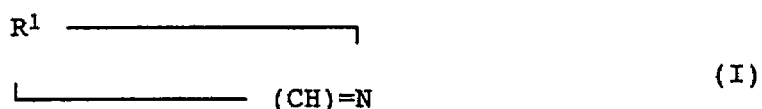


Reducing the level of an unsaturated cyclic imine in a mixture comprising hexamethylenediamine and said imine

5 Description

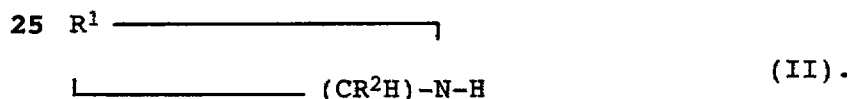
The present invention relates to a process for reducing the level of an unsaturated cyclic imine (I) of the formula (I)

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15 where R¹ is alkenyl having 3, 4, 5, 6, 7, 8, 9, 10, 11 carbon atoms belonging to the ring system,

in a mixture comprising hexamethylenediamine and an imine (I) by
20 electrochemical conversion of an imine (I) in a mixture comprising hexamethylenediamine and an imine (I) in the presence of solvated protons into a saturated cyclic amine of the formula (II)



It is commonly known, for example from Weissermel/Arpe,
30 Industrielle Organische Chemie, Verlag Chemie, third edition, 1988, page 266, and WO-A-96/20166, to hydrogenate adiponitrile in the presence of ammonia under high pressure conditions over heterogeneous catalysts to form 6-aminocapronitrile (ACN) and/or hexamethylenediamine (HMD), which are both important
35 intermediates for the manufacture of polyamides such as nylon-6 and nylon-6,6.

Depending on the catalyst used, this hydrogenation gives rise to varying amounts of undesirable by-products, such as
40 tetrahydroazepine (THA), 1-amino-2-cyanocyclopentene (ICCP), 2-aminomethylcyclopentylamine (AMCPA), 1,2-diaminocyclohexane (DCH) and bis-hexamethylenetriamine (BHMTA), which - unlike the by-produced perhydroazepine (also known as hexamethyleneimine; HMI) - are very difficult to separate from the product of value,
45 ACN and/or HMD.

For instance, US-A-4,282,381 discloses (in column 2 of Table 1) that the hydrogenation of adiponitrile to form HMD in the presence of iron catalysts by-produces, inter alia, on average from 200 to 900 ppm of tetrahydroazepine.

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High levels of THA necessitate a great deal of purification, by distillation, for example, which is reflected in considerable capital expenditure and energy costs or high chemical consumption, especially by complex hydrides such as NaBH_4 or LiAlH_4 .

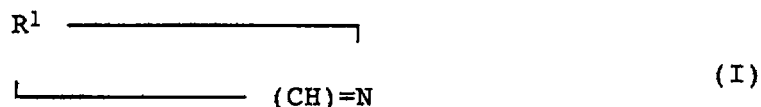
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It is an object of the present invention to provide a process for reducing the THA content of mixtures comprising HMD and THA in a technically simple and economical manner.

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We have found that this object is achieved by the process defined at the beginning. The unsaturated cyclic imine (I) is a compound of the formula

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25 where

R^1 is an alkylene radical having 3, 4, 5, 6, 7, 8, 9, 10, 11 preferably 5, carbon atoms belonging to the ring system.

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The alkylene radical may bear substituents; the alkylene radical is preferably a pure, preferably unbranched, hydrocarbon radical. Preferred alkylene radicals are the trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, undecamethylene groups, especially pentamethylene.

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Compound (I) may be a mixture of different such imines, but preferably is one such imine.

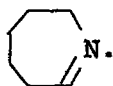
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The amines (II) obtainable by the process of the present invention generally have the same radical R^1 as the imines (I) used as starting material.

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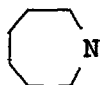
Compound (I) is particularly preferably THA of the formula

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5 The process of the present invention converts it into perhydroazepine of the formula

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as compound (II).

15 According to the present invention, THA is used in mixtures comprising HMD and THA. Such mixtures are obtainable for example in the aforementioned hydrogenation of adiponitrile. The THA contents based on HMD range customarily from 100 to 2500, especially from 200 to 900, ppm.

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A mixture comprising HMD and an imine (I) can be used for the conversion in pure form or preferably in mixtures with liquid diluents.

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Advantageous liquid diluents are hydroxyl-containing compounds, preferably water or alcohols having from 1 to 4 carbon atoms, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methylpropanol, 1-methylpropanol, preferably water or methanol, especially water, or mixtures thereof, and also

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mixtures of such hydroxyl-containing compounds with non-hydroxyl-containing compounds, preferably ethers, such as dimethoxyethane or tetrahydrofuran or mixtures thereof.

