



PCT
WELTORGANISATION FÜR GEISTIGES EIGENTUM
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INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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(21) Internationales Aktenzeichen: PCT/EP97/03098 (22) Internationales Anmeldedatum: 13. Juni 1997 (13.06.97) (30) Prioritätsdaten: 196 23 662.2 13. Juni 1996 (13.06.96) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AK- TIENGESSELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): FUCHS, Eberhard [DE/DE]; Bensheimer Ring 5c, D-67227 Frankenthal (DE). (74) Anwalt: REITSTÖTTER, KINZEBACH & PARTNER; Post- fach 86 06 49, D-81633 München (DE).			(81) Bestimmungsstaaten: AM, AU, AZ, BG, BR, BY, CA, CN, CZ, GE, HU, IL, JP, KG, KR, KZ, LV, MD, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>
(54) Title: METHOD OF PURIFYING ϵ -CAPROLACTAM (54) Bezeichnung: VERFAHREN ZUR REINIGUNG VON ϵ -CAPROLACTAM (57) Abstract The invention concerne a method of purifying ϵ -caprolactam by reacting raw caprolactam with a complex hydride of boron or aluminium. (57) Zusammenfassung Die vorliegende Erfindung betrifft ein Verfahren zur Reinigung von ϵ -Caprolactam durch Umsetzung des rohen Caprolactams mit einem komplexen Hydrid des Bors oder des Aluminiums.			



THIS SHEET HAS BEEN REPLACED

Purification of ϵ -caprolactam

Description

5

The present invention relates to a process for purifying ϵ -caprolactam.

ϵ -Caprolactam is an important starting material for the production
10 of polyamides (nylon 6). There are various ways of producing it
industrially. The most popular option is by Beckmann rearrange-
ment of cyclohexanone oxime (K. Weissermel, H.J. Arpe,
Industrielle Organische Chemie, 4th edition, pp. 272).
Alternatively, cyclohexanecarboxylic acid is produced from
15 toluene via benzoic acid and rearranged with nitrosylsulfuric
acid to the ϵ -caprolactam. Other processes are based on the cy-
clization of ω -aminocaproic acid derivatives, for example 6-ami-
nocaproic esters (EP-A 376 123) or 6-aminocapronitrile
(EP 659 741), in the presence of suitable, typically acidic, cat-
20 alysts to form ϵ -caprolactam.

All ϵ -caprolactam processes give rise to by-products, the nature
and quantity of which depend on the principle of the process, on
the quality of the starting materials and also on the process
25 parameters. On the other hand, the ϵ -caprolactam has to meet high
purity requirements, especially in fibermaking. For this reason,
each manufacturing process requires its own optimized purifica-
tion process. The various purification processes are cited for
example in Process Economics Program Report No. 41 B, Caprolactam
30 and Nylon 6, March 1988, pp. 69.

These purification processes are generally combinations of ex-
traction, distillation and/or crystallization processes. Highly
contaminated caprolactam fractions, for example caprolactam puri-
35 fication residues, are frequently subjected to a catalytic hydro-
genation. Removal of the catalyst is generally followed by a dis-
tillative workup or the return into the purification cycle. In
the case of a catalytic suspension hydrogenation of the crude
 ϵ -caprolactam using Raney nickel (EP-A-138 241, JP-A-60-21145) the
40 removal of the catalyst presents problems. In the case of a hy-
drogenation of the crude ϵ -caprolactam over fixed-bed catalysts
(DE-A-1004616, DD-A-75083), decreasing activity or poisoning of
the catalysts is likely over time.

45 It is an object of the present invention to provide a low-cost
universally deployable purification process for ϵ -caprolactam.

I have found that this object is achieved, surprisingly, by using a complex hydride of aluminum or of boron.

The present invention accordingly provides a process for purifying ϵ -caprolactam, which comprises reacting crude ϵ -caprolactam with a complex hydride of aluminum or of boron.

Suitable complex hydrides of aluminum or of boron for the process of this invention are in particular sodium borohydride, lithium borohydride, potassium borohydride, calcium borohydride, sodium cyanoborohydride, sodium methoxyethoxyaluminum hydride, lithium tri-*t*-butoxyaluminum hydride.

The amount of hydride hydrogen used naturally depends on the concentration of the impurities in the ϵ -caprolactam. It is chosen so that an excess of hydride hydrogen is present, based on the impurities to be reduced. Preference is given to an excess of from 1.5 to five times, based on the stoichiometrically required hydride quantity.

