Title: IMPROVED PROCEDURE FOR THE PRODUCTION OF HIGH-PURITY MELAMINE WITH HIGH YIELDS

Abstract: Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420 °C and a pressure above 7 MPa in which the products of reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the purification and recovery of the melamine, characterized by: the liquid phase output from the pyrolysis Reactor containing melamine, non-reacted urea, intermediate oxidized products of pyrolysis (OAT) and products of deammoniating condensation of the melamine (polycondensates), is sent to a downstream reactor (Post-reactor) that operates in substantially equal temperature and pressure conditions to those of the pyrolysis Reactor; the anhydrous gaseous phase coming from the pyrolysis reactor and from Post-reactor, are subjected to washing with molten urea for the recovery of the melamine contained in it as vapor, before being sent back to the urea synthesis plant for the recovery of NH₃ and CO₂ contained in it; the purified liquid output from the Post-reactor is treated in a Quenching Column at 160-170 °C in the presence of 10% by weight minimum of NH₃ in order to eliminate the polycondensates; the Quenching Column output is cooled and a high purity melamine separated by crystallisation from a mother liquor that is directly recycled in an amount of 80% minimum to the Quenching Column, allowing the costless recovery of ammonia and melamine; the mother liquor not directly recycled is treated for the separation of OAT and then sent back to the Quenching Column realizing the complete recovery of the melamine produced in the reaction system.
"IMPROVED PROCEDURE FOR THE PRODUCTION OF HIGH-PURITY MELAMINE WITH HIGH YIELDS"

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The present invention relates to an improved procedure for the production of high-purity melamine according to a process based on the pyrolysis of the urea under high pressure.

In greater detail, the invention refers to the process that provides for the collection and purification in aqueous solution of melamine produced in a reactor and its separation by crystallization.

It is well known that the overall reaction which transforms urea into melamine follows the stoichiometry shown in the following equation:

\[ 6\text{NH}_2\text{CONH}_2 \rightarrow (\text{CN})_3(\text{NH}_2)_3 + 6\text{NH}_3 + 3\text{CO}_2 \]

urea melamine ammonia carbon dioxide

according to which approximately 1.86 kilograms of a gaseous mixture of NH\(_3\) and CO\(_2\) (called off-gas in their entirety) are formed for every kilogram of melamine produced.

It is also well known that the most widely used process based on the pyrolysis of urea under high pressure is that described in Patent no. US-A-3.161.638 of Allied. The basis of this process is that all effluents from the melamine synthesis reactor are cooled and collected in aqueous ammonia medium. The presence of ammonia as alkaline medium prevents the
precipitation of the intermediate oxidation products of the pyrolysis reaction, called oxyaminotriazines (OAT) and enables the transformation into melamine of the de-ammoniating condensation by-products of the same (polycondensates), thus assuring a high degree of purity of the product.

According to this process a stream of off-gas is also produced containing water vapor derived from the aforementioned treatment of the entire effluent of the reactor with an aqueous medium. This gaseous phase is normally returned to the urea synthesis plant in order to recover the NH₃ and the CO₂ contained in it. However, the presence of water vapor in the off-gas stream can constitute a problem for the urea plant.

Furthermore, the residual aqueous solution (mother liquor) separated from the crystallized melamine according to this process cannot be directly recycled and reused to dissolve the melamine coming out of the reactor, because the concentration of OAT would increase continuously and, once the aqueous medium becomes saturated, OAT would precipitate together with the melamine crystals contaminating the product. For this reason, the said mother liquor must be suitably treated before being recycled, in order to separate OAT and maintain their concentration in the mother liquor at a constant level below the solubility limit. The aforesaid treatment not only renders the aqueous cycle of collection and purification of the melamine more complex, but also adds a source of costs, both in terms of investment and of energy consumption.

A simplified block diagram of an embodiment of the process according to the above-mentioned patent n. US-A-3.161.638 is shown in Figure 1, representing the state of the art for the present invention, with the aim to demonstrate the advantages of the improvements to the aforesaid process brought about by the present invention.
According to the outline in Figure 1, the urea is fed as a liquid at a temperature of 135-140°C to a pyrolysis vat Reactor that works continuously and in which a suitable heating system supplies the necessary calories to the reacting system, maintaining it at a temperature of 360-420°C. The reaction pressure is maintained at a value above 7MPa. The reactor is a single-stage one, and the reacting mass is maintained in strong circulation by the gases that are formed during the pyrolysis of the urea.

