

**PROCESS FOR THE TREATMENT OF LACTAMS AND PROCESS FOR**  
**THE PURIFICATION OF A LACTAM**

The present invention relates to a process  
5 for the treatment of lactams.

It relates more particularly to a process  
which makes it possible to modify the chemical nature  
of the impurities present in a medium comprising  
lactams, either in order to convert them into harmless  
10 compounds or into compounds which can be extracted in  
subsequent purification operations.

Lactams and in particular  $\epsilon$ -caprolactam, a  
monomer in the preparation of polycaproamide (PA6), are  
prepared according to several synthetic processes.

15 The most widely used process industrially  
employs a Beckmann rearrangement reaction of  
cyclohexanone oxime with sulphuric acid or oleum,  
followed by the neutralization of the medium with  
ammonia and then by the separation and purification of  
20 the lactam.

Another process proposed for the synthesis of  
the lactam consists in carrying out a cyclizing  
hydrolysis of an aminoalkylnitrile, such as  
6-aminocapronitrile in the preparation of  
25  $\epsilon$ -caprolactam. This reaction can be carried out in the  
presence or in the absence of a catalyst and in the  
liquid or vapour phase. This reaction releases ammonia.

The latter process is disclosed in numerous patents. Mention may be made, by way of example, of Patents US 2,357,484, US 2,301,964 and FR 2,029,540.

The process for the preparation of lactams by  
5 the vapour-phase cyclizing hydrolysis of aminonitriles is also disclosed in Patent Applications EP 0,659,741 and WO 96/22974.

The conversion of aminocapronitrile to  $\epsilon$ -caprolactam in the presence of water is exemplified  
10 in Patents US 2,245,129 and EP 0,150,295.

Generally, in the latter processes, aminocapronitrile is obtained by hemihydrogenation of adiponitrile by known processes disclosed in particular in Patents DE 836,938, DE 848,654 or US 5,151,543.

15 As the main use of the lactams produced is the manufacture of polymers or copolymers and more particularly of polyamides or copolyamides intended to be shaped for the production of yarns, fibres, moulded items or films, the purity of the lactams must comply  
20 with specific and strict specifications.

Thus, one of the major specifications is the UV absorbance of an aqueous caprolactam solution represented by a UV number. This number is determined by measurement of the absorbance of an aqueous  
25 caprolactam solution (50% by weight) at a wavelength of 290 [lacuna] in a cell with a width of 1 cm.

In order to obtain a low UV number, it is known in particular to subject the lactam to a hydrogenation in the presence of a catalyst.

Thus, German Patent 1,253,716 discloses the  
5 hydrogenation of caprolactam obtained by the Beckmann rearrangement process in the presence of a suspended hydrogenation catalyst.

Likewise, Patent DE 1,004,616 and East German Patent 75 083 discloses a process for the hydrogenation  
10 of caprolactam after treatment with active charcoal and ion-exchange resins.

Patent US 5,496,941 discloses a process for the purification of the lactam obtained by cyclizing hydrolysis of an aminonitrile. This process comprises a  
15 stage of hydrogenation of the lactam in the presence of a hydrogenation catalyst. A solvent, such as water or an alcohol, is preferably present.

The hydrogenation stage is carried out on the isolated lactam separated from the cyclizing hydrolysis  
20 reaction mixture. This is because this process requires the separation from the cyclizing hydrolysis medium of the compounds which are more volatile and less volatile than caprolactam. This separation therefore requires the removal of the ammonia produced and the  
25 distillation of the caprolactam.

These various processes give satisfactory results in the production of a lactam with a low UV

number. However, this purification stage has a disadvantageous effect on the general economics of the process. This is because the efficiency of the catalyst decreases very quickly. This short cycle time of the catalyst requires frequent replacement of the latter and results in the risk of a lactam of unsatisfactory purity being obtained at the end of the catalyst cycle. This process is even more disadvantageous when the catalyst cannot be regenerated by a simple and economic process.