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It has been found that, to obtain an adequate reaction rate in the ϵ -caprolactam purification process of this invention, from 10 to 50 % by weight of water, based on crude ϵ -caprolactam, [lacuna] to be added to the reaction mixture when a borohydride is used.

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In a preferred embodiment, the reaction is carried out in the presence of from 0.5 to 5 mol%, in particular from 1 to 4 mol% of NaBH_4 and of from 10 to 50 % by weight of water, based on crude ϵ -caprolactam. The sodium borohydride can be used in solid form or in the form of a commercially available aqueous solution.

The reaction is preferably carried out within the range from 10 to 150°C, in particular within the range from 20 to 100°C. The reaction time is within the range from 0.5 h to 200 h, preferably within the range from 1 h to 100 h.

After the reaction has ended, water and the reduced impurities are distilled off under a slightly reduced pressure. It is also possible to distil off water and impurities continuously even during the reaction by applying a slight reduced pressure. Thereafter the reaction mixture is subjected to a conventional distillation under reduced pressure (0.5-8 mm Hg). Pure ϵ -caprolactam is obtained as distillate with a UV number < 10 (see below).

The process of this invention is suitable for purifying ϵ -caprolactam produced by any of the conventional manufacturing processes. This process is advantageously suitable for purifying



ϵ -caprolactam produced by cyclization of ω -aminocaproic acid derivatives, for example ω -aminocaproic acid, ω -aminocaproamide, ω -aminocaproic ester and ω -aminocapronitrile.

5 Examples:

Purification of a caprolactam produced by cyclization of ω -aminocapronitrile

- 10 The purity of the ϵ -caprolactam is determined in terms of the UV number. The UV number is defined as the sum of all absorbances of a 50 % strength by weight aqueous caprolactam solution measured at intervals of 10 nm in the wavelength range from 280 nm to 400 nm in a cell having a pathlength of $d = 5$ cm. The UV number
15 of the purified ϵ -caprolactam should not exceed 10.

Example 1

Preparation of ϵ -caprolactam in accordance with DE-A 43 396 48

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- 100 parts by weight of ω -aminocapronitrile were dissolved in 1000 parts by weight of ethanol and 30 parts by weight of water and passed over a fixed bed of titania (anatase) at 220°C with a residence time of 12 min. The solvent was then distilled off. The
25 crude caprolactam thus obtained was used in the following purification stage.

Purification of the crude ϵ -caprolactam

- 30 70 parts by weight of crude caprolactam and 30 parts by weight of water were admixed with 1 % by weight of sodium borohydride (based on crude ϵ -caprolactam) in a stirred vessel equipped with a still head. After 100 h, the reaction mixture was subjected to fractional distillation. ϵ -Caprolactam passed over at 119°C
35 (2 mbar) with a UV number of 3.1.

Example 2

- Crude caprolactam prepared by Beckmann rearrangement (see
40 Progress [sic] Economics Program Report (SRI Report) No. 41 B, Caprolactam and Nylon 6, March 1988) was reacted as described in Example 1 in the presence of 0.4 % by weight NaBH_4 . After 24 h, the reaction mixture was subjected to fractional distillation. ϵ -Caprolactam passed over at 125°C (3 mbar) with a UV number of
45 3.5.

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I claim:

1. A process for purifying ϵ -caprolactam, which comprises
5 reacting ϵ -caprolactam with a complex hydride of aluminum or
of boron.
2. A process as claimed in claim 1, wherein the complex hydride
is selected from the group consisting of NaBH_4 , LiBH_4 , KBH_4 ,
10 $\text{Ca}(\text{BH}_4)_2$, $\text{NaAlH}_2(\text{OCH}_3)(\text{OC}_2\text{H}_5)$, $\text{LiAlH}(\text{Ot-Bu})_3$ and NaBH_3CN .
3. A process as claimed in either of the preceding claims,
wherein from 2 to 20 mol% of hydridic hydrogen is used, based
on the ϵ -caprolactam to be purified.
15
4. A process as claimed in any of claims 2 to 5 [sic], wherein
 ϵ -caprolactam is reacted in the presence of from 0.5 to
5 mol% of NaBH_4 and from 10 to 50 % by weight of water, based
on the ϵ -caprolactam to be purified.
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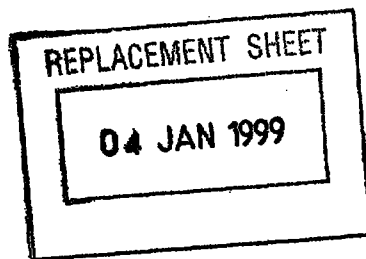


