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(54) Titre : PROCEDE EN CONTINU DE PRODUCTION DE POLYAMIDES A PARTIR D'AMINONITRILES  
 (54) Title: CONTINUOUS METHOD FOR PRODUCING POLYAMIDES FROM AMINONITRILES

(57) **Abrégé/Abstract:**

The invention relates to a continuous method for producing a polyamide by reacting at least one aminonitrile with water. Said method comprises the following steps: (1) at least one aminonitrile is reacted with water in the presence of an organic liquid diluting agent at a temperature of 90 to 400 °C and a pressure of 0.1 to 35 x 10<sup>6</sup> Pa in a stream tube containing a Brønsted acid catalyst selected from a beta-zeolite, phyllosilicate, or titanium dioxide catalyst consisting of 70 to 100 wt. % of anatase and 0 to 30 wt. % of rutile, in which up to 40 wt. % of the titanium dioxide can be replaced by tungsten oxide, in order to obtain a reaction mixture, (2) the reaction mixture is further reacted at a temperature of 150 to 400 °C and a pressure which is lower than the pressure in step 1, in the presence of a Brønsted acid catalyst selected from a beta-zeolite, phyllosilicate, or titanium dioxide catalyst consisting of 70 to 100 wt. % anatase and 0 to 30 wt. % rutile, in which up to 40 wt. % of the titanium dioxide can be replaced by tungsten oxide, the temperature and the pressure being chosen in such a way that a first gas phase and a first liquid phase or a first solid phase or a mixture of a first solid phase and a first liquid phase is obtained, the first gas phase being separated from the first liquid phase or first solid phase or the mixture of the first liquid phase and first solid phase, and (3) the first liquid phase or the first solid phase or the mixture of the first liquid phase and first solid phase is mixed with a gaseous phase or a liquid phase containing water, at a temperature of 150 to 370 °C and a pressure of 0.1 to 30 x 10<sup>6</sup> Pa, in order to obtain a product mixture.

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(54) Title: CONTINUOUS METHOD FOR PRODUCING POLYAMIDES FROM AMINONITRILES

(54) Bezeichnung: KONTINUIERLICHES VERFAHREN ZUR HERSTELLUNG VON POLYAMIDEN AUS AMINONITRILEN

(57) Abstract: The invention relates to a continuous method for producing a polyamide by reacting at least one aminonitrile with water. Said method comprises the following steps: (1) at least one aminonitrile is reacted with water in the presence of an organic liquid diluting agent at a temperature of 90 to 400 °C and a pressure of 0.1 to 35 x 10<sup>6</sup> Pa in a stream tube containing a Brønsted acid catalyst selected from a beta-zeolite, phyllosilicate, or titanium dioxide catalyst consisting of 70 to 100 wt. % of anatase and 0 to 30 wt. % of rutile, in which up to 40 wt. % of the titanium dioxide can be replaced by tungsten oxide, in order to obtain a reaction mixture, (2) the reaction mixture is further reacted at a temperature of 150 to 400 °C and a pressure which is lower than the pressure in step 1, in the presence of a Brønsted acid catalyst selected from a beta-zeolite, phyllosilicate, or titanium dioxide catalyst consisting of 70 to 100 wt. % anatase and 0 to 30 wt. % rutile, in which up to 40 wt. % of the titanium dioxide can be replaced by tungsten oxide, the temperature and the pressure being chosen in such a way that a first gas phase and a first liquid phase or a first solid phase or a mixture of a first solid phase and a first liquid phase is obtained, the first gas phase being separated from the first liquid phase or first solid phase or the mixture of the first liquid phase and first solid phase, and (3) the first liquid phase or the first solid phase or the mixture of the first liquid phase and first solid phase is mixed with a gaseous phase or a liquid phase containing water, at a temperature of 150 to 370 °C and a pressure of 0.1 to 30 x 10<sup>6</sup> Pa, in order to obtain a product mixture.

(57) Zusammenfassung: Das kontinuierliche Verfahren zur Herstellung eines Polyamids durch Umsetzung mindestens eines Aminonitrils mit Wasser umfaßt die folgenden Stufen: (1) Umsetzung mindestens eines Aminonitrils mit Wasser in Gegenwart eines organischen flüssigen Verdünnungsmittels bei einer Temperatur von 90 bis 400 °C und einem Druck von 0,1 bis 35 x 10<sup>6</sup> Pa in einem Strömungsrohr, das einen Brønsted-Säurekatalysator, ausgewählt aus einem Beta-Zeolith-, Schichtsilikat- oder einem Titandioxid-Katalysator aus 70 bis 100 Gew.-% Anatas und 0 bis 30 Gew.-% Rutil, in dem bis zu 40 Gew.-% des Titandioxids durch Wolframoxid ersetzt sein können, enthält, wobei ein Umsetzungsgemisch erhalten wird, (2) weitere Umsetzung des Umsetzungsgemischs bei einer Temperatur von 150 bis 400 °C und einem Druck, der niedriger ist als der Druck in Stufe 1, die in Gegenwart eines Brønsted-Säurekatalysators, ausgewählt aus einem Beta-Zeolith-, Schichtsilikat- oder einem Titandioxid-Katalysator aus 70 bis 100 Gew.-% Anatas und 0 bis 30 Gew.-% Rutil, in dem bis zu 40 Gew.-% des Titandioxids durch Wolframoxid ersetzt sein können, durchgeführt werden kann, wobei die Temperatur und der Druck so gewählt werden, daß eine erste Gasphase und eine erste flüssige oder eine erste feste Phase oder ein Gemisch aus erster fester und erster flüssiger Phase erhalten werden, und die erste Gasphase von der ersten flüssigen oder der ersten festen Phase oder dem Gemisch aus erster flüssiger und erster fester Phase abgetrennt wird, und (3) Versetzen der ersten flüssigen oder der ersten festen Phase oder des Gemischs aus erster flüssiger und erster fester Phase mit einer gasförmigen oder flüssigen Phase, die Wasser enthält, bei einer Temperatur von 150 bis 370 °C und einem Druck, bei einer Temperatur von 150 bis 370 °C und einem Druck von 0,1 bis 30 X 10<sup>6</sup> Pa, wobei ein Produktgemisch erhalten wird.

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CONTINUOUS METHOD FOR PRODUCING POLYAMIDES  
FROM AMINONITRILES

## Description

The present invention relates to a continuous process for preparing polyamides from aminonitriles and water at elevated temperature and elevated pressure.

DE-A-19804023 discloses a continuous process for preparing a polyamide by reacting at least one aminonitrile with water, which comprises:

- 10 (1) reacting at least one aminonitrile with water at from 90 to 400°C and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,
- 20 (2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and
- 30 (3) admixing the first liquid or the first solid phase or the mixture of first liquid and first solid phases with a gaseous or liquid phase comprising water at from 150 to 370°C and from 0.1 to  $30 \times 10^6$  Pa, to obtain a product mixture.

This process provides polyamide in good quality, but there is a need for further improvements in quality.

One problem with the quality of polyamides is the unwanted formation of secondary amines as described in WO 00/24808.

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It is an object of the present invention to provide a process for preparing polyamides from aminonitriles and water that ensures a further quality improvement compared to existing processes.

