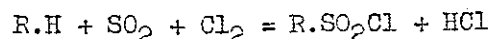


XVI. MERSOL PROCESS

The Mersol reaction consists in treating paraffin hydrocarbons with  $\text{SO}_2$  and chlorine to produce sulphonyl chlorides.



These are subsequently saponified to give the sodium sulphonates.

Scale of Operation:

The Mersol plant at Leuna had a capacity of 50,000 tons per year of products using about 35,000 tons per year of kogasin.

Process Conditions:

The starting material was a kogasin fraction boiling between 220 and 320°C. I.G. would have liked to have included material up to 340°C but this was required for oxidation to fatty acids. The olefin content of the kogasin varied between 5 and 12%, according to the works of origin and the age of the catalyst used in producing it.

The kogasin was subjected to a preliminary hydrogenation at 200-230 atm. pressure to convert the olefins to saturated compounds. Otherwise the olefins absorb chlorine. A nickel tungsten sulphur catalyst was used.

The Mersol reaction was carried out at ordinary temperature and atmospheric pressure using ultra violet light to catalyse the reaction. The reaction was carried out batchwise until the necessary absorption had taken place.  $\text{SO}_2$  and  $\text{Cl}_2$  were blown through the reaction mixture using a small excess of  $\text{SO}_2$ .

The reaction towers were 6-7 m. high and 1.8-2 m. diameter. They were filled to a depth of 4-5 m. with an initial charge of 10-12 tons of material. An increase in volume takes place during the reaction, even though the density increases. Completion of the reaction required about 12-16 hours. The reaction towers were made of steel lined with Igelite (hard PVC).

Ultra violet light was provided by small quartz lamps mounted on a shaft inserted into hard glass tubes of about 120 mm diameter passing through the reaction vessels. Absorption of the shortest wave lengths by the glass tubes is considered desirable as they tend to cause decomposition. These small quartz lamps were about 70 watts each. The power consumption was said to be very small, less than 0.002 KWH per kilo of product.

After the reaction was completed, the product was blown with air or nitrogen to remove HCl. This product, which was known as Mersol D, contained about 82% sulphonyl chlorides and 18% unreacted hydrocarbons. Beyond this stage the reaction becomes very much slower owing to absorption of ultra violet light by the products. There is also a possibility of forming higher sulphonyl chlorides which give inferior products on saponification.

The Mersol D was sent to the soapmakers for saponification. Herold said the soaps made from it were not as good as natural soaps as they lacked colloidal material to maintain the dirt in suspension. For this reason it was usual to add water glass or "Tylosa" (made from sodium cellulose and acetyl chloride). The product was principally used for soap powders. The Mersol soaps, also known as "Mersolates" had been used with kaolin for tablet soap but their high solubility resulted in high consumption. The general practice seems to have been to use the "Mersolates" for soap powders and the fatty acids made by oxidising paraffins for tablet soaps.

Herold said that the synthetic soaps are very good for removing dirt but not so good for removing stains. Repeated washing with them results in a greyish colour and it is difficult to get the pure white colour which is obtained when using pyrophosphate and oxidising materials. Such materials can be used with Mersolate soaps. Herold said that better quality soaps would be obtained by using the longer chain hydrocarbons, which they were not permitted to use owing to the requirements for oxidation to fatty acids. Herold thought that it would be difficult for these synthetic soaps to compete in general with natural soaps but he thought they had a considerable future for special industrial uses, e.g. wool washing. Their advantage was that they were not alkaline and could be used at a low temperature. For removing grease he thought they were better than natural soaps.

Herold said that the Mersol soaps were excellent for emulsion polymerisation and had been widely used in this way for PVC. They were also very effective for Buna, but the rubber manufacturers who had been using "Nekal" (isopropyl sodium sulphonate) for some years were unwilling to risk making a change.

A product known as Mersol 30 was also made at Leuna. For this production, the reaction with  $\text{SO}_2$  and  $\text{Cl}_2$  was only carried to the extent of 30-33%. The product was then esterified with alkali and the separated neutral oil washed and returned to the process. The Mersolate solution was evaporated to give a water-free product and finally cooled in the form of flakes. This product is a thin liquid above 130-150°C. In the evaporation, steam at 15 atm. was used. An advantage of this method of operation is that the lower degree of conversion compared with Mersol D avoids the risk of forming disulphonyl chlorides.