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I claim:

1. A process for purifying ϵ -caprolactam, which comprises
5 treating the ϵ -caprolactam to be purified with a complex
borohydride in the absence of acidic substances.
2. A process as claimed in claim 1, wherein the complex hydride
is selected from the group consisting of NaBH_4 , LiBH_4 , KBH_4 ,
10 $\text{Ca}(\text{BH}_4)_2$ and NaBH_3CN .
3. A process as claimed in either of the preceding claims,
wherein from 2 to 20 mol% of hydridic hydrogen is used, based
on the ϵ -caprolactam to be purified.
15
4. A process as claimed in any of claims 2 to 5 [sic], wherein
the ϵ -caprolactam is treated with from 0.5 to 5 mol% of NaBH_4
and from 10 to 50 % by weight of water, based on the
20 ϵ -caprolactam to be purified.

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REPLACEMENT SHEET

REPLACEMENT SHEETS SG	
☒ Description	: paged 1 to paged 4
☒ Claim(s)	: paged 1 to paged 5
☐ Drawing(s)	: paged 1 to paged 1
☐ Abstract	: paged 1 to paged 1
DATE OF RECEIPT 08/03/99	

Purification of ϵ -caprolactam

Description

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All ϵ -caprolactam processes give rise to by-products, the nature and quantity of which depend on the principle of the process, on the quality of the starting materials and also on the process parameters. On the other hand, the ϵ -caprolactam has to meet high purity requirements, especially in fibermaking. For this reason, each manufacturing process requires its own optimized purification process. The various purification processes are cited for example in Process Economics Program Report No. 41 B, Caprolactam and Nylon 6, March 1988, pp. 69.

These purification processes are generally combinations of extraction, distillation and/or crystallization processes. Highly contaminated caprolactam fractions, for example caprolactam purification residues, are frequently subjected to a catalytic hydrogenation. Removal of the catalyst is generally followed by a distillative workup as for example disclosed in EP-A-641 778 or the return into the purification cycle. In the case of a catalytic suspension hydrogenation of the crude ϵ -caprolactam using Raney nickel (EP-A-138 241, JP-A-60-21145) the removal of the catalyst presents problems. In the case of a hydrogenation of the crude ϵ -caprolactam over fixed-bed catalysts (DE-A-1004616, DD-A-75083 and EP-A-635 487), decreasing activity or poisoning of the catalysts is likely over time.

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REPLACEMENT SHEET
08 MAR 1999

FR-A-1,334,780 discloses a process for the purification of lactams using activated hydrogen in the presence of acidic compounds. The activated hydrogen is generated catalytically or in statu nascendi which, in turn, is generated from boranates or
5 allanates. In the case of boranates this is only possible in the presence of an acidic compound since boranates are stable in neutral environment.

It is an object of the present invention to provide a low-cost
10 universally deployable purification process for ϵ -caprolactam.

We have found that this object is achieved, surprisingly, by using a complex hydride of aluminum or of boron.

15 The present invention accordingly provides a process for purifying ϵ -caprolactam, which comprises reacting crude ϵ -caprolactam with a complex hydride of boron in the presence of acidic compounds.

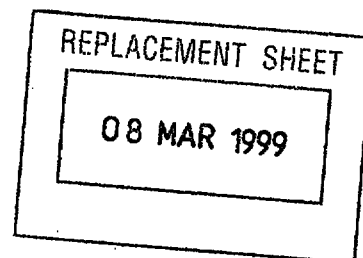
20 Suitable complex hydrides of boron for the process of this invention are in particular sodium borohydride, lithium borohydride, potassium borohydride, calcium borohydride, sodium cyanoborohydride.

25 The amount of hydride hydrogen used naturally depends on the concentration of the impurities in the ϵ -caprolactam. It is chosen so that an excess of hydride hydrogen is present, based on the impurities to be reduced. Preference is given to an excess of from 1.5 to five times, based on the stoichiometrically required hy-
30 dride quantity.

It has been found that, to obtain an adequate reaction rate in the ϵ -caprolactam purification process of this invention, from 10 to 50 % by weight of water, based on crude ϵ -caprolactam, has to
35 be added to the reaction mixture when a borohydride is used.

