ABSTRACT

In this article, the most important technologies to produce fatty amines from fatty acids and fatty alcohols are described. Surprisingly, none of these technologies are practised in the palm oil producing countries. While Southeast Asia became the global leader in the field of fatty acids and fatty alcohols, the area of fatty amines has been completely ignored until now. The reasons for this abstention will be analysed, and possible concepts for a future development of this industry in the region will be evaluated.

INTRODUCTION

Fatty amines are produced by different manufacturing technologies in many countries of the world (Table 1). There is no reliable data concerning the global production of different fatty amines since the amine producers are also producers of derivatives using fatty amines as the starting material (surfactants, biocides, flotation agents, bitumen emulsifier, corrosion inhibitor, etc.). The total global fatty amine production from fatty acids and fatty alcohols is around 800 000 t. Surprisingly none of the major palm oil and palm kernel producing countries are active in this field. The dramatic developments in fatty acid, fatty alcohol, fatty methyl ester and glycerine production in Malaysia and Indonesia have not been seen until recently in the area of fatty amines. So today the world of fatty amines is not too different from that of 20 years ago. Significant investment in new capacity have only been seen in China and India.

Before looking for an explanation of why fatty amines have not developed in the palm oil producing countries, the different manufacturing technologies will be discussed.

MANUFACTURING TECHNOLOGIES

Fatty Amines from Fatty Acids

Primary fatty amines are today only produced in a two-step process from fatty acids (Figure 1). In the first step, in order to produce the nitrile, the handling of liquid ammonia is required. The hydrogenation of the nitrile in the second step has to be carried out in the presence of ammonia if a high yield of primary amine is desired. In the absence of ammonia, the primary amine formed initially is transformed into secondary amine (Figure 2). In a further step, the secondary di-alkyl amine can be

TABLE 1. COUNTRIES PRODUCING FATTY AMINES

<table>
<thead>
<tr>
<th>Country</th>
<th>Company name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>Clariant, Akzo</td>
</tr>
<tr>
<td>Mexico</td>
<td>Quimikao</td>
</tr>
<tr>
<td>USA</td>
<td>Akzo, Evonik, Corsicana, Tomah, Lonza</td>
</tr>
<tr>
<td>Spain</td>
<td>Kao</td>
</tr>
<tr>
<td>France</td>
<td>Ceca</td>
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<tr>
<td>Belgium</td>
<td>Akzo</td>
</tr>
<tr>
<td>Germany</td>
<td>Clariant, Kao, Ecogreen</td>
</tr>
<tr>
<td>India</td>
<td>Indo-Amines</td>
</tr>
<tr>
<td>China</td>
<td>China Resources, Feixiang</td>
</tr>
<tr>
<td>Philippines</td>
<td>Kao</td>
</tr>
<tr>
<td>Japan</td>
<td>Kao, Lion-Akzo, NOF</td>
</tr>
</tbody>
</table>

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Fatty Amines from Palm Oil and Palm Kernel Oil

Transformed into di-alkyl methyl amine, the raw material for the production of di-alkyl di-methyl ammonium chloride (Figure 3).

From primary amines, di-amines and tri-amines are produced through the addition of acrylonitrile followed by hydrogenation in the presence of ammonia (Figure 4). Until about 15 years ago, di-alkyl di-methyl ammonium chlorides were the most important derivates of fatty amines, since they were the basis for fabric softeners in most of the countries of the world. In Europe, they were rapidly replaced by the better biodegradable esterquats, and this led to a large fatty amine over-capacity. Outside Europe this transition was much slower and only partial, so that the problems of over-capacity remained limited. In order to reduce the over-capacity problems in Europe, several plants were closed.

In other countries of the world, only marginal capacity increase projects were carried out, since European producer could service this market with their excess production capacity. Only in the last five years have important capacity increasing projects for fatty amines from fatty acids been carried out, but only in China and India.

Fatty Amines from Fatty Alcohols

Fatty alcohols are increasingly used to produce alkyl di-methyl amines (ADMA) and short chain di-alkyl methyl amines (DAMA) (Figure 5). The main raw materials for ADMAS are C12-14, C16-18 and C20-22 alcohols. DAMA are generally produced from C8-C10 fatty alcohols. These amines can also be produced from fatty acids, via nitrile hydrogenation, but synthesis from fatty alcohols is today the preferred route. Also a different class of amines are produced from fatty alcohols, i.e.,

\[
\begin{align*}
\text{R-CN} + 2 \text{H}_2 & \rightarrow \text{RCH}_2 - \text{NH}_2 \\
2 \text{R-CN}_2 - \text{NH}_2 & \rightarrow (\text{R-CH}_2)_2\text{NH} + \text{NH}_3
\end{align*}
\]

Reaction condition similar to production of primary amines, but reaction proceeds only if formed ammonia is extracted from the reaction.