5 We have found that this object is achieved according to the invention by a continuous process for preparing a polyamide by reacting at least one aminonitrile with water, which comprises:

- 10 (1) reacting at least one aminonitrile with water in the presence of an organic liquid diluent at from 90 to 400°C and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 15 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,
- 20 (2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and 25 in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase 30 is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and
- 35 (3) admixing the first liquid or the first solid phase or the mixture of first liquid and first solid phases with a gaseous or liquid phase comprising water at from 150 to 370°C and from 0.1 to  $30 \times 10^6$  Pa, to obtain a product mixture.

The invention further provides a continuous process for preparing 40 a polyamide by reacting at least one aminonitrile with water, which comprises:

- 45 (1) reacting at least one aminonitrile with water in the presence of an organic liquid diluent at from 90 to 400°C and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst

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comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,

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(2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and

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(3) admixing the first liquid or the first solid phase or the mixture of first liquid and first solid phases with a gaseous or liquid phase comprising water at from 150 to 370°C and from 0.1 to  $30 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a product mixture.

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The above processes preferably further comprise the following step:

(4) postcondensing the product mixture at from 200 to 350°C and a pressure which is lower than the pressure in stage 3, the temperature and pressure being selected so as to obtain a second gas phase, which contains water and ammonia with or without organic diluent, and a second liquid or second solid phase or mixture of second liquid and second solid phases, which each include the polyamide.

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The present invention further provides a continuous process for preparing a polyamide by reaction of at least one aminonitrile with water, which comprises:

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- (1) reacting at least one aminonitrile with water in the presence of an organic liquid diluent at from 90 to 400°C and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,
- (2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and
- (3) postcondensing the first liquid or the first solid phase or the mixture of first liquid and first solid phases at from 200 to 350°C and a pressure which is lower than the pressure in stage 2, the temperature and pressure being selected so as to obtain a second gas phase, which contains water and ammonia with or without organic diluent, and a second liquid or second solid phase or mixture of second liquid and second solid phases, which each include the polyamide.

The principle of the process of the invention is described in DE-A-19804023.

The aminonitrile in the mixture can be in principle any aminonitrile, ie., any compound having both at least one amino group and at least one nitrile group.  $\omega$ -Aminonitriles are preferred, especially  $\omega$ -aminoalkyl nitriles having from 4 to 12 carbon atoms, more preferably 4 to 9 carbon atoms, in the alkylene moiety, or aminoalkylaryl nitriles having from 8 to 13 carbon atoms, preferred aminoalkylaryl nitriles being aminoalkylaryl nitriles which have an alkylene group of at least one carbon atom between the aromatic unit and the amino and nitrile group. Especially preferred aminoalkylaryl nitriles are

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those which have the amino group and nitrile group in the 1,4 position relative to each other.

The  $\omega$ -aminoalkyl nitrile used is more preferably a linear  
5  $\omega$ -aminoalkyl nitrile in which the alkylene moiety (-CH<sub>2</sub>-) preferably contains from 4 to 12 carbon atoms, more preferably from 4 to 9 carbon atoms, such as 6-amino-1-cyanopentane (6-aminocapronitrile), 7-amino-1-cyanoheptane, 8-amino-1-cyanoheptane, 9-amino-1-cyano-octane,  
10 10-amino-1-cyanononane, particularly preferably 6-aminocapronitrile.

6-Aminocapronitrile is customarily obtained by hydrogenation of adiponitrile according to known methods, described for example in  
15 DE-A 836,938, DE-A 848,654 or US-A 5,151,543.

Of course, it is also possible to use mixtures of a plurality of aminonitriles or mixtures of an aminonitrile with further comonomers, for example caprolactam or the below-defined mixture.  
20

In a particular embodiment, especially if copolyamides or branched or chain-lengthened polyamides are to be prepared, the following mixture is used instead of pure 6-aminocapronitrile:

25 from 50 to 99.99, preferably from 80 to 90, % by weight of 6-aminocapronitrile,

from 0.01 to 50, preferably from 1 to 30, % by weight of at least one dicarboxylic acid selected from the group consisting of  
30 aliphatic C<sub>4</sub>-C<sub>10</sub>- $\alpha,\omega$ -dicarboxylic acids, aromatic C<sub>8</sub>-C<sub>12</sub>-dicarboxylic acids and C<sub>5</sub>-C<sub>8</sub>-cycloalkanedicarboxylic acids,

from 0 to 50, preferably from 0.1 to 30, % by weight of an  $\alpha,\omega$ -diamine having from 4 to 10 carbon atoms,  
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from 0 to 50, preferably from 0 to 30, % by weight of an  $\alpha,\omega$ -C<sub>2</sub>-C<sub>12</sub>-dinitrile, and

from 0 to 50, preferably from 0 to 30, % by weight of an  
40  $\alpha,\omega$ -C<sub>5</sub>-C<sub>12</sub>-amino acid or of the corresponding lactam,

from 0 to 10% by weight of at least one inorganic acid or salt thereof,

45 the individual weight percentages adding up to 100%.



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- Suitable dicarboxylic acids include aliphatic  $C_4$ - $C_{10}$ - $\alpha,\omega$ -dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, preferably adipic acid and sebacic acid,
- 5 particularly preferably adipic acid, and aromatic  $C_8$ - $C_{12}$ -dicarboxylic acids such as terephthalic acid and also  $C_5$ - $C_8$ -cycloalkanedicarboxylic acids such as cyclohexanedicarboxylic acid.
- 10 Suitable  $\alpha,\omega$ -diamines having from 4 to 10 carbon atoms include tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine and decamethylenediamine, preferably hexamethylenediamine.
- 15 It is further also possible to use salts of the aforementioned dicarboxylic acids and diamines, especially the salt of adipic acid and hexamethylenediamine, which is known as bb salt.
- 20 The  $\alpha,\omega$ - $C_2$ - $C_{12}$ -dinitrile used is preferably an aliphatic dinitrile such as 1,4-dicyanobutane (adiponitrile), 1,5-dicyanopentane, 1,6-dicyanohexane, 1,7-dicyanoheptane, 1,8-dicyanooctane, 1,9-dicyanononane, 1,10-dicyanodecane, particularly preferably adiponitrile.
- 25 If desired, it is also possible to use diamines, dinitriles and aminonitriles derived from branched alkylene or arylene or alkylarylene compounds.
- 30 The  $\alpha,\omega$ - $C_5$ - $C_{12}$ -amino acid used can be 5-aminopentanoic acid, 6-aminohexanoic acid, 7-aminoheptanoic acid, 8-aminooctanoic acid, 9-aminononanoic acid, 10-aminodecanoic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid, preferably 6-aminohexanoic acid.
- 35 The organic liquid diluent used can in principle be any organic liquid diluent that does not adversely affect the reaction in the first step. Preference is given to organic liquid diluents selected from the group consisting of  $C_1$ - $C_4$ -alkanols such as
- 40 methanol, ethanol, n-propanol, i-propanol, butanols, glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, ethers, such as methyl tert-butyl ether, diethylene glycol diethyl ether, tetrahydrofuran,  $C_6$ - $C_{10}$ -alkanes, such as n-octane, n-decane,  $C_5$ - $C_{10}$ -cycloalkanes, such as
- 45 cyclohexane,  $C_6$ - $C_{10}$ -aromatics, such as benzene, toluene, o-xylene, m-xylene, p-xylene, N- $C_1$ - $C_4$ -alkyllactams, such as N-methylpyrrolidone, N-methylcaprolactam and lactams except

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caprolactam, such as pyrrolidone. Particular preference is given to C<sub>6</sub>-C<sub>10</sub>-aromatics, such as benzene, toluene, o-xylene, m-xylene, p-xylene, especially toluene. It is also possible to use mixtures of such organic liquid diluents.

