

Preparation of melamin cyanurate with low residual melamine

The present invention relates to a method for a preparation of melamin cyanurate comprising the steps of

- a) mixing solid melamine and solid cyanuric acid in a molar ratio in the range from 1.0 : 1.0 to 1.0 : 1.2 to produce a reaction mixture;
- b) continuously adding water to the reaction mixture at a temperature of 80 to 110 °C until a solid content from 72 to 89 wt% is reached to form melamine cyanurate;
- c) holding the temperature of the melamin cyanurate for at least one hour at 40 to 100 °C; and
- d) drying the melamine cyanurate.

- 10 It further relates to a melamin cyanurate obtainable by the method for the preparation of melamin cyanurate, where the melamin cyanurate comprises below 0.1 wt% residual melamine and is free of any additives. Combinations of preferred embodiments with other preferred embodiments are within the scope of the present invention.

- 15 Melamine cyanurate is known for its use in polymers as a flame retardant, e.g. for polyamides, thermoplastic polyurethanes or polybutylene terephthalate. Melamine cyanurate can be used for electrical applications, such as connectors, switches, or housings, cables, tubes made from polyamide or TPU. Flame retardants are added to polymeric materials (synthetic or natural) to enhance the flame retardant properties of the polymers. Depending on their composition, flame retardants may act in the solid, liquid or gas phase either chemically, e.g. as a spumescent by liberation of nitrogen, and/or physically, e.g. by producing a foam coverage. Flame retardants interfere during a particular stage of the combustion process, e.g. during heating, decomposition, ignition or flame spread. Melamine cyanurate can be used alone or in combination with other flame-retardants, thus causing heat sink and dripping of the flame retarded material.

- 25 Commercially available melamine cyanurate comprises trace amounts of melamine. Melamine is labelled as H361f "Suspected of damaging fertility" under the GHS System (Globally Harmonized System of Classification, Labelling and Packaging of Chemicals) of the United Nations.

- 30 Objects were to find a production method for melamine cyanurate which results in a very low concentration of residual melamine. Further objects were to use as few as possible equipment, to avoid the use of additives during the production process, to avoid damage of the production machines due to the sticky or high viscosity reaction mixture, to achieve a high conversion of the educts, to avoid by-products, to avoid the handling of strong acids or bases, or to avoid the presence or addition of high amounts of water which needed to be removed with a lot of energy to prepare a dry melamine cyanurate.

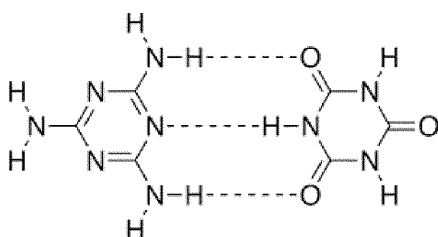
- 35 The object was solved by a method for a preparation of melamin cyanurate comprising the steps of
- a) mixing solid melamine and solid cyanuric acid in a molar ratio in the range from 1.0 : 1.0 to 1.0 : 1.2 to produce a reaction mixture;

- b) continuously adding water to the reaction mixture at a temperature of 80 to 110 °C until a solid content from 72 to 89 wt% is reached to form melamine cyanurate;
- c) holding the temperature of the melamin cyanurate for at least one hour at 40 to 100 °C; and
- d) drying the melamine cyanurate.

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The invention also relates to a melamin cyanurate obtainable by the method for the preparation of melamin cyanurate, where the melamin cyanurate comprises below 0.1 wt% residual melamine and is free of any additives.

Melamine cyanurate is usually a crystalline complex and can be described by the following formula:



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The melamine cyanurate can be in powder form or in granular form. Melamine cyanurate is usually in the crystalline alpha-form or the crystalline beta-form.

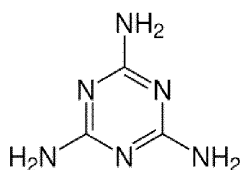
The steps a), b), c) and d) are usually made in the alphabetic order.

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Step a) comprises mixing solid melamine and solid cyanuric acid in a molar ratio in the range from 1.2 : 1 to 1 : 1.2 to produce a reaction mixture.