One of the aims of the present invention is in particular to overcome these disadvantages by providing conditions for implementing the hydrogenation stage which make it possible to greatly increase at least the cycle time of the hydrogenation catalysts and thus the general economics of the process for the manufacture of lactams of high purity.

To this end, a subject-matter of the invention is a process for the treatment of a liquid medium comprising at least one lactam, in particular for decreasing the UV number of the lactam, which consists in subjecting the said medium to a hydrogenation in the presence of a hydrogenation catalyst. The process is characterized by the presence of dissolved ammonia in the said medium.

The presence of ammonia makes it possible to significantly increase the cycle time of the hydrogenation catalyst.

To prevent or limit the condensation reaction of the lactam, the temperature for implementation of the hydrogenation will be carried out at a temperature which makes it possible to have hydrogenation kinetics compatible with an industrial use but which is as low as possible. This temperature is preferably less than 150°C, in particular when the lactam is  $\epsilon$ -caprolactam. The temperature is advantageously between 50°C and 150°C, preferably between 70°C and 130°C.

The concentration of ammonia in the medium can vary within wide proportions but is advantageously greater than 10 g/l, preferably between 50 g/l and 200 g/l.

The medium comprising the lactam comprises, according to one characteristic of the invention, a solvent chosen, for example, from alcohols comprising from 1 to 3 carbon atoms. However, the preferred solvents of the invention are water and water/alcohol mixtures. In addition, it is possible to carry out the hydrogenation of a molten lactam without a solvent other than ammonia.

The treatment process of the invention is carried out in the presence of a hydrogenation catalyst. This catalyst can be suspended in the medium

or present in the form of a fixed bed or fluidized bed deposited in a tubular reactor. The catalyst can be a bulk or supported catalyst.

The preferred catalysts of the invention are  
5 those derived from one or more metals chosen from the group consisting of iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium and platinum.

Use may be made, as catalyst support, of, for example, active charcoal, aluminas, silicas, titanium  
10 oxides, rare earth metal oxides, such as lanthanum or cerium oxides, or zirconium or zinc oxides. Use may also be made of a mixture of these oxides or mixed oxides. Use may also be made, as catalyst support, of magnesium, aluminium or boron silicates or phosphates.

15 In the case of a supported catalyst, the concentration of catalytic element, expressed as weight of metal, is advantageously between 0.01 and 80% of the total weight of the catalyst, preferably from 0.1 to 50% by weight.

20 Furthermore, the catalysts can comprise additives which improve the catalytic effect, such as, for example, zirconium, manganese, copper, chromium, titanium, molybdenum, tungsten, iron or zinc.

These doping elements usually represent from  
25 0 to 15% and preferably from 0.1 to 10% by weight with respect to the catalytically active metal.

The manufacture of these supported or non-supported catalysts is described in numerous documents, such as Ullmann's Encyclopaedia of Industrial Chemistry, Volume A5, pages 348-350, 5th edition.

5           The hydrogenation treatment is carried out either at atmospheric pressure or at a pressure of between 1 and 100 bar.

As is disclosed in the cited documents, this treatment with hydrogen makes it possible to decrease  
10 in particular the UV number of caprolactam. However, the presence of dissolved ammonia makes it possible to obtain a low UV number even after a lengthy continuous operating time for the process, that is to say to treat a large amount of lactam without having to replace or  
15 regenerate the catalyst present in the reactor or by minimizing the consumption of catalyst consumed per kilogram of lactam treated.

The invention applies to the treatment of lactams of various origins, such as those obtained by  
20 the Beckmann rearrangement reaction, lactams obtained by depolymerization of polyamide or lactams obtained by cyclizing hydrolysis of an aminonitrile, for example.

However, the invention applies more particularly to the treatment of the lactam solutions  
25 obtained by hydrolysis of an aminonitrile, either in the vapour phase or in the liquid phase.

Thus, the process of the invention applies more particularly in the hydrogenation stages disclosed in the processes for the purification of caprolactam obtained by cyclizing hydrolysis of an aminonitrile, in 5 the vapour phase or in the liquid phase, disclosed in Patent US 5,496,941 and Patent Application WO 98/05636.

