Process for the production of calcium cyanamide from urea

The invention concerns a process for the production of calcium cyanamide (lime nitrogen) from urea and a calcium compound containing oxygen.

The large-scale production of lime nitrogen has previously been achieved by azotization of calcium carbide. As an alternative to this, processes are already known which are based on the reaction of urea with compounds containing calcium. Thus a two-step process is known from SU-PS 812 713 in which urea is firstly reacted with calcium oxide or calcium oxide hydrate at an increased temperature and subsequently the calcium cyanate that is formed is calcined. A disadvantage of this process is the time-consuming purification of the intermediate.

The process according to SU-PS 1 333 638 appears to be much more simple in which the reaction of calcium oxide or calcium hydroxide with urea is carried out at 130 to 220°C in an inert organic medium and subsequently the reaction mass is heated at 700 to 900°C. Yields of calcium cyanamide of about 80 to 90 % are achieved using this process, the content of cyanamide nitrogen being 28 to 32 % N.

Approximately comparable yields are obtained according to the process of the French Patent Application 2 640 610 according to which 1 mole calcium carbonate is reacted with 2 mole urea at a temperature of 135 to

200°C and subsequently the reaction mixture is subjected to a further temperature treatment between 300 and 500°C.

It is either very difficult or not possible at all to carry out all these said processes on a technical scale because in parts very complicated processing steps are necessary which appear to be extremely problematic also with regard to the profitability of these processes.

The object of the invention is therefore to create a process for the production of calcium cyanamide by reacting urea and an oxygen-containing calcium compound in at least two steps which does not have the said disadvantages of the state of the art but ensures high yields of calcium cyanamide in a technically simple manner. This object is achieved according to the invention in that

a) in a first reaction step the reaction components are allowed to react under compression and/or while being revolved or by applying them to a hot surface at temperatures of 120 to 500°C until a solid is formed and

b) the solid reaction mixture that is formed is subsequently calcined at temperatures of 600 to 900°C.

It surprisingly turned out that high yields of calcium cyanamide can be obtained according to the invention without requiring a complicated processing of the reaction product after the first or second step. In addition high throughputs can be achieved by the process

according to the invention due to the short reaction period which was also not foreseeable.

The process according to the invention includes at least two reaction steps. In the first reaction step urea and the oxygen-containing calcium compound are reacted together at temperatures of 120 to 500°C, preferably 150 to 400°C. In this case burnt lime (calcium oxide (CaO)), calcium hydroxide ($Ca(OH)_2$) or calcium carbonate ($CaCO_3$) and also calcium alcoholates primarily come into consideration as the oxygen-containing calcium compound. The calcium compound is preferably used with a particle size of 0.1 to 1.0 mm. According to a preferred embodiment calcium carbonate is used in a precipitated form which has a particle size of 1 to 200 µm and has a particularly pronounced reactivity due to being finely divided. It is possible in this case within the scope of the invention to use the precipitated calcium carbonate in an impure form as it for example is formed as a usually non-usable by-product in the further processing of lime nitrogen to cyanamide, dicyandiamide or thiourea. The molar ratio of the oxygen-containing calcium compound to urea can be varied within wide limits, however, it has proven to be particularly advantageous to set this molar ratio to 1:1 to 1:4.

An essential feature of the invention is that the reaction components are allowed to react in the first reaction step under compression or/and while being revolved or by application onto a hot surface. The compression or rotation of the reaction components can be preferably accomplished by carrying out the reaction in an extruder, kneader or rotary kiln whereby the oxygen-containing calcium compound and urea are preferably introduced as a mixture into the reactor used

in each case. Conventional technical devices come into consideration as the extruder and kneader such as e.g. a screw extruder in the form of for example single or multiple screw extruders, or kneaders in the form of single, double or multishaft mixers. In these kneaders or extruders the reaction mixture is compressed, homogenized and at the same time transported. In this manner shifting, baking on etc. are also prevented in the reactor.