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Organic liquid diluent can advantageously be used in amounts from 0.1 to 90% by weight, preferably from 1 to 70% by weight, based on the total amount used in the first step.

- 10 According to the invention, the first step (step 1) involves heating an aminonitrile with water in the presence of an organic liquid diluent at a temperature from about 90 to about 400°C, preferably about 180 to about 310°C, especially about 220 to about 270°C, for which a pressure from about 0.1 to about 15 × 10<sup>6</sup> Pa, preferably about 1 to about 10 × 10<sup>6</sup> Pa, especially about 4 to about 9 × 10<sup>6</sup> Pa, is set. In this step, the pressure and temperature can be adjusted relative to each other in such a way as to obtain a liquid or a solid phase and a mixture of liquid or solid phase and a gaseous phase.

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According to the invention, water is used in a molar ratio of aminoalkyl nitrile to water within the range from 1:1 to 1:10, particularly preferably within the range from 1:2 to 1:8, very particularly preferably within the range from 1:2 to 1:6,

- 25 preference being given to the use of water in excess, based on the aminoalkyl nitrile used.

In this embodiment, the liquid or solid phase or the mixture of liquid and solid phase corresponds to the reaction mixture,

- 30 whereas the gaseous phase is separated off. As part of this step, the gaseous phase can be separated from the liquid or solid phase or from the mixture of solid or liquid phase at once, or the synthesis mixture forming within this step can be present in two-phase form: liquid/gaseous, solid/gaseous or liquid-solid/gaseous. Of course, the pressure and temperature can also be adjusted relative to each other in such a way that the synthesis mixture is present as a single solid or liquid phase.

The removal of the gas phase can be effected by the use of

- 40 stirred or unstirred separating vessels or vessel batteries and by the use of evaporator apparatus, for example by means of circulatory evaporators or thin-film evaporators, e.g., film extruders, or by means of annular disk reactors, which ensure an enlarged phase interface. In certain cases, recirculation of the synthesis mixture or the use of a loop reactor may be necessary to increase the phase interface. Furthermore, the removal of the

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gas phase can be furthered by the addition of water vapor or inert gas into the liquid phase.

Preferably, the pressure is adjusted at a preselected temperature  
5 so that the pressure is smaller than the equilibrium vapor pressure of ammonia, but greater than the equilibrium vapor pressure of the other components in the synthesis mixture at the given temperature. This way, it is possible to favor especially the removal of ammonia and thus speed up the hydrolysis of the  
10 nitrile groups.

The two-phase procedure is preferably carried out at a pressure which is greater than the vapor pressure of pure water corresponding to the bulk temperature of the reaction mixture,  
15 but less than the equilibrium vapor pressure of ammonia.

A particularly preferred embodiment of the two-phase procedure utilizes an upright flow tube which is operated under upward flow and optionally has above the product outlet a further opening for  
20 gas phase removal. This tubular reactor can be fully or partially packed with catalyst pellets. In a preferred embodiment, the upright reactor utilized in the two-phase procedure is maximally packed with catalyst material up to the phase boundary.

25 In another, particularly preferred embodiment of the first step, the pressure is selected in such a way that the reaction mixture is present as a single liquid phase, i.e., no gas phase is present in the reactor. For this single-phase procedure, the preferred embodiment is a flow tube packed exclusively with  
30 catalyst material.

According to the invention, the aminonitrile/water/diluent mixture is heated with a heat exchanger before being introduced into the first step. It will be appreciated that the aminonitrile  
35 and the water can also be heated separately from each other and be mixed in the first step by the use of mixing elements.

As regards the residence time of the synthesis mixture in the first step, there are no restrictions whatsoever; however, it is  
40 generally selected within the range from about 10 minutes to about 10 hours, preferably within the range from about 30 minutes to about 6 hours.

Although there are no restrictions whatsoever concerning the  
45 degree of conversion of nitrile groups in step 1 either, economic reasons especially dictate that the conversion of nitrile groups in step 1 be generally not less than about 70 mol%, preferably at

least about 95 mol%, and especially within the range from about 97 to about 99 mol%, each based on the moles of aminonitrile used.

- 5 The nitrile group conversion is customarily determined by means of IR spectroscopy (CN stretching vibration at 2247 wavenumbers), NMR or HPLC, preferably by IR spectroscopy.

Nor does the invention rule out conducting the reaction in step 1  
10 in the presence of oxygen-containing phosphorus compounds, especially phosphoric acid, phosphorous acid and hypophosphorous acid and alkali metal and alkaline earth metal salts and ammonium salts thereof such as  $\text{Na}_3\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_3$ ,  $\text{Na}_2\text{HPO}_3$ ,  $\text{NaH}_2\text{PO}_2$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_3$ ,  $\text{K}_2\text{HPO}_3$ ,  $\text{KH}_2\text{PO}_2$ , in which  
15 case the molar ratio of  $\omega$ -aminonitrile to phosphorus compounds is selected within the range from 0.01:1 to 1:1, preferably within the range from 0.01:1 to 0.1:1.

The reaction in step 1 is carried out in a flow tube containing a  
20 Brønsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide. If a very pure  
25 aminonitrile is used, the proportion of anatase in the titanium dioxide catalyst should be as high as possible. Preferably, a pure anatase catalyst is used. If the aminonitrile used contains impurities, for example from 1 to 3% by weight of impurities, preference is given to using a titanium dioxide catalyst  
30 comprising a mixture of anatase and rutile. Preferably, the proportion of anatase is from 70 to 80% by weight and the proportion of rutile from 20 to 30% by weight. Particular preference is given in this case to using a titanium dioxide catalyst comprising about 70% by weight of anatase and about 30%  
35 by weight of rutile. The catalyst preferably has a pore volume of from 0.1 to 5 ml/g, particularly preferably from 0.2 to 0.5 ml/g. The average pore diameter is preferably within the range from 0.005 to 0.1 mm, particularly preferably within the range from 0.01 to 0.06 mm. If highly viscous products are used, the average  
40 pore diameter should be large. The cutting hardness is preferably greater than 20 N, particularly preferably > 25 N. The BET surface area is preferably more than 40 m<sup>2</sup>/g, particularly preferably more than 100 m<sup>2</sup>/g. If the BET surface area is smaller, the bed volume should be appropriately higher to ensure adequate  
45 catalyst activity. Particularly preferred catalysts have the following properties: 100% of anatase; 0.3 ml/g pore volume; 0.02 mm average pore diameter; 32 N cutting hardness; 116 m<sup>2</sup>/g BET

## 10

surface area or 84% by weight of anatase; 16% by weight of rutile; 0.3 ml/g pore volume; 0.03 mm average pore diameter; 26 N cutting hardness; 46 m<sup>2</sup>/g BET surface area. The catalysts may be prepared from commercial powders as available for example from 5 Degussa, Finti or Kemira. When tungsten oxide is used, up to 40% by weight, preferably up to 30% by weight, particularly preferably from 15 to 25% by weight of the titanium dioxide is replaced by tungsten oxide. The catalysts can be prepared as described in Ertl, Knözinger, Weitkamp: "Handbook of 10 heterogeneous catalysis", VCH Weinheim, 1997, pages 98ff. The catalyst can be used in any desired suitable form. It is preferably used in the form of shaped articles, extrudates or pellets, especially in the form of pellets. The pellets are preferably sufficiently large to be readily separable from the 15 product mixture and not to impair the flowability of the product during the reaction.