In a preferred embodiment, the reaction is carried out in the presence of from 0.5 to 5 mol%, in particular from 1 to 4 mol% of NaBH_4 and of from 10 to 50 % by weight of water, based on crude
40 ϵ -caprolactam. The sodium borohydride can be used in solid form or in the form of a commercially available aqueous solution.

The reaction is preferably carried out within the range from 10 to 150°C, in particular within the range from 20 to 100°C. The
45 reaction time is within the range from 0.5 h to 200 h, preferably within the range from 1 h to 100 h.



After the reaction has ended, water and the reduced impurities are distilled off under a slightly reduced pressure. It is also possible to distil off water and impurities continuously even during the reaction by applying a slight reduced pressure. There-
5 after the reaction mixture is subjected to a conventional distillation under reduced pressure (0.5-8 mm Hg). Pure ϵ -caprolactam is obtained as distillate with a UV number < 10 (see below).

The process of this invention is suitable for purifying ϵ -capro-
10 lactam produced by any of the conventional manufacturing processes. This process is advantageously suitable for purifying ϵ -caprolactam produced by cyclization of ω -aminocaproic acid derivatives, for example ω -aminocaproic acid, ω -aminocaproamide, ω -aminocaproic ester and ω -aminocapronitrile.

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Examples:

Purification of a caprolactam produced by cyclization of ω -aminocapronitrile

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The purity of the ϵ -caprolactam is determined in terms of the UV number. The UV number is defined as the sum of all absorbances of a 50 % strength by weight aqueous caprolactam solution measured at intervals of 10 nm in the wavelength range from 280 nm to
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Example 1

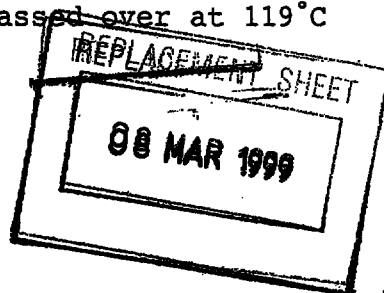
30 Preparation of ϵ -caprolactam in accordance with DE-A 43 396 48

100 parts by weight of ω -aminocapronitrile were dissolved in 1000 parts by weight of ethanol and 30 parts by weight of water and passed over a fixed bed of titania (anatase) at 220°C with a
35 residence time of 12 min. The solvent was then distilled off. The crude caprolactam thus obtained was used in the following purification stage.

Purification of the crude ϵ -caprolactam

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70 parts by weight of crude caprolactam and 30 parts by weight of water were admixed with 1 % by weight of sodium borohydride (based on crude ϵ -caprolactam) in a stirred vessel equipped with a still head. After 100 h, the reaction mixture was subjected to
45 fractional distillation. ϵ -Caprolactam passed over at 119°C (2 mbar) with a UV number of 3.1.



REPLACEMENT SHEET

Example 2

Crude caprolactam prepared by Beckmann rearrangement (see Process Economics Program Report (SRI Report) No. 41 B, Caprolactam and 5 Nylon 6, March 1988) was reacted as described in Example 1 in the presence of 0.4 % by weight NaBH_4 . After 24 h, the reaction mixture was subjected to fractional distillation. ϵ -Caprolactam passed over at 125°C (3 mbar) with a UV number of 3.5.

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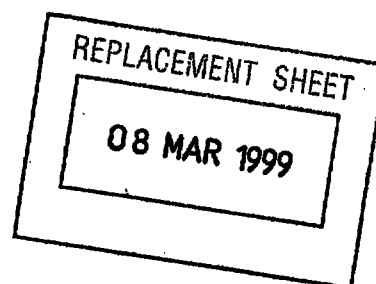
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I claim:

1. A process for purifying ϵ -caprolactam, which comprises
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borohydride in the absence of acidic substances.
2. A process as claimed in claim 1, wherein the complex hydride
10 is selected from the group consisting of NaBH_4 , LiBH_4 , KBH_4 ,
 $\text{Ca}(\text{BH}_4)_2$ and NaBH_3CN .
3. A process as claimed in either of the preceding claims,
wherein from 2 to 20 mol% of hydridic hydrogen is used, based
15 on the ϵ -caprolactam to be purified.
4. A process as claimed in any of claims 2 to 5 [sic], wherein
the ϵ -caprolactam is treated with from 0.5 to 5 mol% of NaBH_4
and from 10 to 50 % by weight of water, based on the
20 ϵ -caprolactam to be purified.

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