

Process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine

5 **Description**

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The invention relates to an improved process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, hereafter also called isophoronediamine or abbreviated to IPDA, from 3-cyano-3,5,5-trimethylcyclohexanone, hereafter also called isophoronenitrile or abbreviated to IPN, by aminating hydrogenation with hydrogen and ammonia in the presence of a fixed bed catalyst. The process according to the invention affords the continuous preparation of isophoronediamine in high yield and high purity.

Isophoronediamine is used as a starting material for the preparation of isophorone diisocyanate, which is an isocyanate component for polyurethane systems, as an amine component for polyamides and as a hardener for epoxy resins. Isophoronediamine is conventionally prepared from isophoronenitrile, the carbonyl group being converted to an amino group and the nitrile group to an aminomethyl group in the presence of ammonia, hydrogen and conventional hydrogenation catalysts. The starting material, isophoronenitrile, can be obtained in conventional manner by the addition of hydrogen cyanide onto isophorone - see DE-OS 39 42 371.

According to the process described in US 3,352,913 for the preparation of isophoronediamine from isophoronenitrile, the hydrogenation is carried out in the presence of ammonia and in the presence of cobalt-, nickel-, iron- or noble metal- containing catalysts known per se, at 50 to 150°C and at a pressure of at least 50 bar. By way of example, the hydrogenation takes place in the presence of methanol

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as a solvent and using suspension or fixed bed catalysts. Apart from the desired isophoronediamine, by-products, such as 3-aminomethyl-3,5,5-trimethylcyclohexanol (isophoroneamino alcohol, IPAA) in particular, are formed
5 in relatively large amounts. The disadvantages of this process are found to be the low yield and a considerable proportion of by-products.

In the quest to obtain a higher yield of IPDA and minimize
10 the unavoidable formation of IPAA, DE-OS 30 11 656 teaches a two-step process; in the first step, IPN is converted with excess ammonia, without a catalyst, to 3-cyano-3,5,5-trimethyliminocyclohexane, and the latter is hydrogenated in the second step to IPDA. The disadvantage of this
15 process is that, as well as the actual hydrogenation reactor, a special imine formation reactor is required.

EP-B 0 042 119 proposes a further improvement to the process, wherein, prior to reaction with ammonia and
20 hydrogen in the presence of hydrogenation catalysts at temperatures of 10 to 120°C and pressures of 1 to 300 bar, the isophoronenitrile is subjected to a preliminary reaction with ammonia in the presence of inorganic and organic ion exchangers in the ammonium form as imine
25 formation catalysts. Whereas the volume ratio of isophoronenitrile to ammonia in the imine formation step is said to be 1:0.5 to 20, this ratio is increased to 1:10 to 20 in the hydrogenation step. Although the process, which can be carried out in trickle bed reactors, leads to a high
30 yield of IPDA and to a high purity, the economy of the process is compromised by the use of two different catalysts and the large excess of ammonia, which necessitates a very high pressure and hence an expensive hydrogenation apparatus.

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EP-B 0 042 119 also discloses a Comparative Example in which isophoronenitrile and liquid ammonia are pumped into



the top of a hydrogenation reactor charged with commercially available cobalt catalyst. The reaction system is kept at 270 bar with H_2 ; a certain gas stream is set up and a certain amount of off-gas is withdrawn. The
5 reaction mixture leaving the bottom of the reactor is then worked up by distillation. Despite approximately quantitative conversion of the isophoronenitrile, this embodiment produces only 48% of isophoronediamine, together with many by-products. Said document does not suggest
10 passing a mixture containing isophorone, ammonia and organic solvent, instead of a mixture of isophoronenitrile and ammonia, over a trickle bed reactor at an essentially low pressure and without the need for a preliminary imine formation reaction.

15 EP-A 0 449 089 discloses another process for the preparation of isophoronediamine: In two spatially separated reaction chambers, a solution of isophorone-nitrile in tetrahydrofuran is initially reacted with excess
20 ammonia on acidic metal catalysts and the reaction mixture is hydrogenated at high pressure in a second reaction chamber with hydrogen in the presence of excess ammonia on catalysts containing cobalt, nickel, ruthenium and/or other noble metals, and optionally basic components. By way of
25 example, the mixture leaving the first reaction step is passed through the hydrogenation reactor from bottom to top; the reactor is operated as a bubble reactor. Said document does not give any indication of also using the reactor as a trickle bed reactor and directly feeding said
30 reactor with a mixture of isophoronenitrile, ammonia and an organic solvent.

EP-A 0 394 967 teaches a process for the amination of carbonylnitriles and iminonitriles and also includes the
35 preparation of isophoronediamine from isophoronenitrile. The starting material is initially converted to the aminonitrile at moderate temperatures under conditions of



reductive amination, i.e. in the presence of hydrogen, ammonia and a hydrogenation catalyst; the nitrile group is then converted to an aminomethyl group at elevated temperature in the presence of a hydrogenation catalyst which is effective in the hydrogenation of nitrile groups. The process can be carried out either in reactors which use suspension catalysts or in reactors which use fixed bed catalysts. Although this process can be carried out at low pressures, the fact that a strictly observed temperature programme has to be operated during both the reaction steps is regarded as a considerable disadvantage since it results in an appreciable lowering of the space-time yield and hence the economy of the process. In addition, unless special promoters are also used, the product quality does not satisfy the requirements because the content of 3-cyano-3,5,5-trimethylaminocyclohexane, which cannot be separated off by distillation, is usually too high.

According to JP-A-4-300852, a pressure reduction in the preparation of isophoronediamine by the aminating catalytic hydrogenation of isophoronenitrile is also made possible by carrying out the hydrogenation in the presence of a supported ruthenium catalyst. However, said document refers only to conditions for suspension hydrogenation and not to conditions using a fixed bed reactor.

SRI International Report no. 1D "Isocyanates" by YU-REN CHIN (July 1983) gave a survey of an industrial process for the preparation of isophoronediamine from isophorone-nitrile: In the process described here, a mixture of isophoronenitrile, methanol and ammonia is passed with hydrogen over a fixed bed reactor containing a supported catalyst of cobalt-on-kieselguhr. In the embodiment described, the catalyst bed is always flooded (bubble column). The operating pressure is given as 150 bar. Also, hydrogen is used in excess and, after the reaction, this excess must be separated from the reaction mixture,

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- purified, compressed and then recycled. The economy of this process is reduced both by the high operating pressure and by the technical cost of recycling the hydrogen. As established by the Inventors of the present invention - see
- 5 Example 3b not according to the invention - this embodiment results in the increased formation of by-products which cannot easily be separated off, and to a lowering of the yield.
- 10 The object of the present invention thus consists in mitigating the disadvantages of the previously known processes for the preparation of isophoronediamine from isophoronenitrile using a reactor charged with a fixed bed catalyst, to the effect that the economy of the process is
- 15 increased. In particular, the cost of the technical equipment should be reduced compared with the previously known processes. It should moreover be possible to obtain isophoronediamine in high yield and to isolate it from the reaction mixture in very pure form by means of conventional
- 20 distillative measures.

A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile, IPN)

25 has been found in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃-alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one

30 hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of

35 isophoronediamine, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling



through the catalyst bed being withdrawn at the bottom end of the reactor.

The reaction according to the invention is carried out in a conventional trickle bed reactor. The designs of such reactors are known to those skilled in the art: The fixed bed catalyst is arranged in the form of one or more layers in a container; the reactor is also equipped with devices for thermostating the catalyst layers in order to ensure that the desired temperature is maintained in the respective catalyst layer. As an alternative to a single trickle bed reactor, several trickle bed reactors can be connected in series, the reaction mixture leaving the first reactor being recharged into the top of the second reactor. The trickle bed reactor or reactors are also equipped with suitable devices for charging the reactants, i.e. in this case the mixture containing isophoronenitrile, ammonia and solvent, and the hydrogen, as well as with devices for distributing the liquid over the surface of the first catalyst bed and, finally, with suitable devices for discharging the reaction mixture leaving the reactor.

An essential feature of the process according to the invention is that the reaction mixture to be hydrogenated trickles over the catalyst bed and also that a sufficiently large gas volume exists within the catalyst bed to enable the hydrogen to be transported through the liquid film onto the catalyst surface. It has been found that the trickle bed process is substantially responsible for obtaining a high product yield and, in particular, a high selectivity. If the reactor is operated not as a trickle bed reactor but as a bubble reactor, in which case the catalyst bed is always flooded, a considerably lower yield of isophoronediamine is obtained under otherwise identical reaction conditions in respect of temperature, pressure and concentration of the reactants; the bubble process also gives a different range of by-products, methylisophorone-



- diamine (methyl-3-aminomethyl-3,5,5-trimethylcyclohexylamine) being formed in particular. Said methylisophoronediamine cannot be separated from isophoronediamine by distillation under conventional
- 5 conditions, so the formation of said by-product must already be avoided in the preparation of the isophoronediamine high product. Surprisingly, said by-product is only formed in very small amounts under the conditions of the process according to the invention. A further
- 10 disadvantage of the bubble process is that hydrogen has to be added in excess in order to achieve saturation of the solution with H_2 ; this entails expensive recycling of the excess H_2 .
- 15 When the process according to the invention is carried out, hydrogen can be fed into the reactor either in excess or in an amount such that no hydrogen has to be discharged from the reactor and recycled. The introduction of hydrogen in excess is less preferable because the technical cost of
- 20 separating off the excess H_2 , condensing ammonia and organic solvent contained in the discharged hydrogen, and compressing the purified hydrogen and recycling it is considerable and reduces the economy of the process on account of the higher investment demanded; moreover, an
- 25 even lower yield of IPDA has been found compared with the process not using excess H_2 . Thus hydrogen is preferably introduced not in excess but only in the amount which is required to maintain the desired operating pressure.
- 30 The aminating hydrogenation is carried out at a pressure in the range 3 to 10 MPa, preferably at 5 to 8 MPa. Said moderate operating pressures, which are possible when using the claimed mixtures of isophoronenitrile, ammonia and solvent and the trickle bed process under the claimed
- 35 temperature conditions, increase the economy, compared with processes which demand a high operating pressure, by



lowering the level of investment required for the apparatus.

The requisite volume of fixed bed catalyst is governed by the LHSV value (liquid hourly space velocity) (dependent on the operating pressure, the temperature and the catalyst activity) which must be observed in order to achieve a quantitative conversion of isophoronenitrile. Conventionally, the LHSV value is 0.5 h^{-1} or preferably above. The LHSV value is preferably between 0.8 and 1.5 h^{-1} . It is particularly good to attain an LHSV value in said range when the reaction is carried out at a temperature in the range between 90 and 130°C and at a pressure of between 5 and 8 MPa .

In addition to the abovementioned parameters of pressure, temperature and catalyst dependence, the LHSV value is also influenced by the chosen concentration ratios of isophorone, ammonia and solvent and by the type of solvent used. The mixture charged onto the catalyst bed conveniently contains 10 to 40% by weight and preferably 10 to 30% by weight of isophoronenitrile and 10 to 40% by weight and preferably 20 to 40% by weight of ammonia. Solvents which can be used are methanol, ethanol, n-propanol and isopropanol. Methanol is the preferred solvent. The isophoronenitrile, ammonia and solvent are mixed in proportions such that an essentially homogeneous solution results. In principle, it is also possible to fall short of or exceed the abovementioned limiting values for ammonia and isophoronenitrile provided a homogeneous solution results. The use of a mixture containing less than 10% by weight of isophoronenitrile has an adverse effect on the economy of the process.

Apart from the constituents mentioned above, the mixture to be charged onto the catalyst can contain fractions, boiling above or below isophoronediamine, from the distillative



working-up of the reaction mixture withdrawn from the trickle bed reactor. In addition to isophoronediamine residues, such fractions can also contain by-products from which isophoronediamine is re-formed under the reaction conditions. The yield of isophoronediamine can be markedly increased by recycling such fractions into the mixture to be used. It is particularly advantageous to feed the fraction boiling after the isophoronediamine, which, in addition to isophoronediamine residues, contains 3,3,5-trimethyl-6-imino-7-azabicyclo[3,2-1]octane as the main product, into the trickle bed reactor together with the mixture of isophoronenitrile, ammonia and solvent. Recycling of the fraction containing the abovementioned byproduct - a bicyclic compound of amidine structure - makes it possible significantly to increase the yield of isophoronediamine and consequently to improve the economy of the process.

The catalysts to be used according to the invention are cobalt and/or ruthenium fixed bed catalysts. These catalysts are conventionally in the form of pellets, extrudates or other mouldings. It is particularly convenient to use supported catalysts, cobalt or ruthenium being present on a support of adequate specific surface area. Conventionally, the specific surface area of the supported catalysts to be used according to the invention is in the range between 5 and 500 m²/g (measured with nitrogen by the BET method).

The cobalt content of the supported catalysts is generally between 10 and 70% by weight and preferably between 30 and 50% by weight, based on the supported catalyst. The surface of the support, which is frequently made up of oxide or silicate materials, is partially or essentially completely covered with cobalt, it also being possible for cobalt oxide to be present underneath the surface due to the method of production. Examples of suitable support



materials are oxides from the group comprising silicon dioxide, aluminium oxide and titanium dioxide, silicates such as aluminium and calcium silicate, and naturally occurring and synthetically produced zeolites and glass
5 frits. Although commercially available supported catalysts with a high Co content, such as catalysts containing 50% by weight of Co on aluminium silicate, are described as being essentially completely covered with Co, it has been found that catalysts with a different support but the same
10 specific surface area thereof and the same Co content have an influence on the selectivity and the range of byproducts. Obviously the surface of the catalyst support is at least partially accessible and intervenes in the catalytic process.

15 For reasons of cost, supported catalysts with ruthenium as the catalytically active component generally contain only a small proportion by weight of ruthenium, being conventionally between 0.5 and 10% by weight and preferably
20 between 2 and 5% by weight. The production of the abovementioned Co and Ru catalysts, which conventionally comprises impregnation, drying and shaping steps, is known to those skilled in the art.

25 It has been established that isophoronediamine is obtainable by the process according to the invention in higher yield when using a supported cobalt catalyst than when using a supported ruthenium catalyst. This is surprising inasmuch as the abovementioned documents JP-A
30 4-300852 and EP-A 0 394 967 have indicated that ruthenium catalysts are particularly effective in the hydrogenation of the nitrile group, which is more difficult to hydrogenate than the carbonyl group.

35 It is known that isophoronediamine exists in the form of cis and trans isomers - see Die Angewandte Makromolekulare Chemie 153 (1987) 1-13, no. 2502. By studying the isomer



- ratio of the isophoronediamine prepared according to the invention, it has been found that the proportion of cis isomer formed is completely predominant when using a ruthenium catalyst: cis/trans isomer ratio according to
- 5 Example 9 / 84 to 16. When using a supported cobalt catalyst, the other conditions being identical, the cis and trans isomers are formed in similar proportions: cis/trans isomer ratio according to Example 8 / 60 to 40.
- 10 It has furthermore been found that it is possible to prepare isophoronediamine with a cis/trans isomer ratio above that which is obtainable using a supported cobalt catalyst, and in high yield, by carrying out the aminating
- 15 layer of a supported ruthenium catalyst and a lower layer of a cobalt fixed bed catalyst are arranged. Particularly suitable catalysts are ruthenium-on- γ -aluminium oxide and a supported cobalt catalyst with an oxide or silicate support and a cobalt content of 10 to 70% by weight, based on the
- 20 catalyst. Instead of having one reactor with two layers of different fixed bed catalysts arranged therein, it is also possible to connect two reactors in series, each containing only one fixed bed catalyst; in this case, the first reactor contains the ruthenium fixed bed catalyst and the
- 25 second reactor contains the cobalt fixed bed catalyst. To obtain a high yield of isophorone with the desired isomer ratio, it is advantageous if the ruthenium fixed bed catalyst, which is positioned first, makes up 3 to 30%, preferably 5 to 20%, of the total catalyst volume.
- 30 As explained earlier, the process according to the invention differs in essential respects from previously known processes of this kind, resulting in substantial advantages. By combining the use of a starting mixture of
- 35 isophoronitrile, ammonia and an alcoholic solvent and the trickle bed operation of the reactor provided with a fixed bed, it is possible to achieve both a high product yield of



isophoronediamine and a high selectivity. The formation of undesired by-products such as methylisophoronediamine, which adversely affects the product quality because it is difficult to separate off, is extensively avoided by the reaction process. The abovementioned combination of essential features of the invention is also such that the aminating hydrogenation can be carried out at moderate pressures, thereby greatly reducing the consequent cost of the pressure apparatus compared with the case of a high-pressure apparatus. As it is not necessary according to the invention to use hydrogen in excess and hence to have to purify and recycle the excess, in contrast to previously known processes using a reactor with a fixed bed catalyst, expensive devices for separating off, purifying and recycling the excess H_2 are dispensed with. Another essential advantage of the process according to the invention is the unexpectedly long service life of the catalysts, which is attributed to the trickle bed process: Even after several months of operation, no reduction in yield, no change in the range of by-products and no change in the isomer ratio were found. A further advantage is the ability to obtain isophoronediamine in high yield with a particular isomer ratio, within certain limits. In the process according to the invention, there is also no need for a preliminary reaction between isophoronenitrile and ammonia in order to form isophoroneimine, which was considered in several documents to be essential for obtaining a high yield and high selectivity in the aminating hydrogenation; according to the invention, by contrast, a solution of isophoronenitrile in the solvent used is mixed with ammonia directly upstream of the trickle bed reactor and the mixture is fed into the reactor.