The reacted mass (liquid and gas) is continuously discharged into an apparatus (Quench) where its temperature is lowered to approximately 160°C in the presence of a water solution. Under these conditions, all the melamine, the non-reacted urea and the various impurities, pass into solution and are sent downstream to be processed, while a gaseous phase, consisting substantially of NH₃ and CO₂, is separated and recycled to the urea synthesis plant, together with the amount of water vapor corresponding to the thermodynamic equilibrium in the Quench condition.

The aqueous solution from the Quench also contains a certain amount of dissolved ammonia and CO₂ that is eliminated in the following CO₂ Stripper. The elimination of the CO₂ is necessary in order to get a high degree of purity of melamine in the down-stream treatment.

The aqueous stream from the bottom of the CO₂ Stripper, containing a residual amount of CO₂ of the order of 0.3-0.5% by weight, contains melamine at a concentration of 6-12% by weight, together with OAT and the polycondensates. The polycondensates, given their low solubility, must be eliminated before sending said aqueous stream to the Crystallizer for the recovery of the melamine.

In order to eliminate the polycondensates the solution is heated to approximately 170°C in the presence of ammonia in a suitable column, called Hydrolizer, in which ammonia is added to the warm solution until it reaches the level of 12-15% by weight. During the stay in the
Hydrolizer under these conditions, the polycondensates are almost totally transformed into melamine and, to a lesser extent, into OAT.

The purified ammoniacal solution from the Hydrolizer is fed to the Crystallizer where the temperature is lowered to 40-50° C, thus allowing the crystallization of the greater part of the melamine. The presence of ammonia in the Crystallizer serves to maintain OAT in solution and thus to separate a product characterized by a high degree of purity (+99.9 % weight).

In the following operation of Liquid/Solid Separation, the crystallized melamine is separated from an aqueous stream containing the OAT formed in reaction and in the various equipments of the aqueous circuit due to the hydrolysis of melamine.

This aqueous stream (called mother liquor) in which the residual melamine is present at a concentration of 0.8-1% by weight, cannot be recycled directly to the Quench because, otherwise, OAT content would continue to increase and, once the saturation concentration is reached, they would precipitate in the Crystallizer contaminating the product. On the other hand, the mother liquor cannot be discharged into the ambient because of the presence of large amounts of ammonia and other organic materials. Other than that, dumping these mother liquor would correspond to a heavy economic loss because of its melamine and ammonia content.

Therefore, the process according to patent n. US-A-3,161,368 provides for the treatment of the mother liquor in an Ammonia Recovery Section. Here the ammonia is completely recovered and an ammonia-free solution is produced; this solution contains almost exclusively melamine and OAT. Cooling this solution to room temperature causes the Precipitation and Separation of OAT which are thus eliminated from the aqueous cycle, allowing the re-circulation of the purified mother liquor and the recovery of the melamine it contains.
The process illustrated here above is currently in use industrially in numerous plants, but it requires a certain consumption of steam due to the necessity to treat almost the whole amount of the OAT-containing mother liquor. Furthermore, the presence of water in the stream of ammonia and carbon dioxide (off-gas) that are returned to the urea synthesis plant requires some adjustments in the operative conditions of this latter.

The object of the present invention is a process for the production of melamine which is greatly improved compared to the state of the art because: a) it enables a substantially total recovery at low cost of the melamine dissolved in the mother liquor; b) it separates and restitutes to the urea synthesis plant a gaseous stream containing CO₂ and NH₃ completely free of water; c) it obtains a substantial increase in the total yield of the plant in terms of urea consumption; d) it considerably reduces the energy consumption of the whole process; e) it reduces the number of processing steps, increasing the stream factor and the investment cost of the plant.

The object of the invention is achieved by a process that introduces simple but substantial modifications to the state of the art.

The main variations consist of the separation of off-gases from the product of pyrolysis of the urea before the treatment of melamine in the aqueous medium, and the introduction of a Post-reactor, downstream of the pyrolysis Reactor, fed with the liquid phase containing all the melamine produced. The employment of a Post-reactor allows urea conversion to reach practically 100% and the amount of OAT produced in the reaction to be drastically reduced.

The reduction of OAT allows, in the down stream, most of the mother liquor to be recycled directly to the Quench without any treatment, permitting the direct recovery, without loss, of the corresponding amount of ammonia and melamine it contains. In this way the mother liquor treated in the Ammonia Recovery Section and in the OAT Precipitation and Separation
Section, can be drastically reduced in comparison to the actual state of the art, with consequent reduction of investment and energy consumption.

