36th
Syngas | Ammonia | Urea | Nitrates | Methanol | GTL | Hydrogen
CRU Nitrogen + Syngas 2023
International Conference & Exhibition

Euromel® G5 new generation: The green and energy saving melamine technology

GIUSEPPE DI RUOCCO

Eurotecnica Contractors and Engineers SpA

Milan, Italy

Eurotecnica Contractors and Engineers S.p.A. was established in Milan, Italy, in 1962.

Across a few decades Eurotecnica has reached a leading position in the melamine industry as technology provider, designer and implementer of high-pressure plants.

Eurotecnica's proprietary Euromel® Melamine Process, has been licensed for 28 plants and a total nameplate capacity exceeding 1 million tonnes per year.

The ultimate 5th generation (G5), has already been gained a massive popularity being licensed for 3 large-scale plants, as it features the lowest OPEX in the melamine industry, a reduced CAPEX because of the leaner process, the evergreen performances such as zero liquid effluents and zero solid wastes, thanks to having a purification by ammonia.

Ammonia is easily available in any fertilizer complex whereto is fully returned (therefore its consumption is zero). The water-free high-pressure reaction off-gas provide excellent performance in terms of easy and efficient recycle to the upstream urea plant.

Eurotecnica is the technology arm of the Proman family of companies, a global leader in natural gas derived products and services (www.proman.org).

INTRODUCTION

Melamine (2,4,6-triamino-1,3,5-triazine) is a thermally stable crystalline compound derived from urea.

Along with ammonia, melamine features the highest nitrogen content among the other nitrogen-based compounds.

Ammonia plays a significant role in the synthesis of Euromel® Melamine, as it uses ammonia in the reaction section to achieve high yields and push the reaction towards maximizing melamine opposing the formation of oxyaminotriazines (OAT) and polycondensates.

After Euromel® melamine outflows the Reaction Section is quenched in an ammonia-water solution for stopping the reaction mechanisms. Then it goes through a Filtering Section and the Crystallization Section where Euromel® melamine crystals are formed and physically separated from the mother liquor containing OAT still in solution.

The alkaline environment in the melamine plant purification section is essential for the final product quality, since the pH of the purification solution is sufficiently high to keep the OAT products in solution during the melamine crystallization, thus avoiding product off-spec.

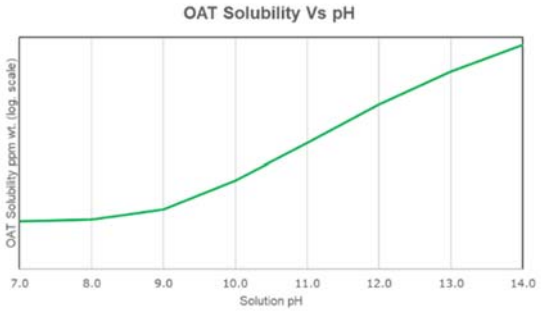


Fig. 1: Semi-log Graph; OAT solubility Vs. the pH of Solution.

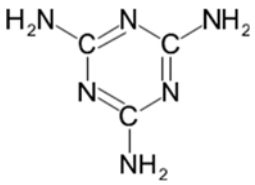
In the Euromel® Melamine Process, ammonia features an additional and very important role, as it is also used in the purification section in place of costly and erratically fluctuating add-on chemicals.

The use of ammonia in the purification of melamine provides the Euromel® Melamine plant operators with the advantage of being free from the generation of liquid effluents and solid wastes, notably unwelcome because not every country or region allows them to be released into the environment at some points.

To better understand ammonia's essential role in the purification section, the synthesis of melamine is highlighted hereunder.