The process according to the invention is illustrated in greater detail with the aid of the following Examples, without implying a limitation.



Example 1

A reaction tube is filled with 200 ml of hydrogenation catalyst. The feed solution containing IPN and methanol, and liquid NH_3 , are pumped into the top of the reactor. Hydrogen also flows into the tube from the top. The reaction temperature is kept at 120°C by means of oil heating. The pressure is regulated at 60 bar. The liquid is collected in a separating vessel. The gas stream at the reactor inlet is adjusted so that a gas stream of 100 Nl/h is established downstream of the separating vessel.

The catalyst used was a commercially available solid Co catalyst (ca. 50% Co on silicate support) in the form of extrudates of 4-5 mm in diameter and length. The feed solution contained 24% by weight of IPN and 76% by weight of methanol. 130 ml/h thereof and 70 ml/h of NH_3 were mixed directly before being charged into the reactor, and the mixture was pumped into the reactor; the LHSV value was thus 1 h^{-1} . According to analysis of the product mixture, the yield of IPDA was 88.7%, based on IPN used. The product mixture also contained 5% of 2-aza-4,6,6-trimethylbicyclo[3,2,1]octane (= bicyclic compound) and 4.3% of 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane (= amidine).

Example 2

The experiment was carried out in the same experimental set-up as already described in Example 1, except that no gas stream was withdrawn from the separating vessel, so only the consumed hydrogen was replaced in order to keep the reaction pressure at 60 bar. The catalyst, liquid streams and liquid composition were the same as described in Example 1.

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Analysis of the product mixture of this experiment showed an IPDA yield of 89.2%, based on IPN used. The product mixture also contained 4.5% of bicyclic compound and 4.4% of amidine. Surprisingly, an even higher yield of IPDA and a reduction in the "bicyclic" by-product are made possible by the process without excess H_2 . This experiment was run for 2000 h with no observable loss of yield or change in the range of products.

10 Examples 3a and 3b

The experimental set-up used was the same as in Experiment 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. The H_2 stream was adjusted so that 100 NL/h of H_2 were withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were pumped into the reactor together with 50 ml/h of liquid NH_3 . 200 ml of cobalt catalyst were introduced as the catalyst. Two processes were studied. In the trickle bed process (3a), gas and liquid flowed through the reactor from top to bottom; in the bubble column process (3b), the reactor was in the flooded state and they flowed through it from bottom to top.

A yield of 87.1% was achieved in the trickle bed process (3a). After purification by distillation, the product purity was 99.8%; methyl-IPDA was detectable in an amount of only about 200 ppm.

A yield of 85.5% was achieved in the experiment by the bubble column process (3b). Purification by distillation gave a product purity of only 99.5%. Analysis showed that the pure product still contained 3000 ppm of methyl-IPDA. The methyl-IPDA by-product, which has a very adverse effect on the quality of the IPDA product, is practically inseparable by distillation.



Examples 4 to 6

The experiments were carried out in the same experimental set-up and under the same reaction conditions as described in Example 1. Only the catalyst was varied. The results are given in the Table.

Example	Catalyst	Yield of IPDA (%)
4	5% Ru/ γ -Al ₂ O ₃	82.1
5	Ni	55.3
6	2% Pd/ γ -Al ₂ O ₃	4

Both the Ru and the Pd were applied to γ -Al₂O₃ extrudates as the support. Examples 5 and 6 clearly show that the yields obtained with Ni and Pd catalysts are not satisfactory compared with the process according to the invention.

Example 7

The low-boiling components, namely methanol, NH₃, H₂O and the bicyclic compound, were removed from 8770 g of the reaction solution of Example 2 by fractional distillation.

1292 g of a crude solution remained. 1190 g of IPDA were distilled off from this solution at a bottom temperature of 147°C and at a pressure of 20 mbar. This corresponds to an isolation yield of 87.3%. 98 g remained as the bottom product of the distillation. A further high-boiling fraction of 74 g was distilled off from this bottom product under reduced pressure (10 mbar) and at a temperature of 162°C. It contained 20% of IPDA and 74% of amidine. This resulting fraction of 74 g corresponds to 5.6% of the amount of IPN used.

In another experiment, which was carried out analogously to Example 2, the high-boiling fraction, i.e. 5.6% based on



the amount of IPN used, was added. After hydrogenation and separation of the low-boiling components and purification of the IPDA by distillation, the isolation yield found was 92.3%. Accordingly, it was possible to achieve a 5% increase in the isolation yield of IPDA by recycling the high-boiling fraction containing the amidine.

The yield of IPDA can be increased by a further 4% by catalytically hydrogenating the fraction containing the bicyclic compound (boiling point below that of IPDA) in a separate hydrogenation reactor under elevated temperature conditions.

Examples 8 to 11

The experimental set-up used was the same as in Experiment 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. No H₂ was withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were mixed with 50 ml/h of liquid NH₃ and pumped into the reactor. This experimental set-up was operated with a ruthenium catalyst, a cobalt catalyst and various combinations of the two. The results of this experiment are shown in the Table.

	Example	Catalyst*)	Yield (%)	Isomer ratio cis:trans
30	8	200 ml Co	87.2	60:40
	9	200 ml Ru	81.5	84:16
	10	100 ml Ru + 100 ml Co	83.7	81:19
	11	10 ml Ru +	86.9	78:22
	35	190 ml Co		

*) Ru catalyst: 5% Ru on γ -Al₂O₃ extrudates

Co catalyst: 50% Co on Al silicate extrudate

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By combining an Ru catalyst and a Co catalyst, the Ru catalyst being arranged as the upper layer in the reactor, it is possible to obtain IPDA with a high cis/trans isomer ratio in higher yield than by using an Ru catalyst on its own.

Example 12

A reaction tube (diameter 16 mm) of a trickle bed hydrogenation apparatus was filled with 120 ml of commercially available supported Co catalyst (Co on aluminium silicate, 50% by weight of Co; BET surface area (N_2) ca. 200 m^2/g). The experiment was carried out analogously to Example 1. The reaction temperature was adjusted to 110°C and the total pressure (sum of the partial pressures of H_2 , NH_3 and methanol) was adjusted to 60 bar. The starting solution contained 15% by weight of isophoronenitrile, 65% by weight of methanol and 20% by weight of ammonia. 100 ml of this starting solution were introduced onto the trickle bed per hour. After the solution had passed through the trickle bed, the reaction mixture contained the following (mol% based on isophorone-nitrile in the starting solution):

Isophoronediamine (IPDA)	89.2%
Isophoroneamino alcohol (IPAA)	2.1%
Amidine (see Example 1)	4.0%
Bicyclic compound (see Example 1)	3.8%

Example 13

Example 12 was repeated, the only difference being that another commercially available supported Co catalyst was used - Co on silica, 25% by weight of Co, BET surface area (N_2) ca. 200 m^2/g . The reaction mixture contained the following (data in mol% based on starting isophorone-nitrile):

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IPDA	87.4%
IPAA	1.2%
Amidine	4.3%
5 Bicyclic compound	5.1%

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Claims

1. A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophorone-nitrile, IPN) in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃-alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronediamine, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling through the catalyst bed being withdrawn at the bottom end of the reactor.
2. A process for the preparation of isophoronediamine according to Claim 1, characterized in that the hydrogenation is carried out at a temperature in the range 90 to 130°C and at a pressure of 5 to 8 MPa.
3. A process according to Claim 1 or 2, characterized in that methanol is used as the solvent, the mixture charged onto the catalyst bed contains 10 to 40% by weight, preferably 10 to 30% by weight, of isophorone-nitrile and 10 to 40% by weight, preferably 20 to 40% by weight, of ammonia and the mixture forms a homogeneous solution.





4. A process according to one or more of Claims 1 to 3, characterized in that the hydrogenation catalyst used is a supported catalyst consisting essentially of an inorganic support material, preferably an oxide or silicate support material, and cobalt, the catalyst containing a total of 10 to 70% by weight of cobalt.
5. A process according to one or more of Claims 1 to 4, characterized in that a high-boiling fraction distilling after the isophoronediamine main fraction in the distillative working-up of the reaction mixture, and containing, in addition to isophoronediamine residues, 3,3,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane as the main component, is fed into the trickle bed reactor together with the mixture of isophoronitrile, solvent and ammonia.
6. A process according to one or more of Claims 1 to 5, characterized in that the aminating hydrogenation is carried out in a trickle bed reactor with an upper layer of a supported ruthenium catalyst, preferably ruthenium-on- γ -aluminium oxide, and a lower layer of a cobalt fixed bed catalyst arranged therein, it being possible for said upper layer and said lower layer also to be arranged in two separate reactors connected in series in the stated order, instead of in one reactor.
7. A process according to Claim 6, characterized in that the volume of the ruthenium-containing fixed bed catalyst makes up 3 to 30%, preferably 5 to 20%, of the total volume of fixed bed catalysts.
8. A process according to one or more of Claims 1 to 7, characterized in that hydrogen is fed into the top or bottom end of the trickle bed reactor in an amount



such that no hydrogen has to be discharged from the reactor and recycled.

9. A process according to one or more of Claims 1 to 8,
characterized in that the mixture of isophorone-
nitrile, solvent and ammonia, which preferably
contains 10 to 30% by weight of isophoronenitrile,
20 to 40% by weight of ammonia and methanol as the
solvent, is allowed to trickle over the catalyst bed
of the reactor with an LHSV value (liquid hourly space
velocity) of 0.8 to 1.5 h⁻¹.

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Process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine

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Abstract

The invention relates to an improved process for the continuous preparation of 3-aminomethyl-3,5,5-trimethyl-
10 cyclohexylamine in high yield and high purity (isophorone-diamine) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile) by aminating hydrogenation with hydrogen and ammonia in the presence of a fixed bed catalyst. Isophoronediamine is a raw material for the
15 preparation of isophorone diisocyanate, an amine component for polyamides and a hardening component for epoxy resins.

According to the invention, the aminating hydrogenation is carried out by allowing a mixture of isophoronenitrile,
20 ammonia and a C_1 - C_3 -alcohol, in the presence of hydrogen, to trickle over a trickle bed reactor provided with a Co and/or Ru fixed bed catalyst, at 3 to 8 MPa and at a temperature of 40 to 150°C, preferably 90 to 130°C, and working up the reaction mixture by distillation.
25 Preferably, a high-boiling by-product fraction, containing a bicyclic amidine, is added to the mixture to be hydrogenated, thereby appreciably increasing the yield.

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PROCESS FOR THE PREPARATION OF ISOPHORONEDIAMINE

INTRODUCTION AND BACKGROUND

The present invention relates to a process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, hereafter also called isophoronediamine or abbreviated as IPDA, from 3-cyano-3,5,5-trimethylcyclohexanone, hereafter also called isophorononitrile or abbreviated as IPN, by an aminating hydrogenation reaction with hydrogen and ammonia in the presence of a fixed bed catalyst. The process according to the present invention affords the continuous preparation of isophoronediamine in high yield and high purity.

Isophoronediamine is used as a starting material for the preparation of isophorone diisocyanate, which is used as an isocyanate component for polyurethane systems, as an amine component for polyamides, and as a hardener for epoxy resins. Isophoronediamine is conventionally prepared from isophorononitrile, the carbonyl group being converted to an amino group and the nitrile group to an aminomethyl group in the presence of ammonia, hydrogen and conventional hydrogenation catalysts. The starting material, isophorononitrile, can be obtained in a conventional manner by the addition of hydrogen cyanide onto isophorone (see U.S. Pat. No. 5,091,554 which is incorporated by reference in its entirety; DE-OS 39 42 371).

According to the process described in U.S. Pat. No. 3,352,913 (which is incorporated by reference in its entirety) for the preparation of isophoronediamine from isophorononitrile, the hydrogenation is carried out in the presence of ammonia and in the presence of cobalt-, nickel-, iron- or noble metal-containing catalysts known per se, at 50° to 150° C. and at a pressure of at least 5 MPa. By way of example, the hydrogenation takes place in the presence of methanol as a solvent. Apart from the desired isophoronediamine, by-products, such as 3-aminomethyl-3,5,5-trimethylcyclohexanol (isophoroneamino alcohol, abbreviated as IPAA) in particular, are formed in relatively large amounts. The disadvantages of this process are found to be the low yield and a considerable proportion of by-products.

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In the quest to obtain a higher yield of IPDA and minimize the unavoidable formation of IPAA, DE-OS 30 11 656 teaches a two-step process; in the first step, IPN is converted with excess ammonia, without a catalyst, to 3-cyano-3,5,5-trimethyliminocyclohexane which is hydrogenated in the second step to IPDA. The disadvantage of this process is that, as well as the actual hydrogenation reactor, a special imine formation reactor is required.

EP-B 0 042 119 (U.S. Pat. No. 4,429,157) proposes a further improvement to the process of producing IPDA, wherein, prior to reaction with ammonia and hydrogen in the presence of hydrogenation catalysts at temperatures of 10° to 120° C. and pressures of 0.1 to 30 MPa, the isophoronenitrile is subjected to a preliminary reaction with ammonia in the presence of inorganic and organic ion exchangers in the ammonium form as imine formation catalysts. Whereas the volume ratio of isophoronenitrile to ammonia in the imine (isophoroneimine or Schiff's base) formation step is said to be 1:0.5 to 20, this ratio is increased to 1:10 to 20 in the hydrogenation step. The economy of the process is compromised by the use of two different catalysts and the large excess of ammonia, which necessitates a very high pressure and hence an expensive hydrogenation apparatus.

EP-B 0 042 119 also discloses a Comparative Example in which isophoronenitrile and liquid ammonia are pumped into the top of a hydrogenation reactor charged with commercially available cobalt catalyst. The reaction system is kept at 270 bar with H₂; a certain gas stream is set up and a certain amount of off-gas is withdrawn. The reaction mixture leaving the bottom of the reactor is then worked up by distillation. Despite approximately quantitative conversion of the isophoronenitrile, this embodiment produces only 48% of isophoronediamine, together with many by-products. EP-B 0 042 119 does not suggest passing a mixture containing isophoronenitrile, ammonia and organic solvent, instead of a mixture of isophoronenitrile and ammonia, over a trickle bed reactor at an essentially low pressure and without the need for a preliminary imine formation reaction.

EP-A 0 449 089 (CA 2,039,328) discloses another process for the preparation of isophoronediamine. In two spatially separated reaction chambers, a solution of isophoronenitrile in tetrahydrofuran is initially reacted with excess ammonia on acidic metal catalysts to form 3-cyano-3,5,5-trimethylcyclohexylimine and the reaction mixture is hydrogenated at



high pressure in a second reaction chamber with hydrogen in the presence of excess ammonia on catalysts containing cobalt, nickel, ruthenium and/or other noble metals, and optionally basic components. By way of example, the mixture leaving the first reaction step is passed through the hydrogenation reactor from bottom to top; the reactor is operated as a bubble reactor. EP-A 0 49 089 does not give any indication of also using the reactor as a trickle bed reactor and directly feeding said reactor with a mixture of isophoronenitrile, ammonia and an organic solvent.

EP-A 0 394 967 teaches a process for the amination of carbonylnitriles and iminonitriles and also includes the preparation of isophoronediamine from isophoronenitrile. The starting material is initially converted to the aminonitrile at moderate temperatures under conditions of reductive amination, i.e. in the presence of hydrogen, ammonia and a hydrogenation catalyst; the nitrile group is then converted to an aminomethyl group at elevated temperature in the presence of a hydrogenation catalyst which is effective in the hydrogenation of nitrile groups. Although this process can be carried out at low pressures, the fact that a strictly observed temperature program has to be operated during both the reaction steps is regarded as a considerable disadvantage since it results in an appreciable lowering of the space-time yield and hence the economy of the process. In addition, unless special promoters are also used, the product quality does not satisfy the requirements of low by-products because the content of 3-cyano-3,5,5-trimethylaminocyclohexane, which cannot be separated off by distillation, is usually too high.