The pellet form of the catalyst makes it possible to remove the catalyst mechanically at the point of exit from the first step.

20 For example, mechanical filters or sieves are provided at the point of exit from the first step for this purpose. If the catalyst is additionally used in the second and/or third step, it is preferably present in the same form.

25 According to the invention, the reaction mixture obtained in the first step is further reacted in step 2 at a temperature from about 200 (150) to about 350 (400)°C, preferably at a temperature within the range from about 210 (200) to about 330 (330)°C, especially within the range from about 230 (230) to about 270 30 (290)°C, and a pressure which is lower than the pressure in step 1. The pressure in step 2 is preferably at least about  $0.5 \times 10^6$  Pa lower than the pressure in step 1, and generally the pressure will be within the range from about 0.1 to about  $35 \times 10^6$  Pa, preferably within the range from about 0.5 to about  $15 \times 10^6$  Pa, 35 especially within the range from about 2 to about  $6 \times 10^6$  Pa (values in brackets: without catalyst).

In step 2, the temperature and pressure are selected so as to obtain a first gas phase and a first liquid or first solid phase 40 or a mixture of first liquid and first solid phase, and the first gas phase is separated from the first liquid or first solid phase or from the mixture of first liquid and first solid phases.

The first gaseous phase, which consists essentially of ammonia 45 and water vapor, is generally removed continuously by means of a distillation apparatus, for example a distillation column. Any organic constituents of the distillate coremoved in the course of

## 11

this distillation, predominantly unconverted aminonitrile with or without organic diluent, can be wholly or partly recycled into step 1 and/or step 2.

- 5 The residence time of the reaction mixture in step 2 is not subject to any restrictions whatsoever, but is generally within the range from about 10 minutes to about 5 hours, preferably within the range from about 30 minutes to about 3 hours.
- 10 The product line between the first and second steps optionally contains packing elements, for example Raschig rings or Sulzer mixing elements, which facilitate a controlled expansion of the reaction mixture into the gas phase. This relates, in particular, to the single-phase procedure.
- 15 Preferably, the reactor of the second step likewise contains the catalyst material of the invention, especially in pellet form. The reactor provides a further improvement in product properties compared with a catalyst-free reactor especially at higher
- 20 pressures and/or in the presence of a large amount of excess water in the reaction mixture. Temperature and pressure should be selected in such a way that the viscosity of the reaction mixture remains sufficiently small to prevent any blinding of the catalyst surface. According to the invention, the point of exit
- 25 from the second process step too is equipped with sieves or filters which guarantee the purity of the reaction mixture and separate the catalyst from the reaction mixture.

In step 3, the first liquid or the first solid phase or the

30 mixture of first liquid and first solid phase is admixed with a gaseous or liquid phase comprising water, preferably water or water vapor. This is done continuously. The amount of water added (as liquid) is preferably within the range from about 10 to about 1500 ml, more preferably within the range from about 50 to about

35 500 ml, based in each case on 1 kg of the first liquid or first solid phase or of the mixture of first liquid and first solid phase. This addition of water primarily compensates the water losses incurred in step 2 and furthers the hydrolysis of acid nitrile groups in the synthesis mixture. This results in a

40 further advantage of this invention, that the mixture of the starting materials as used in step 1 can be used with a small excess of water only.

The water-comprising gaseous or liquid phase is preferably

45 preheated in a heat exchanger before being introduced into step 3 and then mixed with the first liquid or the first solid phase or the mixture of first solid and first liquid phase. The reactor

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may optionally be fitted with mixing elements which further the mixing of the components.

Step 3 can be operated at a temperature from 150 to 370°C and a pressure from 0.1 to  $30 \times 10^6$  Pa; if a catalyst bed according to the invention is present, the conditions applicable to step 1 can be employed. Otherwise, the temperature is preferably 180-300°C, particularly preferably 220-280°C. The pressure is preferably from 1 to  $10 \times 10^6$  Pa, particularly preferably from  $2 \times 10^6$  to  $7 \times 10^6$  Pa.

The pressure and temperature can be adjusted to each other in such a way that the synthesis mixture is present as a single liquid or solid phase. In another embodiment, the pressure and temperature are selected so that a liquid or a solid phase or a mixture of solid and liquid phase and also a gaseous phase are obtained. In this embodiment, the liquid or solid phase or the mixture of liquid and solid phase corresponds to the product mixture, whereas the gaseous phase is separated off. As part of this step, the gaseous phase can be separated from the liquid or solid phase or from the mixture of solid and liquid phase at once, or the synthesis mixture forming within this step can be present in two-phase form: liquid/gaseous, solid/gaseous or liquid-solid/gaseous.

25

The pressure can be adjusted at a preselected temperature so that the pressure is smaller than the equilibrium vapor pressure of ammonia, but greater than the equilibrium vapor pressure of the other components in the synthesis mixture at the given temperature. This way, it is possible to favor especially the removal of ammonia and thus speed up the hydrolysis of the nitrile groups.

The apparatus/reactors usable in this step can be identical to those of step 1, discussed above.

The residence time of this step is likewise not subject to any restrictions, but economic reasons generally dictate a range from about 10 minutes to about 10 hours, preferably about 60 to about 8 hours, particularly preferably about 60 minutes to about 6 hours.

The product mixture obtained in step 3 can then be further processed as described below.

45

## 13

In a preferred embodiment, the product mixture of step 3 is subjected to a postcondensation in step 4 at temperatures from about 200 to about 350°C, preferably at temperatures from about 220 to 300°C, especially from about 240 to 270°C. Step 4 is  
5 carried out at a pressure which is below the pressure of step 3 and is preferably be within the range from about 5 to  $1000 \times 10^3$  Pa, more preferably within the range from about 10 to about  $300 \times 10^3$  Pa. In the context of this step, the temperature and pressure  
10 liquid or solid phase or a mixture of second liquid and second solid phase which each comprise the polyamide.

The postcondensation of step 4 is preferably carried out in such a way that the relative viscosity (measured at a temperature of  
15 25°C and a concentration of 1 g of polymer per 100 ml in 96% strength by weight of sulfuric acid) of the polyamide assumes a value within the range from about 1.6 to about 3.5.

In a preferred embodiment, any water present in the liquid phase  
20 can be expelled by means of an inert gas such as nitrogen.

The residence time of the reaction mixture in step 4 depends especially on the desired relative viscosity, the temperature, the pressure and the amount of water added in step 3.

25

If step 3 is operated as a single-phase regime, the product line between step 3 and step 4 may optionally contain packing elements, for example Raschig rings or Sulzer mixing elements, which allow a controlled expansion of the reaction mixture in the  
30 gas phase.

The fourth step too can be operated using the catalyst of the invention. The use of the catalyst in step 4 improves the molecular weight buildup especially when the relative viscosity  
35 of the effluent from the third or - in the case of the three-step procedure - second step is less than  $RV = 1.6$  - and/or the molar nitrile group and acid amide content in the polymer is greater than 1%, each based on the moles of aminonitrile used.