Another subject-matter of the invention is a process for the purification of a lactam obtained by cyclizing hydrolysis of an aminonitrile in the vapour 10 phase and more particularly a process for the purification of  $\epsilon$ -caprolactam obtained by cyclizing hydrolysis in the vapour phase of 6-aminocapronitrile.

This process consists:

- in cooling the hydrolysis reaction mixture to a 15 temperature of less than 150°C,
- in subjecting the cooled reaction mixture, at least partially comprising the ammonia formed, to a hydrogenation in the presence of a hydrogenation catalyst,
- 20 - after hydrogenation, in optionally separating the ammonia from the reaction mixture,
- and in subjecting the reaction mixture to one or more purification processes, in order to obtain a lactam which satisfies the desired purity specifications.

25 The hydrogenation treatment, carried out directly on the reaction mixture resulting from the cyclizing hydrolysis, makes it possible to use the

ammonia produced in order to carry out this hydrogenation under satisfactory economic conditions, in particular with a cycle time of the catalyst which is compatible with an economic industrial use. If  
5 necessary, it is possible to adjust the concentration of ammonia, either by addition of ammonia or partial evaporation of the ammonia produced by the hydrolysis reaction.

In addition, it also has the effect of  
10 reducing the deterioration in the UV number which is observed during the separation of the light fractions from the reaction mixture, in particular during the distillation of the ammonia and optionally of the water or of the solvent present in the mixture.

15 According to the invention, the lactam recovered after the hydrogenation treatment and optionally the separation of the ammonia can be subjected to various known purification stages described in numerous patents, such as, for example  
20 Patent US 5,496,941, WO 98/05636, and the like.

The possible treatments are oxidation, distillation in acidic or basic medium, liquid/liquid extraction, treatment over ion-exchange resins, or crystallization, for example.

25 All these treatments are given solely by way of example, it is possible for all of them to be carried out or just some of them, in any order.

Other advantages and details of the invention will become more clearly apparent in the light of the examples given below solely by way of indication, without any limiting effect on the invention.

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**Comparative Example 1**

An aqueous solution composed of 60% of caprolactam resulting from a cyclizing hydrolysis of 6-aminocapronitrile, the conditions of which are  
10 disclosed in French Patent Application 2,714,379, is continuously introduced into a hydrogenation reactor at 80°C under 25 bar charged with 5% of Raney nickel as hydrogenation catalyst.

This caprolactam solution no longer comprises  
15 ammonia, the latter having been distilled off on leaving the cyclizing hydrolysis stage.

The UV number of this measured solution is 24 at 290 nm.

The UV number of the solution exiting from  
20 the hydrogenation stage is periodically monitored in order to determine the efficiency of the hydrogenation and thus the activity of the catalyst.

The results are shown in the table hereinbelow.

|                |      |      |      |       |       |
|----------------|------|------|------|-------|-------|
| Operating time | 24 h | 48 h | 72 h | 120 h | 192 h |
| UV number      | 9.7  | 22   | 22   | 23    | 23    |

The results show that the catalyst has lost its activity from the 2nd day of operating.

### Example 2

5            Example 1 is repeated but using as solution of caprolactam in water to which has been added ammonia, in order to obtain a solution comprising 90 g/l of ammonia and 61% of caprolactam.

10           The caprolactam solution, before treatment, exhibits a UV number, measured at 290 nm, of 1.6.

The results are shown in the following table.

|                |      |       |       |
|----------------|------|-------|-------|
| Operating time | 48 h | 120 h | 192 h |
| UV number      | 0.8  | 0.8   | 0.8   |

15           These results clearly show the effect of the presence of ammonia on the preservation of the activity of the catalyst. Thus, after operating for eight days, the UV number of the resulting solution is identical to that obtained at the beginning of the operation. The hydrogenation treatment retains its efficiency.