According to JP-A-4-300852, a pressure reduction in the preparation of isophoronediamine by the aminating catalytic hydrogenation of isophoronenitrile is also made possible by carrying out the hydrogenation in the presence of a supported ruthenium catalyst. However, JP-A-4-300852 refers only to conditions for suspension hydrogenation and not to conditions using a fixed bed reactor.

SRI International Report No. 1D, "Isocyanates" by YUREN CHIN (July 1983), gave a survey of an industrial process for the preparation of isophoronediamine from isophoronenitrile. In the process described therein, a mixture of isophoronenitrile, methanol and ammonia is passed with hydrogen over a fixed bed reactor containing a supported



catalyst of cobalt-on-kieselguhr. In the embodiment described, the catalyst bed is always flooded (bubble column). The operating pressure is given as 150 bar. Also, hydrogen is used in excess and, after the reaction, this excess must be separated from the reaction mixture, purified, compressed and then recycled. The economy of this process is reduced both by the high operating pressure and by the technical cost of recycling the hydrogen. As established in comparative Example 3b below, this embodiment results in the increased formation of by-products which cannot easily be separated off, and to a lowering of the yield.

SUMMARY OF THE INVENTION

One object of the present invention is to mitigate the disadvantages of the previously known processes for the preparation of isophoronediamine from isophoronenitrile using a reactor charged with a fixed bed catalyst, to the effect that the economy of the process is increased. In particular, the cost of the technical equipment should be reduced compared with the previously known processes. It should moreover be possible to obtain isophoronediamine in high yield and to isolate it from the reaction mixture in very pure form by means of conventional distillative measures.

According to the present invention, isophoronediamine is prepared from a mixture of isophoronenitrile, an organic solvent, and ammonia which is hydrogenated with hydrogen at a pressure sufficient to enable hydrogen to be transported through the liquid to the catalyst surface, in the presence of at least one hydrogenation catalyst, and the isophoronediamine is recovered from the reaction mixture by distillation. The aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronenitrile, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling through the catalyst bed being withdrawn at the bottom end of the reactor.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will be further understood with reference to the drawing, wherein:

FIG. 1-(a) is a schematic drawing showing a trickle bed reactor which can contain one or more layers of fixed bed catalyst; and

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FIG. 1-(b) is a schematic representation of trickle bed reactors connected in series.

DETAILED DESCRIPTION OF THE INVENTION

According to a more detailed aspect of the present invention, isophoronediamine is prepared from a mixture of isophoronitrile, an organic solvent (e.g., lower alkyl alcohol), and ammonia which is hydrogenated with hydrogen at a pressure sufficient to enable hydrogen to be transported through the liquid to the catalyst surface (e.g., in the range 3 to 10 MPa) and at a temperature in the range 80° to 150° C. in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the isophoronediamine is recovered from the reaction mixture by distillation. The aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronitrile, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling through the catalyst bed being withdrawn at the bottom end of the reactor.

The reaction according to the present invention is carried out in a conventional trickle bed reactor. The designs of such reactors are known to those skilled in the art. The fixed bed catalyst is arranged in the form of one or more layers in a container; the reactor is also equipped with devices for thermostating the catalyst layers in order to control the heat and to ensure that the desired temperature is maintained in the respective catalyst layer (see FIG. 1a). As an alternative to a single trickle bed reactor, several trickle bed reactors can be connected in series, the reaction mixture leaving the first reactor being recharged into the top of the second reactor and so on (FIG. 1b). The trickle bed reactor or reactors are also equipped with suitable devices for charging the reactants (i.e., in this case the mixture containing isophoronitrile, ammonia and solvent, and the hydrogen) as well as with devices for distributing the liquid over the surface of the first catalyst bed and, finally, with suitable devices for discharging the reaction mixture leaving the reactor. Such equipment is well known in the art, see for example Kirk-Othmer's *Encyclopedia of Chemical Technology*, Third Edition, Volume 19, pages 880-914 (this excerpt is entirely incorporated herein by reference), especially page 884.



An essential feature of the process according to the present invention is that the reaction mixture to be hydrogenated trickles over the catalyst bed and also that a sufficiently large gas volume exists within the catalyst bed to enable the hydrogen to be transported through the liquid film onto the catalyst surface. It has been found that the trickle bed process is substantially and surprisingly responsible for obtaining a high product yield and, in particular, a high selectivity. As used herein, "sufficiently large gas volume" means at least 50% of the volume of the catalyst particles; the "gas volume" is the space between the catalyst particles (approximately pellets) and is inclusive of the pore volume of the catalyst particles.

The yield in the present process with recycling of the high boiling (amidine containing) fraction lies preferably between greater than 91% and 95%; without recycling of the high boiling fraction, the yield most often lies between about 87% and 90% (preferably 87%-90%). The purity of the products lies in general above 99.6% preferably between 99.7 and 99.9%

If the reactor is operated not as a trickle bed reactor (where the liquid flows as a continuous film over the catalyst; the liquid mixture is allowed to trickle over the catalyst bed in the presence of hydrogen) but as a bubble reactor, in which case the catalyst bed is always flooded (the liquid reaction mixture is conveyed from bottom to top so that the reactor is always flooded), a considerably lower yield of isophoronediamine is obtained under otherwise identical reaction conditions with respect to temperature, pressure and concentration of the reactants; the bubble process also gives a different range of by-products, methylisophoronediamine (methyl-3-aminomethyl-3,5,5-trimethylcyclohexylamine) being formed in particular. Methylisophoronediamine cannot be separated from isophoronediamine by distillation under conventional conditions, so the formation of such by-products must already be avoided in the preparation of the isophoronediamine crude product. Surprisingly, such by-products are only formed in very small amounts under the conditions of the process according to the present invention. A further disadvantage of the bubble process is that hydrogen has to be added in excess in order to achieve saturation of the solution with H_2 ; this entails expensive recycling of the excess H_2 .



When the process according to the present invention is carried out, hydrogen can be fed into the reactor either in excess or in an amount such that no hydrogen has to be discharged from the reactor and recycled. The introduction of hydrogen in excess is less preferable because the technical cost of separating off the excess H_2 , condensing ammonia and organic solvent contained in the discharged hydrogen, and compressing the purified hydrogen and recycling it is considerable and reduces the economy of the process on account of the higher investment demanded. Moreover, an even lower yield of IPDA has been found compared with the process not using excess H_2 . Thus, hydrogen is preferably introduced not in excess but only in the amount which is required to maintain the desired operating pressure.

The aminating hydrogenation reaction is carried out at a pressure in the range 3 to 10 MPa, preferably at 5 to 8 MPa. Such moderate operating pressures, which are possible when using the mixtures of isophoronenitrile, ammonia and solvent and the trickle bed process under the temperature conditions according to the present invention, increase the economy, compared with processes which demand a high operating pressure, by lowering the level of investment required for the apparatus.

The requisite volume of fixed bed catalyst is governed by the LHSV value (liquid hourly space velocity which is dependent on the operating pressure, the temperature and the catalyst activity) which must be observed in order to achieve a quantitative conversion of isophoronenitrile. Generally, the LHSV value is 0.5 h^{-1} or preferably above. The LHSV value is preferably between 0.8 and 1.5 h^{-1} ; it is particularly good to attain an LHSV value in this range when the reaction is carried out at a temperature in the range between 90° and 130° C. and at a pressure of between 5 and 8 MPa.

In addition to the above mentioned parameters of pressure, temperature and catalyst activity, the LHSV value is also influenced by the chosen concentration ratios of isophoronenitrile, ammonia and solvent and by the type of solvent used. The mixture charged onto the catalyst bed conveniently contains 10 to 40% by weight and preferably 10 to 30% by weight of isophoronenitrile and 10 to 40% by weight and preferably 20 to 40% by weight of ammonia. Organic solvents which can be used are lower alkyl alcohols such as methanol, ethanol, n-propanol and isopropanol. Methanol is the preferred solvent. These solvents are inert to



production. Examples of suitable support materials are oxides from the group comprising silicon dioxide, aluminum oxide and titanium dioxide, silicates such as aluminum and calcium silicate, and naturally occurring and synthetically produced zeolites and glass frits. Although commercially available supported catalysts with a high Co content, like catalysts with 50% by weight of Co on aluminum silicate, are being described as essentially completely covered with cobalt, it has been found that catalysts with different supports but with the same specific surface and the same Co content influence the selectivity and the spectrum of side products. Obviously, the surface of the support of the catalyst is at least partially accessible and interferes with the catalytic process.

For reasons of cost, supported catalysts with ruthenium as the catalytically active component generally contain only a small proportion by weight of ruthenium, being generally between 0.5 and 10% by weight and preferably between 2 and 5% by weight.

The production of the above mentioned Co and Ru catalysts, which conventionally comprises impregnation, drying and shaping steps, is known to those skilled in the art; see U.S. Pat. No. 3,352,913 (which is incorporated by reference in its entirety), especially column 2, lines 28-41, and "Heterogeneous Catalysis In Industrial Practice" by Charles N. Satterfield, 2nd edition, 1991, McGraw Hill Inc., chapter 4, pages 87-130 (which is incorporated by reference in its entirety).

It has been established that isophoronediamine is obtainable by the process according to the present invention in higher yield when using a supported cobalt catalyst than when using a supported ruthenium catalyst. This is surprising inasmuch as JP-A 4-300852 and EP-A 0 394 967 have indicated that ruthenium catalysts are particularly effective in the hydrogenation of the nitrile group, which is more difficult to hydrogenate than the carbonyl group.

It is known that isophoronediamine exists in the form of cis and trans isomers (see *Die Angewandte Makromolekulare Chemie* 153 (1987) 1-13, No. 2502). By studying the isomer ratio of the isophoronediamine prepared according to the present invention, it has been found that the proportion of cis isomer formed is completely predominant when using a ruthenium catalyst: cis/trans isomer ratio according to Example 9 (below) = 84 to 16. When using a supported

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the reaction. The isophoronenitrile, ammonia and solvent are mixed in proportions such that an essentially homogeneous solution results. In principle, it is also possible to fall short of or exceed the above mentioned limiting values for ammonia and isophoronenitrile provided a homogeneous solution results. The use of a mixture containing less than 10% by weight of isophoronenitrile has an adverse effect on the economy of the process.

Apart from the constituents mentioned above, the mixture to be charged onto the catalyst can contain fractions, boiling above or below isophoronediamine, from the distillative recovery of the reaction mixture withdrawn from the trickle bed reactor. In addition to isophoronediamine residues, such fractions can also contain by-products from which isophoronediamine is re-formed under the reaction conditions. The yield of isophoronediamine can be markedly increased by recycling such fractions into the mixture to be used. It is particularly advantageous to feed the fraction boiling after the isophoronediamine, which, in addition to isophoronediamine residues, contains 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane as the main product, into the trickle bed reactor together with the mixture of isophoronenitrile, ammonia and solvent. Recycling of the fraction containing the 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane, a bicyclic compound of amidine structure, makes it possible to significantly increase the yield of isophoronediamine and consequently to improve the economy of the process.

The catalysts to be used according to the present invention are cobalt and/or ruthenium fixed bed catalysts; these catalysts are conventionally in the form of pellets, extrudates or other moldings known in the art. It is particularly convenient to use supported catalysts, cobalt or ruthenium being present on a support of adequate specific surface area. Conventionally, the specific surface area of the supported catalysts to be used according to the present invention is in the range between 5 and 500 m²/g (measured with nitrogen by the BET method).

The cobalt content of the supported catalyst is generally between 10 and 70% by weight and preferably between 30 and 50% by weight, based on the supported catalyst. The surface of the support, which is frequently made up of oxide or silicate materials, is partially or essentially completely covered with cobalt, it also being possible for cobalt oxide to be present underneath the surface due to the method of

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cobalt catalyst, the other conditions being identical, the cis and trans isomers are formed in somewhat equal proportions: cis/trans isomer ratio according to Example 8 (below) = 60 to 40.

It has furthermore been found that it is possible to prepare isophoronediamine with a cis/trans isomer ratio above that which is obtainable using a supported cobalt catalyst, and in high yield, by carrying out the aminating hydrogenation reaction in a trickle bed reactor in which an upper layer of a supported ruthenium catalyst and a lower layer of a cobalt fixed bed catalyst are arranged. The cis/trans isomer ratio is dependent upon the reaction temperature and/or the choice of catalyst (see our copending U.S. application corresponding to DE 43 43 891.1); for example, at a temperature of 120° C. (single step temperature method) the cis/trans ratio with a Co-catalyst is between approximately 60 to 40, with a catalyst combination of Ru-Co in dependence from the amount of Ru to Co the cis/trans ratio is from 90 to 10.

Particularly suitable catalysts are ruthenium-on- γ -aluminum oxide and a supported cobalt catalyst with an oxide or silicate support and a cobalt content of 10 to 70% by weight, based on the catalyst. Instead of having one reactor with two layers of different fixed bed catalysts arranged therein, it is also possible to connect two reactors in series, each containing only one fixed bed catalyst; in this case, the first reactor contains the ruthenium fixed bed catalyst and the second reactor contains the cobalt fixed bed catalyst. To obtain a high yield of isophoronediamine with the desired isomer ratio, it is advantageous if the ruthenium fixed bed catalyst, which is positioned first, makes up 3 to 30%, preferably 5 to 20%, of the total catalyst volume.

As explained earlier, the process according to the present invention differs in essential respects from previously known processes, resulting in substantial advantages. By combining the use of a starting mixture of isophoronenitrile, ammonia and an alcoholic solvent with the trickle bed operation of the reactor provided with a fixed bed, it is possible to surprisingly achieve both a high product yield of isophoronediamine and a high selectivity. The formation of undesired by-products, such as methylisophoronediamine, which adversely affects the product quality because it is difficult to separate off, is extensively avoided by the reaction process of the present invention; less than 3000 ppm (preferably 200 ppm or less) of by-products such as methylisophoronediamine are produced. The above mentioned

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combination of essential features of the present invention is also such that the aminating hydrogenation can be carried out at moderate pressures, thereby greatly reducing the consequent cost of the pressure apparatus compared with the case of a high-pressure apparatus. As it is not necessary according to the present invention to use hydrogen in excess and hence to have to purify and recycle the excess, in contrast to previously known processes using a reactor with a fixed bed catalyst, expensive devices for separating off, purifying and recycling the excess H_2 are dispensed with.

Another essential advantage of the process according to the present invention is the unexpectedly long service life of the catalysts, which is attributed to the trickle bed process. Even after several months of operation, no reduction in yield, no change in the range of by-products, and no change in the isomer ratio were found. A further advantage is the ability to obtain isophoronediamine in high yield with a particular isomer ratio, within certain limits.

In the process according to the present invention, there is also no need for a preliminary reaction between isophoronitrile and ammonia in order to form isophoroneimine, which was considered by the art to be essential for obtaining a high yield and high selectivity in the aminating hydrogenation. In contrast, according to the present invention, a solution of isophoronitrile in the solvent used is mixed with ammonia directly upstream of the trickle bed reactor and the mixture is fed into the reactor.

The process according to the present invention is illustrated in greater detail with the aid of the following Examples, without implying a limitation.

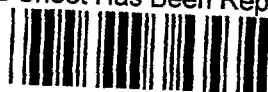
EXAMPLE 1

A vertical reaction tube is filled with 200 ml of hydrogenation catalyst. The feed solution containing IPN and methanol, and liquid NH_3 , are pumped into the top of the reactor. Hydrogen also flows into the tube from the top. The reaction temperature is kept at $120^\circ C$. by means of oil heating. The pressure is regulated at 6 MPa. The liquid is collected in a separating vessel. The gas stream at the reactor inlet is adjusted so that a gas stream of 100 NI/h is established downstream of the separating vessel.

The catalyst used was a commercially available solid Co catalyst (ca. 50% Co on silicate support) in the form of extrudates of 4-5 mm in diameter and length. The feed solution contained 24% by weight of IPN and 76% by

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weight of methanol. 130 ml/h thereof and 70 ml/h of NH_3 were mixed directly before being charged into the reactor, and the mixture was pumped into the reactor; the LHSV value was thus 1 h^{-1} . According to analysis of the product mixture, the yield of IPDA was 88.7%, based on IPN used. The product mixture also contained 5% of 2-aza-4,6,6-trimethylbicyclo[3,2,1]octane (bicyclic compound) and 4.3% of 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane (amidine).