40 In a further embodiment of the invention, step 3 may be dispensed with and the polyamide is prepared by carrying out steps (1), (2) and (4).

This variant is preferably carried out as follows:

45

In step 1, the reaction is carried out as described above.



## 14

The reaction mixture is treated in step 2 as described above or at a temperature within the range from about 220 to about 300°C and a pressure within the range from about 1 to about  $7 \times 10^6$  Pa, the pressure in step 2 being at least  $0.5 \times 10^6$  Pa lower than in  
5 step 1. At the same time, the resulting first gas phase is separated from the first liquid phase.

The first liquid phase obtained in step 2 is treated in step 4 as in step 1 or at a temperature within the range from about 220 to  
10 300°C and a pressure within the range from about 10 to about  $300 \times 10^3$  Pa, the resulting second gas phase, which contains water and ammonia with or without organic diluent, being separated from the second liquid phase. Within this step, the relative viscosity (measured as defined above) of the resulting polyamide is  
15 adjusted to a desired value within the range from about 1.6 to about 3.5 through choice of temperature and residence time.

The resulting second liquid phase is then conventionally discharged and, if desired, worked up.

20

In a further preferred embodiment of the present invention, at least one of the gas phases obtained in the respective steps can be recycled into at least one of the preceding steps.

It is further preferable to select the temperature and pressure  
25 in step 1 or in step 3 or in both step 1 and step 3 so as to obtain a liquid or a solid phase or a mixture of liquid and solid phase and a gaseous phase and to separate off the gaseous phase.

An apparatus for carrying out the process according to the  
30 invention is described for example in DE-A-19804023 and a schematic representation is evident from Fig. 1 in the drawing therein.

Furthermore, in the context of the process of the invention, it  
35 is also possible to carry out a chain extension or branching or a combination thereof. For this purpose, polymer branching or chain-extending substances known to a person skilled in the art are added in the individual steps. These substances are preferably added in step 3 or 4.

40

Usable substances are:

Trifunctional amines or carboxylic acids as branchers or crosslinkers. Examples of suitable at least trifunctional amines  
45 or carboxylic acids are described in EP-A-0 345 648. The at least trifunctional amines have at least three amino groups which are capable of reaction with carboxylic acid groups. They preferably

## 15

- do not have any carboxylic acid groups. The at least trifunctional carboxylic acids have at least three carboxylic acid groups which are capable of reaction with amines and which can also be present, for example, in the form of their derivatives, such as esters. The carboxylic acids preferably do not contain any amino groups capable of reaction with carboxylic acid groups. Examples of suitable carboxylic acids are trimesic acid, trimerized fatty acids, preparable for example from oleic acid and having from 50 to 60 carbon atoms,
- 10 naphthalenepolycarboxylic acids, such as naphthalene-1,3,5,7-tetracarboxylic acid. The carboxylic acids are preferably defined organic compounds and not polymeric compounds.
- 15 Examples of amines having at least 3 amino groups are nitrilotrialkylamine, especially nitrilotriethaneamine, dialkylenetriamines, especially diethylenetriamine, trialkylenetetramines and tetraalkylenepentamines, the alkylene moieties preferably being ethylene moieties. Furthermore,
- 20 dendrimers can be used as amines. Dendrimers preferably have the general formula I



## 25 where

R is H or  $-(CH_2)_n-NR^1_2$  where  
 $R^1$  is H or  $-(CH_2)_n-NR^2_2$  where  
 $R^2$  is H or  $-(CH_2)_n-NR^3_2$  where  
 $R^3$  is H or  $-(CH_2)_n-NH_2$ ,

- 30 n is an integer from 2 to 6, and  
 x is an integer from 2 to 14.

- Preferably, n is 3 or 4, especially 3, and x is an integer from 2 to 6, preferably from 2 to 4, especially 2. The radicals R can also have the stated meanings independently of one another.
- 35 Preferably, R is a hydrogen atom or a  $-(CH_2)_n-NH_2$  radical.

- Suitable carboxylic acids are those having from 3 to 10 carboxylic acid groups, preferably 3 or 4 carboxylic acid groups.
- 40 Preferred carboxylic acids are those having aromatic and/or heterocyclic nuclei. Examples are benzyl, naphthyl, anthracene, biphenyl, triphenyl radicals or heterocycles such as pyridine, bipyridine, pyrrole, indole, furan, thiophene, purine, quinoline, phenanthrene, porphyrin, phthalocyanine, naphthalocyanine.
- 45 Preference is given to 3,5,3',5'-biphenyltetracarboxylic acid, phthalocyanine, naphthalocyanine, 3,5,3',5'-biphenyltetracarboxylic acid,

## 16

1,3,5,7-naphthalenetetracarboxylic acid,  
2,4,6-pyridinetricarboxylic acid,  
3,5,3',5'-bipyridyltetracarboxylic acid,  
3,5,3',5'-benzophenonetetracarboxylic acid,  
5 1,3,6,8-acridinetetracarboxylic acid, particularly preferably  
1,3,5-benzenetricarboxylic acid (trimesic acid) and  
1,2,4,5-benzenetetracarboxylic acid. Such compounds are  
commercially available or can be prepared by the process  
described in DE-A-4 312 182. If ortho-substituted aromatic  
10 compounds are used, imide formation is preferably prevented  
through the choice of suitable reaction temperatures.

These substances are at least trifunctional, preferably at least  
tetrafunctional. The number of functional groups can be from 3 to  
15 16, preferably from 4 to 10, particularly preferably from 4 to 8.  
The processes of the invention are carried out using either at  
least trifunctional amines or at least trifunctional carboxylic  
acids, but not mixtures of such amines or carboxylic acids.  
However, small amounts of at least trifunctional amines may be  
20 present in the trifunctional carboxylic acids, and vice versa.

The substances are present in an amount from 1 to 50 mmol/kg of  
polyamide, preferably from 1 to 35, particularly preferably from  
1 to 20, mmol/kg of polyamide. The substances are preferably  
25 present in an amount from 3 to 150, particularly preferably from  
5 to 100, especially from 10 to 70, mmol of equivalents/kg of  
polyamide. The equivalents are based on the number of functional  
amino groups or carboxylic acid groups.

30 Difunctional carboxylic acids or difunctional amines serve as  
chain extenders. These have 2 carboxylic acid groups which can be  
reacted with amino groups, or 2 amino groups which can be reacted  
with carboxylic acids. The difunctional carboxylic acids or  
amines, besides the carboxylic acid groups or amino groups, do  
35 not contain any further functional groups capable of reaction  
with amino groups or carboxylic acid groups. Preferably, they do  
not contain any further functional groups. Examples of suitable  
difunctional amines are those which form salts with difunctional  
carboxylic acids. They can be linear aliphatic, such as  
40 C<sub>1-14</sub>-alkylenediamine, preferably C<sub>2-6</sub>-alkylenediamine, for example  
hexylenediamine. They can also be cycloaliphatic. Examples are  
isophoronediamine, dicycycan, laromine. Branched aliphatic  
diamines are likewise usable, an example being Vestamin TMD  
(trimethylhexamethylenediamine, from Hüls AG). Also, the diamines  
45 may be aromatic/aliphatic; m-xylylenediamine may be used, for

## 17

example. The said amines can each be substituted by C<sub>1-12</sub>-alkyl, preferably C<sub>1-14</sub>-alkyl, radicals on the carbon skeleton.