Instead of compressing or/and revolving the reaction components, these can also be applied in the first reaction step to a hot surface which is preferably kept moving. A technical method of realizing this variant of the process is to use drum or band dryers on which the reaction components are applied. After the reaction is completed, the solid reaction product can then be mechanically removed again from the hot surface of the apparatus for example with the aid of scrapers, scratchers etc.. The first reaction step is carried out until formation of the solid occurs or until the generation of ammonia has ended. This is usually the case after 0.25 to 2 hours depending on the reaction temperature. The first reaction step a) is preferably carried out continuously.

According to a preferred embodiment the reaction components are converted completely or partially into a molten form before carrying out the first reaction step. It is expedient to accomplish this by heating the reaction components to a temperature between 130 and 250°C during which the reaction mixture at least partially melts and the desired reaction starts. This melting reaction of the starting products is preferably carried out in a heated tubular reactor and in

particular in a heated screw conveyor or in a stirred tank. The residence time in these melting units is normally between 5 and 30 minutes depending on the size. This pretreatment of the reaction components enables a particularly rapid and complete conversion to the desired reaction product. The ammonia which is formed during this pretreatment step and also in the first reaction step can be collected and reused almost quantitatively.

In the second reaction step, the reaction mixture obtained in the first reaction step is then calcined at a temperature of 600 to 900°C without further processing or purification. This reaction can be carried out in conventional devices such as e.g. a rotary kiln, settling furnace or even in a fluidized bed, continuous processing being preferred. If this second reaction step is carried out in a revolving tube, it is advisable to carry out the calcination in the presence of grinding balls composed of an inert material such as e.g. porcelain or steel which preferably have a diameter of 1 to 100 mm in order to comminute the material and to improve heat transfer. In order to avoid undesired side reactions which can lead to appreciable losses in yield, oxygen and water are preferably excluded in the second reaction step. Therefore the calcination is particularly preferably carried out under an inert gas atmosphere e.g. under nitrogen or out of contact with air under the waste gases of the reaction.

The second reaction step, which is usually also completed after 0.25 to 2 hours, yields calcium cyanamide in good purity and in high yields. The yields of calcium cyanamide are up to 97 % and its content of cyanamide nitrogen is up to 34 %. As a result of these

good yields and the technically simple reaction procedures, the process according to the invention is particularly suitable for the technical scale.

It is intended to elucidate the invention in more detail by the following examples.

Examples

Example 1

500 g urea and the amount corresponding to the respective molar ratio (186 or 155 g) of calcium oxide (particle size < 500 µm) were melted in a tubular reactor at 150°C (residence time 7 minutes) and subsequently applied to a rotating roller dryer which had been heated to various temperatures as stated in Table 1. The solid reaction product that formed was scratched off with the aid of scrapers after a residence time of 10 minutes and then calcined for 1 hour in a rotating tube under a nitrogen atmosphere at a temperature of 750°C. The results are shown in Table 1:

Table 1

Molar ratio CaO/urea	Temperature of the drum dryer	Yield of calcium cyanamide [g]	N content [weight %]
a) 1:2.5	380°C 520°C	232 247	30.6 30.1
b) 1:3.0	300°C 280°C	212 210	34.1 33.8

Example 2

500 g urea and the amount corresponding to the respective molar ratio (233 or 186 g) of precipitated lime (particle size < 200 μm) are melted down in a tubular reactor at 150°C (residence time 12 minutes) and subsequently reacted for 1 hour at 350°C in a rotating tube in the presence of porcelain balls (diameter 20 mm).

After the first reaction step is completed, the reaction product is calcined for 1 hour at 750°C in a settling furnace under a nitrogen atmosphere. The results are shown in Table 2:

Table 2

	Molar ratio $CaCO_3$: urea	Yield of calcium cyanamide [g]	N content [weight %]
a)	1:2	281	29.5
b)	1:3	290	30.1

Example 3

73 kg/h urea and 27 kg/h CaO are melted down in a stirred tank at ca. 160°C (residence time ca. 10 minutes) and the melt is continuously rolled and compressed in a subsequent heated kneader. The temperature at the entrance of the kneader is ca. 235°C, and ca. 275°C at the product discharge point. After a throughput of 1400 kg reaction mixture, 884 kg of

product are obtained which is converted into a lime nitrogen with a nitrogen content of 30.0 % by weight by calcination at 750°C (20 minutes) in a rotating tube in the absence of air. The results are shown in Table 3.