EXAMPLE 2

The experiment was carried out in the same experimental set-up as described in Example 1, except that no gas stream was withdrawn from the separating vessel so only the consumed hydrogen was replaced in order to keep the reaction pressure at 60 bar. The catalyst, liquid streams and liquid composition were the same as described in Example 1.

Analysis of the product mixture of this experiment showed an IPDA yield of 89.2%, based on IPN used. The product mixture also contained 4.5% of bicyclic compound and 4.4% of amidine. Surprisingly, an even higher yield of IPDA and a reduction in the "bicyclic" by-product are made possible by the process without excess H_2 . This experiment was run for 2000 h with no observable loss of yield or change in the range of products.

EXAMPLES 3a and 3b

The experimental set-up used was the same as in Example 1. The hydrogenation pressure was 6 MPa and the reaction temperature was 120°C . The H_2 stream was adjusted so that 100 Nl/h of H_2 were withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were pumped into the reactor together with 50 ml/h of liquid NH_3 . 200 ml of cobalt catalyst were introduced as the catalyst.

Two processes were studied: In the trickle bed process (3a), gas and liquid flowed through the reactor from top to bottom; in the bubble column process (3b), the reactor was in the flooded state and gas and liquid flowed through it from bottom to top.

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A yield of 87.1% was achieved in the trickle bed process (3a). After purification by distillation, the product purity was 99.8%; methyl-IPDA was detectable in an amount of only about 200 ppm.

A yield of 85.5% was achieved in the experiment by the bubble column process (3b). Purification by distillation gave a product purity of only 99.5%. Analysis showed that the pure product still contained 3000 ppm of methyl-IPDA. The methyl-IPDA by-product, which has a very adverse effect on the quality of the IPDA product, is practically inseparable by distillation.

The difference in yield between 3a and 3b is 1.6% which is statistically significant in a commercial process. The difference in purity (3a: 99.8% with 200 ppm methyl-IPDA; 3b: 99.5% with 3000 ppm of methyl-IPDA) is of great practical significance because the methyl-IPDA cannot be separated by distillation. The difference in yield and purity between 3a and 3b shows the unexpected superiority of the present invention over the process of EP-A 0 394 967.

EXAMPLES 4 to 6

These experiments were carried out in the same experimental set-up and under the same reaction conditions as described in Example 1. Only the catalyst was varied. The results are given in the following Table:

Example	Catalyst	Yield of IPDA (%)
4	5% Ru/ γ -Al ₂ O ₃	82.1
5	Ni	55.3
6	2% Pd/ γ -Al ₂ O ₃	4

Both the Ru and the Pd were applied to γ -Al₂O₃ extrudates as the support. Examples 5 and 6 clearly show that the yields obtained with Ni and Pd catalysts are not satisfactory compared with the process according to the present invention.

EXAMPLE 7

The low-boiling components, namely methanol, NH₃, H₂O and the bicyclic compound, were removed from 8770 g of the reaction solution of Example 2 by fractional

distillation. 1292 g of a crude solution remained. 1190 g of IPDA were distilled off from this solution at a bottom temperature of 147° C. and at a pressure of 2 kPa. This corresponds to an isolation yield of 87.3%. 98 g remained as the bottom product of the distillation. A further high-boiling fraction of 74 g was distilled off from this bottom product under reduced pressure (1 kPa) and at a temperature of 162° C. It contained 20% of IPDA and 74% of amidine. This resulting fraction of 74 g corresponds to 5.6% of the amount of IPN used.

In another experiment, which was carried out analogously to Example 2, the high-boiling fraction (i.e., 5.6% based on the amount of IPN used) was added. After hydrogenation and separation of the low-boiling components and purification of the IPDA by distillation, the isolation yield found was 92.3%. Accordingly, it was possible to achieve a 5% increase in the isolation yield of IPDA by recycling the high-boiling fraction containing the amidine.

The yield of IPDA can be increased by a further 4% by catalytically hydrogenating the fraction containing the bicyclic compound (boiling point below that of IPDA) in a separate hydrogenation reactor under elevated temperature conditions (150°–200° C.).

EXAMPLES 8 to 11

The experimental set-up used was the same as in Example 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120° C. No H₂ was withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were mixed with 50 ml/h of liquid NH₃ and pumped into the reactor. This experimental setup was operated with a ruthenium catalyst, a cobalt catalyst and various combinations of the two. The results of this experiment are shown in the following Table:

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Example	Catalyst*	Yield (%)	Isomer ratio cis:trans
8	200 ml Co	87.2	60:40
9	200 ml Ru	81.5	84:16
10	100 ml Ru + 100 ml Co	83.7	81:19
11	10 ml Ru + 190 ml Co	86.9	78:22

*Ru catalyst: 5% Ru on γ -Al₂O₃ extrudates; Co catalyst: 50% Co on Al silicate extrudates

Use of a Co catalyst alone increases the yield compared to use of a Ru catalyst alone. Use of a Ru catalyst alone increases the cis/trans isomer ratio compared to use of a Co catalyst alone. By combining a Ru catalyst and a Co catalyst, the Ru catalyst being arranged as the upper layer in the reactor, it is possible to obtain IPDA with a high cis/trans isomer ratio in higher yield than by using an Ru catalyst on its own.

EXAMPLE 12

A reaction tube (diameter 16 mm) of a trickle bed hydrogenation apparatus was filled with 120 ml of a commercial Co support catalyst (Co on aluminum silicate, 50% by weight Co; specific surface (BET (N₂)) approximately 200 m²/g). The example was performed in a similar manner as Example 1. The reaction temperature was regulated to 110° C., the total pressure (sum of the partial pressures for H₂, NH₃, methanol) to 6 MPa. The feed solution contained 15% by weight isophorononitrile, 65% by weight methanol, and 25% by weight ammonia. 100 ml of said feed solution was pumped onto the top of the trickle bed. After trickling of said solution through the trickle bed, the reaction mixture contained (mole % related to isophorononitrile in the feed solution):

Isophoronediamine (IPDA)	89.2%
Isophoroneaminoalcohol (IPAA)	2.1%
Amidine compound (see example 1)	4.0%
Bicyclic compound (see example 1)	3.8%

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EXAMPLE 13

Example 12 was repeated with the only difference in that another commercial Co support catalyst was used (Co on silica, 25% by weight Co, specific surface (BET (N₂)) approximately 200 m²/g). The reaction mixture contained (mole % related to isophoronenitrile in the feed solution):

Isophoronediamine (IPDA)	87.4%
Isophoroneaminoalcohol (IPAA)	1.2%
Amidine compound (see example 1)	4.3%
Bicyclic compound (see example 1)	5.1%

Further variations and modifications of the foregoing will be apparent to those skilled in the art and such variations and modifications are attended to be encompassed by the claims that are appended hereto.

What is claimed:

1. A process for the preparation of isophoronediamine from isophoronenitrile, said process comprising charging a reaction mixture of isophoronenitrile, an organic inert solvent, and ammonia onto a catalyst bed at the top end of a trickle bed reactor with hydrogen at a sufficient pressure and at a temperature in the range 80° to 150° C., and withdrawing said reaction mixture after trickling through said catalyst bed at the bottom end of said trickle bed reactor; wherein said catalyst bed contains at least one hydrogenation catalyst selected from the group consisting of cobalt and ruthenium fixed bed catalysts.

2. The process according to claim 1, further comprising working up the reaction mixture by distillation.

3. The process according to claim 1, wherein the LHSV is 0.8–1.5 h⁻¹ and said temperature is in the range 90° to 130° C. and said pressure is in the range of 5 to 8 MPa.

4. The process according to claim 1, wherein said temperature is in the range 40° to 150° C. and said pressure is in the range of 3 to 8 MPa.

5. The process according to claim 1, wherein said isophoronenitrile in said solvent is mixed with said ammonia directly upstream of said trickle bed reactor and said mixture is fed into said reactor.

6. The process according to claim 1, wherein said solvent is selected from the group consisting of methanol, ethanol, n-propanol, and isopropanol.

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EXAMPLE 13

Example 12 was repeated with the only difference in that another commercial Co support catalyst was used (Co on silica, 25% by weight Co, specific surface (BET (N_2)) approximately 200 m^2/g). The reaction mixture contained (mole % related to isophoronenitrile in the feed solution):

Isophoronediamine (IPDA)	87.4%
Isophoroneaminoalcohol (IPAA)	1.2%
Amidine compound (see example 1)	4.3%
Bicyclic compound (see example 1)	5.1%

Further variations and modifications of the foregoing will be apparent to those skilled in the art and such variations and modifications are attended to be encompassed by the claims that are appended hereto.

What is claimed:

1. A process for the preparation of isophoronediamine from isophoronenitrile, said process comprising charging a reaction mixture of isophoronenitrile, an organic inert solvent, and ammonia onto a catalyst bed at the top end of a trickle bed reactor with hydrogen at a sufficient pressure and at a temperature in the range 80° to 150° C., and withdrawing said reaction mixture after trickling through said catalyst bed at the bottom end of said trickle bed reactor; wherein said catalyst bed contains at least one hydrogenation catalyst selected from the group consisting of cobalt and ruthenium fixed bed catalysts.

2. The process according to claim 1, further comprising working up the reaction mixture by distillation.

3. The process according to claim 1, wherein the LHSV is 0.8–1.5 h^{-1} and said temperature is in the range 90° to 130° C. and said pressure is in the range of 5 to 8 MPa.

4. The process according to claim 1, wherein said temperature is in the range 40° to 150° C. and said pressure is in the range of 3 to 8 MPa.

5. The process according to claim 1, wherein said isophoronenitrile in said solvent is mixed with said ammonia directly upstream of said trickle bed reactor and said mixture is fed into said reactor.

6. The process according to claim 1, wherein said solvent is selected from the group consisting of methanol, ethanol, n-propanol, and isopropanol.

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7. The process according to claim 6, wherein said solvent is methanol.

8. The process according to claim 1, wherein said reaction mixture comprises 10 to 40% by weight of isophoronenitrile and 10 to 40% by weight of ammonia and said reaction mixture forms a homogeneous solution.

9. The process according to claim 8, wherein said reaction mixture comprises 10 to 30% by weight of isophoronenitrile and 20 to 40% by weight of ammonia.

10. The process according to claim 1, wherein the LHSV is greater than or equal to 0.5 h^{-1} .

11. The process according to claim 10, wherein said LHSV is $0.8\text{--}1.5 \text{ h}^{-1}$.

12. The process according to claim 1, wherein said hydrogenation catalyst is a supported catalyst consisting essentially of (a) an inorganic support material and (b) 10 to 70% by weight of cobalt or 0.5 to 10% by weight of ruthenium.

13. The process according to claim 12, wherein said hydrogenation catalyst is a supported catalyst consisting essentially of (a) an inorganic support material and (b) 30 to 50% by weight of cobalt or 2 to 5% by weight of ruthenium.

14. The process according to claim 12, wherein said supported catalyst has a BET specific surface area of $5\text{--}500 \text{ m}^2/\text{g}$.

15. The process according to claim 12, wherein said support material is selected from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, aluminum silicate, calcium silicate, zeolite and glass frit.

16. The process according to claim 1, wherein an excess of hydrogen is not used.

17. The process according to claim 1, wherein said hydrogen is present in an amount required to maintain said pressure.

18. The process according to claim 2, further comprising feeding back into said trickle bed reactor a high-boiling fraction distilling after the isophoronediamine main fraction in the distillative working-up of the reaction mixture.

19. The process according to claim 18, wherein said high-boiling fraction contains 3,5,5-trimethyl-6-imino-7-azabicyclo(3,2,1)octane.

20. The process according to claim 12, wherein said hydrogenation catalyst is a supported catalyst consisting essentially of (a) an inorganic support material and (b) 30 to 50% by weight of cobalt.

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34. The process according to claim 1, wherein said pressure is in the range 3 to 10 MPa.

35. The process according to claim 1, wherein less than 3000 ppm of methylisophoronediamine is produced.

36. The process according to claim 35, wherein less than or equal to 200 ppm of methylisophoronediamine is produced.

37. The process according to claim 18, wherein the yield of isophoronediamine is greater than 91% to 95%.

38. The process according to claim 1, wherein the yield of isophoronediamine is about 87% to 90%.

39. The process according to claim 38, wherein the yield of isophoronediamine is 87% to 90%.

40. The process according to claim 1, wherein the purity of isophoronediamine is greater than 99.6%.

41. The process according to claim 40, wherein the purity of isophoronediamine is 99.7% to 99.9%.

42. The process according to claim 1, consisting essentially of charging a reaction mixture of isophoronenitrile, an organic inert solvent, and ammonia onto a catalyst bed at the top end of a trickle bed reactor with hydrogen at a sufficient pressure and at a temperature in the range 80° to 150° C., and withdrawing said reaction mixture after trickling through said catalyst bed at the bottom end of said trickle bed reactor; wherein said catalyst bed contains at least one hydrogenation catalyst selected from the group consisting of cobalt and ruthenium fixed bed catalysts.

43. A process for the preparation of isophoronediamine from isophoronenitrile, said process comprising charging a reaction mixture of isophoronenitrile, an organic inert solvent, and ammonia onto a catalyst bed at the top end of a trickle bed reactor with hydrogen at a sufficient pressure and at a temperature in the range 80° to 150° C., and withdrawing said reaction mixture after trickling through said catalyst bed at the bottom end of said trickle bed reactor; wherein said catalyst bed contains at least one hydrogenation catalyst which comprises a cobalt fixed bed catalyst.

44. The process according to claim 43, wherein said hydrogenation catalyst is a supported catalyst consisting essentially of (a) an inorganic support material and (b) 10 to 70% by weight of cobalt.

45. The process according to claim 44, wherein said hydrogenation catalyst is a supported catalyst consisting essentially of (a) an inorganic support material and (b) 30 to 50% by weight of cobalt.



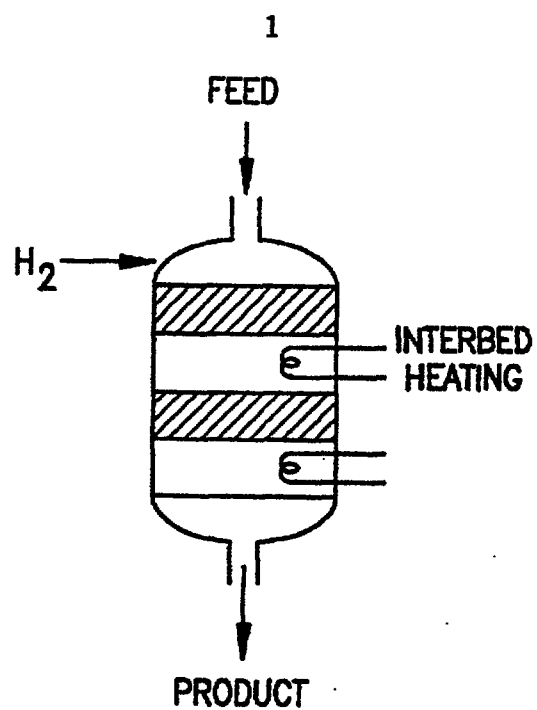


FIG. 1a

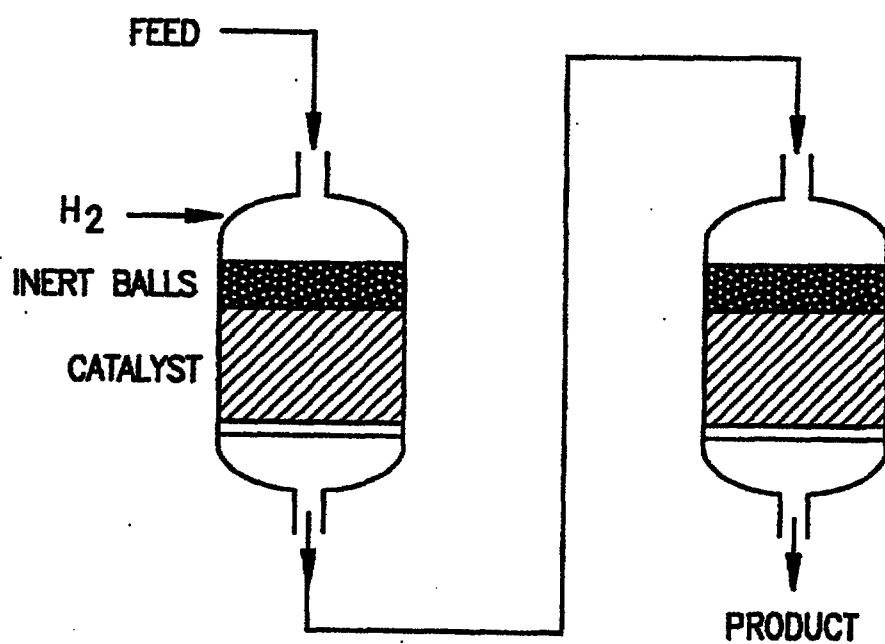


FIG. 1b

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1

Process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine

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Description

The invention relates to an improved process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, hereafter also called isophoronediamine or abbreviated to IPDA, from 3-cyano-3,5,5-trimethylcyclohexanone, hereafter also called isophoronenitrile or abbreviated to IPN, by aminating hydrogenation with hydrogen and ammonia in the presence of a fixed bed catalyst. The process according to the invention affords the continuous preparation of isophoronediamine in high yield and high purity.