Mersol D can only be made from kogasin but Mersol 30 can also be made from other materials. Kogasin has the advantage that it is more transparent to ultra violet light. If other oils are used, the olefins and aromatics must be hydrogenated to prevent an excessive chlorine consumption. When chlorination takes place, this results in the formation of hydroxyl groups after the saponification and the oil returned to the Mersol reaction must be hydrogenated again to remove them as they interfere with the reaction. The Mersol plant at Leuna was started with oil from the hydrogenation plant, but they preferred the paraffinic Fischer-Tropsch material as it requires a smaller hydrogenation plant and a smaller consumption of chlorine. This applies even more strongly to natural petroleum fractions. Herold said that with kogasin at 30 pf. per kilo and petroleum oil at 18 pf. per kilo, there is not much difference in the cost of the final product.

XVII. METHYLAMINE

The following information was obtained from Dr. Helmut Hanisch on 12th and 14th May. Reference should be made to Figure XXXVII.

About 80 T/month of mono- and di-methylamine were made. A batch mixture was made up, presumably at pressure above atmospheric, containing 4 to 5 mols  $\text{H}_2$  to 1 mol  $\text{CH}_3\text{OH}$ , and the mixture was pumped at the rate of about 1000 l/hr. to a converter. This was run at any pressure from 60 to 200 ats, but the effect of pressure was not ascertained. The converter and inter-changer were both made of S1 steel (low carbon steel) with copper lining and the electrical preheater was copper-covered. The converter was 500 mm I.D. and 8000 mm long, containing about 900 l. of catalyst. There was said to be little difference in performance between catalyst 6069 (90%  $\text{Al}_2\text{O}_3$  and 10% kaolin) and catalyst 6067 (50%  $\text{Al}_2\text{O}_3$  and 50% kaolin), samples of which were obtained.

The make was let-down into a reservoir kept at 25 ats. The de-watering still was copper-lined and filled with 18 m of porcelain Raschig rings, run at a pressure of 20 ats.

Trimethylamine (TMA) and excess  $\text{NH}_3$  were then separated from the mono- and di- (MMA and DMA) in a continuous double still run at 15 ats. The top column contained bubble-plates, with a TMA- $\text{NH}_3$  azeotrope taken overhead and  $\text{NH}_3$  taken from the bottom. The bottom column was filled with Raschig rings, with crude MMA and DMA mixture taken off the bottom.

The TMA- $\text{NH}_3$  azeotrope was fed back continuously into a similar converter, for partial reconversion to MMA and DMA. The product was fed into the same de-watering still as the main stream.

Final purification of the crude MMA and DMA mixture was carried out in a batch still. A batch consisted of 30  $\text{M}^3$  of the crude mixture, with 5  $\text{M}^3$   $\text{NH}_3$  added to provide  $\text{NH}_3$  for TMA separation. The still had an I.D. of 700 mm and was packed with 18 m of Raschig rings. With the top temperature kept at  $40^\circ\text{C}$  and the bottom temperature at  $55^\circ$  to  $60^\circ\text{C}$ , the TMA- $\text{NH}_3$  azeotrope was taken off as the pressure was dropped from 15 to 10 ats, then MMA as the pressure was dropped further to 8 ats. and then DMA as the pressure was dropped to 5 ats, with water left behind. The MMA and DMA fractions were then given a further final purification.

Dr. Hanisch said that copper could be used in this process if care was taken to exclude oxygen.

ISOBUTYLAMINE MANUFACTURE

Dr. Hanisch said that 20 to 25 T/month of higher alkyl amines were made and gave the following details of the manufacture of isobutylamine as typical.

In contrast to methylamines, which were made from methanol and ammonia over a dehydrating catalyst, isobutylamine was made from the aldehyde and ammonia in the presence of hydrogen.