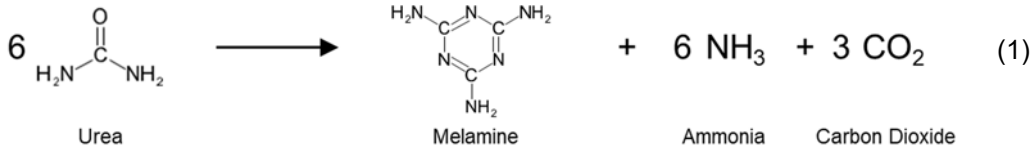
HP MELAMINE SYNTHESIS – MECHANISM OF REACTION

Melamine is the amide of cyanic acid and has the following formula:

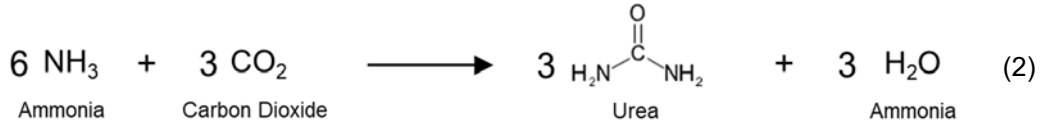


In the high-pressure non-catalytic process, the melamine synthesis occurs in the liquid phase via a multistep reaction mechanism, which results in:

six moles of urea are converted into one mole of melamine, plus six moles of ammonia (NH_3) and three moles of carbon dioxide (CO_2):



The ammonia and carbon dioxide, released in the melamine synthesis, are returned to the upstream urea plant, for reconversion into urea, according to the following reaction:



Considering the sum of reactions no. 1 and 2, the net stoichiometric urea consumption is:

$$Net\ Urea\ Consumption = \frac{3 * MW_{Urea}}{1 * MW_{Melamine}} = \frac{3 * 60.06 \left[\frac{kg_{Urea}}{kmol}\right]}{1 * 126.12 \left[\frac{kg_{Mel}}{kmol}\right]} = \frac{180.18}{126.12} = 1.4286 \left[\frac{kg_{Urea}}{kg_{Mel}}\right]$$

Where:

- MW_{Urea}= 60.06 kg/kmol;
- $MW_{Melamine}$= 126.12 kg/kmol.

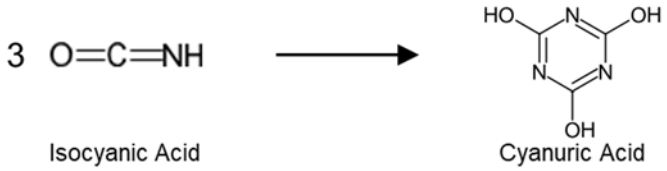
In the Euromel® process, the urea conversion occurs at high-pressure pressure and high temperature.

The overall reaction is highly endothermic, the required heat of reaction is usually provided by the circulation of heated molten salts. The reaction mechanism is based on a reaction's intermediate named "cyanuric acid", which is progressively converted into melamine through replacement of the hydroxyl groups (-OH) with three ammino groups ($-NH_2$). The main reaction's steps are the following:

1) Urea decomposes to isocyanic acid and ammonia:

(3)

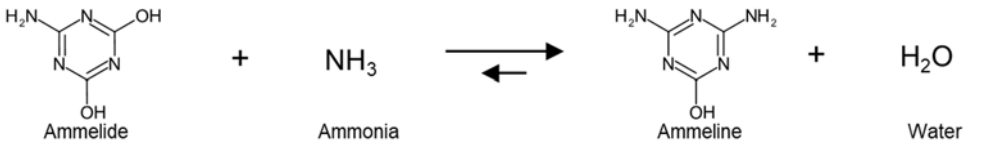
2) Isocyanic acid trimerizes to cyanuric acid:



(4)

3) cyanuric acid reacts stepwise with ammonia, by releasing water and by forming first ammelide, then ammeline and finally melamine.

(5)



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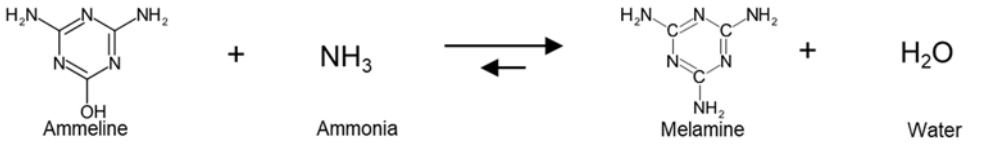
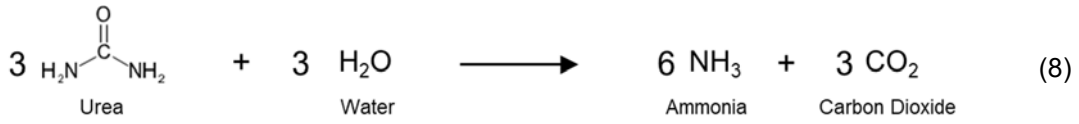


(7)

Ammelide and ammeline are also called "oxyaminotriazines" ("OAT"). Reactions no. 5, 6 and 7 are reversible at synthesis operating conditions, therefore the intermediates conversion toward melamine is pushed by means of an extra injection of ammonia in the high-pressure non-catalytic melamine synthesis section.