Figure 2. Production of secondary amines from fatty acids.

Figure 3. Production of di-alkyl di-methyl ammonium chloride from secondary amines.
the ether amines (Figure 6), which are produced by reacting fatty alcohols with acrylonitrile followed by a hydrogenation in the presence of ammonia.

**Fatty Amines from Petrochemical Raw Materials**

Until recently ADMA and DAMA were produced on a large scale from alfa-olefins in the USA by Albemarle and Procter & Gamble (Figure 7). About a year ago, Procter & Gamble announced that it had stopped this production and is now sourcing the amines from Feixiang (China) which produces ADMA and DAMA from fatty alcohols. This development is comparable to the gradual replacement of petrochemical fatty alcohols by natural fatty alcohols, which has been seen over the last 20 years.

**THE ABSENCE OF FATTY AMINE PRODUCERS IN PALM OIL PRODUCING COUNTRIES**

It seems that the following factors are the reason why the production of fatty amines did not develop in Malaysia and Indonesia in the same way as the production of fatty acids, fatty alcohols, glycerine or methyl esters.

**Step 1**

\[
R\text{-NH}_2 + CH_2=CH-CN \rightarrow R\text{-NH-CH}_2\text{-CH}_2\text{-CN}
\]

**Step 2**

\[
R\text{-NH-CH}_2\text{-CH}_2\text{-CN} + 2H_2 \rightarrow R\text{-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2
\]

Trough repetition of Step 1 and 2, Tri-amines can be produced from Di-amines

\[
R\text{-OH} + HN\text{-CH}_3 \rightarrow RN\text{-CH}_3 + H_2O
\]

ADMA

\[
2 R\text{-OH} + H_2N\text{-CH}_3 \rightarrow R\text{-N-CH}_3 + 2 H_2O
\]

DAMA

Catalyst: CuCr, CuNi, CuZn, CuCrBa, Pd, etc.
Reaction Temperature: 160°C - 180°C
Reaction Pressure: < 2 bar hydrogen

*Figure 4. Di-amines and tri-amines from primary amines.*

*Figure 5. Fatty amines from fatty alcohols.*
For the traditional production of C16/C18 fatty amines, tallow is the preferred raw material. From the technical point of view tallow can be replaced without any problem by palm oil, palm stearin or even palm fatty acid distilled (PFAD). Since in most of the countries in which fatty amines are produced tallow is cheaper than palm oil, there is no incentive to change raw material. The movement toward vegetable raw materials, which took place in the field of fatty acids and fatty alcohols, has not been observed with fatty amines, probably because fatty amines from fatty acids are mostly used in technical areas. It seems obvious that any fatty amine capacity in Southeast Asia would use vegetable raw materials (PFAD, palm stearin) instead of tallow.

The Handling of Liquid Ammonia and Short-chain Amines

The oleochemical industry in Southeast Asia is not accustomed to work with liquid ammonia and methyl amines. Also as a by-product, large amounts of diluted ammonia solutions must be handled. The ammonia must be recovered through distillation, or a use of the aqueous ammonia solution must be found, since it cannot be released into the environment.

Lack of Marketing Know-how

Fatty amines are more difficult to sell than fatty acids or fatty alcohols. Fatty amines are sold in many different markets which require also applied research know-how, which is not generally available in the region. It seems logical that any activity in the fatty amine area in palm oil producing countries be best carried out together with a traditional amine producer from Japan, Europe or the USA.

The Historical Capacity Excess in Europe

The excess capacity which existed in Europe in the past is one reason why the established producers of fatty amines are hesitant to invest in palm oil producing countries. It must also be considered that leading traditional fatty amine producers (such as Kao or Akzo) are already producing fatty amines in Asia, which makes it difficult to justify an investment in Malaysia or Indonesia. However, recent capacity increases in India and China by local companies (Indo-Amines, China Resources and Feixiang) indicate that there is a growing demand for fatty amines in Asia.

The Availability of Manufacturing Technology

In contrast to fatty acids, fatty alcohols, glycerine or methyl ester, the technology to manufacture the different types of fatty amines is closely protected.
by traditional producers and is thus not easily available for new entrants. Although there are engineering companies offering fatty amine production technology, their know-how is limited because of the lack of investment activity in past years.

**SUMMARY**

The market for the different types of fatty amines is growing in Asia, as shown by recent investments in additional capacity. Recently, Feixiang, the largest Chinese fatty amine producer, which in the meantime is one of the largest in the world, has been sold to the French group Rhodia for around USD 490 million. This price (equivalent to an EBITDA of nine times sales), for a company with around USD 250 million, can only be justified by strong growth expectation. The difficulties in entering the fatty amine market for oleochemical companies in palm oil producing countries can be best overcome by cooperation with an established producer, who is not present in Asia and wants to develop a position in this growing market.