Difunctional carboxylic acids are for example those which form  
5 salts with difunctional diamines. They can be linear aliphatic dicarboxylic acids, which are preferably C<sub>4-20</sub>-dicarboxylic acids. Examples are adipic acid, azelaic acid, sebacic acid, suberic acid. They can also be aromatic. Examples are isophthalic acid, terephthalic acid, naphthalenedicarboxylic acid, as well as  
10 dimerized fatty acids.

The difunctional basic building blocks (c) are preferably used in amounts from 1 to 55, particularly preferably from 1 to 30, especially from 1 to 15, mm/kg of polyamide.

15

According to the invention, the product mixture obtained in step 3, or the second liquid or second solid phase or the mixture of second liquid and second solid phase (from step 4) which each comprise the polyamide, preferably a polymer melt, is discharged  
20 from the reaction vessel in a conventional manner, for example by means of a pump. Subsequently, the polyamide obtained can be worked up according to conventional methods, as described for example in DE-A 4 321 683 (page 3 line 54 to page 4 line 3) at length.

25

In a preferred embodiment, the level of cyclic dimer in the nylon-6 obtained according to the invention can be further reduced by extracting the polyamide first with an aqueous solution of caprolactam and then with water and/or subjecting it  
30 to a gas phase extraction (described in EP-A-0 284 968, for example) and/or extraction using an aminonitrile, such as 6-aminocapronitrile. The low molecular weight constituents obtained in this aftertreatment, such as caprolactam, linear caprolactam oligomer and cyclic caprolactam oligomer, can be  
35 recycled into the first and/or second and/or third step.

The starting mixture and the reaction mixture can be admixed in all steps with chain regulators such as aliphatic and aromatic carboxylic and dicarboxylic acids, and catalysts such as  
40 acid-containing phosphorus compounds in amounts within the range from 0.01 to 5% by weight, preferably within the range from 0.2 to 3% by weight, based on the amount of polyamide-forming monomers and aminonitriles used. Suitable chain regulators include for example propionic acid, acetic acid, benzoic acid,  
45 terephthalic acid and triacetonediamine.

## 18

Additives and fillers such as pigments, dyes and stabilizers are generally added to the synthesis mixture prior to pelletization, preferably in the second, third and fourth steps. Particular preference is given to using fillers and additives whenever the  
5 synthesis or polymer mixture will not encounter fixed bed catalysts in the rest of the processing. One or more impact-modifying rubbers may be present in the compositions as additives in amounts from 0 to 40% by weight, preferably from 1 to 30% by weight, based on the entire composition.

10

It is possible to use, for example, customary impact modifiers which are suitable for polyamides and/or polyarylene ethers.

Rubbers which enhance the toughness of polyamides generally have  
15 two essential features: they have an elastomeric portion which has a glass transition temperature of less than  $-10^{\circ}\text{C}$ , preferably less than  $-30^{\circ}\text{C}$ , and they contain at least one functional group which is capable of interaction with the polyamide. Suitable functional groups include for example carboxylic acid, carboxylic  
20 anhydride, carboxylic ester, carboxylic amide, carboxylic imide, amino, hydroxyl, epoxide, urethane and oxazoline groups.

Rubbers which enhance the toughness of the blends include for example:

25

EP and EPDM rubbers grafted with the above functional groups. Suitable grafting reagents include for example maleic anhydride, itaconic acid, acrylic acid, glycidyl acrylate and glycidyl methacrylate.

30

These monomers can be grafted onto the polymer in the melt or in solution, in the presence or absence of a free-radical initiator such as cumene hydroperoxide.

35 A further group of suitable elastomers are core-shell graft rubbers. These are graft rubbers which are produced in emulsion and which have at least one hard and one soft constituent. A hard constituent is customarily a polymer having a glass transition temperature of at least  $25^{\circ}\text{C}$ , while a soft constituent is a  
40 polymer having a glass transition temperature of not more than  $0^{\circ}\text{C}$ . These products have a structure made up of a core and at least one shell, the structure being the result of the order in which the monomers are added. The soft constituents are generally derived from butadiene, isoprene, alkyl acrylates, alkyl  
45 methacrylates or siloxanes and optionally further comonomers. Suitable siloxane cores can be prepared for example starting from cyclic oligomeric octamethyltetrasiloxane or

tetravinyltetramethyltetrasiloxane. These can be, for example, reacted with  $\gamma$ -mercaptopropylmethyldimethoxysilane in a ring-opening cationic polymerization, preferably in the presence of sulfonic acids, to form the soft siloxane cores. The siloxanes  
5 can also be crosslinked by, for example, conducting the polymerization reaction in the presence of silanes having hydrolyzable groups such as halogen or alkoxy groups such as tetraethoxysilane, methyltrimethoxysilane or phenyltrimethoxysilane. Suitable comonomers here include for  
10 example styrene, acrylonitrile and crosslinking or grafting monomers having more than one polymerizable double bond such as diallyl phthalate, divinylbenzene, butanediol diacrylate or triallyl (iso)cyanurate. The hard constituents are generally derived from styrene,  $\alpha$ -methylstyrene and copolymers thereof,  
15 preferred comonomers being acrylonitrile, methacrylonitrile and methyl methacrylate.

Preferred core-shell graft rubbers have a soft core and a hard shell or a hard core, a first soft shell and at least one further  
20 hard shell. The incorporation of functional groups such as carbonyl, carboxylic acid, acid anhydride, acid amide, acid imide, carboxylic ester, amino, hydroxyl, epoxy, oxazoline, urethane, urea, lactam or halobenzyl groups is here preferably effected by the addition of suitably functionalized monomers  
25 during the polymerization of the last shell. Suitable functionalized monomers include for example maleic acid, maleic anhydride, mono- or diesters or maleic acid, tert-butyl (meth)acrylate, acrylic acid, glycidyl (meth)acrylate and vinyloxazoline. The proportion of monomers having functional  
30 groups is generally within the range from 0.1 to 25% by weight, preferably within the range from 0.25 to 15% by weight, based on the total weight of the core-shell graft rubber. The weight ratio of soft to hard constituents is generally within the range from 1:9 to 9:1, preferably within the range from 3:7 to 8:2.

35 Such rubbers, which enhance the toughness of polyamides, are known per se and described in EP-A-0 208 187, for example.

A further group of suitable impact modifiers are thermoplastic  
40 polyester elastomers. Polyester elastomers are segmented copolyetheresters containing long-chain segments, generally derived from poly(alkylene) ether glycols, and short-chain segments, derived from low molecular weight diols and dicarboxylic acids. Such products are known per se and are  
45 described in the literature, for example in US 3,651,014. Corresponding products are also commercially available under the

## 20

names of Hytrel<sup>®</sup> (Du Pont), Arnitel<sup>®</sup> (Akzo) and Pelprene<sup>®</sup> (Toyobo Co. Ltd.).

It will be appreciated that it is also possible to use mixtures  
5 of different rubbers.

As further additives there may be mentioned for example processing aids, stabilizers and oxidation retardants, agents against thermal decomposition and decomposition by ultraviolet  
10 light, lubricating and demolding agents, flame retardants, dyes and pigments and plasticizers. The proportion thereof is generally up to 40%, preferably up to 15%, by weight, based on the total weight of the composition.