4) the water released in the aforesaid reactions (no. 5, 6 and 7) decomposes urea to ammonia and carbon dioxide



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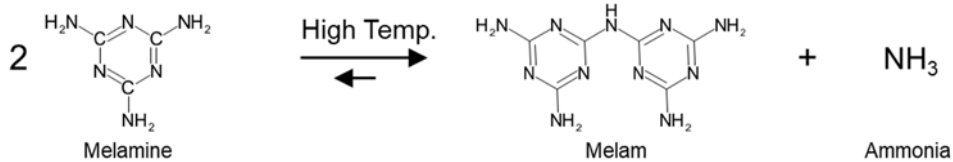
The produced melamine at the high temperature further reacts with other melamine molecules (see reactions no. 9 and 10) forming condensation compounds such as melam and melem (collectively called "polycondensates"), releasing ammonia.



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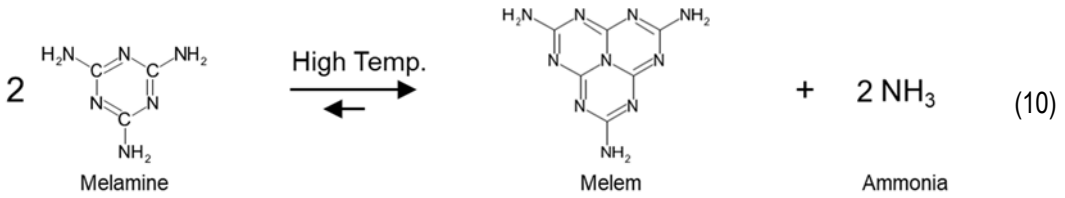


(10)

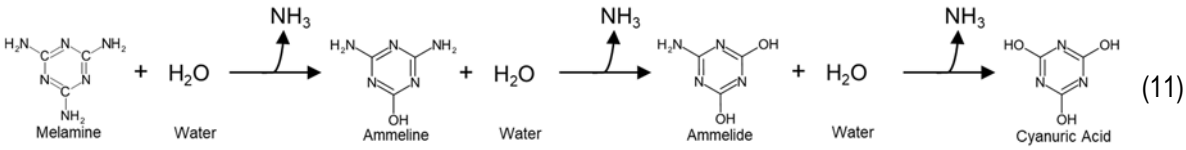
THE STRATEGIC ROLE OF AMMONIA IN THE FINISHING SECTION

Euromel® Melamine Process is characterized by using ammonia not only in the Reaction section but also in the Purification Section, where ammonia is a key player to achieve the superior performances of the Euromel® process, such as product purity, consistency, high yield and environmental friendliness.

The utilization of ammonia in the Purification Section is the best solution for both the logistics and the operations point of view, since ammonia is already available in any fertilizer complex.

Compared to other basic or alkali substances, ammonia does not require any additional facility nor special operation for unloading, storage and conditioning, neither in the melamine plant ISBL nor in the OSBL.

In the purification section ammonia has a double purpose: on one hand it raises the pH of the purification solution thus increasing the OAT solubility (as shown in fig.1). This avoids any OAT precipitation during melamine crystallization. On the other hand the high concentration of ammonia in the mother liquor is exploited so to maximize the process yield and minimize the loss of melamine due to hydrolysis reactions.