35 The amount of liquid diluent is easily ascertained in a few simple preliminary tests.

For an HMD/THA mixture having a THA content within the range from 100 to 2500, especially from 200 to 900, ppm, the presence of

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water and/or methanol, especially water, in an amount of from 0.01 to 20% by weight based on the total mixture will be particularly advantageous.

The electrochemical conversion is suitably carried out using

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electrolysis cells having one, preferably more than one, such as 2, 3 or 4, especially 2, cell compartments. If a plurality of

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Advantageously, the catholyte may include a material which is catalytically active for the reaction and which is preferably heterogeneous with regard to the catholyte, such as finely divided metal, preferably iron, Raney cobalt or Raney nickel, especially Raney nickel, in amounts from 1 to 20% by weight based on the catholyte. After the reaction, such catalytically active materials can be separated from the mixture in a conventional and simple manner, as by filtration.

- 10 Filter materials of the cathode for this elementary reaction of the electrolysis cell are known per se and commercially available. It may be advantageous to use metal filters such as stainless steel filters or filters composed of platinized titanium.

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The reaction is customarily carried out at a temperature at which anolyte and catholyte are present in liquid form, preferably at from 10 to 60°C, especially at from 36 to 40°C.

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The current density is advantageously from 1 to 30 mA/cm², preferably from 15 to 30 mA/cm², which results in voltages from 14.4 to 58 V, preferably from 14.4 to 36 V.

- 25 The compound (II) which is formed from the starting mixture of the invention, comprising HMD and imine (I), can be separated from the product mixture in a conventional manner, as by distillation, crystallization or extraction.

30 Example

The examples were carried out under the following conditions:

35 Table 1

40	Cell type	Divided cell, 2 compartments
	Anode	Heraeus Pita 64, oxygen-evolving
	Cathode	Edge gap element composed of platinized titanium, gap width: 100 µm
	Electrode surface area	100 cm ²
	Membrane	Nafion 324
	Electrolysis temperature	38°C

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Anolyte	1200 g of aqueous 1% strength sulfuric acid
Catholyte	Catalyst: 50 g of Raney nickel Remainder: see Table 2

Table 2

10	HMD [g]	1120	840	1120	1120	1120
	Methanol [g]	-	560	-	-	-
	H ₂ O [g]	280	-	280	280	180
	LiCl [g]	-	28	-	-	-
	Adipic acid [g]	-	-	-	21	21
15	Current density [mA/cm ²]	1.6-2.9	30	0.5-0.9	15	15
	Voltage (start) [V]	58.0	14,4	57.9	36.8	47.6
	Voltage (end) [V]	58.1	25.7	56.3	22.9	20.3
	THA start [ppm]	1399	753	1530	775	829
	THA end [ppm]	91/30	37	81/41	185/62/46	196/55/15
20	Time [h]	10/50	4	10/43	5/10/20	5/10/15
	THA reduced by [%]	93/98	95	95/97	76/92/94	76/93/98

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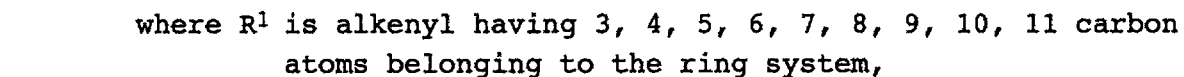
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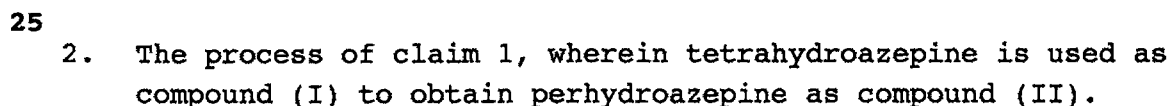
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5 1. The process for reducing the level of an unsaturated cyclic imine (I) of the formula (I)



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7. The process of claim 6, wherein the organic acid used is a mono- or dicarboxylic acid.
- 5 8. The process of claim 7, wherein the monocarboxylic acid used is adipic acid.

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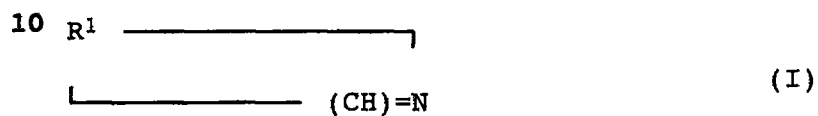
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Reducing the level of an unsaturated cyclic imine in a mixture comprising hexamethylenediamine and said imine

5 Abstract

The level of an unsaturated cyclic imine (I) of the formula (I)



15 where R^1 is alkenyl having 3, 4, 5, 6, 7, 8, 9, 10, 11 carbon atoms belonging to the ring system,

in a mixture comprising hexamethylenediamine and an imine (I) is reduced by electrochemical conversion of an imine (I) in a mixture comprising hexamethylenediamine and an imine (I) in the presence of solvated protons into a saturated cyclic amine of the formula (II)