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Melamine can be described by the following formula:



Examples of solid forms of **melamine** are powder or granules, where powder form is preferred.

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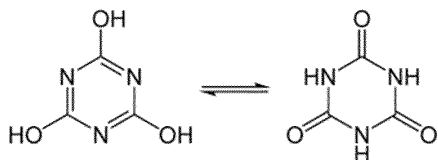
The melamine may contain up to 2 wt%, preferably up to 0.5 wt% and in particular up to 0.2 wt% of water. The water content can be determined gravimetrically by drying for 2 h at 120 °C.

The melamine may have a purity of at least 95 wt%, preferably at least 98 wt%, and in particular at least 99 wt%.

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Examples of solid forms of **cyanuric acid** are powder or granules, where powder form is preferred.

Cyanuric acid can be described by the following tautomeric formulae:



- 5 Cyanuric acid can have two tautomers, one being in the enol form and the other in the keto form. In literature the enol form is often called "cyanuric acid" and the keto form is often called "isocyanuric acid". Cyanuric acid usable in the present invention, however, does not mean only the enol form but include both the enol form and the keto form.

- 10 The cyanuric acid may contain up to 2 wt%, preferably up to 0.5 wt% and in particular up to 0.2 wt% of water. The water content can be determined gravimetrically by drying for 2 h at 120 °C.

The cyanuric acid may have a purity of at least 95 wt%, preferably at least 98 wt%, and in particular at least 99 wt%.

- 15 The solid cyanuric acid can be mechanically comminuted before mixing with the solid melamine, e.g. by milling, grinding, crushing, cutting, or vibrating.

The **molar ratio** of the melamine to the cyanuric acid can be in the range from 1.0 : 1.0 to 1.0 : 1.2, preferably from 1.0 : 1 to 1 : 1.1, and in particular from 1.00 : 1 to 1 : 1.03.

- 20 The solid melamine and solid cyanuric acid can be mixed by a **solid-solid mixer**, such as tumble mixers, and vertical or horizontal convection mixers (e.g. ribbon mixer, paddle mixer, ploughshare mixer, vertical screw blender, turbine blender), where horizontal convection mixer are preferred. The melamine and the cyanuric acid are preferably mixed in a horizontal convection mixer.

- 25 A horizontal convection mixer has usually a cylindrical mixing drum, and a mixing tool can be attached to a central mixing shaft. For particularly intensive mixing, a planetary stirring system can also be applied. In a horizontal mixer the product can be fed through nozzles or flaps on the top of the cylindrical mixing drum. Discharging can also be effected by means of nozzles or flaps, which can be located in the lower part of the mixer. A double jacket may effect the heating or cooling of the mixture. If required, it is possible to mix under vacuum or pressure conditions.

- 30 The steps a), b), c) and d) can be made in a solid-solid mixer (e.g. a convection mixer), preferably they are made in the same solid-solid mixer. Typically, the steps a), b), c) and d) are made in one and the same solid-solid mixer, which is preferably a convection mixer, in particular a horizontal convection mixer (e.g. a ribbon mixer, paddle mixer, ploughshare mixer).

Typically, in step a) no other compounds are added, such as additives, beside the melamine and the cyanuric acid. Preferably, the reaction mixture is obtained by mixing only melamine and cyanuric acid.

5 The reaction mixture produced in step a) may have a solid content of at least 95, 96, 97, 98 or 99 wt%. The reaction mixture produced in step a) may have a solid content up to 100 wt%. The solid content can be determined gravimetrically by drying for 2 h at 120 °C.

10 **Step b)** comprises continuously adding water to the reaction mixture at a temperature of 80 to 110 °C until a solid content from 72 to 89 wt% is reached to form melamine cyanurate.

The step b) may directly follow the step a), e.g. without any additional purification or workup steps. The step b) usually starts directly when the mixing in step a) was finished.

15 During the addition of water the reaction mixture is usually mixed, such as in the solid-solid mixer.

The water added in step b) may have distilled water quality, such as distilled water or osmosis water.

