XVI. MERSOL PROCESS

The Mersol reaction consists in treating paraffin hydrocarbons with SO_2 and chlorine to produce sulphonyl chlorides.

$$R.H + SO_2 + Cl_2 = R.SO_2Cl + HCl$$

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. SO_2 and Cl_2 were blown through the reaction mixture using a small excess of 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 "Tylose" (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 SO_2 and 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.

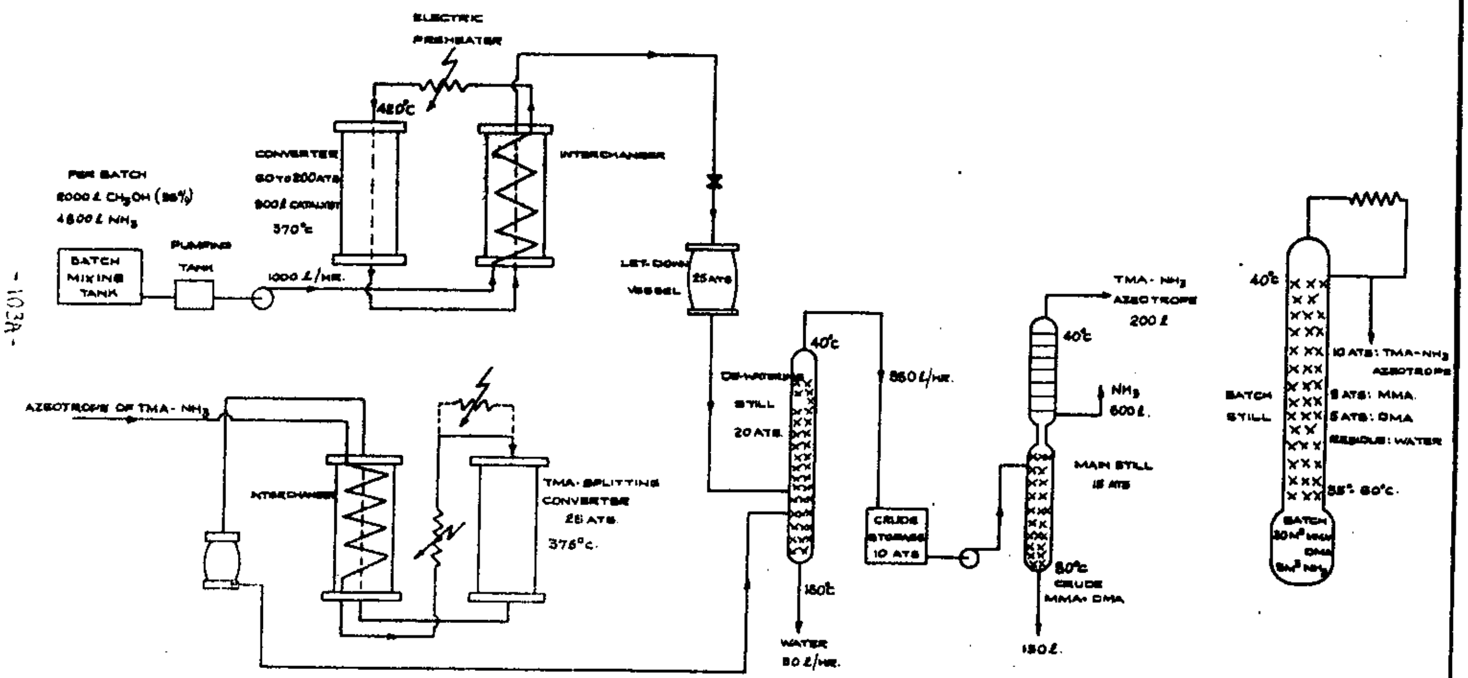

FIG XXXVII METHYLAMINE MANUFACTURE