

Separation of 6-aminocapronitrile from mixtures containing
6-aminocapronitrile, adipodinitrile and hexamethylenediamine

- 5 The present invention relates to a process for the distillative separation of 6-aminocapronitrile from mixtures containing 6-aminocapronitrile, adipodinitrile and hexamethylenediamine, wherein
- 10 a) the hexamethylenediamine is separated from the mixture to give a mixture (I) with a hexamethylenediamine content of less than 1% by weight;
- 15 b) all or part of the 6-aminocapronitrile is separated from the mixture (I) to give a mixture (II) whose content of substances which boil above 6-aminocapronitrile under distillation conditions and cannot be formed by dimerization reactions of 6-aminocapronitrile under thermal stress is less than 1% by weight; and
- 20 c) all or part of the hexamethylenediamine present is separated from the mixture (II) to give a mixture (IV) whose hexamethylenediamine content is higher than that of the mixture (II), and a mixture (V) whose hexamethylenediamine
- 25 content is lower than that of the mixture (II).

It is known that 6-aminocapronitrile can be used for the preparation of caprolactam or polyamides. The 6-aminocapronitrile must have a high purity for such purposes.

- 30 6-Aminocapronitrile is conventionally prepared by the partial catalytic hydrogenation of adipodinitrile, which can be obtained by the double hydrocyanation of butadiene in the presence of catalysts. This normally gives a mixture containing
- 35 6-aminocapronitrile, unreacted adipodinitrile and hexamethylenediamine, optionally together with solvents, substances boiling below hexamethylenediamine, substances boiling above adipodinitrile, and other by-products.

- 40 Numerous processes for the separation of 6-aminocapronitrile from such mixtures to give a 6-aminocapronitrile of said high purity are known, for example from WO 96/20931 and WO 97/23454.

- The disadvantage of these processes is the high energy
- 45 expenditure required to recover 6-aminocapronitrile of sufficient purity from the mixture.

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It is an object of the present invention to provide a process which makes it possible, in a technically simple and economic manner and avoiding said disadvantages, to recover 6-aminocapronitrile of sufficient purity from mixtures containing
5 6-aminocapronitrile, adipodinitrile, hexamethylenediamine and optionally solvents and other secondary components.

We have found that this object is achieved by the process defined at the outset.

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Processes for the preparation of mixtures containing 6-aminocapronitrile, adipodinitrile, hexamethylenediamine and optionally solvents, substances boiling below hexamethylenediamine, substances boiling above adipodinitrile,
15 and other by-products are known per se.

Thus mixtures containing 6-aminocapronitrile, adipodinitrile and hexamethylenediamine can be obtained by the partial catalytic hydrogenation of adipodinitrile.

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Based on the sum of 6-aminocapronitrile, adipodinitrile and hexamethylenediamine, such mixtures conventionally contain from 5 to 90% by weight, preferably from 10 to 80% by weight and particularly preferably from 20 to 70% by weight of
25 6-aminocapronitrile and from 5 to 90% by weight, preferably from 10 to 80% by weight and particularly preferably from 20 to 70% by weight of hexamethylenediamine, the remainder being unreacted adipodinitrile.

30 In the light of previous observations, the catalyst used for the hydrogenation is not critical in terms of the process according to the invention. The mixture can take place [sic] from the catalyst after the hydrogenation in a manner known per se, for example by filtration, this being preferred in the case of a
35 suspension hydrogenation, or by removal of the mixture from the reaction vessel to leave the catalyst in the reaction vessel, this being preferred in the case of a fixed bed hydrogenation.

The hydrogenation can advantageously be carried out in the
40 presence of a solvent. Suitable solvents are organic solvents such as alcohols, preferably alkanols and especially C₁-C₄ alkanols like methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol or s-butanol, esters, preferably esters of an alkanecarboxylic acid, especially a C₁-C₄ alkanecarboxylic acid
45 like formic acid, acetic acid, propionic acid or butyric acid, with an alkanol, especially a C₁-C₄ alkanol like methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol or

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- s-butanol, ethers such as linear or cyclic ethers, for example dimethyl ether, diethyl ether, methyl t-butyl ether or tetrahydrofuran, hydrocarbons such as aliphatic or aromatic hydrocarbons, for example benzene, toluene, ethylbenzene,
- 5 o-xylene, m-xylene or p-xylene, amines such as primary, secondary or tertiary amines, lactones such as butyrolactone, lactams such as caprolactam, pyrrolidone or N-methylpyrrolidone, and amides, or inorganic solvents such as ammonia, or mixtures thereof.
- 10 Preferred solvents are alcohols, especially methanol and ethanol, aromatic hydrocarbons, especially toluene, and ammonia, or mixtures thereof.