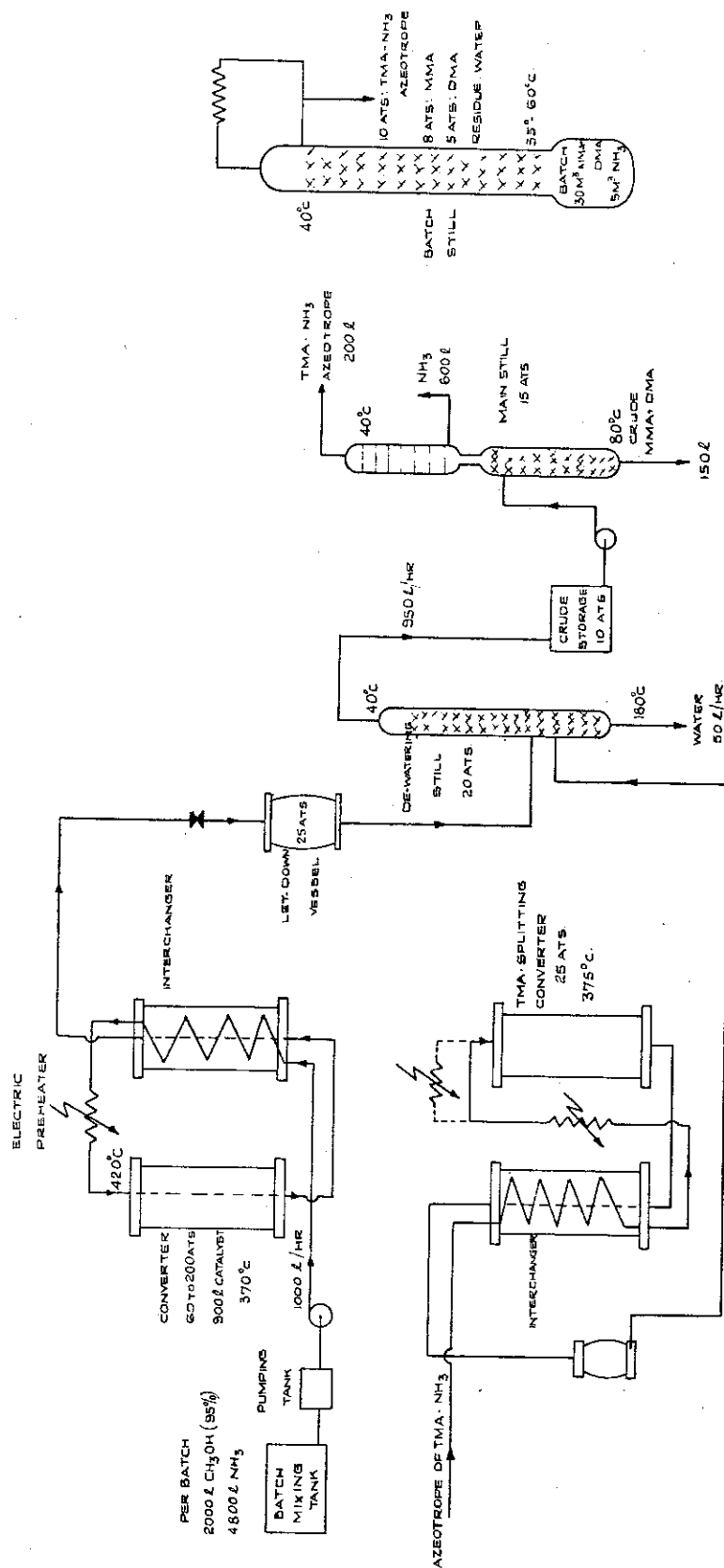
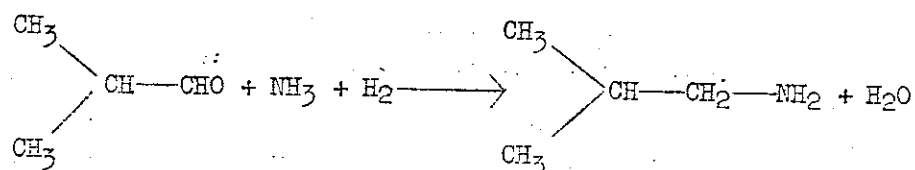


