FEEL THE CHEMISTRY

AGROLINZ

MELAMINE

INTERNATIONAL

AMI
Development of AMI Melamine Technology

Low pressure versus High pressure
Agenda

- History
- Chemistry
- Overview on Melamine Process
- AMI Melamine Processes
• Melamine was first described by Liebig in 1834

• Approx. 100 years later the condensation with formaldehyde as an important application was discovered

• 1943 American Cyanamid Co discovered that Melamine could be obtained by thermal decomposition of urea

• Until 1960 Melamine was manufactured from dicyandiamide in autoclaves in batch processes
History 2/2

• 1960 Allied Chemical operated first urea-based high pressure melamine plant (license from American Cyanamid)
• During same period Nissan Chemical and Montedison developed their own high pressure process
• Between 1960 and 1965 BASF, DSM/Stamicarbon and AMI\(^*\) developed their own low pressure technology
• 1990 AMI bought the Montedison process and developed the high pressure technology further (mid 1990’s).
• Today both types, high and low pressure processes, are worldwide in operation

\(^*\) at that time Österreichische Stickstoffwerke, later Chemie Linz
**Chemistry**

**Urea decomposition:**

\[ 6 \text{(NH}_2\text{)}_2\text{CO} \rightleftharpoons 6 \text{HNCO} + 6 \text{NH}_3 \]

Urea \quad \text{Isocyanic Acid} + \text{Ammonia}

**Melamine formation:**

\[ 6 \text{HNCO} \rightleftharpoons \text{C}_3\text{N}_3(\text{NH}_2)_3 + 3 \text{CO}_2 \]

Isocyanic Acid \quad \text{Melamine} + \text{Carbon Dioxide}

**Overall:**

\[ 6 \text{(NH}_2\text{)}_2\text{CO} \rightleftharpoons \text{C}_3\text{N}_3(\text{NH}_2)_3 + 6 \text{NH}_3 + 3 \text{CO}_2 \]

Urea \quad \text{Melamine} + \text{Ammonia} + \text{Carbon Dioxide}

\[ \Delta H > 0 \]

\[ \Delta H < 0 \]
Today all industrial processes use Urea as feedstock

Off-Gas recycle to Urea Plant for efficient feedstock use
Process Basics

High Pressure Synthesis

- Synthesis Conditions:
  370 - 400 °C
  80 - 150 bar

- **No** catalyst required

- Reaction in Liquid Phase

Low Pressure Synthesis

- Synthesis Conditions:
  370 - 400 °C
  1 - 7 bar

- Catalyst required

- Reaction in Fluidized/Fixed Bed
## Competing Technologies in Melamine Recovery

<table>
<thead>
<tr>
<th>High Pressure</th>
<th>Low Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aqueous Recovery</strong></td>
<td><strong>Aqueous Recovery</strong></td>
</tr>
<tr>
<td>- AMI Agrolinz</td>
<td>- AMI Agrolinz</td>
</tr>
<tr>
<td>- Nissan</td>
<td>- DSM / Stamicarbon</td>
</tr>
<tr>
<td>- Eurotechnica ¹</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dry Recovery</th>
<th>Dry Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>- DSM (SLP) ²</td>
<td>- BASF</td>
</tr>
<tr>
<td>- LURGI/Tsingda Huaye</td>
<td></td>
</tr>
</tbody>
</table>

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¹ Formerly Allied Chemicals  
² Formerly MCI (Melamine Chemicals)
AMI LP-Process 1/2

• Two stage, low pressure, vapour phase, catalytic process
• Decomposition of Urea and synthesis of Melamine in separate reactors
• Melamine will be recovered from reactor effluent by quenching with mother liquor
• Removal of unreacted urea by thermal treatment of mother liquor and re-crystallization of the Melamine obtained in this process
• Product purity > 99,8 %
• Off-gas treatment is integral part of the plant; NH$_3$ and CO$_2$ are obtained as pure gases
• By-product Guanidin Carbonate (approx. 3%)
Ammonia gas preheating (salt) → Ammonia gas preheating (Dowtherm) → Ammonia gas preheating (steam) → Ammonia compression → Offgas recovery and treatment → CO₂ + H₂O

Urea decomposition (sand fluidized bed reactor) → NH₃ + HNCO → Melamine catalyst fix bed reactor → NH₃ + CO₂ + Melamine + HNCO → Quenching → NH₃ + CO₂ + H₂O → Melamine filtration → H₂O → Melamine drying → Melamine to storage

Molten salt heating unit → natural gas → molten urea → Urea decomposition

NH₃ gas for export → Ammonia compression enters the ammonia treatment section → Offgas recovery and treatment

