

The production of methylamines and their derivatives

Introduction

1. MMA, DMA and TMA are predominantly used for manufacturing derivative products. Figure 1 summarizes the reactions involved in producing the methylamines and the derivatives relevant to this inquiry: DMF, choline chloride and the three AAAs: MMEA, DMAE and MDEA.

FIGURE 1

Methylamines and their derivatives

<i>Inputs</i>	<i>Methylamines</i>	<i>Inputs</i>	<i>Derivatives</i>	<i>Key end use</i>
Methanol + Ammonia	= { MMA { { DMA { { TMA	MMA + Ethylene oxide (EO)	= { AAAs { MMEA { { MDEA	Coatings Brightening agent
		DMA + EO	= DMAE	Fabric softener Gas treatment
	= DMA	DMA + carbon monoxide	= <i>DMF</i> DMF	Water treatment
	= TMA	TMA + hydrochloric acid and EO	= <i>Choline chloride</i> Choline chloride	Solvents
				Animal feed

Source: CC, based on information from the parties.

2. The parties told us that producers of all these products could expand capacity significantly by optimizing the performance of their existing plants and making de-bottlenecking investments.

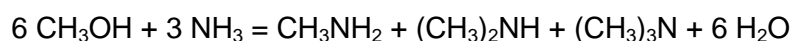
Methylamines

3. The three methylamines are colourless, highly reactive, flammable gasses or volatile liquids with distinct odours resembling that of ammonia with a fishy undertone. They and their derivatives are classified as volatile organic compounds that are harmful to inhale and irritate the respiratory system. The methylamines are predominantly used as building blocks to produce methylamine derivatives. In Europe, these activities are usually vertically integrated: both Taminco and AP use around [X] per cent of the methylamines they produce internally.
4. MMA has the chemical formula CH_3NH_2 , DMA has the formula $(\text{CH}_3)_2\text{NH}$ and TMA has the formula $(\text{CH}_3)_3\text{N}$. Their molecules are thus essentially ammonia (NH_3) molecules with one or more hydrogen atoms (H) replaced by methyl (CH_3) groups. As a result they share many of the chemical properties of ammonia.
5. All manufacturers of methylamines produce the three compounds simultaneously in one reaction. This involves reacting methanol¹ (CH_3OH) with ammonia under high

¹Also known as methyl alcohol.

pressure and temperature and in the presence of a fixed catalyst; it results in a mix of MMA, DMA and TMA and water (H₂O). At a molecular level, one or more hydrogen atoms in each ammonia molecule are replaced by a methyl group; if one is replaced it results in MMA, if two are replaced it results in DMA and if all three are replaced it results in TMA.

6. The quantities of each methylamine produced are dependent on the reaction procedure, the reaction conditions and the catalyst used. On average, Taminco mix of [x] per cent MMA, [x] per cent DMA and [x] per cent TMA. The proportions of MMA, DMA and TMA produced by a plant can be altered significantly within four days. The reaction is as follows:



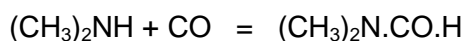
7. A production unit consists of a synthesis section and a distillation section. In the synthesis section, measured quantities of methanol and ammonia are fed continuously through evaporators and heat exchangers into a reactor filled with a catalyst. As the reaction is an equilibrium reaction, MMA, DMA or TMA can be fed back into the synthesis section to change the mix of products produced. This may be economic when the commercial outlets for a particular product are limited. The resulting mixture is separated, and the methylamines purified, by means of a number of distillation columns, connected in series. The whole installation runs continuously and is completely automated.
8. The anhydrous amines are stored as liquified gases in pressure tanks. They are transported by means of trucks or railway containers. Some customers require aqueous solutions of MMA and DMA, which can be produced by mixing the anhydrous products with demineralized water. These solutions are shipped in bulk or drums.

Methylamine derivatives

9. There are over 200 highly varied end-uses for the methylamine derivatives relevant to this inquiry, including agricultural chemicals, electronics, explosives, fuel additives and chemicals for the paper industry.