The process of melamine synthesis according to the invention and the advantages that derive from it can best be understood from the following description of an embodiment of the present invention, with the aid of the attached Fig. 2. The description and the related outline of the process should not be considered as limiting the scope of the invention.

The block-diagram of Fig. 2 shows substantially the main equipment and the flow lines of the products and reagents of the process according to the invention.

The Reactor of Fig. 2 works in the same conditions as Fig. 1 with the difference that there are two separate outputs from the Reactor: the off-gases output and the raw liquid melamine output. Neither of these outputs contain water.

The gaseous anhydrous stream of NH₃ and CO₂ containing vaporized melamine, according to its vapor pressure, is fed to an off-gas Washing Section, operating at the same pressure as the pyrolysis reactor. In the off-gas Washing Section the melamine is removed by direct contact with molten urea fed at a temperature of 135-140°C. By this operation, in which the considerable heat content of the off-gases is recovered as steam, the melamine is completely recovered by the molten urea and the resulting liquid mixture constitutes the input to the pyrolysis Reactor. The off-gases thus purified, leaving the Washing Section at a temperature of 170-200°C, are returned to the urea plant for the total recovery of NH₃ and CO₂. In a variant of the process, the gaseous fraction formed in the pyrolysis reaction can be separated in a suitable vessel placed downstream of the Reactor or in the same Post-reactor that, in such case, also acts as a separator.

The molten urea containing the melamine recovered from the Washing Section goes to feed the Reactor by gravity or by means of a suitable pump.
The liquid stream of raw melamine leaving the Reactor is sent to the Post-reactor, which works under the same conditions of temperature and pressure of the Reactor, where it comes into intimate contact with superheated anhydrous gaseous ammonia added in amounts equal to from 1:10 to 1:1 typically 1:3 by weight on the raw liquid melamine.

The superheated ammonia passing through the liquid mass of the raw melamine extracts the dissolved CO₂ and permits the complete transformation of OAT into melamine.

The residence time of the melamine stream in the Post-reactor can vary from 0 to 2 hours, preferably from 15 to 45 minutes, obtaining a reduction of OAT content to a value lower than 6,000 ppm.

This further residence time of the liquid raw melamine stream in the Post-reactor also permits the completion of the conversion of the urea. Moreover, with the elimination of the CO₂, the partial pressure of ammonia in the Post-reactor increases with consequent reduction of the polycondensates concentration.

The purified melamine exits from the Post-reactor containing reduced amounts of OAT and polycondensates and practically no residual urea.

The superheated ammonia blown into the Post-reactor remains substantially in the vapor phase and, exiting from the Post-reactor separately from the purified liquid melamine, joins the output gas from the Reactor before the off-gases Washing Section, where the recovery of the melamine present in the vapor phase occurs.

The purified liquid melamine stream is fed to the Quenching Column which, due to the absence of a gaseous phase, operates completely full of liquid. The purified liquid melamine enters at the bottom of the Quenching Column, which is kept strongly agitated by mechanical means, and is brought into intimate contact at a temperature of 160-170°C with a water and ammonia solution coming from the purification circuit. The solution thus formed, in which
the NH\textsubscript{3} content is maintained at a value above 10\% by weight, proceeds upwards for sufficient contact time to transform the residual polycondensates coming from the Post-reactor into melamine. Since the concentration of CO\textsubscript{2} in the Quenching Column is very low (less than 0.1\% by weight), effective hydrolysis of polycondensates is obtained in this column with very short contact times (under 30 minutes).

The aqueous solution of melamine from the head of the Quenching Column is fed directly to the Crystallizer where the temperature is lowered to 40-50°C, causing precipitation of crystals of very high-purity melamine which are separated from the mother liquor in the next stage, the Liquid/Solid Separator.

The mother liquor in output from the Liquid/Solid Separator contains a reduced amount of OAT, far from the saturation value, since the latter have been drastically reduced in the Post-reactor. Therefore the greatest part of the mother liquor can be recycled to the Quenching Column, without any treatment, with no risk of OAT reaching the saturation value in the Crystallizer with consequent precipitation.