Isophoronediamine is used as a starting material for the preparation of isophorone diisocyanate, which is an isocyanate component for polyurethane systems, as an amine component for polyamides and as a hardener for epoxy resins. Isophoronediamine is conventionally prepared from isophoronenitrile, the carbonyl group being converted to an amino group and the nitrile group to an aminomethyl group in the presence of ammonia, hydrogen and conventional hydrogenation catalysts. The starting material, isophoronenitrile, can be obtained in conventional manner by the addition of hydrogen cyanide onto isophorone - see DE-OS 39 42 371.

According to the process described in US 3,352,913 for the preparation of isophoronediamine from isophoronenitrile, the hydrogenation is carried out in the presence of ammonia and in the presence of cobalt-, nickel-, iron- or noble metal- containing catalysts known per se, at 50 to 150°C and at a pressure of at least 50 bar. By way of example, the hydrogenation takes place in the presence of methanol

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as a solvent and using suspension or fixed bed catalysts. Apart from the desired isophoronediamine, by-products, such as 3-aminomethyl-3,5,5-trimethylcyclohexanol (isophoroneamino alcohol, IPAA) in particular, are formed in relatively large amounts. The disadvantages of this process are found to be the low yield and a considerable proportion of by-products.

In the quest to obtain a higher yield of IPDA and minimize the unavoidable formation of IPAA, DE-OS 30 11 656 teaches a two-step process; in the first step, IPN is converted with excess ammonia, without a catalyst, to 3-cyano-3,5,5-trimethyliminocyclohexane, and the latter is hydrogenated in the second step to IPDA. The disadvantage of this process is that, as well as the actual hydrogenation reactor, a special imine formation reactor is required.

EP-B 0 042 119 proposes a further improvement to the process, wherein, prior to reaction with ammonia and hydrogen in the presence of hydrogenation catalysts at temperatures of 10 to 120°C and pressures of 1 to 300 bar, the isophoronenitrile is subjected to a preliminary reaction with ammonia in the presence of inorganic and organic ion exchangers in the ammonium form as imine formation catalysts. Whereas the volume ratio of isophoronenitrile to ammonia in the imine formation step is said to be 1:0.5 to 20, this ratio is increased to 1:10 to 20 in the hydrogenation step. Although the process, which can be carried out in trickle bed reactors, leads to a high yield of IPDA and to a high purity, the economy of the process is compromised by the use of two different catalysts and the large excess of ammonia, which necessitates a very high pressure and hence an expensive hydrogenation apparatus.

EP-B 0 042 119 also discloses a Comparative Example in which isophoronenitrile and liquid ammonia are pumped into



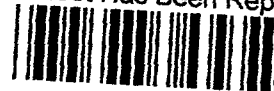
the top of a hydrogenation reactor charged with commercially available cobalt catalyst. The reaction system is kept at 270 bar with H_2 ; a certain gas stream is set up and a certain amount of off-gas is withdrawn. The reaction mixture leaving the bottom of the reactor is then worked up by distillation. Despite approximately quantitative conversion of the isophoronenitrile, this embodiment produces only 48% of isophoronediamine, together with many by-products. Said document does not suggest passing a mixture containing isophorone, ammonia and organic solvent, instead of a mixture of isophoronenitrile and ammonia, over a trickle bed reactor at an essentially low pressure and without the need for a preliminary imine formation reaction.

EP-A 0 449 089 discloses another process for the preparation of isophoronediamine: In two spatially separated reaction chambers, a solution of isophorone-nitrile in tetrahydrofuran is initially reacted with excess ammonia on acidic metal catalysts and the reaction mixture is hydrogenated at high pressure in a second reaction chamber with hydrogen in the presence of excess ammonia on catalysts containing cobalt, nickel, ruthenium and/or other noble metals, and optionally basic components. By way of example, the mixture leaving the first reaction step is passed through the hydrogenation reactor from bottom to top; the reactor is operated as a bubble reactor. Said document does not give any indication of also using the reactor as a trickle bed reactor and directly feeding said reactor with a mixture of isophoronenitrile, ammonia and an organic solvent.

EP-A 0 394 967 teaches a process for the amination of carbonylnitriles and iminonitriles and also includes the preparation of isophoronediamine from isophoronenitrile. The starting material is initially converted to the aminonitrile at moderate temperatures under conditions of

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reductive amination, i.e. in the presence of hydrogen, ammonia and a hydrogenation catalyst; the nitrile group is then converted to an aminomethyl group at elevated temperature in the presence of a hydrogenation catalyst which is effective in the hydrogenation of nitrile groups. The process can be carried out either in reactors which use suspension catalysts or in reactors which use fixed bed catalysts. Although this process can be carried out at low pressures, the fact that a strictly observed temperature programme has to be operated during both the reaction steps is regarded as a considerable disadvantage since it results in an appreciable lowering of the space-time yield and hence the economy of the process. In addition, unless special promoters are also used, the product quality does not satisfy the requirements because the content of 3-cyano-3,5,5-trimethylaminocyclohexane, which cannot be separated off by distillation, is usually too high.

According to JP-A-4-300852, a pressure reduction in the preparation of isophoronediamine by the aminating catalytic hydrogenation of isophoronenitrile is also made possible by carrying out the hydrogenation in the presence of a supported ruthenium catalyst. However, said document refers only to conditions for suspension hydrogenation and not to conditions using a fixed bed reactor.

SRI International Report no. 1D "Isocyanates" by YU-REN CHIN (July 1983) gave a survey of an industrial process for the preparation of isophoronediamine from isophoronenitrile: In the process described here, a mixture of isophoronenitrile, methanol and ammonia is passed with hydrogen over a fixed bed reactor containing a supported catalyst of cobalt-on-kieselguhr. In the embodiment described, the catalyst bed is always flooded (bubble column). The operating pressure is given as 150 bar. Also, hydrogen is used in excess and, after the reaction, this excess must be separated from the reaction mixture,

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purified, compressed and then recycled. The economy of this process is reduced both by the high operating pressure and by the technical cost of recycling the hydrogen. As established by the Inventors of the present invention - see Example 3b not according to the invention - this embodiment results in the increased formation of by-products which cannot easily be separated off, and to a lowering of the yield.

The object of the present invention thus consists in mitigating the disadvantages of the previously known processes for the preparation of isophoronediamine from isophoronenitrile using a reactor charged with a fixed bed catalyst, to the effect that the economy of the process is increased. In particular, the cost of the technical equipment should be reduced compared with the previously known processes. It should moreover be possible to obtain isophoronediamine in high yield and to isolate it from the reaction mixture in very pure form by means of conventional distillative measures.

A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile, IPN) has been found in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃-alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronediamine, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling



through the catalyst bed being withdrawn at the bottom end of the reactor.

The reaction according to the invention is carried out in a conventional trickle bed reactor. The designs of such reactors are known to those skilled in the art: The fixed bed catalyst is arranged in the form of one or more layers in a container; the reactor is also equipped with devices for thermostating the catalyst layers in order to ensure that the desired temperature is maintained in the respective catalyst layer. As an alternative to a single trickle bed reactor, several trickle bed reactors can be connected in series, the reaction mixture leaving the first reactor being recharged into the top of the second reactor. The trickle bed reactor or reactors are also equipped with suitable devices for charging the reactants, i.e. in this case the mixture containing isophoronenitrile, ammonia and solvent, and the hydrogen, as well as with devices for distributing the liquid over the surface of the first catalyst bed and, finally, with suitable devices for discharging the reaction mixture leaving the reactor.

An essential feature of the process according to the invention is that the reaction mixture to be hydrogenated trickles over the catalyst bed and also that a sufficiently large gas volume exists within the catalyst bed to enable the hydrogen to be transported through the liquid film onto the catalyst surface. It has been found that the trickle bed process is substantially responsible for obtaining a high product yield and, in particular, a high selectivity. If the reactor is operated not as a trickle bed reactor but as a bubble reactor, in which case the catalyst bed is always flooded, a considerably lower yield of isophoronediamine is obtained under otherwise identical reaction conditions in respect of temperature, pressure and concentration of the reactants; the bubble process also gives a different range of by-products, methylisophorone-

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diamine (methyl-3-aminomethyl-3,5,5-trimethylcyclohexylamine) being formed in particular. Said methylisophoronediamine cannot be separated from isophoronediamine by distillation under conventional conditions, so the formation of said by-product must already be avoided in the preparation of the isophoronediamine high product. Surprisingly, said by-product is only formed in very small amounts under the conditions of the process according to the invention. A further disadvantage of the bubble process is that hydrogen has to be added in excess in order to achieve saturation of the solution with H_2 ; this entails expensive recycling of the excess H_2 .

When the process according to the invention is carried out, hydrogen can be fed into the reactor either in excess or in an amount such that no hydrogen has to be discharged from the reactor and recycled. The introduction of hydrogen in excess is less preferable because the technical cost of separating off the excess H_2 , condensing ammonia and organic solvent contained in the discharged hydrogen, and compressing the purified hydrogen and recycling it is considerable and reduces the economy of the process on account of the higher investment demanded; moreover, an even lower yield of IPDA has been found compared with the process not using excess H_2 . Thus hydrogen is preferably introduced not in excess but only in the amount which is required to maintain the desired operating pressure.

The aminating hydrogenation is carried out at a pressure in the range 3 to 10 MPa, preferably at 5 to 8 MPa. Said moderate operating pressures, which are possible when using the claimed mixtures of isophoronenitrile, ammonia and solvent and the trickle bed process under the claimed temperature conditions, increase the economy, compared with processes which demand a high operating pressure, by

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lowering the level of investment required for the apparatus.

The requisite volume of fixed bed catalyst is governed by the LHSV value (liquid hourly space velocity) (dependent on the operating pressure, the temperature and the catalyst activity) which must be observed in order to achieve a quantitative conversion of isophoronenitrile.

Conventionally, the LHSV value is 0.5 h^{-1} or preferably above. The LHSV value is preferably between 0.8 and 1.5 h^{-1} . It is particularly good to attain an LHSV value in said range when the reaction is carried out at a temperature in the range between 90 and 130°C and at a pressure of between 5 and 8 MPa .

In addition to the abovementioned parameters of pressure, temperature and catalyst dependence, the LHSV value is also influenced by the chosen concentration ratios of isophorone, ammonia and solvent and by the type of solvent used. The mixture charged onto the catalyst bed conveniently contains 10 to 40% by weight and preferably 10 to 30% by weight of isophoronenitrile and 10 to 40% by weight and preferably 20 to 40% by weight of ammonia. Solvents which can be used are methanol, ethanol, n-propanol and isopropanol. Methanol is the preferred solvent. The isophoronenitrile, ammonia and solvent are mixed in proportions such that an essentially homogeneous solution results. In principle, it is also possible to fall short of or exceed the abovementioned limiting values for ammonia and isophoronenitrile provided a homogeneous solution results. The use of a mixture containing less than 10% by weight of isophoronenitrile has an adverse effect on the economy of the process.

Apart from the constituents mentioned above, the mixture to be charged onto the catalyst can contain fractions, boiling above or below isophoronediamine, from the distillative

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working-up of the reaction mixture withdrawn from the trickle bed reactor. In addition to isophoronediamine residues, such fractions can also contain by-products from which isophoronediamine is re-formed under the reaction conditions. The yield of isophoronediamine can be markedly increased by recycling such fractions into the mixture to be used. It is particularly advantageous to feed the fraction boiling after the isophoronediamine, which, in addition to isophoronediamine residues, contains 3,3,5-trimethyl-6-imino-7-azabicyclo[3,2-1]octane as the main product, into the trickle bed reactor together with the mixture of isophoronenitrile, ammonia and solvent. Recycling of the fraction containing the abovementioned byproduct - a bicyclic compound of amidine structure - makes it possible significantly to increase the yield of isophoronediamine and consequently to improve the economy of the process.

The catalysts to be used according to the invention are cobalt and/or ruthenium fixed bed catalysts. These catalysts are conventionally in the form of pellets, extrudates or other mouldings. It is particularly convenient to use supported catalysts, cobalt or ruthenium being present on a support of adequate specific surface area. Conventionally, the specific surface area of the supported catalysts to be used according to the invention is in the range between 5 and 500 m²/g (measured with nitrogen by the BET method).

The cobalt content of the supported catalysts is generally between 10 and 70% by weight and preferably between 30 and 50% by weight, based on the supported catalyst. The surface of the support, which is frequently made up of oxide or silicate materials, is partially or essentially completely covered with cobalt, it also being possible for cobalt oxide to be present underneath the surface due to the method of production. Examples of suitable support

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materials are oxides from the group comprising silicon dioxide, aluminium oxide and titanium dioxide, silicates such as aluminium and calcium silicate, and naturally occurring and synthetically produced zeolites and glass frits. Although commercially available supported catalysts with a high Co content, such as catalysts containing 50% by weight of Co on aluminium silicate, are described as being essentially completely covered with Co, it has been found that catalysts with a different support but the same specific surface area thereof and the same Co content have an influence on the selectivity and the range of byproducts. Obviously the surface of the catalyst support is at least partially accessible and intervenes in the catalytic process.

For reasons of cost, supported catalysts with ruthenium as the catalytically active component generally contain only a small proportion by weight of ruthenium, being conventionally between 0.5 and 10% by weight and preferably between 2 and 5% by weight. The production of the abovementioned Co and Ru catalysts, which conventionally comprises impregnation, drying and shaping steps, is known to those skilled in the art.

It has been established that isophoronediamine is obtainable by the process according to the invention in higher yield when using a supported cobalt catalyst than when using a supported ruthenium catalyst. This is surprising inasmuch as the abovementioned documents JP-A 4-300852 and EP-A 0 394 967 have indicated that ruthenium catalysts are particularly effective in the hydrogenation of the nitrile group, which is more difficult to hydrogenate than the carbonyl group.

It is known that isophoronediamine exists in the form of cis and trans isomers - see Die Angewandte Makromolekulare Chemie 153 (1987) 1-13, no. 2502. By studying the isomer

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ratio of the isophoronediamine prepared according to the invention, it has been found that the proportion of cis isomer formed is completely predominant when using a ruthenium catalyst: cis/trans isomer ratio according to Example 9 / 84 to 16. When using a supported cobalt catalyst, the other conditions being identical, the cis and trans isomers are formed in similar proportions: cis/trans isomer ratio according to Example 8 / 60 to 40.

It has furthermore been found that it is possible to prepare isophoronediamine with a cis/trans isomer ratio above that which is obtainable using a supported cobalt catalyst, and in high yield, by carrying out the aminating hydrogenation in a trickle bed reactor in which an upper layer of a supported ruthenium catalyst and a lower layer of a cobalt fixed bed catalyst are arranged. Particularly suitable catalysts are ruthenium-on- γ -aluminium oxide and a supported cobalt catalyst with an oxide or silicate support and a cobalt content of 10 to 70% by weight, based on the catalyst. Instead of having one reactor with two layers of different fixed bed catalysts arranged therein, it is also possible to connect two reactors in series, each containing only one fixed bed catalyst; in this case, the first reactor contains the ruthenium fixed bed catalyst and the second reactor contains the cobalt fixed bed catalyst. To obtain a high yield of isophorone with the desired isomer ratio, it is advantageous if the ruthenium fixed bed catalyst, which is positioned first, makes up 3 to 30%, preferably 5 to 20%, of the total catalyst volume.