FIG XXXVII METHYLAMINE MANUFACTURE



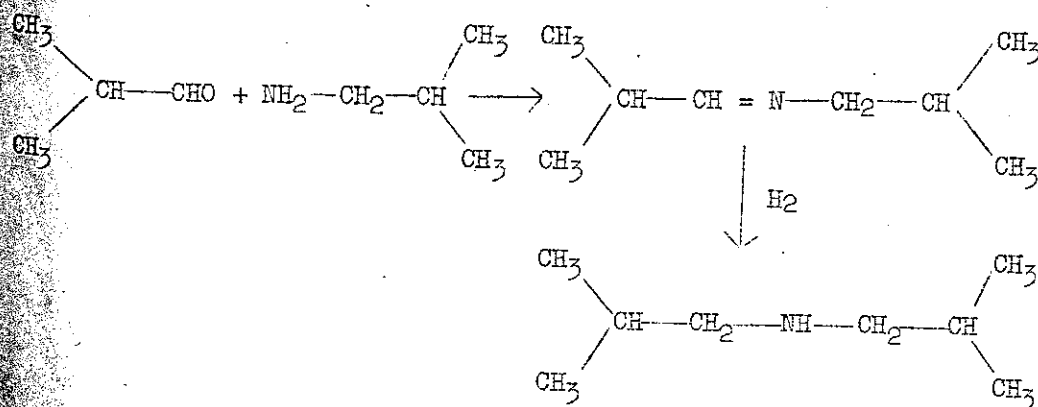
The only details obtained of the manufacture of isobutyraldehyde were that, whereas formerly this had been made by passing isobutanol at 1 at. and 370°C over 2493 (zinc sulphide on pumice, a sample of which was obtained), the method now preferred was to pass isobutanol with air over a silver gauze.

The synthesis of isobutylamine was carried out at 220 ats. over catalyst 3076, NiS.WS<sub>2</sub>, a sample of which was obtained, at a temperature of 300°C. 1800 to 2000 M<sup>3</sup>/hr. H<sub>2</sub> and 600 to 800 l/hr. NH<sub>3</sub> were circulated with a feed of 60 l/hr. isobutyraldehyde over 90 to 100 l catalyst. The product was separated after cooling and the surplus H<sub>2</sub> recirculated. The crude was stored at 50 ats. and distilled for purification, releasing surplus NH<sub>3</sub>, which was recirculated.

Amines of other higher alcohols were made in a similar way.

#### SCHIFF'S BASE

Dr. Henisch said this was made by reacting isobutylamine and isobutyraldehyde at 1 at (the catalyst, if any, was not specified) and hydrogenating the product at 200-220 ats.

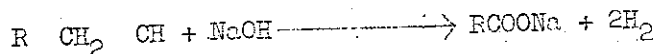


The hydrogenation was carried out in apparatus similar to that used for the manufacture of isobutylamine, using the same catalyst, NiS.WS<sub>2</sub>. The feed rate at Schiff's base was 40 l/hr. and the make-up H<sub>2</sub> rate was 40 to 50 M<sup>3</sup>/hr, the temperature being 220 to 310°C; the catalyst volume was only 40 l.

## XVIII. MANUFACTURE OF CARBOXYLIC ACIDS.

Information on this process was obtained from Dr. Gericke, the plant foreman, with whom the installation was inspected.

The process is based on the following reaction:



It is carried out by vaporising the alcohol and passing the alcohol vapor into a mixture of NaOH and alcohol maintained at 446 - 518°F; the violent mixing obtained in this way is important for successful operation. An excess of 17% NaOH beyond the amount required for complete conversion of the total quantity of alcohol is used in the reaction. The resulting sodium salt of the carboxylic acid is subsequently converted into the free acid. N-butyl, iso-butyl, hexyl and heptyl alcohols have been successfully processed but the C<sub>8</sub>-C<sub>12</sub> alcohols were most frequently used because the resulting acids were utilised in the preparation of the lubricating oil inhibitor "R". Another use of these acids consisted in the preparation of metal salts (Zn, Ca, Mg) to be used as substitute protective coatings. The alcohols were obtained in the course of the isobutyl-alcohol synthesis.

The production of this plant amounted to 60 - 70 tons/month (132,000 - 154,000 lbs/month). Capacity was 150 tons/month.

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XIX. POLYMERISATION OF C<sub>6</sub> AND C<sub>7</sub> OLEFINES.

The information on this process was obtained by plant inspection and interrogation of Dr. Gericke, the foreman in charge of the plant.

