



Diamine purification method

The present invention relates to a process for the purification of diamines obtained by hydrogenation of dinitriles.

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It relates more particularly to the purification of hexamethylenediamine obtained from the hydrogenation of adiponitrile.

10 Diamines are important chemical intermediates, in particular in the manufacture of polymers. Thus, hexamethylenediamine is an important monomer in the manufacture of polyamides, in particular for the production of poly(hexamethylene adipamide).

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For the manufacture of such polyamides, it is important and necessary for the hexamethylenediamine to exhibit very high purity characteristics. This is because the presence of impurities causes difficulties in obtaining
20 a high degree of polymerization and results in particular in polymers with a yellowish colour. Furthermore, significant difficulties are encountered in the use of these polymers, in particular in the preparation of yarns or fibres, such as, for example, a
25 high degree of breakage on spinning and drawing. In addition, these impurities can result in irregularities in the structure of the polymer and the cross section of the yarns, producing unevennesses in dyeing which are very harmful to the quality of the textile
30 surfaces.

These characteristics of dyeing evenness are essential in the production of textile surfaces for clothing or for surface coverings.

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Consequently, many studies have been carried out over very many years in order to obtain hexamethylenediamine with the highest possible purity or at least comprising



the minimum of compounds which bring about declines in characteristics indicated above, when these were able to be identified.

- 5 Thus, a first process proposed which makes it possible to purify hexamethylenediamine consists in distilling this diamine in the presence of a base. Such a process is disclosed, for example, in Patents US 2 987 452, EP 497 333 and GB 1 238 351. However, there are
- 10 disadvantages to this process, such as, for example:
- the control of the solubility of the bases,
 - the incineration of the heavy compounds formed during the distillation,
 - the need to use special materials which are
- 15 resistant to corrosive media in the construction of the plants.

Other processes have been provided, such as, for example, the distillation of hexamethylenediamine in the presence of water or of an inert compound

20 (WO 98/34900, WO 98/34901, WO 98/34902).

One of the aims of the present invention is to provide a novel process for the purification of diamines and more particularly of hexamethylenediamine which makes

25 it possible to obtain significant removal of the troublesome compounds and thus a diamine which can be used in particular in processes for the manufacture of polyamides, more particularly polyamides for the manufacture of yarns or fibres.

30 To this end, the invention provides a process for the purification of aliphatic diamines which consist in treating the diamine or the reaction medium resulting from the synthesis of the diamine with hydrogen or a

35 gas comprising hydrogen in the presence of a catalyst comprising an element chosen from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, nickel and cobalt.

In a preferred embodiment of the invention, the diamine to be purified is present in the reaction medium resulting from its synthesis. The synthetic processes most generally used employ a hydrogenation of dinitrile compounds, such as the hydrogenation of adiponitrile to hexamethylenediamine, in the presence of a hydrogenation catalyst, such as Raney metals, for example Raney nickel.

10 In this embodiment, the hydrogenation treatment of the invention is carried out directly on the reaction medium resulting from the synthesis stage, optionally after separation of the unconverted dinitrile.

15 In another embodiment, the hydrogenation treatment of the invention can be carried out with a diamine extracted from the reaction medium, for example by distillation.

20 Whatever the embodiment of the treatment, the catalytic system used is advantageously of the supported catalyst type. The catalytic element or elements mentioned above are deposited, precipitated or adsorbed on a generally inert support according to techniques known to a person skilled in the art. Any support conventionally used in the field of supported catalysis can be used in the present invention.

30 By way of indication, mention may be made, as examples of a support suitable for the invention, of charcoals, titanium, zirconium or magnesium oxides, alumina or the like.

The concentration by weight of catalytic element is generally between 0.1% and 16% with respect to the element/support catalytic system.

Likewise, the hydrogenation stage of the invention can be carried out according to the usual techniques.

Preferably, the techniques used are either the use of a stationary or fluidized bed catalytic system or suspending the catalyst in the reaction medium and recovering the catalyst by filtration or separation by settling.

The conditions for the implementation of the hydrogenation reaction are those known to a person skilled in the art for hydrogenation reactions. By way of indication, the reaction temperature is between 50°C and 200°C, the hydrogen pressure being between 0.1 MPa and 5 MPa. Furthermore, it is possible to use a gas comprising hydrogen or to add, to the reaction medium, a hydrogen-generating compound.

After hydrogenation, the diamine is advantageously extracted from the medium by distillation, according to the usual techniques, or the hydrogenation treatment of the invention can be carried out directly on the reaction medium.

In another preferred embodiment of the invention, the process for the purification of the diamines is carried out concomitantly with the stage of distillation of the diamines.