Table 3

Molar ratio CaO : urea	Yield of calcium cyanamide	N content [weight %]
1:2.5	36.0 kg/h	30.0

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Claims

1. Process for the production of calcium cyanamide by reacting urea with an oxygen-containing calcium compound in at least two steps
w h e r e i n
a) in a first reaction step the reaction components are allowed to react under compression and/or while being revolved or by applying them to a hot surface at temperatures of 120 to 500°C until a solid is formed and
b) the solid reaction mixture that is formed is subsequently calcined at temperatures of 600 to 900°C.

2. Process as claimed in claim 1,
w h e r e i n
the oxygen-containing calcium compound represents burnt lime and/or calcium hydroxide and/or calcium carbonate.

3. Process as claimed in claim 1,
w h e r e i n
precipitated calcium carbonate is used as the oxygen-containing calcium compound.

4. Process as claimed in claim 3,
w h e r e i n
the precipitated calcium carbonate is used in an impure form.

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5. Process as claimed in one of the claims 1 to 4,
w h e r e i n
the molar ratio of oxygen-containing calcium compound to urea is 1:1 to 1:4.

6. Process as claimed in one of the previous claims,
w h e r e i n
the first reaction step is carried out in an extruder.

7. Process as claimed in one of the previous claims,
w h e r e i n
the first reaction step is carried out in a kneader.

8. Process as claimed in one of the previous claims,
w h e r e i n
the reaction components in the first reaction step are applied to a hot surface and the solid that is formed is then mechanically scraped off the surface.

9. Process as claimed in claim 8,
w h e r e i n
the reaction components are applied to a drum or band dryer.

10. Process as claimed in one of the previous claims,
w h e r e i n
the first reaction step a) is carried out continuously.

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11. Process as claimed in one of the previous claims,
w h e r e i n
the reaction components are completely or partially converted into a molten form by heating to temperatures of 130 to 250°C before carrying out the first reaction step.

12. Process as claimed in claim 11,
w h e r e i n
the reaction components are melted in a heated tubular reactor, in particular in a heated screw conveyor or in a stirred tank.

13. Process as claimed in one of the previous claims,
w h e r e i n
ammonia that is formed in the first reaction step is collected and reused.

14. Process as claimed in one of the previous claims,
w h e r e i n
the second reaction step is carried out in a rotating tube.

15. Process as claimed in claim 14,
w h e r e i n
the calcination in the rotating tube is carried out in the presence of balls made of an inert material.

16. Process as claimed in one of the previous claims,
w h e r e i n
the second reaction step is carried out in a settling furnace.

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17. Process as claimed in one of the previous claims, w h e r e i n the second reaction step is carried out in a fluidized bed reactor.

18. Process as claimed in one of the previous claims, w h e r e i n the second reaction step is carried out in the absence of oxygen and water.

19. Process as claimed in claim 18, w h e r e i n the second reaction step is carried out under an inert gas atmosphere.

20. Process as claimed in one of the previous claims, w h e r e i n the second reaction step b) is carried out continuously.

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Abstract

In order to produce calcium cyanamide by reacting urea with an oxygen-containing calcium compound in at least two steps

a) in a first step the reaction components are allowed to react under compression and/or while being revolved or by applying them to a hot surface at temperatures of 120 to 500°C until a solid is formed and

b) the solid reaction mixture that is formed is subsequently calcined at temperatures of 600 to 900°C.

In this process it is possible to obtain high yields and throughputs of calcium cyanamide without requiring a time-consuming processing of the reaction product after the first or second step.