**Example 3**

The caprolactam solution treated by hydrogenation according to the conditions of Example 1 is the reaction mixture resulting from the reaction of 6-aminocapronitrile with water. This mixture was subjected to rapid cooling to a temperature of 80°C at the reactor outlet, in order to prevent polycondensation of the caprolactam. The mixture comprises 90 g/l of ammonia produced by the reaction. This mixture exhibits a UV number at 290 nm of 1.8. The mixture is subjected directly to a hydrogenation according to the conditions of Example 1. The results obtained are given in the table hereinbelow.

| Hydrogenation<br>operating time | 48 h | 120 h | 192 h |
|---------------------------------|------|-------|-------|
| UV number                       | 0.8  | 0.8   | 0.8   |

Furthermore, the aminocapronitrile which has not been converted to caprolactam is completely hydrogenated to hexamethylenediamine, even after the hydrogenation catalyst has been operating for 192 hours.

**CLAIMS**

1. Process for the treatment of a liquid medium comprising at least one lactam which consists in  
5 subjecting the said medium to a hydrogenation in the presence of a hydrogenation catalyst, characterized in that the medium comprises dissolved ammonia.

2. Process according to claim 1, characterized in that the medium comprises a solvent  
10 chosen from the group consisting of alcohols having from 1 to 3 carbon atoms, water and water/alcohol mixtures.

3. Process according to claim 1 or 2, characterized in that the hydrogenation treatment is  
15 carried out at a temperature of less than 150°C.

4. Process according to claim 3, characterized in that the hydrogenation treatment is carried out at a temperature of between 50 and 150°C, preferably between 70°C and 130°C.

20 5. Process according to one of the preceding claims, characterized in that the concentration of dissolved ammonia is greater than 10 g/l.

6. Process according to one of the  
25 preceding claims, characterized in that the hydrogenation catalyst is chosen from the group consisting of iron, nickel, cobalt, ruthenium, rhodium,



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palladium, osmium, iridium and platinum, taken alone or in combination.

7. Process according to claim 6,  
characterized in that the catalyst is a bulk catalyst  
5 or a supported catalyst.

8. Process according to either of claims 6  
and 7, characterized in that the catalyst comprises at  
least one additive chosen from the group consisting of  
zirconium, manganese, copper, chromium, titanium,  
10 molybdenum, tungsten, iron and zinc.

9. Process according to either of claims 7  
and 8, characterized in that the support of the  
catalyst is chosen from the group consisting of active  
charcoals, aluminas, silicas, titanium oxide, rare  
15 earth metal oxides, zirconium oxides, zinc oxides,  
magnesium and/or aluminium silicates or phosphates, and  
boron phosphates.

10. Process according to one of claims 7 to  
9, characterized in that the concentration of catalytic  
20 element in the supported catalysts is between 0.01% and  
80% by weight, expressed as metal element, with respect  
to the weight of catalyst.

11. Process according to one of the  
preceding claims, characterized in that the lactam is  
25 obtained by cyclizing hydrolysis of an aminonitrile.



12. Process according to one of the preceding claims, characterized in that the lactam is  $\epsilon$ -caprolactam.

13. Process for the purification of lactams  
5 obtained by cyclizing hydrolysis of an aminonitrile, characterized in that it consists in:

- converting an aminonitrile to the lactam by reaction with water in the vapour phase and production of ammonia,
- 10 - cooling the cyclizing hydrolysis reaction mixture to a temperature of less than 150°C,
- subjecting the said cooled reaction mixture, at least partially comprising the ammonia produced by the reaction, to a hydrogenation in the presence of a  
15 hydrogenation catalyst according to one of claims 1 to 12,
- in optionally separating the ammonia from the reaction mixture,
- and optionally subjecting the said reaction mixture  
20 to one or more stages of separation and of purification of the lactam, in order to obtain a lactam which satisfies the desired purity specifications.

14. Process according to claim 13,  
25 characterized in that the stages of separation or of purification of the lactam are chosen from the group consisting of distillation, oxidation, treatment over



ion-exchange resins, distillation in the presence of acid or of base, crystallization or liquid/liquid extraction, one or more of these stages being carried out in any order.



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This Sheet Has Been Replaced