15 Pigments and dyes are generally present in amounts of up to 4%, preferably from 0.5 to 3.5%, especially from 0.5 to 3%, by weight.

The pigments for coloring thermoplastics are commonly known, see  
20 for example R. Gächter and H. Müller, Taschenbuch der Kunststoffadditive, Carl Hanser Verlag, 1983, pages 494 to 510. The first preferred group of pigments to be mentioned are white pigments such as zinc oxide, zinc sulfide, lead white (2  $\text{PbCO}_3$   $\text{Pb(OH)}_2$ ), lithopone, antimony white and titanium dioxide. Of  
25 the two most common crystal polymorphs (rutile and anatase) of titanium dioxide, the rutile form is preferred for use as white pigment for the molding compositions of the invention.

Black pigments which can be used according to the invention are  
30 iron oxide black ( $\text{Fe}_3\text{O}_4$ ), spinel black ( $\text{Cu(Cr,Fe)}_2\text{O}_4$ ), manganese black (mixture of manganese dioxide, silicon dioxide and iron oxide), cobalt black and antimony black and also, particularly preferably, carbon black, which is usually used in the form of furnace or gas black (see G. Benzing, Pigmente für  
35 Anstrichmittel, Expert-Verlag (1988), p. 78ff).

It will be appreciated that inorganic color pigments such as chromium oxide green or organic color pigments such as azo pigments and phthalocyanines can be used according to the  
40 invention to obtain certain hues. Such pigments are generally commercially available.

It can further be of advantage to use the abovementioned pigments or dyes in a mixture, for example carbon black with copper  
45 phthalocyanines, since this generally facilitates the dispersion of color in the thermoplastic.

## 21

Oxidation retardants and thermal stabilizers which can be added to the thermoplastic compositions of the invention include for example halides of metals of group I of the periodic table, e.g., sodium halides, potassium halides, lithium halides, optionally in  
5 conjunction with copper(I) halides, for example chlorides, bromides or iodides. The halides, especially of copper, may also contain electron-rich p-ligands. Examples of such copper complexes are copper halide complexes with triphenylphosphine, for example. It is further possible to use zinc fluoride and zinc  
10 chloride. Other possibilities are sterically hindered phenols, hydroquinones, substituted representatives of this group, secondary aromatic amines, optionally in conjunction with phosphorus-containing acids and salts thereof, and mixtures of these compounds, preferably in a concentration up to 1% by  
15 weight, based on the weight of the mixture.

Examples of UV stabilizers are various substituted resorcinols, salicylates, benzotriazoles and benzophenones, which are generally used in amounts of up to 2% by weight.

20

Lubricating and demolding agents, which are generally included in the thermoplastic material in amounts of up to 1% by weight, are stearic acid, stearyl alcohol, alkyl stearates and  
N-alkylstearamides and also esters of pentaerythritol with  
25 long-chain fatty acids. It is also possible to use salts of calcium, of zinc or of aluminum of stearic acid and also dialkyl ketones, for example distearyl ketone.

The present invention further provides a polyamide preparable by  
30 any of the foregoing processes.

The examples which follow illustrate the invention.

## Examples

35

## Analysis

The relative viscosity (RV), a measure of the molecular weight buildup and the degree of polymerization, was measured in 1%  
40 strength by weight solution of extracted material in 96% strength sulfuric acid, at 25°C using an Ubbelohde viscometer.

Secondary amines were determined following total hydrolysis of the sample in aqueous hydrochloric acid. The species with  
45 secondary amine units was identified by the method described in detail in WO 00/24808. The hydrolysis product iminobishexanoic acid, which is a measure of the number of branching products in



the polymer chain, was derivatized with N-dimethylformamide dimethyl acetal to make it possible for it to be quantitatively detected by gas chromatography. The number of branches was then determined in milliequivalents of iminobishexanoic acid (IBHA) 5 per kilogram of polymer.

For extraction, 100 parts by weight of polymer were stirred with 400 parts by weight of completely ion-free water at 100°C for 32 hours under reflux and, after removal of the water, dried gently, 10 i.e., without postcondensation, at 100°C under reduced pressure for 20 hours.

The inventive and comparative examples were carried out in an apparatus as per Figure 1 of DE-A-19804023 using 15 aminocapronitrile (ACN) and water (H<sub>2</sub>O) as reactants. The organic diluent used was ethanol (EtOH). The reactants and the organic diluent were initially charged to feed vessel V of the apparatus mentioned.

20 The first process stage (1), having an empty volume of 1 liter and an internal length of 1000 mm, was packed with titanium dioxide pellets prepared according to Ertl, Knözinger, Weitkamp: "Handbook of heterogeneous catalysis", VCH Weinheim, 1997; page 98ff. The pellets were 100% TiO<sub>2</sub> in the anatase form and had a 25 strand length within the range from 2 to 14 mm, a strand thickness of about 2 mm and a specific surface area of 110 m<sup>2</sup>/g.

The second stage (2) was a 2 liter capacity separating vessel.

30 The third stage (3), having an empty volume of 1 liter and an internal length of 1000 mm, was packed with the titanium dioxide pellets described under process stage (1). In this flow tube, the reaction mixture could be additionally mixed with water from a feed vessel (see Figure 1 mentioned).

35

The fourth stage (4) was in turn a separating vessel (5 liter capacity), from which the polymer melt prepared was extruded in strand form (A) with the aid of a gear pump.

40 The results of the inventive and comparative examples are evident from the table which follows. The abbreviations in the table have the following meanings:

The throughput D is the mass flow of reaction mixture from the 45 feed vessel through the first process stage/step.

## 23

To enable the examples to be compared, the ACN space velocity of the first process stage is reported. It is the ratio of the throughput of ACN (kg/h) in stage 1 and the empty volume of the first stage (liters).

5

WZ signifies the amount of water added in the third stage. It is based on the throughput of the reaction mixture into the first stage and is reported in percent.

10 The numerals 1, 2, 3 and 4 appended in the table to the temperature (T) and pressure (P) data signify the first, second, third and fourth stages of the apparatus.

The IBHA content indicates the number of branches in  
15 milliequivalents of iminobisshexanoic acid (IBHA) per kilogram of polymer.

The residence time of the reaction mixture in the second stage was 1 h in all examples. To ensure this, given varying  
20 throughputs in the first stage, the fill level in the second stage was adapted. The residence time in the fourth stage was 5 h in all examples.