As explained earlier, the process according to the invention differs in essential respects from previously known processes of this kind, resulting in substantial advantages. By combining the use of a starting mixture of isophoronenitrile, ammonia and an alcoholic solvent and the trickle bed operation of the reactor provided with a fixed bed, it is possible to achieve both a high product yield of

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isophoronediamine and a high selectivity. The formation of undesired by-products such as methylisophoronediamine, which adversely affects the product quality because it is difficult to separate off, is extensively avoided by the reaction process. The abovementioned combination of essential features of the invention is also such that the aminating hydrogenation can be carried out at moderate pressures, thereby greatly reducing the consequent cost of the pressure apparatus compared with the case of a high-pressure apparatus. As it is not necessary according to the invention to use hydrogen in excess and hence to have to purify and recycle the excess, in contrast to previously known processes using a reactor with a fixed bed catalyst, expensive devices for separating off, purifying and recycling the excess H_2 are dispensed with. Another essential advantage of the process according to the invention is the unexpectedly long service life of the catalysts, which is attributed to the trickle bed process: Even after several months of operation, no reduction in yield, no change in the range of by-products and no change in the isomer ratio were found. A further advantage is the ability to obtain isophoronediamine in high yield with a particular isomer ratio, within certain limits. In the process according to the invention, there is also no need for a preliminary reaction between isophoronenitrile and ammonia in order to form isophoroneimine, which was considered in several documents to be essential for obtaining a high yield and high selectivity in the aminating hydrogenation; according to the invention, by contrast, a solution of isophoronenitrile in the solvent used is mixed with ammonia directly upstream of the trickle bed reactor and the mixture is fed into the reactor.

The process according to the invention is illustrated in greater detail with the aid of the following Examples, without implying a limitation.

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Example 1

A reaction tube is filled with 200 ml of hydrogenation catalyst. The feed solution containing IPN and methanol, and liquid NH_3 , are pumped into the top of the reactor. Hydrogen also flows into the tube from the top. The reaction temperature is kept at 120°C by means of oil heating. The pressure is regulated at 60 bar. The liquid is collected in a separating vessel. The gas stream at the reactor inlet is adjusted so that a gas stream of 100 Nl/h is established downstream of the separating vessel.

The catalyst used was a commercially available solid Co catalyst (ca. 50% Co on silicate support) in the form of extrudates of 4-5 mm in diameter and length. The feed solution contained 24% by weight of IPN and 76% by weight of methanol. 130 ml/h thereof and 70 ml/h of NH_3 were mixed directly before being charged into the reactor, and the mixture was pumped into the reactor; the LHSV value was thus 1 h^{-1} . According to analysis of the product mixture, the yield of IPDA was 88.7%, based on IPN used. The product mixture also contained 5% of 2-aza-4,6,6-trimethylbicyclo[3,2,1]octane (= bicyclic compound) and 4.3% of 3,5,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane (= amidine).

Example 2

The experiment was carried out in the same experimental set-up as already described in Example 1, except that no gas stream was withdrawn from the separating vessel, so only the consumed hydrogen was replaced in order to keep the reaction pressure at 60 bar. The catalyst, liquid streams and liquid composition were the same as described in Example 1.

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Analysis of the product mixture of this experiment showed an IPDA yield of 89.2%, based on IPN used. The product mixture also contained 4.5% of bicyclic compound and 4.4% of amidine. Surprisingly, an even higher yield of IPDA and a reduction in the "bicyclic" by-product are made possible by the process without excess H_2 . This experiment was run for 2000 h with no observable loss of yield or change in the range of products.

Examples 3a and 3b

The experimental set-up used was the same as in Experiment 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. The H_2 stream was adjusted so that 100 NL/h of H_2 were withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were pumped into the reactor together with 50 ml/h of liquid NH_3 . 200 ml of cobalt catalyst were introduced as the catalyst. Two processes were studied. In the trickle bed process (3a), gas and liquid flowed through the reactor from top to bottom; in the bubble column process (3b), the reactor was in the flooded state and they flowed through it from bottom to top.

A yield of 87.1% was achieved in the trickle bed process (3a). After purification by distillation, the product purity was 99.8%; methyl-IPDA was detectable in an amount of only about 200 ppm.

A yield of 85.5% was achieved in the experiment by the bubble column process (3b). Purification by distillation gave a product purity of only 99.5%. Analysis showed that the pure product still contained 3000 ppm of methyl-IPDA. The methyl-IPDA by-product, which has a very adverse effect on the quality of the IPDA product, is practically inseparable by distillation.

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**Examples 4 to 6**

The experiments were carried out in the same experimental set-up and under the same reaction conditions as described in Example 1. Only the catalyst was varied. The results are given in the Table.

Example	Catalyst	Yield of IPDA (%)
4	5% Ru/ γ -Al ₂ O ₃	82.1
5	Ni	55.3
6	2% Pd/ γ -Al ₂ O ₃	4

Both the Ru and the Pd were applied to γ -Al₂O₃ extrudates as the support. Examples 5 and 6 clearly show that the yields obtained with Ni and Pd catalysts are not satisfactory compared with the process according to the invention.

Example 7

The low-boiling components, namely methanol, NH₃, H₂O and the bicyclic compound, were removed from 8770 g of the reaction solution of Example 2 by fractional distillation. 1292 g of a crude solution remained. 1190 g of IPDA were distilled off from this solution at a bottom temperature of 147°C and at a pressure of 20 mbar. This corresponds to an isolation yield of 87.3%. 98 g remained as the bottom product of the distillation. A further high-boiling fraction of 74 g was distilled off from this bottom product under reduced pressure (10 mbar) and at a temperature of 162°C. It contained 20% of IPDA and 74% of amidine. This resulting fraction of 74 g corresponds to 5.6% of the amount of IPN used.

In another experiment, which was carried out analogously to Example 2, the high-boiling fraction, i.e. 5.6% based on



the amount of IPN used, was added. After hydrogenation and separation of the low-boiling components and purification of the IPDA by distillation, the isolation yield found was 92.3%. Accordingly, it was possible to achieve a 5% increase in the isolation yield of IPDA by recycling the high-boiling fraction containing the amidine.

The yield of IPDA can be increased by a further 4% by catalytically hydrogenating the fraction containing the bicyclic compound (boiling point below that of IPDA) in a separate hydrogenation reactor under elevated temperature conditions.

Examples 8 to 11

The experimental set-up used was the same as in Experiment 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. No H₂ was withdrawn from the separating vessel. The feed solution contained 30% by weight of IPN and 70% by weight of methanol. 130 ml/h thereof were mixed with 50 ml/h of liquid NH₃ and pumped into the reactor. This experimental set-up was operated with a ruthenium catalyst, a cobalt catalyst and various combinations of the two. The results of this experiment are shown in the Table.

Example	Catalyst*)	Yield (%)	Isomer ratio cis:trans
8	200 ml Co	87.2	60:40
9	200 ml Ru	81.5	84:16
10	100 ml Ru + 100 ml Co	83.7	81:19
11	10 ml Ru + 190 ml Co	86.9	78:22

*) Ru catalyst: 5% Ru on γ -Al₂O₃ extrudates

Co catalyst: 50% Co on Al silicate extrudate

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By combining an Ru catalyst and a Co catalyst, the Ru catalyst being arranged as the upper layer in the reactor, it is possible to obtain IPDA with a high cis/trans isomer ratio in higher yield than by using an Ru catalyst on its own.

Example 12

A reaction tube (diameter 16 mm) of a trickle bed hydrogenation apparatus was filled with 120 ml of commercially available supported Co catalyst (Co on aluminium silicate, 50% by weight of Co; BET surface area (N_2) ca. 200 m^2/g). The experiment was carried out analogously to Example 1. The reaction temperature was adjusted to 110°C and the total pressure (sum of the partial pressures of H_2 , NH_3 and methanol) was adjusted to 60 bar. The starting solution contained 15% by weight of isophoronenitrile, 65% by weight of methanol and 20% by weight of ammonia. 100 ml of this starting solution were introduced onto the trickle bed per hour. After the solution had passed through the trickle bed, the reaction mixture contained the following (mol% based on isophorone-nitrile in the starting solution):

Isophoronediamine (IPDA)	89.2%
Isophoroneamino alcohol (IPAA)	2.1%
Amidine (see Example 1)	4.0%
Bicyclic compound (see Example 1)	3.8%

Example 13

Example 12 was repeated, the only difference being that another commercially available supported Co catalyst was used - Co on silica, 25% by weight of Co, BET surface area (N_2) ca. 200 m^2/g . The reaction mixture contained the following (data in mol% based on starting isophorone-nitrile):

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IPDA	87.4%
IPAA	1.2%
Amidine	4.3%
Bicyclic compound	5.1%

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Claims

1. A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophorone-nitrile, IPN) in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃-alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronediamine, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling through the catalyst bed being withdrawn at the bottom end of the reactor.
2. A process for the preparation of isophoronediamine according to Claim 1, characterized in that the hydrogenation is carried out at a temperature in the range 90 to 130°C and at a pressure of 5 to 8 MPa.
3. A process according to Claim 1 or 2, characterized in that methanol is used as the solvent, the mixture charged onto the catalyst bed contains 10 to 40% by weight, preferably 10 to 30% by weight, of isophorone-nitrile and 10 to 40% by weight, preferably 20 to 40% by weight, of ammonia and the mixture forms a homogeneous solution.



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4. A process according to one or more of Claims 1 to 3, characterized in that the hydrogenation catalyst used is a supported catalyst consisting essentially of an inorganic support material, preferably an oxide or silicate support material, and cobalt, the catalyst containing a total of 10 to 70% by weight of cobalt.
5. A process according to one or more of Claims 1 to 4, characterized in that a high-boiling fraction distilling after the isophoronediamine main fraction in the distillative working-up of the reaction mixture, and containing, in addition to isophoronediamine residues, 3,3,5-trimethyl-6-imino-7-azabicyclo[3,2,1]octane as the main component, is fed into the trickle bed reactor together with the mixture of isophoronitrile, solvent and ammonia.
6. A process according to one or more of Claims 1 to 5, characterized in that the aminating hydrogenation is carried out in a trickle bed reactor with an upper layer of a supported ruthenium catalyst, preferably ruthenium-on- γ -aluminium oxide, and a lower layer of a cobalt fixed bed catalyst arranged therein, it being possible for said upper layer and said lower layer - also to be arranged in two separate reactors connected in series in the stated order, instead of in one reactor.
7. A process according to Claim 6, characterized in that the volume of the ruthenium-containing fixed bed catalyst makes up 3 to 30%, preferably 5 to 20%, of the total volume of fixed bed catalysts.
8. A process according to one or more of Claims 1 to 7, characterized in that hydrogen is fed into the top or bottom end of the trickle bed reactor in an amount



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such that no hydrogen has to be discharged from the reactor and recycled.

9. A process according to one or more of Claims 1 to 8, characterized in that the mixture of isophorone-nitrile, solvent and ammonia, which preferably contains 10 to 30% by weight of isophoronenitrile, 20 to 40% by weight of ammonia and methanol as the solvent, is allowed to trickle over the catalyst bed of the reactor with an LHSV value (liquid hourly space velocity) of 0.8 to 1.5 h⁻¹.

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Process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine

Abstract

The invention relates to an improved process for the continuous preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine in high yield and high purity (isophoronediamine) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile) by aminating hydrogenation with hydrogen and ammonia in the presence of a fixed bed catalyst. Isophoronediamine is a raw material for the preparation of isophorone diisocyanate, an amine component for polyamides and a hardening component for epoxy resins.

According to the invention, the aminating hydrogenation is carried out by allowing a mixture of isophoronenitrile, ammonia and a C_1 - C_3 -alcohol, in the presence of hydrogen, to trickle over a trickle bed reactor provided with a Co and/or Ru fixed bed catalyst, at 3 to 8 MPa and at a temperature of 40 to 150°C, preferably 90 to 130°C, and working up the reaction mixture by distillation. Preferably, a high-boiling by-product fraction, containing a bicyclic amidine, is added to the mixture to be hydrogenated, thereby appreciably increasing the yield.

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purified, compressed and then recycled. The economy of this process is reduced both by the high operating pressure and by the technical cost of recycling the hydrogen. As established by the Inventors of the present invention - see Example 3b not according to the invention - this embodiment results in the increased formation of by-products which cannot easily be separated off, and to a lowering of the yield.

The object of the present invention thus consists in mitigating the disadvantages of the previously known processes for the preparation of isophoronediamine from isophoronenitrile using a reactor charged with a fixed bed catalyst, to the effect that the economy of the process is increased. In particular, the cost of the technical equipment should be reduced compared with the previously known processes. It should moreover be possible to obtain isophoronediamine in high yield and to isolate it from the reaction mixture in very pure form by means of conventional distillative measures.

A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile, IPN) has been found in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃- alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronenitrile, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling

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diamine (methyl-3-aminomethyl-3,5,5-trimethylcyclohexylamine) being formed in particular. Said methylisophoronediamine cannot be separated from isophoronediamine by distillation under conventional conditions, so the formation of said by-product must already be avoided in the preparation of the isophoronediamine crude product. Surprisingly, said by-product is only formed in very small amounts under the conditions of the process according to the invention. A further disadvantage of the bubble process is that hydrogen has to be added in excess in order to achieve saturation of the solution with H_2 ; this entails expensive recycling of the excess H_2 .

When the process according to the invention is carried out, hydrogen can be fed into the reactor either in excess or in an amount such that no hydrogen has to be discharged from the reactor and recycled. The introduction of hydrogen in excess is less preferable because the technical cost of separating off the excess H_2 , condensing ammonia and organic solvent contained in the discharged hydrogen, and compressing the purified hydrogen and recycling it is considerable and reduces the economy of the process on account of the higher investment demanded; moreover, an even lower yield of IPDA has been found compared with the process not using excess H_2 . Thus hydrogen is preferably introduced not in excess but only in the amount which is required to maintain the desired operating pressure.

The aminating hydrogenation is carried out at a pressure in the range 3 to 10 MPa, preferably at 5 to 8 MPa. Said moderate operating pressures, which are possible when using the claimed mixtures of isophoronenitrile, ammonia and solvent and the trickle bed process under the claimed temperature conditions, increase the economy, compared with processes which demand a high operating pressure, by

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lowering the level of investment required for the apparatus.

The requisite volume of fixed bed catalyst is governed by the LHSV value (liquid hourly space velocity) (dependent on the operating pressure, the temperature and the catalyst activity) which must be observed in order to achieve a quantitative conversion of isophoronenitrile.

Conventionally, the LHSV value is 0.5 h^{-1} or preferably above. The LHSV value is preferably between 0.8 and 1.5 h^{-1} . It is particularly good to attain an LHSV value in said range when the reaction is carried out at a temperature in the range between 90 and 130°C and at a pressure of between 5 and 8 MPa .

In addition to the abovementioned parameters of pressure, temperature and catalyst activity, the LHSV value is also influenced by the chosen concentration ratios of isophorone, ammonia and solvent and by the type of solvent used. The mixture charged onto the catalyst bed conveniently contains 10 to 40% by weight and preferably 10 to 30% by weight of isophoronenitrile and 10 to 40% by weight and preferably 20 to 40% by weight of ammonia. Solvents which can be used are methanol, ethanol, n-propanol and isopropanol. Methanol is the preferred solvent. The isophoronenitrile, ammonia and solvent are mixed in proportions such that an essentially homogeneous solution results. In principle, it is also possible to fall short of or exceed the abovementioned limiting values for ammonia and isophoronenitrile provided a homogeneous solution results. The use of a mixture containing less than 10% by weight of isophoronenitrile has an adverse effect on the economy of the process.

Apart from the constituents mentioned above, the mixture to be charged onto the catalyst can contain fractions, boiling above or below isophoronediamine, from the distillative

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ratio of the isophoronediamine prepared according to the invention, it has been found that the proportion of cis isomer formed is completely predominant when using a ruthenium catalyst: cis/trans isomer ratio according to Example 9 = 84 to 16. When using a supported cobalt catalyst, the other conditions being identical, the cis and trans isomers are formed in similar proportions: cis/trans isomer ratio according to Example 8 = 60 to 40.

It has furthermore been found that it is possible to prepare isophoronediamine with a cis/trans isomer ratio above that which is obtainable using a supported cobalt catalyst, and in high yield, by carrying out the aminating hydrogenation in a trickle bed reactor in which an upper layer of a supported ruthenium catalyst and a lower layer of a cobalt fixed bed catalyst are arranged. Particularly suitable catalysts are ruthenium-on- γ -aluminium oxide and a supported cobalt catalyst with an oxide or silicate support and a cobalt content of 10 to 70% by weight, based on the catalyst. Instead of having one reactor with two layers of different fixed bed catalysts arranged therein, it is also possible to connect two reactors in series, each containing only one fixed bed catalyst; in this case, the first reactor contains the ruthenium fixed bed catalyst and the second reactor contains the cobalt fixed bed catalyst. To obtain a high yield of isophoronediamine with the desired isomer ratio, it is advantageous if the ruthenium fixed bed catalyst, which is positioned first, makes up 3 to 30%, preferably 5 to 20%, of the total catalyst volume.