If the hydrogenation is carried out in the presence of a solvent,

15 the reaction mixture will then contain this solvent. Prior to the process according to the invention, the solvent can advantageously be separated from the reaction mixture in a manner known per se, for example by distillation or rectification.

- 20 This separation can advantageously be performed by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

Suitable apparatuses are those conventionally used for

25 distillation, for example those described in: Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve-plate columns, bubble-cap columns or packed columns, with or without a side discharge.

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By-products, for example substances boiling below hexamethylenediamine and/or substances boiling above adipodinitrile, can be formed in the hydrogenation.

- 35 In terms of the present invention, substances boiling below hexamethylenediamine are understood as meaning compounds which have a boiling point below that of hexamethylenediamine under the appropriate distillation conditions.

- 40 Examples of possible substances boiling below hexamethylenediamine are hexamethyleneimine, hexylamine, aminomethylcyclopentylamine and diaminocyclohexane. Such compounds are present in the mixtures obtained from the hydrogenation in overall amounts of up to 10% by weight,
- 45 preferably of up to 5% by weight, based on the sum of 6-aminocapronitrile, adipodinitrile and hexamethylenediamine.

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Prior to the process according to the invention, substances boiling below hexamethylenediamine can advantageously be separated from the reaction mixture in a manner known per se, for example by distillation or rectification.

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15 side discharge.

Any solvent used and any substances present which boil below hexamethylenediamine can be separated off simultaneously in step a or beforehand. Preferably, any solvent used is separated off
20 first (step a0), followed by any substances present which boil below hexamethylenediamine (step a1).

Step a1 should advantageously be carried out at a pressure below ambient atmospheric pressure, preferably at an absolute pressure
25 below 500 mbar.

According to the invention, hexamethylenediamine is separated from the mixture in step a to give a mixture (I) with a hexamethylenediamine content below 5% by weight, preferably below
30 1% by weight, based on the mixture (I).

This separation can advantageously be performed by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

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40 columns, bubble-cap columns or packed columns, with or without a side discharge, preferably with a side discharge.

Step a should advantageously be carried out at a pressure below ambient atmospheric pressure, preferably at an absolute pressure
45 below 500 mbar.

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In one preferred embodiment, hexamethylenediamine and components boiling below hexamethylenediamine can be separated off together, i.e. steps a1 and a can be carried out together.

- 5 In this operation, hexamethylenediamine can advantageously be recovered at a side discharge.

In one particularly preferred embodiment, the column used has a separating plate in the region between the feed and the side
10 discharge.

According to the invention, all or part of the 6-aminocapronitrile is separated from the mixture (I) in step b to give a mixture (II) whose content of substances which boil
15 above 6-aminocapronitrile under distillation conditions and cannot be formed by dimerization reactions of 6-aminocapronitrile under thermal stress is less than 2% by weight, preferably less than 0.1% by weight.

- 20 This separation can advantageously be performed by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

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25 distillation, for example those described in: Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve-plate columns, bubble-cap columns or packed columns, with or without a side discharge, preferably with a side discharge.

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Step b should advantageously be carried out at a pressure below ambient atmospheric pressure, preferably at an absolute pressure below 500 mbar.

- 35 According to the invention, all or part of the hexamethylenediamine present is separated from the mixture (II) in step c to give a mixture (IV) whose hexamethylenediamine content is higher than that of the mixture (II), and a mixture (V) whose hexamethylenediamine content is lower than that of the
40 mixture (II).

This separation can advantageously be performed by fractional distillation in one or more, such as 2 or 3, distillation apparatuses.

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Suitable apparatuses are those conventionally used for distillation, for example those described in: Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve-plate
5 columns, bubble-cap columns or packed columns, with or without a side discharge.

Step c should advantageously be carried out at a pressure below ambient atmospheric pressure, preferably at an absolute pressure
10 below 500 mbar.

In one preferred embodiment, the pressure in step a should be lower than the pressure in step c.

15 In another preferred embodiment, the mixture (IV) obtained in step c can be recycled into step a, the mixture (IV) preferably being vaporous.

In another embodiment of step b in terms of the present
20 invention, it is possible to allow a higher content of substances boiling above 6-aminocapronitrile to give a mixture (IIa) and separate components boiling above 6-aminocapronitrile from the mixture (IIa) to give a mixture (VI) whose 6-aminocapronitrile content is higher than that of the mixture (II), and a mixture
25 (VII) whose 6-aminocapronitrile content is lower than that of the mixture (II).

In another preferred embodiment, the mixture (VII) can be recycled into step b.

30 The hexamethylenediamine content of the mixture (V) should advantageously be at most 5000 ppm, preferably 0 to 1000 ppm and particularly preferably 0 to 200 ppm, based on the weight of the mixture (V). The sum of the components of the mixture (V) other
35 than 6-aminocapronitrile should advantageously be at most 5000 ppm, preferably 0 to 500 ppm and particularly preferably 0 to 200 ppm, based on the weight of the mixture (V).