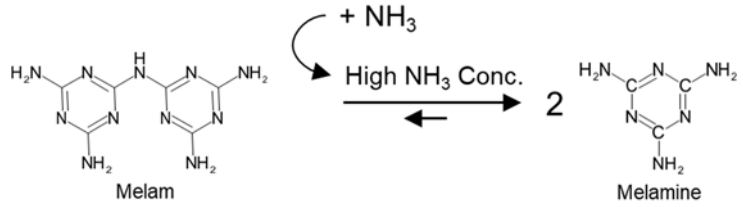


(11)

The melamine hydrolysis proceeds stepwise with the loss of one, two or three amino groups and consequent ammonia release.

The above-mentioned reactions, in Euromel® Melamine Process, are slowed down due to the high ammonia concentration in the purification solution, with the beneficial effect of reducing the melamine losses and increasing the product yield.

The high concentration of ammonia in mother liquor has an also additional benefit in supporting the condensation compounds (polycondensates) re-conversion to melamine, as per the following reactions:



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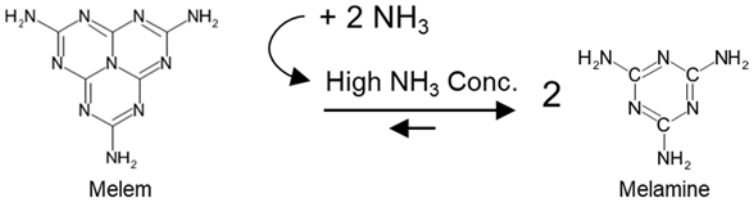


(13)

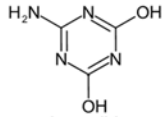
After crystallization, the melamine crystals are sent to the last stage of the melamine finishing section, where the melamine crystals are separated from the mother liquor by means of a solid-liquid decanter. Finally, the melamine crystals are dried at atmospheric pressure and sent to storage and bagging.

Also in this last section, the final product stability and purity take advantage of using ammonia which has high volatility: ammonia is fully removed during the drying stage by evaporation, so the final product purity is never affected by any foreign substances.

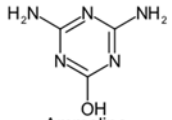
Finally, ammonia has paramount importance for the environmental sustainability of the process, thus achieving the Total-Zero-Pollution feature which is one of the main characteristics of Euromel® Melamine.

Since add-on chemicals are never used in any section of the Euromel® Melamine Process, no foreign substances pollute the process water, allowing it to be directly treated inside the melamine plant battery limits where ammonia is

recovered by distillation. The ammonia is re-used within the Euromel® Melamine Process, while the treated process water is sent to the Process Water Recovery section, where the side products (i.e., Oxyaminotryazine OAT, produced as per reaction mechanism no.11) are converted into ammonia and carbon dioxide by hydrolysis at high temperature, as per the following reaction:



Ammelide + $4H_2O$ (Water) → $4NH_3$ (Ammonia) + $3CO_2$ (Carbon Dioxide) (14)



Ammeline + $5H_2O$ (Water) → $5NH_3$ (Ammonia) + $3CO_2$ (Carbon Dioxide) (15)

The resulting pure process water is finally recycled to one of the key items of Euromel® Melamine Recovery section, named Ammonia Absorber (fig. 2), where the ammonia-rich water solution (alias mother liquor) is regenerated absorbing the gaseous ammonia previously recovered in the Ammonia Recovery section.

Fig. 2: Detail of Ammonia Absorber - XLX Euromel® Melamine Plant, Xinjiang, China – World's largest single-train HP melamine plant, 60,000 MTPY, operating since 2016

CONCLUSION

Ammonia is naturally present in any Fertilizer Complex, as shown by chemistry it has an important role in the Euromel® Melamine Process synthesis to minimize side products. Furthermore the use of ammonia in the purification section contributes to achieving the superior performances of the Euromel® Melamine Process itself, maximizing the product yields, guaranteeing product purity and stability while achieving, at the same time, the ambitious feature of Total-Zero-Pollution process.

ACKNOWLEDGMENT

Giuseppe Di Ruocco serves as the Engineering Director of Eurotecnica Contractors and Engineers SpA and leads all the engineering and process department of the Company. Eurotecnica is part of Proman Group, a multi-assets corporation engaged as global leader in the production of methanol, ammonia, nitrogen-based fertilizers and melamine. He holds a Master Degree in Chemical Engineering from Università di Salerno, Italy, in 2005.