As explained earlier, the process according to the invention differs in essential respects from previously known processes of this kind, resulting in substantial advantages. By combining the use of a starting mixture of isophoronenitrile, ammonia and an alcoholic solvent and the trickle bed operation of the reactor provided with a fixed bed, it is possible to achieve both a high product yield of





Claims

1. A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophorone-nitrile, IPN) in which a mixture of isophoronenitrile, an organic solvent from the group comprising C₁- to C₃-alcohols, and ammonia is hydrogenated with hydrogen at a pressure in the range 3 to 10 MPa and at a temperature in the range 80 to 150°C, in the presence of at least one hydrogenation catalyst from the group comprising cobalt and/or ruthenium fixed bed catalysts, and the reaction mixture is worked up by distillation, said process being characterized in that the aminating hydrogenation is carried out in a trickle bed reactor, the mixture of isophoronenitrile, organic solvent and ammonia being charged onto the catalyst bed at the top end of the reactor, and the reaction mixture obtained after trickling through the catalyst bed being withdrawn at the bottom end of the reactor.
2. A process for the preparation of isophoronediamine according to Claim 1, characterized in that the hydrogenation is carried out at a temperature in the range 90 to 130°C and at a pressure of 5 to 8 MPa.
3. A process according to Claim 1 or 2, characterized in that methanol is used as the solvent, the mixture charged onto the catalyst bed contains 10 to 40% by weight, preferably 10 to 30% by weight, of isophorone-nitrile and 10 to 40% by weight, preferably 20 to 40% by weight, of ammonia and the mixture forms a homogeneous solution.



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Process For The Preparation of 3-Aminomethyl-3,5,5-Trimethylcyclohexylamine

The invention is directed towards an improved process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine, hereinafter also referred to as isophoronediamine or as its abbreviation IPDA, from 3-cyano-3,5,5-trimethylcyclohexanone, hereinafter also referred to as isophorone nitrile or as its abbreviation IPN, by means of aminating hydrogenation using hydrogen and ammonia in the presence of a fixed-bed catalyst. The process according to the invention permits the continuous preparation of isophoronediamine in high yield and in high purity.

Isophoronediamine is used as starting material for the preparation of isophorone diisocyanate, an isocyanate component for polyurethane systems, as an amine component for polyamides and as a curing agent for epoxy resins. Isophoronediamine is generally prepared from isophorone nitrile, the carbonyl group being converted into an amino group and the nitrile group being converted into an aminomethyl group in the presence of ammonia, hydrogen and conventional hydrogenation catalysts. The starting material isophorone nitrile can be obtained in known manner by addition of hydrogen cyanide to isophorone - see DE-OS 39 42 371.

According to the process for the preparation of isophoronediamine from isophorone nitrile described in US 3,352,913, the hydrogenation is carried out in the presence of ammonia and in the presence of known per se catalysts containing cobalt, nickel, iron or precious metals at 50°C to 150°C and at a pressure of at least 50 bar. In the examples, the hydrogenation is carried out in the presence of methanol as solvent, with suspension catalysts or fixed-bed catalysts being used. In addition to the desired isophoronediamine, large amounts of by-products are formed, such as in particular 3-aminomethyl-3,5,5-trimethylcyclohexanol (isophorone aminoalcohol, IPAA). The

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low yield and a considerable proportion of by-products have proved to be disadvantageous in this process.

In an endeavour to obtain a higher yield of IPDA and to
5 minimise the unavoidable accumulation of IPAA, DE-OS 30 11
656 discloses a two-step process wherein in the first step,
in the absence of catalyst and with excess ammonia, IPN is
converted into 3-cyano-3,5,5-trimethyliminocyclohexane
which, in the second step, is hydrogenated to IPDA. A
10 disadvantage of this process is that a special imine-
forming reactor is necessary in addition to the actual
hydrogenation reactor.

According to EP-B 0 042 119, a further improvement to the
15 process is seen in subjecting the isophorone nitrile, prior
to the reaction thereof with ammonia and hydrogen in the
presence of hydrogenation catalysts at temperatures of 10°C
to 120°C and pressures of 1 to 300 bar, to a preliminary
reaction with ammonia in the presence of inorganic and
20 organic ammonium-form ion exchangers serving as catalysts
promoting imine formation. Whereas the volume ratio of
isophorone nitrile to ammonia in the imine-forming step is
to be 1 to 0.5 up to 1 to 20, in the hydrogenation step
this ratio is increased to 1 to 10 up to 1 to 20. The
25 process, which can be carried out in trickle-bed reactors,
leads to a high yield of IPDA and to a high purity, but the
economic efficiency of the process is lowered by the use of
two different catalysts and by the high excess of ammonia,
which renders necessary very high pressures and
30 consequently an expensive hydrogenation apparatus.

EP-B 0 042 119 also discloses a comparative example wherein
isophorone nitrile and liquid ammonia are pumped from above
into a hydrogenation reactor filled with a commercially
35 available cobalt catalyst. The reaction system is
maintained at 270 bar by means of H₂; a certain gas stream
is established and a certain quantity of waste gas is

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transferred out. The reaction mixture leaving the reactor at the bottom is led away for working up by distillation. In this embodiment, in spite of an approximately quantitative conversion of the isophorone nitrile, only
5 48 % of isophorone diamine is obtained, together with many by-products. One cannot draw from this document an idea to pass through a trickle-bed reactor, instead of a mixture of isophorone nitrile and ammonia, a mixture containing isophorone, ammonia and organic solvent at considerably low
10 pressure and without the necessity of a previous imine-forming reaction.

Another process for the preparation of isophoronediamine is known from EP-A 0 449 089. In two reaction chambers
15 spatially separated from one another, a solution of isophorone nitrile in tetrahydrofuran is first of all reacted with excess ammonia on acidic metal catalysts, and in a second reaction chamber the reaction mixture is hydrogenated at high pressure with hydrogen in the presence
20 of excess ammonia on catalysts containing cobalt, nickel, ruthenium and/or other precious metals and optionally basic components. In the example, the mixture leaving the first reaction step is passed from below upwards through the hydrogenation reactor; the reactor is operated as a bubble
25 reactor. One cannot derive from this document instructions to use the reactor also as a trickle-bed reactor and immediately to supply thereto a mixture of isophorone nitrile, ammonia and an organic solvent.

30 EP-A 0 394 967 discloses a process for the amination of carbonyl nitriles and iminonitriles and also includes the preparation of isophoronediamine from isophorone nitrile. The starting material is first converted into the aminonitrile under conditions of reductive amination, that
35 is, in the presence of hydrogen, ammonia and a hydrogenation catalyst at moderate temperatures; the nitrile group is then converted into an aminomethyl group

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in the presence of a hydrogenation catalyst which actively hydrogenates nitrile groups at a more elevated temperature. The process can be carried out both in reactors with the use of suspension catalysts and in reactors with the use of
5 fixed-bed catalysts. Although this process can be carried out at low pressures, it is regarded as a considerable disadvantage that a rigidly maintained temperature programme has to be operated during the two stages of the reaction, as a result of which the space-time yield and
10 consequently the economic efficiency of the process decline considerably. Furthermore, unless special promoters are used in addition, the product quality does not meet the requirements, owing to the generally excessively high content of 3-cyano-3,5,5-trimethylaminocyclohexane, which
15 cannot be separated by distillation.

A lowering of the pressure during the preparation of isophoronediamine by aminating catalytic hydrogenation of isophorone nitrile is also possible, according to JP-A-4-
20 300852, by carrying out hydrogenation in the presence of a supported catalyst containing ruthenium. But this document relates only to conditions for the suspension hydrogenation and not those where a fixed-bed catalyst is used.

25 A general idea of an industrially used process for the preparation of isophorone diamine from isophorone nitrile has become known from SRI International Report No. 1D "Isocyanates" by YU-REN CHIN (July 1983). In the process described here, a mixture of isophorone nitrile, methanol
30 and ammonia is sent together with hydrogen over a fixed-bed reactor containing a supported catalyst - cobalt on kieselguhr. The catalyst bed in the embodiment described is always flooded (bubble column). The operating pressure is given as 150 bar. Furthermore, hydrogen is added in excess
35 and after the reaction this excess has to be separated from the reaction mixture, purified and then returned after compression. Both the high operating pressure and the

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technical expenditure of returning the hydrogen lessen the economic efficiency of this process. As the inventor of the present invention has found - see Example 3b, not according to the invention - this embodiment results in an increased
5 formation of by-products which are difficult to separate, and in a decrease in the yield.

The object of the present invention, accordingly, is to correct the disadvantages of the previously known processes
10 for the preparation of isophoronediamine from isophorone nitrile using a reactor filled with a fixed-bed catalyst, in such a way as to increase the economic efficiency of the process. In particular the expenditure on the technical equipment is to be decreased as compared with the
15 previously known processes. Isophoronediamine is moreover to be obtained in high yield and is to be isolable in very pure form from the reaction mixture by means of conventional distillation steps.

20 A process has been found for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) from 3-cyano-3,5,5-trimethylcyclohexanone (isophorone nitrile, IPN), wherein a mixture of isophorone nitrile, an organic solvent selected
25 from the C₁- to C₃- alcohols and ammonia, at a pressure in the range from 3 to 10 MPa and at a temperature in the range from 80 to 150°C, is hydrogenated by hydrogen in the presence of at least one hydrogenation catalyst selected from the cobalt and/or ruthenium fixed-bed catalysts and
30 the reaction mixture is worked up by distillation, characterised in that the aminating hydrogenation is carried out in a trickle-bed reactor, the mixture of isophorone nitrile, organic solvent and ammonia being introduced at the upper end of the reactor onto the
35 catalyst bed and the reaction mixture obtained after the reactants have trickled through the catalyst bed being withdrawn at the lower end of the reactor.

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The reaction according to the invention is carried out in a conventional trickle-bed reactor. The construction of reactors of this kind is known to the person skilled in the art. The fixed-bed catalyst is arranged in the form of one or more layers in a container; the reactor has in addition devices for tempering the layers of catalyst in order to ensure that the required temperature is maintained in the respective layer of catalyst. Instead of a single trickle-bed reactor, several trickle-bed reactors may also be connected one behind the other, with the reaction mixture leaving the first reactor being added again at the head of the second reactor. The trickle-bed reactor or reactors has/have in addition suitable devices for charging the reactants, in the present instance the mixture containing isophorone nitrile, ammonia and solvent as well as the hydrogen, and also devices for distributing the liquid on the surface of the first catalyst bed and, finally, suitable discharging devices for the reaction mixture leaving the reactor.

It is an essential characteristic of the process according to the invention that the reaction mixture being hydrogenated trickles over the catalyst bed and that within the catalyst bed there is also a volume of gas large enough to enable hydrogen to be transported through the liquid film at the catalyst surface. It has been found that the trickle-bed mode of operation is instrumental in attaining a high product yield and above all is responsible for a high selectivity. If the reactor is operated not as a trickle-bed reactor but as a bubble reactor, and the catalyst bed is therefore always flooded, under otherwise identical reaction conditions as regards temperature, pressure and concentration of the reactants, a considerably smaller yield of isophoronediamine is obtained; the bubble mode of operation also leads to a different range of by-products, with the formation in particular of methylisophoronediamine (methyl-3-aminomethyl-3,5,5-

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trimethylcyclohexylamine). The said methylisophoronediamine cannot be separated from isophoronediamine by distillation under conventional conditions, so that the formation of the above-mentioned by-product during the preparation of the
5 isophoronediamine raw product must be avoided.

Surprisingly, the above-mentioned by-product is formed in only very small quantities under the conditions of the process according to the invention. A further disadvantage of the bubble mode of operation is that hydrogen has to be
10 added in excess in order to saturate the solution with H_2 , the consequence of which is an expensive recirculation of the excess H_2 .

When the process according to the invention is carried out,
15 hydrogen can be supplied to the reactor either in excess or in a quantity such that no hydrogen is discharged from the reactor and has to be recirculated. Supply of the hydrogen in excess is less preferred, because the technical expenditure required for the separation of the H_2 excess,
20 for the condensation of ammonia and organic solvents contained in the hydrogen discharged, and for the compression of the purified hydrogen and recirculation of the latter is considerable and lessens the economic efficiency of the process because of the greater investment
25 entailed thereby. Moreover, an even smaller yield of IPDA was found compared with the operation without an H_2 excess. Hydrogen is therefore preferably not supplied in excess, but only in such a quantity as is necessary for maintaining the required operating pressure.

30 The aminating hydrogenation is carried out at a pressure within the range of from 3 to 10 MPa, preferably at 5 to 8 MPa. As a result of the above-mentioned moderate operating pressures, which are feasible when the mixtures of
35 isophorone nitrile, ammonia and solvent according to the Claims are used and the trickle-bed mode of operation under the temperature conditions according to the Claims is

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applied, the economic efficiency is increased as compared with processes requiring a high operating pressure, while the apparatus requires a smaller volume of investment.

- 5 The required volume of fixed-bed catalyst is determined by the LHSV value (liquid hourly space velocity) - which depends on the operating pressure, on the temperature and on catalyst activity - which has to be maintained in order to achieve a quantitative conversion of isophorone nitrile.
- 10 The LHSV value is generally equal to or, better, above 0.5 h^{-1} . The LHSV value is preferably between 0.8 and 1.5 h^{-1} . It is particularly good to achieve an LHSV value within the last-named range when the reaction is carried out at a temperature within the range of between 90°C and
- 15 130°C and at a pressure of between 5 and 8 MPa.

In addition to the above-mentioned variables pressure, temperature and activity of the catalyst, the LHSV value is also influenced by the chosen ratios of concentrations of

20 isophorone nitrile, ammonia and solvent, and on the nature of the solvent used. The mixture applied to the catalyst bed usefully contains from 10 to 40 wt.%, preferably 10 to 30 wt.% of isophorone nitrile, and from 10 to 40 wt.%, preferably 20 to 40 wt.%, of ammonia. The solvents used may

25 be methanol, ethanol, n-propanol and isopropanol. The preferred solvent is methanol. Isophorone nitrile, ammonia and the solvent are mixed in a ratio such that the resulting solution is substantially homogeneous. In principle, the limiting values for ammonia and isophorone

30 nitrile given above can even be fallen short of or exceeded, provided that a homogeneous solution results. The use of a mixture containing less than 10 wt.% of isophorone nitrile has an adverse effect on the economic efficiency of the process.

35

In addition to the above-mentioned components, the mixture applied to the catalyst may contain fractions boiling

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higher or lower than isophoronediamine, which are obtained from the process of distilling the reaction mixture withdrawn from the trickle-bed reactor. Such fractions may also contain, besides residues of isophoronediamine, those by-products from which isophorone is formed once more under the conditions of the reaction. The yield of isophoronediamine can be distinctly increased by returning such fractions to the mixture to be introduced. It is particularly advantageous to pass the fraction boiling after isophoronediamine, which besides residues of isophoronediamine contains 3,3,5-trimethyl-6-imino-7-azabicyclo-[3,2,1]-octane as the main product, to the trickle-bed reactor together with the mixture of isophorone nitrile, ammonia and solvent. By returning the fraction containing the above-mentioned by-product - a bicyclic compound having an amidine structure - it is possible to increase considerably the yield of isophorone and consequently to increase the economic efficiency of the process.

20

The catalysts to be used according to the invention are cobalt fixed-bed catalysts and/or ruthenium fixed-bed catalysts. These catalysts are generally available as pellets, extrudates or other shapes. It is particularly advisable to use supported catalysts wherein cobalt or ruthenium are on a support having a sufficiently large specific surface. The specific surface of the supported catalysts which can be used according to the invention is generally within the range of between 5 and 500 qm/g (measured by the BET method using nitrogen).

The cobalt content of the supported catalysts is generally between 10 and 70 wt.% and preferably between 30 and 50 wt.%, referred to the supported catalyst. The surface of the catalyst, which in many cases is an oxide or silicate material, is partly or substantially completely covered with cobalt and, because of the preparative conditions,

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cobalt oxide may also be present beneath the surface. Examples of suitable supporting material are oxides selected from silicon dioxide, aluminium oxide and titanium dioxide, also silicates such as aluminium silicate and calcium silicate, as well as naturally occurring and synthetically prepared zeolites and glass frits. Although commercially available supported catalysts having a high Co content, such as catalysts containing 50 wt.% Co on aluminium silicate, are described as being substantially completely covered with Co, it was found that catalysts having a different support but the same specific surface and the same Co content influence the selectivity and the range of by-products. Evidently the surface of the support of the catalyst is at least partly accessible and influences the catalytic process.