According to the proposed process which characterizes the invention, in order to stabilize the concentration of OAT in the circulating aqueous solution at a value prudentially far away from the value corresponding to the saturation in the Crystallizer condition, it is sufficient to send only a small part of the mother liquor to the Ammonia Recovery Section and to the OAT Precipitation and Separation system. The portion of mother liquor which undergoes treatment is in fact less than 20\% of the output from the Liquid/Solid Separator. The less the amount of OAT output from the Post-reactor, the smaller this quantity will be. In other words the higher the efficiency of the Post-reactor in reducing OATs, the smaller is the portion of mother liquor which must be sent to the treatment and the greater is the economic saving obtained in terms of investment cost and energy consumption.
The portion of mother liquor not directly recycled to the Quenching Column is subject to the same treatment as in the cycle illustrated in figure 1 and, after the separation and the recovery of the ammonia in the Ammonia Recovery Section and the elimination of OAT in the OAT Precipitation and Separation section, is also recycled to the Quenching Column, permitting the total recovery of the melamine and ammonia. The concentration of CO₂, present in minimal amount in the purified output from the Post-reactor, is maintained constant in the circulating aqueous solution by continuously extracting a stream rich of CO₂ from a suitable point of the Ammonia Recovery Section.

The process proposed gives the following considerable advantages:

1. Production of off-gases without water (anhydrous off-gas) and at a higher pressure that facilitates their recovery in the urea plant to which they are returned. The economic value of anhydrous off-gases is higher than that of wet, lower pressure, off-gases produced by the current process.

2. The simplification of the aqueous purification circuit and the drastic reduction in the dimensions of the Ammonia Recovery Section and the OAT Precipitation and Separation Section involve a net reduction of the investment cost which exceeds the added investment for the Post-reactor vessel and the off-gas Washing Section. The system based on the process object of the present invention provides for an investment reduction in excess of 15% compared with the classic plant.

3. The total conversion of urea and the almost complete transformation of OAT into melamine in the Post-reactor involves an increase in overall yield of the process corresponding to a reduction of at least 8% in consumption of the urea, compared to the existing technology.
4. A further increase in overall yield of the process is due to the reduction of hydrolysis of the melamine into OAT in the aqueous cycle because of the smaller numbers and volume of the equipments in which the melamine remains in contact with aqueous solutions at high temperature. The reduction of number and volume of the equipments in the aqueous cycle is consequent to the simplification of the same cycle and the drastic reduction in capacity of the Ammonia Recovery Section.

5. The direct recycling of the greatest part of mother liquor from the Liquid/Solid Separator to the Quenching Column (with the consequent reduction of the fraction to be treated in the Ammonia Recovery Section), allows a reduction in energy consumption of more than 40% compared to the current process.

Example:

In a high-purity melamine production plant built in accordance with the invention and comprising all the stages included in the process of Fig. 2, 950 kg of molten urea at a temperature of 135°C are introduced into the Washing Section of the anhydrous off-gases coming from the reaction section.

The Washing operation is conducted at a pressure of 8 MPa and at a temperature of 185°C. From the Washing Section are obtained 746 kg/h of anhydrous off-gases, free of melamine, that are sent to the adjacent urea synthesis plant, and a liquid mixture containing urea and the recovered melamine that is fed by gravity to the Reactor.

In the Reactor the temperature is maintained at 380°C and the pressure to 8 MPa for a residence time (calculated on the entering molten urea stream) of approximately 50 minutes. From the Reactor exit a raw melamine liquid stream containing 91% by weight of melamine and, separately, a gaseous mixture of CO₂ and NH₃ saturated with melamine vapors which is sent to the off-gas Washing Section for the recovery of the melamine. The liquid stream is fed
to the Post-reactor where, under the same conditions of the Reactor, it is treated with a
gaseous stream of 100 Kg/h of superheated anhydrous ammonia that almost totally eliminates
the dissolved CO₂. The residence time of the liquid melamine in this equipment is 45 minutes.
The ammonia and gaseous CO₂ output from the Post-reactor joins the off-gases output from
the Reactor and are fed together to the off-gas Washing equipment.
Molten melamine flows from the Post-reactor containing approximately 6000 ppm by weight
of OAT and less than 1% by weight of polycondensates.
This purified melamine stream is fed to the Quenching Column where it passes entirely into
aqueous solution under conditions of 2.5 MPa and 170°C. The concentration of NH₃ in the
Quenching Column is maintained above 13% by weight.
The aqueous solution in output from the Quenching Column contains 7.8% by weight of
melamine, less than 2500 ppm of OAT and less than 10 ppm of polycondensates. It is
brought to almost atmospheric pressure and 45°C in the Crystallizer. Under these conditions
320 Kg/h of high-purity melamine (99.95% by weight) crystallizes and is separated in the
Liquids/Solids Separator and dried. In the Liquid/Solid Separator 4.85 m³/h of mother liquor
are recovered of which 4m³/h return directly to the Quenching Column to dissolve the
melamine coming from the Post-reactor, while the remaining 0.85 m³/h are distilled in the
Ammonia Recovery Section where 70 kg/h of anhydrous ammonia and, as side-stream, 90
Kg/h of aqueous ammonia solution containing the CO₂ are recovered.
The deammoniated mother liquor from the Ammonia Recovery Section, containing less than
700 ppm of NH₃, is cooled to 50°C and the pH adjusted to the value of 7 by the addition of a
small quantity of CO₂ in order to reduce the solubility of OAT to a minimum and cause its
almost total precipitation. The precipitated OAT is separated by filtering and eliminated from
the water cycle. The filtrate, consisting in a 1% melamine solution containing less than 200
ppm of OAT, is recycled to the Quenching Column thus recovering the melamine contained in it.
1. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine, characterized in that:

a) the liquid phase from the pyrolysis Reactor containing melamine, non-reacted urea, intermediate oxidized products of pyrolysis (OAT) and products of de-ammoniating condensation of melamine (polycondensates), are sent to a downstream Post-reactor that operates under substantially equal conditions of temperature and pressure as those of the pyrolysis Reactor and into which is also fed gaseous superheated anhydrous ammonia under pressure in order to eliminate the dissolved CO₂, to complete the pyrolysis reaction of the urea and to transform the greater part of OAT into melamine, reducing at the same time also the polycondensates concentration;

b) the liquid product from the Post-reactor is dissolved in aqueous solution in the Quenching Column in the presence of ammonia, maintaining all in controlled conditions of temperature and residence time, to give a solution substantially free of polycondensates that is successively subjected to crystallization to give high-purity melamine and an aqueous mother liquor containing melamine and reduced quantities of OAT that is recycled for the greater part to the Quenching Column without any treatment.

c) the anhydrous gaseous phase coming from the pyrolysis Reactor and Post-reactor, is subjected to washing with molten urea to recover the melamine contained in it as vapor, before being sent back to the urea synthesis plant for the recovery of NH₃ and CO₂ contained in it.
2. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that the smaller portion of aqueous mother liquor of which at point b) of Claim 1, not recycled to the Quenching Column, is subject to treatment in an Ammonia Recovery Section for the recovery of the NH₃ and the elimination of the CO₂ dissolved in it and then being sent to the OAT Precipitation and Separation Section whose function is to maintain the concentration of the aforesaid OAT in aqueous cycle constant at a level below their solubility.

3. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that gaseous, anhydrous and superheated ammonia is blown into the Post-reactor in amount equal to 1:10 until to 1:1, preferably equal to 1:3, by weight with respect to the raw liquid phase.

4. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that the residence time of the liquid stream in Post-reactor is comprised between 0 and 2 hours and preferably between 15 and 45 minutes.
5. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that the recovery of the melamine in vapor phase is realized at the pressure of the Reactor and in anhydrous conditions by means of washing of the gaseous stream (off-gas) with molten urea.

6. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase are subjected to successive treatments for the recovery of the melamine, according to Claim 1, characterized in that the aqueous solution containing melamine in the Quenching Column is maintained at a temperature of 160-170°C in the presence of ammonia at a concentration above 10% by weight, for a residence time of less than 30 minutes.

7. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that Post-reactor is of the same type as the synthesis Reactor.

8. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that the Post-Reactor is of the piston flow type.
9. Process for the production of high-purity melamine with high yields by means of pyrolysis of urea at a temperature comprised between 360 and 420°C and a pressure higher than 7 MPa in which the products of the reaction, comprising a gaseous phase and a liquid phase, are subjected to successive treatments for the recovery of the melamine according to Claim 1, characterized in that the aqueous mother liquor subject to treatment in the Ammonia Recovery Section and the OAT Precipitation and Separation Section is in the amount comprised between 0 and 20% of the aqueous mother liquor recovered from the Liquid/Solid Separator.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D251/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Patent family members are listed in annex.

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Date of the actual completion of the international search

18 October 2002

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25/10/2002

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