20 In step b) the water can be **sprayed** on the reaction mixture while mixing the reaction mixture, e.g. in the solid-solid mixer.

In step b) the water can preferably be sprayed through nozzles on the reaction mixture while mixing the reaction mixture, such as in the solid-solid mixer. Suitable nozzles are for example solid stream nozzle; deflector; swirl nozzle with hollow-cone pattern; solid-cone or full-cone nozzles; flat fan pattern nozzles; spiral nozzles; liquid-liquid impingement; poppet nozzles; rotary nozzles; or ultrasonic nozzles.

25 In step b) the water is continuously added, which usually means that the addition is not intentionally interrupted for a substantial period (e.g. a period less than 20 %, preferably, less than 10 %, and in particular less than 1 % of the whole time during which the water is added).

30 The water is usually added to the reaction mixture in an amount of 30 to 1000 kg water per hour and per ton of melamine, preferably of 50 to 800 kg water per hour and per ton of melamine, and in particular 80 to 600 kg water per hour and per ton of melamine.

35 The water can be added to the reaction mixture at a **temperature** of 80 to 110 °C, preferably of 85 to 105 °C, and in particular of 90 to 100 °C. The temperature of the reaction mixture can be achieved by applying the same or higher jacket temperatures to the vessel, e.g. the solid-solid mixer.

The water can be added to the reaction mixture at a ambient pressure (e.g. about 1013 mbar) or a small excess of pressure, e.g. an excess of up to 500, 200 or 100 mbar.

5 The water can be added to the reaction mixture until the **solid content** from 72 to 89 wt%, preferably 74 to 87, more preferably 76 to 86, even more preferably 78 to 85, and in particular 80 to 84 wt% is reached.

10 Usually, the amount of water which is required to reach the desired solid content can be calculated based on the amount of melamine and cyanuric acid mixed in step a). The calculation of the required amount of water can be done before the step b) started.

While continuously adding water to the reaction mixture the added water may partly evaporate. The evaporated water may be a) condensed and optionally collected, or b) discharged, e.g. as water steam in the environment.

15 In a preferred form of step b) the added water partly evaporates and the evaporated water is condensed and the amount of condensed water determined.

20 In another preferred form of step b) the added water partly evaporates, the evaporated water is condensed, the amount of condensed water is determined, and the determined amount of condensed water is added to the reaction mixture.

25 In another form of step b) the evaporated water is discharged, e.g. as water steam in the environment, and the solid content of the reaction mixture can be analyzed to determine the amount of evaporated water, and further water can be added to the reaction mixture to until the desired solid content (usually 72 to 89 wt%, preferably 74 to 87, more preferably 76 to 86, even more preferably 78 to 85, and in particular 80 to 84 wt%) is reached.

Typically, in step b) no other compounds are added, such as additives, beside the water.

30 The **step c)** comprise holding the temperature of the melamin cyanurate for at least one hour at 40 to 100 °C.

In step c) the temperature of the melamine cyanurates can be held for at least 60, 90, 120, or 180 min.

In step c) the temperature of the melamine cyanurates can be held for up to 10, 9, 8, 7, 6, 5, 4, 3, or 2 hours.

35 In step c) the temperature of the melamine cyanurates can be held one hour to 10 hours, or one hour to 8 hours, or one hour to 6 hours, or one hour to 4 hours, or one hour to 3 hours, or 1.5 hours to 10 hours, or 1.5 hours to 8 hours, or 1.5 hours to 6 hours, or 1.5 hours to 4 hours.