Supported catalysts containing ruthenium as the catalytically active component for reasons of cost generally contain only a small per cent by weight of ruthenium, usually between 0.5 and 10 wt.%, preferably between 2 and 5 wt.%. The production of the above-mentioned Co catalysts and Ru catalysts, which generally includes an impregnating step, a drying step and forming step, is known to those skilled in the art.

It has been found that when a cobalt supported catalyst is used, isophoronediamine is obtainable by the process according to the invention in higher yield than in the case when a ruthenium supported catalyst is used. This is surprising, because in the above-mentioned documents JP-A 4-300852 and EP-A 394 967, ruthenium catalysts were described as being particularly active with regard to the hydrogenation of the nitrile group, which is more difficult to hydrogenate compared with the carbonyl group.

It is generally known that isophoronediamine exists in the form of cis and trans isomers; see Die Angewandte

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Makromolekulare Chemie 153 (1987) 1-13, No. 2502. In the analysis of the ratio of the isomers of isophoronediamine prepared according to the invention, it was found that the cis isomer is very predominantly formed when a ruthenium catalyst is used: ratio of cis/trans isomers as in Example 9 (84 : 16). Under otherwise identical conditions, but with the use of a cobalt supported catalyst, the cis isomer and the trans isomer are formed in a similar quantity: ratio of cis/trans isomers as in Example 8 (60 : 40).

10

It was also found that isophoronediamine containing a ratio of cis/trans isomers above that obtainable with the use of a cobalt supported catalyst can be prepared in high yield if the aminating hydrogenation is carried out in a trickle-bed reactor wherein are arranged an upper layer consisting of a ruthenium supported catalyst and a lower layer consisting of a cobalt fixed-bed catalyst. Particularly suitable catalysts are ruthenium on γ -aluminium oxide and a cobalt supported catalyst having an oxide or silicate support and a cobalt content of from 10 to 70 wt.%, referred to the catalyst. Instead of one reactor containing two layers of different fixed-bed catalysts arranged therein, two reactors can also be connected one behind the other, each containing only one fixed-bed catalyst; in this case the first reactor contains the ruthenium fixed-bed catalyst and the second reactor contains the cobalt fixed-bed catalyst. To obtain a high yield of isophorone diamine containing the required ratio of isomers, it is advantageous that the ruthenium fixed-bed catalyst placed in the first position constitute 3 to 30 %, preferably 5 to 20 %, of the total volume of the catalyst.

As explained above, the process according to the invention differs in important respects from previously known processes of the same type and these differences result in considerable advantages. By combining the use of a starting mixture of isophorone nitrile, ammonia and an alcoholic

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solvent and the trickle-bed mode of operation of the reactor equipped with a fixed bed, it is possible to obtain a high product yield of isophoronediamine as well as a high selectivity. The formation of undesirable by-products such as methylisophoronediamine which, because it is difficult to separate off, adversely affects the product quality, is largely avoided by the procedure for carrying out the reaction. Through the previously mentioned combination of features essential to the invention, it is possible to carry out the aminating hydrogenation at moderate pressures, so that the expenditure on the pressure apparatus necessitated thereby is far lower than in the case of an apparatus designed for high pressures. Since, contrary to previously known processes using a reactor containing a fixed-bed catalyst, according to the invention it is unnecessary to use hydrogen in excess and consequently to have to purify and to recirculate the excess, expensive devices for separating, purifying and recirculating the H_2 excess are not required. Another considerable advantage of the process according to the invention is the unexpectedly high useful life of the catalysts, which can be attributed to the trickle bed mode of operation. Even after several months of operation, neither a decrease in yield nor an alteration in the range of by-products nor an alteration in the ratio of isomers was detected. A further advantage is that isophoronediamine having a particular ratio of isomers within certain limits can be obtained in high yield. In the process according to the invention, a preliminary reaction between the isophorone nitrile and ammonia to form the isophorone imine is also unnecessary. In some documents this preliminary reaction has been considered essential in order to obtain a high yield and high selectivity during the aminating hydrogenation; according to the invention, in contrast, a solution of the isophorone nitrile in the solvent used is mixed with ammonia immediately in front of the trickle-bed reactor and the mixture is fed into the reactor.

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The process according to the invention is further explained, but is not limited, by the following Examples.

Example 1

5

A reaction tube is filled with 200 ml of hydrogenation catalyst. The solution introduced, which contains IPN and methanol, as well as liquid NH_3 , is pumped in at the top of reactor. The hydrogen also flows into the tube from above.

10 The reaction temperature is maintained at 120°C by oil heating. The pressure is adjusted to 60 bar. The liquid is collected in a receiving vessel. The gas flow at the inlet to the reactor is adjusted so that after the receiving vessel a gas flow of 100 Nl/h is established.

15

The catalyst used was a commercially available Co whole contact (approx. 50 % Co on a silicate support) in the form of extrudates of 4 to 5 mm in diameter and length. The introduced solution contained 24 wt.% IPN and 76 wt.%

20 methanol. 130 ml/h of this solution and 70 ml/h of NH_3 were mixed immediately prior to the addition to the reactor, and the mixture was pumped into the reactor; the LHSV value was therefore 1 h^{-1} . The analysis of the product mixture indicated a yield of 88.7 % IPDA, referred to IPN used. The

25 product mixture contained in addition 5 %
2-aza-4,6,6-trimethylbicyclo-[3,2,1]-octane (= bicyclic compound) and 4.3 % 3,3,5-trimethyl-6-imino-7-azabicyclo-[3,2,1]-octane (= amidine).

30 Example 2

The experiment was carried out in the same experimental unit as that already described in Example 1, except that no flow of gas was transferred out of the receiving vessel, so

35 that only the spent hydrogen was replenished in order to maintain the reaction pressure of 60 bar. Catalyst, liquid

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flows and liquid composition were the same as those described in Example 1.

The analysis of the product mixture obtained in this experiment indicated a yield of 89.2 % IPDA, referred to IPN used. The product mixture contained in addition 4.5 % bicyclic compound and 4.4 % amidine. Surprisingly, in the mode of operation without an H₂ excess, an even higher yield of IPDA and a decrease in the yield of the by-product "bicyclic compound" are made possible. This experiment was carried out for 2000 h, with no loss of yield nor altered range of products being observed.

Examples 3a and 3b

15

The experimental unit used was the same as in Example 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. The H₂ flow was adjusted so that H₂ was transferred out of the receiving vessel at a rate of 100Nl/h. The introduced solution contained 30 wt.% IPN and 70 wt.% methanol. 130 ml/h of this solution and in addition 50 ml/h of liquid NH₃ were pumped into the reactor. 200 ml of cobalt contact was added as catalyst. Two modes of operation were investigated. In the trickle-bed mode of operation (3a) gas and liquid flowed through the reactor from top to bottom; in the bubble column mode of operation (3b) the passage was from the bottom to the top of the reactor in the flooded state.

30 In the trickle-bed mode of operation (3a) a yield of 87.1 % was obtained. After purification by distillation, the product purity was 99.8 %; methyl IPDA was detectable only in a quantity of about 200 ppm.

35 In the experiment using the bubble column mode of operation (3b) a yield of 85.5 % was obtained. Purification by distillation resulted in a product purity of 99.5 %. The

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analysis showed that 3000 ppm of methyl IPDA was still present in the pure product. The by-product methyl IPDA, which has a very adverse effect on the product quality of IPDA, is not in practice separable by distillation.

5

Examples 4 to 6

The experiments were carried out in the same experimental unit and under the same reaction conditions as described in Example 1. Only the catalyst was varied. The results are shown in the Table.

	Example	Catalyst	Yield of IPDA (%)
15	4	5 % Ru/ γ -Al ₂ O ₃	82.1
	5	Ni	55.3
	6	2 % Pd/ γ -Al ₂ O ₃	4

20

The Ru and Pd were each applied to γ -Al₂O₃ extrudates as supports. Examples 5 and 6 show clearly that the yields obtained by using Ni catalysts and Pd catalysts are not satisfactory compared with the yield from the process according to the invention.

25

Example 7

8770 g of the reaction solution from Example 2 was freed from the low-boiling components methanol, NH₃, H₂O and bicyclic compound by means of fractional distillation. A crude solution weighing 1292 g remained. 1190 g of IPDA was distilled off from this solution at a temperature of 147°C at the bottom of the column and at a pressure of 20 mbar. This corresponds to a yield of 87.3 % of isolated product. 98 g remained at the bottom of the distillation

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column. A further high-boiling fraction of 74 g in weight was distilled off from this bottom material at reduced pressure (10 mbar) and at a temperature of 162°C. This fraction contained 20 % IPDA and 74% amidine. This fraction of 74 g obtained corresponds to 5.6 % of the initially introduced quantity of IPN.

In an additional experiment, which was carried out in a manner similar to Example 2, the high-boiling fraction corresponding to 5.6 % of the initially introduced quantity of IPN was added. After the hydrogenation and separation of the low-boiling components and purification of IPDA by distillation, a yield of 92.3 % of isolated product was obtained. As a result of recirculating the high-boiling fraction containing the amidine, the yield of IPDA isolated could therefore be increased by 5 %.

By means of a catalytic hydrogenation of the fraction containing the bicyclic compound (boiling point below that of IPDA) under conditions of elevated temperature in a separate hydrogenation reactor, it is possible to increase the yield of IPDA by a further 4 %.

Examples 8 to 11

The experimental unit used was the same as in Example 1. The hydrogenation pressure was 60 bar and the reaction temperature was 120°C. No H₂ was transferred out of the receiving vessel. The introduced solution contained 30 wt.% IPN and 70 wt.% methanol. 130 ml/h of this solution and in addition 50 ml/h of liquid NH₃ were mixed and then pumped into the reactor. This variation of the experiment was carried out using a ruthenium catalyst, a cobalt catalyst and different combinations of these. The results of this experiment are shown in the Table.

Example	Catalyst *)	Yield (%)	Ratio of isomers cis:trans
5	8 200 ml Co	87.2	60 : 40
	9 200 ml Ru	81.5	84 : 16
10	10 100 ml Ru + 100 ml Co	83.7	81 : 19
10	11 10 ml Ru + 190 ml Co	86.9	78 : 22

*) Ru catalyst: 5 % Ru on γ -Al₂O₃ extrudates
 15 Co catalyst: 50 % Co on Al silicate extrudate

Through the combination of an Ru catalyst with a Co catalyst, with the Ru catalyst being arranged as the upper layer in the reactor, IPDA containing a high ratio of cis to trans isomers is successfully obtained in a higher yield than that obtained when only an Ru catalyst is used.

Example 12

25 A reaction tube (diameter 16 mm) of a trickle-bed hydrogenation apparatus was filled with 120 ml of a commercially available Co supported catalyst (Co on aluminium silicate, 50 wt.% Co; BET (N₂) surface area approx. 200 m²/g). The experiment was carried out in a
 30 manner similar to Example 1. The reaction temperature was adjusted to 110°C; the total pressure (sum of the partial pressures of H₂, NH₃ and methanol) was adjusted to 60 bar. The introduced solution contained 15 wt.% isophorone nitrile, 65 wt.% methanol and 20 wt.% ammonia. This
 35 introduced solution was applied at a rate of 100 ml per hour to the trickle bed. After the passage of the solution through the trickle bed, the reaction mixture contained the

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following (mol-%, referred to isophorone nitrile in the solution introduced):

	isophoronediamine (IPDA)	89.2 %
5	isophorone aminoalcohol (IPAA)	2.1 %
	amidine (see Example 1)	4.0 %
	bicyclic compound (see Example 1)	3.8 %

Example 13

10

Example 12 was repeated, with the only variation that a different commercially available Co supported catalyst was used - Co on silica, 25 wt.% Co, BET (N₂) surface area approx. 200 m²/g. The reaction mixture contained the
15 following (data in mol-%, referred to isophorone nitrile introduced):

	IPDA	87.4 %
	IPAA	1.2 %
20	amidine	4.3 %
	bicyclic compound	5.1 %

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Claims

1. A process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA)
5 from 3-cyano-3,5,5-trimethylcyclohexanone (isophorone nitrile, IPN), wherein a mixture of isophorone nitrile, an organic solvent selected from the C₁- to C₃- alcohols and ammonia, at a pressure in the range from 3 to 10 MPa and at a temperature in the range
10 from 80 to 150°C, is hydrogenated by hydrogen in the presence of at least one hydrogenation catalyst selected from the cobalt and/or ruthenium fixed-bed catalysts and the reaction mixture is worked up by distillation, characterised in that the aminating
15 hydrogenation is carried out in a trickle-bed reactor, the mixture of isophorone nitrile, organic solvent and ammonia being introduced at the upper end of the reactor onto the catalyst bed and the reaction mixture obtained after the reactants have trickled through the
20 catalyst bed being withdrawn at the lower end of the reactor.
2. The process for the preparation of isophorone diamine according to claim 1, characterised in that the
25 hydrogenation is carried out at a temperature in the range of from 90 to 130°C and at a pressure of from 5 to 8 MPa.
3. The process according to claim 1 or 2, characterised
30 in that the solvent used is methanol, the mixture introduced onto the catalyst bed contains from 10 to 40 wt.%, preferably 10 to 30 wt.%, of isophorone nitrile and from 10 to 40 wt.%, preferably 20 to 40 wt.%, of ammonia and the mixture forms a homogeneous
35 solution.

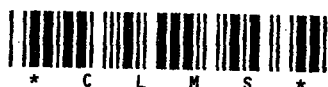


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4. The process according to one or more of claims 1 to 3, characterised in that the hydrogenation catalyst used is a supported catalyst which consists substantially of an inorganic supporting material, preferably an oxide or silicate supporting material, and cobalt, the catalyst containing in total from 10 to 70 wt.% of cobalt.
5. The process according to one or more of claims 1 to 4, characterised in that a high-boiling fraction which distils off after the isophoronediamine main fraction during the working up of the reaction mixture by distillation and which contains, in addition to residues of isophoronediamine, 3,3,5-trimethyl-6-imino-7-azabicyclo-[3,2,1]octane as main component together with the mixture of isophorone nitrile, solvent and ammonia, is passed to the trickle-bed reactor.
6. The process according to one or more of claims 1 to 5, characterised in that the aminating hydrogenation is carried out in a trickle-bed reactor having an upper layer arranged therein consisting of a ruthenium supported catalyst, preferably ruthenium on γ -aluminium oxide, and a lower layer consisting of a cobalt fixed-bed catalyst, the said upper layer and the said lower layer possibly also being arranged, instead of in one reactor, in two separate reactors arranged one behind the another in the sequence referred to.
7. The process according to claim 6, characterised in that the volume of the fixed-bed catalyst containing ruthenium constitutes 3 to 30%, preferably 5 to 20%, of the total volume of fixed-bed catalyst.

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8. The process according to one or more of claims 1 to 7,
characterised in that hydrogen is supplied at the
upper or lower end of the trickle-bed reactor in a
quantity such that no hydrogen is discharged from the
reactor and has to be recirculated.
9. The process according to one or more of claims 1 to 8,
characterised in that the mixture of isophorone
nitrile, solvent and ammonia, which preferably
contains from 10 to 30 wt.% of isophorone nitrile and
from 20 to 40 wt.% of ammonia and methanol as solvent,
is caused to trickle over the catalyst bed of the
reactor at an LHSV value (liquid hourly space
velocity) of from 0.8 to 1.5 h⁻¹.



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Process for the preparation of 3-aminomethyl-3,5,5-trimethylcyclohexylamine

5

Abstract

The invention relates to an improved process for the continuous preparation of 3-aminomethyl-3,5,5-trimethyl-
10 cyclohexylamine in high yield and high purity (isophorone-diamine) from 3-cyano-3,5,5-trimethylcyclohexanone (isophoronenitrile) by aminating hydrogenation with hydrogen and ammonia in the presence of a fixed bed catalyst. Isophoronediamine is a raw material for the
15 preparation of isophorone diisocyanate, an amine component for polyamides and a hardening component for epoxy resins.

According to the invention, the aminating hydrogenation is carried out by allowing a mixture of isophoronenitrile,
20 ammonia and a C₁-C₃-alcohol, in the presence of hydrogen, to trickle over a trickle bed reactor provided with a Co and/or Ru fixed bed catalyst, at 3 to 8 MPa and at a temperature of 40 to 150°C, preferably 90 to 130°C, and working up the reaction mixture by distillation.
25 Preferably, a high-boiling by-product fraction, containing a bicyclic amidine, is added to the mixture to be hydrogenated, thereby appreciably increasing the yield.

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