Melamine to recrystallization → Mother liquor recovery and compression → NH₃ liquid → Quenching → NH₃ + H₂O → NH₃ slurry → Melamine filtration → H₂O → Melamine drying → Melamine to storage

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• Two stage, high pressure, liquid phase, non-catalytic process
• Urea scrubber for off-gas treatment; off-gas is dry and has same pressure as reactor
• Melamine recovered from reactor effluent (2\textsuperscript{nd} stage) by quenching with mother liquor and process condensate
• Purification by decomposition of poly-condensated by-products with caustic soda
• Treatment with activated carbon before crystallization
• Product purity: > 99,8 %
• Off-gas can be condensed without additional water in an Urea plant
AMI HP-Process 2/2

High pressure section

- Urea scrubber
  - molten Urea
  - steam
  - condensate

- Melamine reactor (1st stage)
  - molten Urea
  - molten Melamine
  - natural gas
  - molten salt heating unit

- CO2 Stripper (2nd stage)
  - molten Melamine

- Quenching
  - molten Melamine

- Decomposer
  - Caustic soda

Low pressure section

- Ammonia gas
- Ammonium carbonate solution
- waste water treatment
- waste water to sewer
- Melamine to storage
- Melamine drying
- Melamine solid wet

- Melamine filtration

- Crystallization
- Melamine solution

- Filtration and activated carbon treatment

- Ammonia water
- H2O
- mother liquor
- mother liquor

- Ammonia water

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AMI steps in HP-Technology

- 1990: Acquisition of Montedison process and Castellanza (I) site
- 1990’s: Laboratory tests in Linz (A) and Castellanza
- 1996/97: Pilot plant in Castellanza
- 2000: Start-up of 30,000 mtpa production plant in Linz
- 2001: Start-up of 30,000 mtpa production plant in Castellanza
- 2004: Start-up of 80,000 mtpa production plant in Piesteritz (D)
- 2006: Process design for 80,000 mtpa production plant in Ruwais (UAE)
Lates Improvements in AMI HP-Process

• Urea scrubber for off-gas treatment
  => dry off-gas at p> 80 bar can be condensed and fed to the reactor of an Urea plant

• Quantitative removal of CO\textsubscript{2} from melamine melt
  => no CO\textsubscript{2} entering in LP-section

• Less by-products in melamine melt
  => higher yield on urea

• Lower temperature and pressure required for by-products degradation in LP-section

• Reduction of specific urea consumption

• Reduction of specific steam and cooling water consumption
<table>
<thead>
<tr>
<th>LP-Process</th>
<th>HP-Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>• High gas volumina</td>
<td>• No gas circulation</td>
</tr>
<tr>
<td>• Catalyst</td>
<td>• Off-gas condensation produces energy</td>
</tr>
<tr>
<td>• High energy demand for separation of off-gas</td>
<td>• Product is recrystallized</td>
</tr>
<tr>
<td>• High energy demand for compression and recompression of ammonia/carbon dioxide</td>
<td>• Thermal degradation of by-products</td>
</tr>
<tr>
<td>• Off-spec product in start-up-phase (catalyst fines)</td>
<td>• Recycling of ammonia carbonate solution to urea plant</td>
</tr>
<tr>
<td></td>
<td>• On-spec product shotly after start-up</td>
</tr>
</tbody>
</table>
## Consumption figures Melamine-Processes

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>AMI-HP</th>
<th>AMI-LP</th>
<th>Other-HP</th>
<th>Other-LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea Melt</td>
<td>t</td>
<td>3,10</td>
<td>3,25</td>
<td>3.00 - 3.26</td>
<td>3.01 - 3.10</td>
</tr>
<tr>
<td>Ammonia</td>
<td>t</td>
<td>0,2</td>
<td>0,3</td>
<td>0.6 - 0.7</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>catalyst</td>
<td>kg</td>
<td>-</td>
<td>1,5</td>
<td>-</td>
<td>3 - 6</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>kg</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>el. Power</td>
<td>kWh</td>
<td>300</td>
<td>880</td>
<td>490 - 530</td>
<td>500 - 1250</td>
</tr>
<tr>
<td>Steam</td>
<td>t</td>
<td>2,2</td>
<td>8,7</td>
<td>0.7 - 10.0</td>
<td>0.8 - 7.4</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>m³</td>
<td>180</td>
<td>500</td>
<td>40 - 900</td>
<td>20 - 700</td>
</tr>
<tr>
<td>Fuel Gas</td>
<td>GJ</td>
<td>6,8</td>
<td>11,9</td>
<td>7.0 - 7.5</td>
<td>9.7 - 15.8</td>
</tr>
</tbody>
</table>

*1) per metric ton melamine
Thank you for your attention!