- In another form of step c) the temperature of the melamine cyanurates can be held at 55 to 100 °C for one hour to 10 hours, or one hour to 8 hours, or one hour to 6 hours, or one hour to 4 hours, or one hour to 3 hours, or 1.5 hours to 10 hours, or 1.5 hours to 8 hours, or 1.5 hours to 6 hours, or 1.5 hours to 4 hours.
- 5 In another form of step c) the temperature of the melamine cyanurates can be held at 65 to 100 °C for one hour to 10 hours, or one hour to 8 hours, or one hour to 6 hours, or one hour to 4 hours, or one hour to 3 hours, or 1.5 hours to 10 hours, or 1.5 hours to 8 hours, or 1.5 hours to 6 hours, or 1.5 hours to 4 hours.
- In step c) the temperature of the melamine cyanurates can be held at 40 to 100 °C, preferably at 55 to 100 °C, and in particular at 65 to 100 °C. The temperature of the melamine cyanurates can be achieved by applying the same or higher jacket temperatures to the vessel, e.g. the solid-solid mixer.
- 10 In step c) the melamin cyanurate is usually mixed (such as in the solid-solid mixer) during the holding of the temperature, preferably it is continuously mixed during step c).
- 15 The step c) may directly follow the step b), e.g. without any additional purification or workup steps or without any addition of water or of additives.
- The step c) usually starts directly when the addition of water in step b) has stopped. In step c) usually no water is added.
- 20 The **step d)** comprises drying the melamine cyanurate.
- The step d) may directly follow the step c), e.g. without any additional purification or workup steps or without any addition of water or of additives. The step d) usually starts directly when the holding of the temperature in step c) has stopped. The drying in step d) is usually made in the same vessel as the step c).
- 25 The melamine cyanurate can be **dried** by evaporating the water in a vacuum while mixing, such as in the solid-solid mixer. The water can be evaporated in a vacuum of below 900, 700, 500, 400, 200, or 100 mbar. The vacuum can be increased over time, e.g. until the desired water content is reached.
- 30 The evaporation of the water in the vacuum can be done at a temperature of the melamine cyanurate of at least 50, 60, 70, 80 or 90 °C, such as 60 to 150 °C, or 80 to 130 °C.
- 35 The mixing (such as in the solid-solid mixer) is usually continued without interruption during the drying.
- The method for the preparation of melamin cyanurate, especially the step d), is usually free of spray drying the melamin cyanurate.

The melamine cyanurate can be dried in step d) until the water content is below 1 wt%, preferably below 0.5 wt%, and in particular below 0.2 wt%. The water content may be determined gravimetrically by drying samples at 120 °C for 2 hours.

- 5 The concentration of **free melamin** in the melamin cyanurate is usually below 0.5 wt%, preferably below 0.2 wt%, and in particular below 0.1 wt% after the drying in step d). The melamine concentration can be determined by HPLC analysis, such as on a cation-exchange stationary phase.

- 10 Typically, no additives are added in the method for the preparation of the melamin cyanurate. Examples of the additives which are not added are polymers (such as styrene/maleic anhydride copolymers), diallyldialkylammonium chloride or a homopolymer or a copolymer thereof, organic auxiliary material with a melting or softening temperature higher than 40 °C (e.g. polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl caprolactam), a fluid thermoplastic polymer (e.g. nylon, polyethylene, polyolefin, polyvinylidene chloride, polystyrene, polyacrylonitrile, polycarbonate, or polybutadiene), a metal oxide (e.g. silica oxide, alumina oxide, or antimony oxide).

- 15 Typically, no other compounds are added beside the melamine and the cyanuric acid in the method for the preparation of the melamin cyanurate.

- 20 Typically, no pH adjustment is made during the method for the preparation of the melamin cyanurate, such as by addition of a base (e.g. sodium hydroxide, potassium hydroxide, or sodium carbonate) or an acid (e.g. a strong mineral acid).

- The melamine cyanurate which is obtained at the end of step d) may be further comminuted to a powder form, or it may be processed to a granular form.

- 25 The melamine cyanurate in powder form may have particles with an **average size** d_{50} of 0.1 - 50 μm , preferably 0.2 to 10 μm , and in particular 0.5 to 6 μm . The average size d_{50} mean usually the average of the largest size and the smallest size, this size also being the average over the total number of the agglomerates. The particles are usually substantially of a round shape. The melamine cyanurate can be grinded to a desired particle size.

- 30 The melamine cyanurate in granular form can be prepared for example by kneaders, extruders (e.g. single or twin screw extruders), and from powders by pressurized compaction.