The process consists of the polymerisation of C<sub>6</sub> and C<sub>7</sub> olefines to C<sub>12</sub> and C<sub>14</sub> olefines which were used in the alkylation of phenol in the course of the manufacturing process for a detergent. This part of the synthesis was carried out at Höchst and only the C<sub>12</sub>, C<sub>14</sub> polymers were prepared at Leuna.

The feed stock was made by dehydration of the alcohols boiling in the iso-hexyl and iso-heptyl alcohol range and obtained in the isobutylalcohol synthesis. The olefine fraction of maximum boiling point of 203°F was used as feed stock.

Olefine and sulphuric acid (85%) were mixed at a rate of 105 gals. of olefine to 663 gals. of acid per hour. The mixture was preheated in a 2-1/2" diameter lead coil (steam heating of a water bath) to about 120°F and introduced into a lead-lined tower of 3 ft. diameter and about 80 ft. height packed with iron Raschig rings. The mixture passed from the bottom of the tower into a settler from where it was recycled. Circulation was continued until a hydrocarbon sample withdrawn from the settler indicated that the desired polymerisation had taken place as shown by the results of a laboratory fractional distillation. The product was then caustic washed, water washed and distilled. The yield of desired polymer, boiling between 324 and 446°F, amounted to 50% by wt. of the olefine feed. The distillation range of the total reaction product and its utilisation are given as follows:

<u>% by wt. of</u> <u>feed stock</u>	<u>Boiling Range</u> <u>°F</u>	<u>Utilisation</u>
5 - 10	140 - 203	Recycled
5 - 10	203 - 324	Blended with heavy polymer.
50	324 - 446	Sp.g. product at 20°C = 0.730..
20 - 30	Above 446	Heavy polymer to hydro- genation plant.

The design capacity of the plant was 440,000 lbs. of product/month but actual output of C<sub>12</sub>, C<sub>14</sub> polymers was only 66,000 - 88,000 lbs/month. Samples of the olefine feed stock and polymers product were obtained for detailed examination.

XX. FERTILISERS AND NITRIC ACID

This Division covers the manufacture of Ammonium Sulphate, Nitric Acid, Calcium Nitrate (Kalksalpeter), Ammonium Nitrate and Calcium Carbonate mixture (Kalkamonsalpeter, equivalent to Nitro Chalk), Leuna Salpeter, and Phosphate Fertilisers. Dr. Ernst Willfroth was interrogated on May 12th; he was the Manager of the Nitrogen Division. There appeared to have been no major developments in what were old-established processes.

Ammonium Sulphate

This was made by the reaction of Anhydrite with  $\text{NH}_3$  and  $\text{CO}_2$ . The capacity of the plant up to 1935 was 500 T/D N; in 1935 a part of the building was taken over to produce Leuna Salpeter, so that the capacity of Sulphate dropped to 300 T/D N.

Carbonated liquor was manufactured by the Ammonia Division by scrubbing out  $\text{CO}_2$  from catalysed gas at 1 at. This liquor contained 14% as  $(\text{NH}_4)_2\text{CO}_3$ . These scrubbers were followed by a Sulphuric Acid wash to recover Ammonia.

The reaction with Anhydrite was carried out in the presence of excess  $\text{NH}_3$ , and after filtering the liquor could either be decomposed by heating to recover  $\text{NH}_3$  or else it could be neutralised with 60%  $\text{H}_2\text{SO}_4$  (Sulphuric Acid was made on site, the source of Sulphur being  $\text{H}_2\text{S}$  in water gas recovered in an Alkacid Plant and converted to Sulphur in a Claus Plant).

The filtered mud contained 0.5% Nitrogen (= 2% Ammonium Sulphate) on a dry basis. Rotary filters were installed but Dr. Willfroth preferred the old wooden plate type, which was still in use; these had plates suspended inside large wooden troughs.

The evaporation of the liquor was done in double-effect evaporators. The first effect was merely a concentrator, without salting; the steam pressure was 7 lbs. g, the temperature of the solution  $106^\circ\text{C}$  and the internal pressure 100-200 mm.Hg. The second evaporator ran with steam vapours at 0.2 ats. abs. with a steam temperature of  $56-62^\circ\text{C}$  and a liquid temperature of  $46-52^\circ\text{C}$ , the final vapour pressure being 65 mm.Hg. Each evaporator had a heating surface of  $124 \text{ M}^2$ , and the combined output was 170 T/D Ammonium Sulphate. Steam consumption was about 0.9 T/T Sulphate.