In this embodiment, the reaction medium resulting from the hydrogenation of the dinitriles to diamines is fed, after extraction of the unreacted dinitriles, to a stage of distillation of the diamines, generally in the lower part of a distillation column. In such a process, the pure diamine is recovered at the column top.

According to the invention, a portion of the liquid stream circulating in the distillation column is withdrawn and fed to a hydrogenation reactor. The hydrogenation stage in accordance with the invention is carried out in this reactor. The resulting stream is fed to the distillation column, advantageously to a

region situated upstream or downstream of the withdrawal region described above.

5 The process of the invention applies more particularly to the purification of linear or branched aliphatic diamines which comprise from 2 to 10 carbon atoms.

10 Hexamethylenediamine and methylpentanediamine, which are obtained by hydrogenation of adiponitrile or of methylglutaronitrile, are the preferred diamines among these diamines.

15 The purification process of the invention makes it possible to remove impurities present in these compounds, such as, in particular, tetrahydroazepine (THA).

20 Other impurities can be present in the diamine, such as hexamethylene or iminocyanocyclopentane (ICCP), for example.

25 In order to assess the quality of the diamines and in particular of hexamethylenediamine, in particular for use as monomer in the production of polyamide, it is conventional to determine the polarographic index of this compound, referred to as POLI.

30 This polarographic index represents in particular the concentration of imine compounds in the medium. It is determined by polarography and is expressed in moles of imine functional group per tonne of sample to be quantitatively determined.

35 Other details and advantages of the invention will become more clearly apparent in the light of the examples given below by way of illustration. These examples have a purely indicative nature.

Example 1

Hexamethylenediamine obtained by hydrogenation of adiponitrile in the presence of Raney nickel was distilled.

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The concentration by weight of the main impurities is as follows:

% by weight of THA: 0.113%

POLI, mmol/t: 7900

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The hexamethylenediamine is introduced into a stirred reactor comprising a palladium-on-charcoal catalyst comprising 0.5% of palladium. The catalyst is sold by Engelhard.

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The hydrogen pressure is 18 bar.

After reacting at 120°C for 120 minutes, the hexamethylenediamine recovered comprises 0.0043% of THA and exhibits a POLI of 4000.

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Example 2

A similar test to Example 1 was carried out in treating a hexamethylenediamine comprising 0.1066% of THA and a POLI of 12 000.

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After treating at 120°C for 120 minutes, the THA content fell to 0.0072% and the POLI to 1900.

30 Example 3

A purification of a hexamethylenediamine comprising 0.0406% of THA and a POLI of 4671 was treated at a temperature of 135°C for 60 minutes according to the procedure of Example 1.

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The hexamethylenediamine obtained exhibits a THA concentration of 0.00036% and a POLI of 244.

CLAIMS

1. Process for the purification of aliphatic diamines, characterized in that it comprises a stage of hydrogenation of the diamine in the presence of a catalyst comprising an element chosen from the group consisting of platinum, palladium, ruthenium, rhodium, iridium, nickel and cobalt.
2. Process according to Claim 1, characterized in that the catalyst of the hydrogenation is a supported catalyst, the support of the catalytic element being chosen from the group consisting of charcoals, titanium, zirconium and magnesium oxides, and alumina.
3. Process according to Claim 1 or 2, characterized in that the diamine is extracted from the medium after hydrogenation by distillation.
4. Process according to one of the preceding claims, characterized in that the hydrogenation treatment is carried out on a reaction medium resulting from the synthesis of the diamine.
5. Process according to Claim 4, characterized in that the diamine is synthesized by hydrogenation of a dinitrile compound.
6. Process according to Claim 5, characterized in that the dinitrile present in the resulting reaction medium is separated before the stage of hydrogenation of the said resulting reaction medium.
7. Process according to one of the preceding claims, characterized in that the hydrogenation of the diamine is carried out with a catalyst in the form

of a stationary or fluidized bed.

- 5 8. Process according to one of Claims 1 to 6,
characterized in that the hydrogenation of the
diamine is carried out in the presence of a
catalyst suspension.
- 10 9. Process according to one of the preceding claims,
characterized in that the diamine or the reaction
medium from the synthesis is fed to a distillation
column and in that a portion of the liquid stream
circulating in the distillation column is
withdrawn from a withdrawal point situated along
the distillation column and is subjected to a
15 hydrogenation stage in the presence of a catalyst
comprising an element chosen from the group
consisting of platinum, palladium, ruthenium,
rhodium, iridium, nickel and cobalt, the said
stream withdrawn after hydrogenation being fed
20 back to the column upstream or downstream of the
withdrawal point.
- 25 10. Process according to one of the preceding claims,
characterized in that the diamine is chosen from
the group consisting of hexamethylenediamine and
methylpentanediamine.