- The melamin cyanurate in powder form or in granular form may have a bulk density of 50 to 1500 kg/m^3 , preferably 35 80 to 1100 kg/m^3 , and in particular 100 to 800 kg/m^3 .

The melamine cyanurate can be **used** as flame retardant in various polymers, such as polystyrene, polyolefins (e.g. polyethylenes, polypropylenes), polybutylene terephthalate, acrylonitrile butadiene styrene, polyurethanes, polyvinyl chloride, or natural and synthetic rubbers.

- 5 The melamine cyanurate can be used alone or together with other flame retardant compounds, including halogen containing and halogen-free ones. However, preference is given to halogen-free flame retardant compounds, including triazine compounds such as melamine, ammeline and/or ammelide, higher condensation products thereof such as melem and/or melam; melamine derivatives such as melamine phosphate, melamine acetate, melamine pyrophosphate, melamine polyphosphate and/or melamine ammonium polyphosphate; metal compounds such as
- 10 aluminium hydroxide, magnesium hydroxide, antimony trioxide, Sb₂O₅, zinc oxide, sodium antimonate, zinc stannate and/or zinc borate with or without water of crystallization.

Examples

15 Example 1

Melamine cyanurate (CAS no. 37640-57-6) was prepared as follows:

- Melamine powder (purity >99 wt%, <0.1 wt% water) and cyanuric acid (purity >99 wt%, <0.2 wt% water) and were
- 20 loaded in a molar ratio 1 : 1 in a horizontal solid-solid mixer and heated to 95 °C while mixing. In case the cyanuric acid has formed chunks depending on the storage conditions, the chunks are mechanically comminuted before mixing with the melamine.

- The amount of water was calculated which is required to reach a solid content in the mixture of 81.5 wt%. This
- 25 calculated amount of water (distilled water quality) was continuously added during about four hours (350 liter/hour) by spraying via nozzles on the mixture while mixing it in the horizontal solid-solid mixer (corresponding to 113 kg water per hour and per ton melamin) at a heating jacket temperature of 95 °C.

- During this addition of water the product temperature raised to about 100 °C due to the exothermic reaction and the
- 30 added water partly evaporated (roughly about 10 wt%). The amount of evaporated water was determined by condensing and analyzing it in a separated vessel. The amount of evaporated water was additionally dosed to the above mixture in order to reach a solid content of 81.5 wt%.

- Once the addition of water was finished then the product temperature was hold for 3 hours at 95 °C while the mixing
- 35 in the horizontal solid-solid mixer was continued at a heating jacket temperature of 95 °C.

Then the product was dried to a water content of below 0.1 wt% (determined gravimetrically by drying samples at 120 °C for 2 hours) by increasing the heating jacket temperature to 140 °C and applying a vacuum of around 50

mbar while the mixing in the horizontal solid-solid mixer was continued. The drying was finished when the product temperature raised to about 115 °C.

- Finally, the heating jacket temperature was lowered to cool down the product and a white odourless coarse powder was obtained (pH value 5-6 as saturated solution in water at 20 °C; specific gravity 1.7 g/cm³; solubility in water below 5 mg/l; decomposed without melting at a decomposition point of above 350 °C (DTA)).

The melamine cyanurate contained less than 0.2 % free cyanuric acid as determined by titration.

- 10 The melamine cyanurate contained less than 0.1 % free melamine. The melamine concentration was determined by HPLC on a Partisil® 10 SCX (strong cation-exchange phase based on benzenesulphonic acid, 25 cm length, particle size 10 µm) at 40 °C. The mobile phase (0.7 ml/min) was water, buffer KH₂PO₄/H₃PO₄. Melamine was detected at around 5.4 min by a Diode-Array Detection DAD detector at 210 nm.

15 Example 2

The process as described in Example 1 was repeated with the following differences:

- 20 Water was added with an amount of 1000 liter/hour (instead of 350 liter/hour as in Example 1), which corresponded to 250 kg water per hour and per ton melamin.

Once the addition of water was finished then the temperature was hold for 3 hours at 75 °C (instead of 95 °C as describe in Example 1) while the mixing was continued.