The solution prior to evaporation at density of 1.24, contained 530-540 g/l Ammonium Sulphate and about 0.2 g/l  $\text{H}_2\text{SO}_4$ , with a pH of about 5.

The evaporators were lead covered throughout, but it was not stated whether any alloying metal was included. The evaporator tubes were 50 mm. I. D. and 78 mm. O. D.

The anhydrite used came from a quarry in the Harz about 130 km. away. Fuller mills were originally used, and some of these were still there, but others had been replaced by Lösscher mills, which occupied far less space but had the same energy consumption. These mills worked on the principle



of one roll working on a vertical axis, with two inclined rolls running on the top, the ground material being removed by hot air.

The plant itself was very old and there had been no advances made in recent years; the double-effect evaporation has been in use for many years. The plant has been shut down since May of 1944, owing to non-availability of  $\text{NH}_3$ . Direct air raid damage was not very great, and the plant personnel estimated that they could make 100 T/D N after 4-6 weeks and 300 T/D N after 10 months.

### Nitric Acid

The plant was built in 1927 and was said to be the only plant in Germany working at 5 ats. The original capacity was 150 T/D N, but it had been enlarged (during the war?) to 260 T/D. Most, if not all the other I. G. plants erected elsewhere operated at 1 at. The main advantage of using a pressure process was stated to be the saving of space for the absorption system, and the process was economic if energy was not too expensive.

Power was recovered from the hot let down gases by passing them through a turbine working on the same axis as the air compressor.

The catalyst favoured was platinum with 5% rhodium. This catalyst was much better than 1% rhodium, but in a pressure process 10% rhodium was stated to give no better results.  $\text{NH}_3$  conversion efficiency was stated to be 96% on the gauze and 92-94% after absorption. Final scrubbing of the gases was done with a lime solution. The final acid contained 48%  $\text{HNO}_3$  and was all used for making Nitrate of Lime and Ammonium Nitrate mixtures.

It had been found that if welding took place in the neighbourhood of the air compressors, poisoning of the catalyst resulted, and this was put down to the presence of poisons such as  $\text{PH}_3$  in the acetylene.

The plant was not inspected closely but from a distance it appeared to be relatively undamaged.

### Concentrated Nitric Acid

This was not made by working up 48%  $\text{HNO}_3$ , but was made directly from the nitric acid oxidation gases. Gases after the waste heat boiler were further cooled and then oxidation of  $\text{NO}$  to  $\text{NO}_2$  allowed to take place. The gases were then indirectly cooled with water to remove  $\text{H}_2\text{O}$  as weak  $\text{HNO}_3$ . The gases were then further cooled to  $-10^\circ\text{C}$  to give liquid  $\text{NO}_2$ . This  $\text{NO}_2$  was then treated in an autoclave at 80-100 ats. and  $70^\circ\text{C}$  with dilute Nitric Acid and Oxygen, yielding pure  $\text{HNO}_3$  plus  $\text{N}_2\text{O}_4$ . On distillation this mixture evolved  $\text{NO}_2$ , which was returned to the process and gave 99%  $\text{HNO}_3$  at the bottom of the still.

### Ammonium Nitrate

Only a small quantity of the pure material was made; the bulk was made into Kalkammonsalpeter. This latter plant was not investigated but the process was said to be very similar to that used in making Nitro-Chalk. A spray tower was at the end of the building.

I.C. 7370

Calcium Nitrate (Kalksalpeter)

This plant was very heavily damaged but the material could be produced in the Nitro-Chalk plant, although not at the same time as Nitro-Chalk.

Phosphate Fertilisers

This was contained in the same building as Ammonium Sulphate, but none had been made during the war, owing to shortage of phosphates.

Leuna Salpeter (Amm. Sulphate & Nitrate)

This plant also formed part of the Ammonium Sulphate plant, but was not inspected in detail; it had suffered little air raid damage.

Ammonium Chloride Fertilisers

No work had been done on developing Ammonium Chloride fertilisers, which were said to be unsuitable for German soils.