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Example	Reactant ACN:H <sub>2</sub> O:EtOH [mol:mol:mol]	D [kg/h]	Space velocity [kg/(h*liter)]	T(1) [°C]	P(1) [bar]	T(2) [°C]	P(2) [bar]	T(3) [°C]	P(3) [bar]	WZ [%]	T(4) [°C]	P(4) [bar]	RV	IBHA content
1	1:6:0	0.6	0.3	240	85	259	28	250	56	10	255	1	2.03	4.2
2	1:6:4	1.0	0.29	240	87	257	26	252	55	6	255	1	2.07	2.8
3	1:6:6	1.3	0.3	241	84	257	28	250	55	5	255	1	2.03	2.5
4	1:6:8	1.6	0.3	240	85	258	27	250	58	4	254	1	2.09	2.1

We claim:-

1. A continuous process for preparing a polyamide by reacting at  
5 least one aminonitrile with water, which comprises:
  - (1) reacting at least one aminonitrile with water in the  
presence of an organic liquid diluent at from 90 to 400°C  
and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a  
10 Brönsted acid catalyst selected from a beta-zeolite  
catalyst, a sheet-silicate catalyst or a titanium dioxide  
catalyst comprising from 70 to 100% by weight of anatase  
and from 0 to 30% by weight of rutile and in which up to  
15 40% by weight of the titanium dioxide may be replaced by  
tungsten oxide, to obtain a reaction mixture,
  - (2) further reacting the reaction mixture at from 150 to  
400°C and a pressure which is lower than the pressure in  
stage 1 in the presence of a Brönsted acid catalyst  
20 selected from a beta-zeolite catalyst, a sheet-silicate  
catalyst or a titanium dioxide catalyst comprising from  
70 to 100% by weight of anatase and from 0 to 30% by  
weight of rutile and in which up to 40% by weight of the  
titanium dioxide may be replaced by tungsten oxide, the  
25 temperature and pressure being selected so as to obtain a  
first gas phase and a first liquid phase or a first solid  
phase or a mixture of first solid and first liquid phases  
and so that the first gas phase is separated from the  
first liquid phase or first solid phase or from the  
30 mixture of first liquid and first solid phases, and
  - (3) admixing the first liquid or the first solid phase or the  
mixture of first liquid and first solid phases with a  
gaseous or liquid phase comprising water at from 150 to  
35 370°C and from 0.1 to  $30 \times 10^6$  Pa, to obtain a product  
mixture.
2. A continuous process for preparing a polyamide by reacting at  
40 least one aminonitrile with water, which comprises:
  - (1) reacting at least one aminonitrile with water in the  
presence of an organic liquid diluent at from 90 to 400°C  
and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a  
45 Brönsted acid catalyst selected from a beta-zeolite  
catalyst, a sheet-silicate catalyst or a titanium dioxide  
catalyst comprising from 70 to 100% by weight of anatase  
and from 0 to 30% by weight of rutile and in which up to

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40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,

- 5 (2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and
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- 20 (3) admixing the first liquid or the first solid phase or the mixture of first liquid and first solid phases with a gaseous or liquid phase comprising water at from 150 to 370°C and from 0.1 to  $30 \times 10^6$  Pa in a flow tube containing a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a product mixture.
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3. A process as claimed in claim 1 or 2, further comprising the following stage:
- 35 (4) postcondensing the product mixture at from 200 to 350°C and a pressure which is lower than the pressure in stage 3, the temperature and pressure being selected so as to obtain a second, water- and ammonia-containing gas phase and a second liquid or second solid phase or a mixture of second liquid and second solid phases, which each include the polyamide.
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4. A continuous process for preparing a polyamide by reacting at least one aminonitrile with water, which comprises:
- 45 (1) reacting at least one aminonitrile with water in the presence of an organic liquid diluent at from 90 to 400°C and from 0.1 to  $35 \times 10^6$  Pa in a flow tube containing a

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- Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, to obtain a reaction mixture,
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- (2) further reacting the reaction mixture at from 150 to 400°C and a pressure which is lower than the pressure in stage 1 in the presence of a Brönsted acid catalyst selected from a beta-zeolite catalyst, a sheet-silicate catalyst or a titanium dioxide catalyst comprising from 70 to 100% by weight of anatase and from 0 to 30% by weight of rutile and in which up to 40% by weight of the titanium dioxide may be replaced by tungsten oxide, the temperature and pressure being selected so as to obtain a first gas phase and a first liquid phase or a first solid phase or a mixture of first solid and first liquid phases and so that the first gas phase is separated from the first liquid phase or first solid phase or from the mixture of first liquid and first solid phases, and
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- (4) postcondensing the first liquid or the first solid phase or the mixture of first liquid and first solid phases at from 200 to 350°C and a pressure which is lower than the pressure in stage 3, the temperature and pressure being selected so as to obtain a second, water- and ammonia-containing gas phase and a second liquid or second solid phase or a mixture of second liquid and second solid phases, which each include the polyamide.
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5. A process as claimed in any of claims 1 to 4, wherein the temperature and pressure in stage 1 or in stage 3 or in both stage 1 and stage 3 are selected so as to obtain a liquid or a solid phase or a mixture of liquid and solid phases and a gaseous phase and so that the gaseous phase is separated off.
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6. A process as claimed in any of claims 1 to 5, wherein the reaction of stage 1 is carried out using a molar ratio from 1:1 to 1:30 for aminonitrile to water.
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7. A process as claimed in any of claims 1 to 6, wherein in stage 3 the gaseous or liquid phase which contains water is added in an amount from 50 to 1500 ml of water per 1 kg of first liquid or first solid phase or mixture of first liquid and first solid phases.
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8. A process as claimed in any of claims 1 to 7, wherein at least one of the gas phases obtained in the respective stages is recycled into at least one of the preceding stages.
- 5 9. A process as claimed in any of claims 1 to 8, wherein the aminonitrile used is an  $\omega$ -aminoalkyl nitrile having an alkylene moiety (-CH<sub>2</sub>-) of from 4 to 12 carbon atoms or an aminoalkylaryl nitrile having from 8 to 13 carbon atoms.
- 10 10. A process as claimed in any of claims 1 to 9, wherein the following mixture is used:
- from 50 to 99.99% by weight of 6-aminocapronitrile,  
from 0.01 to 50% by weight of at least one dicarboxylic acid  
15 selected from the group consisting of aliphatic C<sub>4</sub>-C<sub>10</sub>- $\alpha,\omega$ -dicarboxylic acids, aromatic C<sub>8</sub>-C<sub>12</sub>-dicarboxylic acids and C<sub>5</sub>-C<sub>8</sub>-cycloalkanedicarboxylic acids,  
20 from 0 to 50% by weight of an  $\alpha,\omega$ -diamine having 4 - 10 carbon atoms,  
from 0 to 50% by weight of an  $\alpha,\omega$ -C<sub>2</sub>-C<sub>12</sub>-dinitrile and  
from 0 to 50% by weight of an  $\alpha,\omega$ -C<sub>5</sub>-C<sub>12</sub>-amino acid or of the  
25 corresponding lactam,  
from 0 to 10% by weight of at least one inorganic acid or salt thereof,
- the individual weight percentages adding up to 100%.
- 30 11. A process as claimed in any of claims 1 to 10, wherein the organic liquid diluent used is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub>-alkanols, glycols, ethers, C<sub>6</sub>-C<sub>10</sub>-alkanes, C<sub>5</sub>-C<sub>10</sub>-cycloalkanes, C<sub>6</sub>-C<sub>10</sub>-aromatics, N-C<sub>1</sub>-C<sub>4</sub>-alkyllactams and  
35 lactams except caprolactam.
12. A process as claimed in any of claims 1 to 11, wherein the organic liquid diluent used is selected from the group consisting of benzene, toluene, o-xylene, m-xylene and  
40 p-xylene.
13. A process as claimed in any of claims 1 to 12, wherein the organic liquid diluent is used in amounts from 0.1 to 90% by weight, based on the total mixture used in the first stage.  
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14. A polyamide preparable by a process as claimed in any of claims 1 to 13.