Dimethylformamide

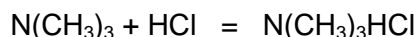
10. DMF is used as a solvent and has the chemical formula (CH₃)₂N.CO.H. It is produced commercially through the following continuous reaction between DMA and carbon monoxide (CO) at high temperature and pressure in the presence of a liquid catalyst dissolved in methanol:



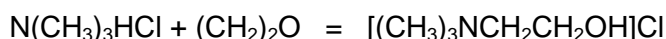
11. Carbon monoxide may be replaced by methyl formate in the above reaction. After separating the catalyst, the product is sent to a distillation section to be purified.
12. AP's plant was also capable of producing dimethylacetamide.

Choline chloride

13. Choline chloride, which is also known as vitamin B4, is used primarily as an additive in animal feed.² It has the chemical formula $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]\text{Cl}$. Choline chloride is produced in two reaction stages using TMA, ethylene oxide³ (EO) and hydrochloric acid (HCl). In the first, batch production stage TMA, which is strongly basic,⁴ is added steadily to hydrochloric acid and reacts vigorously:



14. Further TMA is added to the solution until its acidity has been almost neutralized.
15. Then, in the second, continuous production stage, the resulting trimethyl ammonium hydrochloride is pumped into a reactor, where it reacts with the unstable EO $(\text{CH}_2)_2\text{O}$:



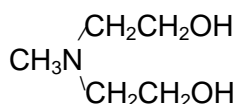
16. The resulting aqueous choline chloride solution is partially evaporated to achieve a choline chloride concentration of about 75 per cent.

Alkylalkanolamines

17. AAAs are a class of chemicals whose molecules each consist of an alkyl component, such as a methyl, ethyl or propyl group, combined with an alkanol component, such as an ethanol or propanol group, and an amine component. The three AAAs relevant to this inquiry are derived from methylamines. They are all produced by reactions between individual methylamines and EO. The technology used to produce the different AAAs is similar and most AAA producers produce all three. They can switch production between them using the same reactor; the parties told us that switching production is relatively inexpensive and takes at most three days. MDEA and DMAE are by far the most commercially important of the AAAs. MMEA production accounts for only approximately 5 per cent of total AAA production.

Monomethylethanolamine and methyldiethanolamine

18. MMEA is used in specialty coatings, as a brightening agent, and as an intermediate in the manufacture of antihistamines. It has the chemical formula $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{OH}$.
19. MDEA is used as a fabric softener or for gas treatment and has the following chemical structure:



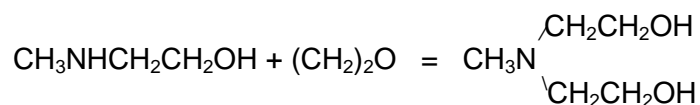
20. The production process that produces both these compounds involves a two-stage reaction between MMA and EO at high temperature. This simultaneously produces a

²Small quantities of highly purified choline chloride are also produced for human consumption. Neither of the main parties produces this grade of choline chloride.

³EO is a highly unstable compound which requires handling with great care.

⁴A base is a chemical compound that reacts with acids to form salts.

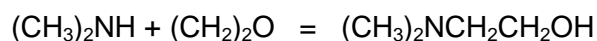
mixture of MMEA and MDEA. MMA and EO are added continuously to the reactor whilst maintaining an excess of MMA. The two reaction stages are:



21. MMEA and MDEA are then separated and purified in a number of distillation stages. The excess MMA is recycled.

Dimethylaminoethanol

22. DMAE is also known as dimethylethanolamine (DMEA). It is used in water treatment products as a flocculant. DMAE has the chemical formula $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$ and is produced commercially by a reaction between DMA and EO at high temperature and pressure:



23. The reaction normally takes place without any solvent or catalyst. (Some producers may, however, use solvents such as methanol to reduce the reaction temperature.) DMA is fed into a reactor that is essentially a long pipe into which EO is introduced. There has to be a slight excess of DMA to ensure that all the EO is consumed. After the reaction is complete, the mixture is cooled down and degassed before the DMAE is purified by distillation. The excess DMA is recycled.