The total energy consumption of the process according to the
40 invention, calculated as the sum of the energy consumptions in steps a, b and c, and optionally a0 and a1, is lower than the energy consumption required when the separation is carried out in only two steps a and c, and optionally a0 and a1, to achieve the same hexamethylenediamine content in the 6-aminocapronitrile
45 separated off.

Example

- In a distillation column K1, 200 kg/h of a hydrogenation mixture containing 29% of hexamethylenediamine, 42% of
- 5 6-aminocapronitrile, 27% of adipodinitrile, 0.5% of low-boiling components and 1.5% of high-boiling components were separated off so that 1.5 kg/h containing essentially low-boiling components were withdrawn at the top.
- 10 58 kg/h of hexamethylenediamine with a 6-aminocapronitrile content of 110 ppm were withdrawn at a side discharge. 156.5 kg/h with a hexamethylenediamine content of 0.2% were withdrawn at the bottom of the column K1. Said column was operated with 90 kg/h of steam. In a second distillation column K2, the bottom product
- 15 withdrawn from column K1 was distilled so that 116.5 kg/h of 6-aminocapronitrile with a hexamethylenediamine content of 0.3% were withdrawn at the top. 58 kg/h with a 6-aminocapronitrile content of 2% were withdrawn at the bottom. The top product of column K2 was distilled in a third column K3 so that 17 kg/h of
- 20 vapor were withdrawn at the top and recycled into column K1. Column K2 was operated with 30 kg/h of steam. 99.5 kg/h of 6-aminocapronitrile with a hexamethylenediamine content of 45 ppm were withdrawn from column K3 at a side discharge. Column K3 was operated with 5 kg/h of steam. The steam consumption of columns
- 25 K1 + K3 was 95 kg/h.

Comparative Example

- In distillation column K1 according to the Example, 200 kg/h of a
- 30 hydrogenation mixture containing 29% of hexamethylenediamine, 42% of 6-aminocapronitrile, 27% of adipodinitrile, 0.5% of low-boiling components and 1.5% of high-boiling components were separated off so that 1.5 kg/h containing essentially low-boiling components were withdrawn at the top.
- 35 58 kg/h of hexamethylenediamine with a 6-aminocapronitrile content of 115 ppm were withdrawn at a side discharge. 156.5 kg/h with a hexamethylenediamine content of 0.05% were withdrawn at the bottom of column K1. 140 kg/h of steam were necessary to
- 40 obtain this hexamethylenediamine content at the bottom of the column. In a second distillation column K2, the bottom product withdrawn from column K1 was distilled so that 116.5 kg/h of 6-aminocapronitrile were withdrawn at the top. The hexamethylenediamine content of the top discharge was 800 ppm.
- 45 The column was operated with 30 kg/h of steam.

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Despite the fact that the energy consumption of column K1 in the Comparative Example (140 kg/h) was higher than the sum of the energy consumptions in columns K1 and K3 in the Example (95 kg/h overall), the ACN purity achieved was markedly poorer in the

5 Comparative Example.

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We claim:-

1. A process for the distillative separation of
5 6-aminocapronitrile from mixtures containing
6-aminocapronitrile, adipodinitrile and hexamethylenediamine,
wherein
 - 10 a) the hexamethylenediamine is separated from the mixture to
give a mixture (I) with a hexamethylenediamine content of
less than 1% by weight;
 - 15 b) all or part of the 6-aminocapronitrile is separated from
the mixture (I) to give a mixture (II) whose content of
substances which boil above 6-aminocapronitrile under
distillation conditions and cannot be formed by
dimerization reactions of 6-aminocapronitrile under
thermal stress is less than 1% by weight; and
 - 20 c) all or part of the hexamethylenediamine present is
separated from the mixture (II) to give a mixture (IV)
whose hexamethylenediamine content is higher than that of
the mixture (II), and a mixture (V) whose
25 hexamethylenediamine content is lower than that of the
mixture (II).
2. A process as claimed in claim 1 wherein hexamethylenediamine
is recovered at a side discharge in step a.
- 30 3. A process as claimed in claim 1 or 2 wherein
hexamethylenediamine and components boiling below
hexamethylenediamine are separated off together.
4. A process as claimed in any of claims 1 to 3 wherein all or
35 part of the mixture (IV) separated off in step c is recycled
into step a.
5. A process as claimed in claim 4 wherein the mixture (IV)
recycled from step c into step a is vaporous.
- 40 6. A process as claimed in claim 5 wherein all or part of the
mixture (VII) is recycled into step b.
7. A process as claimed in any of claims 1 to 6 wherein the
45 pressure in step b is chosen so that the bottom temperature
does not exceed 185°C.