- 25 The melamine cyanurate contained less than 0.1 % of free melamine.

Example 3

The process as described in Example 1 was repeated with the following difference:

- 30 Water was added with an amount of 1700 liter/hour (instead of 350 liter/hour as in Example 1), which corresponded to 425 kg water per hour and per ton melamin.

The melamine cyanurate contained less than 0.1 % of free melamine.

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Comparative Example A

The process as described in Example 1 was repeated with the following differences:

The amount of water was calculated which is required to reach a solid content in the mixture of 70 wt% (instead of 81.5 wt% as in Example 1). This calculated amount of water (osmosis water quality) was continuously added with an amount of 1000 liter/hour as in Example 2.

- 5 Towards the end of the water addition the horizontal mixer showed increased vibrations. Additionally, the torque rate or the mixer increased which led to an automatic safety shutdown of the mixer.

This comparative example demonstrated that a lower solid content (which means a higher water content) during the synthesis has negative consequences on the manufacturing process.

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Comparative Example B

The process as described in Example 1 was repeated with the following differences:

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The amount of water was calculated which is required to reach a solid content in the mixture of 90 wt% (instead of 81.5 wt% as in Example 1). This calculated amount of water (osmosis water quality) was continuously added with an amount of 1000 liter/hour as in Example 2.

- 20 The final product was coarsely granular and contained insoluble agglomerates of cyanuric acid.

This comparative example demonstrated that a higher solid content (which means a lower water content) during the synthesis has negative consequences on the product quality.

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Claims

1. A method for a preparation of melamine cyanurate comprising the steps of
 - a) mixing solid melamine and solid cyanuric acid in a molar ratio in the range from 1.0 : 1.0 to 1.0 : 1.2 to
5 produce a reaction mixture;
 - b) continuously adding water to the reaction mixture at a temperature of 80 to 110 °C until a solid content
from 72 to 89 wt% is reached to form melamine cyanurate;
 - c) holding the temperature of the melamine cyanurate for at least one hour at 40 to 100 °C; and
 - d) drying the melamine cyanurate.
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2. The method according to claim 1 where in step b) the water is sprayed on the reaction mixture while mixing the
reaction mixture.
3. The method according to claim 2 where in step b) the water is sprayed through nozzels.
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4. The method according any of claims 1 to 3 where in step b) the water is added to the reaction mixture in an
amount of 30 to 1000 kg water per hour and per ton of melamine.
5. The method according any of claims 1 to 4 where in step b) the added water partly evaporates, the evaporated
20 water is condensed, the amount of condensed water is determined, and the determined amount of condensed
water is added to the reaction mixture.
6. The method according any of claims 1 to 5 where the steps a), b), c) and d) are made in a solid-solid mixer,
preferably in the same solid-solid mixer.
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7. The method according any of claims 1 to 6 where in step d) the melamine cyanurate is dried by evaporating the
water in a vacuum while mixing.
8. The method according any of claims 1 to 7 where the melamine cyanurate is dried in step d) until the water
30 content is below 1 wt%.
9. The method according any of claims 1 to 8 where the method is free of spray drying the melamin cyanurate.
10. The method according any of claims 1 to 9 where in step a) the solid cyanuric acid is mechanically comminuted
35 before mixing with the solid melamine.
11. The method according any of claims 1 to 10 where in step c) no water is added.

12. The method according any of claims 1 to 11 where the water added in step b) has distilled water quality.
13. The method according any of claims 1 to 12 where the concentration of free melamin in the melamin cyanurate is below 0.5 wt%, preferably below 0.2 wt%, and in particular below 0.1 wt% after the drying in step d).
- 5 14. The method according any of claims 1 to 13 where no additives are added in the method for the preparation of the melamin cyanurate.
- 10 15. The method according any of claims 1 to 14 where no pH adjustment is made during the method for the preparation of the melamin cyanurate.
- 15 16. A melamin cyanurate obtainable by the method for the preparation of melamin cyanurate as defined in any of claims 1 to 15, where the melamin cyanurate comprises below 0.1 wt% residual melamine and is free of any additives.