

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 NH_3 to 1 mol CH_3OH , 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 interchanger were both made of SI steel (low carbon steel) with copper lining and the electrical preheater was copper-covered. The converter was 500 mms I.D. and 8000 mms long, containing about 900 l. of catalyst. There was said to be little difference in performance between catalyst 6069 (90% Al_2O_3 and 10% kaolin) and catalyst 6067 (50% Al_2O_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 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- NH_3 azeotrope taken overhead and 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- 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.

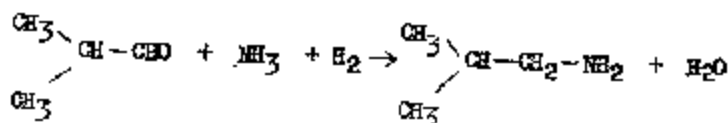
Final purification of the crude MMA and DMA mixture was carried out in a batch still. A batch consisted of 30 M³ of the crude mixture, with 5 M³ NH_3 added to provide NH_3 for TMA separation. The still had an I.D. of 700 mm and was packed with 18 m of Raschig rings. With the top temperature kept at 40°C and the bottom temperature at 55° to 60°C, the TMA- 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.



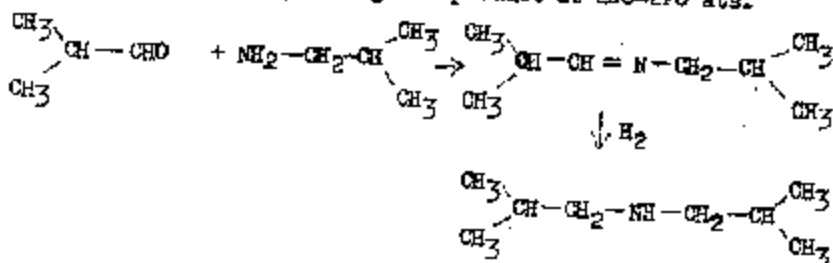
The only details obtained of the manufacture of isobutyraldehyde were that, whereas formerly this had been made by passing isobutanol at 1 at. and 370°C over 2493 (zinc sulphide on pumice, a sample of which was obtained), the method now preferred was to pass isobutanol with air over a silver gauze.

The synthesis of isobutylamine was carried out at 220 ats. over catalyst 3076, NiS.NH₂, a sample of which was obtained, at a temperature of 300°C. 1800 to 2000 M³/hr. H₂ and 600 to 800 l/hr. NH₃ 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 H₂ recirculated. The crude was stored at 50 ats. and distilled for purification, releasing surplus NH₃, which was recirculated.

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

SCHIFF'S BASE

Dr Hanisch 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.WS₂. The feed rate of Schiff's base was 40 l/hr. and the make-up H₂ rate was 40 to 50 M³/hr, the temperature being 220 to 310°C; the catalyst volume was only 40 l.