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RECLAIMING ϵ -CAPROLACTAM FROM CARPET WASTE

The invention relates to the reclamation of ϵ -caprolactam from carpet waste, and more particularly to a method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam has been obtained by means of depolymerisation of nylon-6 originating from carpet waste.

Such a method is disclosed in US-A-5169870. Said patent specification describes a method in which nylon-6 from carpet made from nylon-6 fibers is depolymerised in the presence of phosphoric acid and steam. The phosphoric acid serves as depolymerisation catalyst. The carpet is traditionally composed of nylon-6 tufts and of a, for example, jute, polypropylene or latex backing. Also, the latex may contain fillers. The post-consumer carpet will also contain various sorts of dirt. These materials are present during depolymerization, due to the difficulty of fully separating the nylon-6 from the non-nylon-6 material, according to US-A-5169870. This non-nylon-6 material will result in impurities which have to be removed from the ϵ -caprolactam in order to obtain ϵ -caprolactam reusable for making nylon-6. According to US-A-5169870 this so-called "carpet" ϵ -caprolactam should be purified in the following manner. The volatile components and added steam, which are released during depolymerisation, are condensed and fractionated to separate some non-aqueous contamination from this crude mixture containing water and ϵ -caprolactam. This crude water- ϵ -caprolactam mixture is then further purified by adding potassium permanganate for an oxidative treatment in order to oxidize the impurities which are not removed by the fractionation.

The addition of potassium permanganate is disadvantageous because solid manganese dioxide (MnO_2) is

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produced during the purification. This solid manganese dioxide has to be removed by means of, for example, filtration. The removal of manganese dioxide is troublesome, particularly in a continuous process. A
5 further disadvantage is that manganese dioxide is a valueless by-product which causes environmental pollution.

The object of this invention is to provide a method of purifying contaminated ϵ -caprolactam obtained from carpet waste in which the quality of the final
10 product, ϵ -caprolactam, is at least as good as that of the ϵ -caprolactam obtained by the known method described above but which method does not result in the production of solid manganese dioxide.

This object is achieved in that the mixture of
15 water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.

It has been found that, if the contaminated ϵ -caprolactam is purified by the method according to the invention, the final product has the same or better
20 quality features as ϵ -caprolactam obtained by the method described in US-A-5169870. These quality features are for example °Hazen (ISO 8112), PM number, Abs 290 (ISO 7059), Alkalinity VI bases (ISO 8661) and PAN (ISO 8660).

An additional advantage of the process according
25 to the invention is that hydrogen is easier to obtain and to process than potassium permanganate. The method according to the invention therefore also offers an economically and also environmentally attractive process for reclaiming ϵ -caprolactam from carpet waste.

30 Another advantage of the process according to the invention will be elucidated below. When starting from different types of nylon-6 containing carpets, it appeared that ϵ -caprolactam obtained from some carpets and purified with KMnO_4 according to US-A-5169870 shows a visual
35 turbidity (hazy shine in contrast with the normally observed water clear solution) when dissolved in water.



This turbidity indicates impurities which make the ϵ -caprolactam not suitable for further reuse in making nylon-6 fibres. The turbidity makes it for example impossible to measure the extinction at 290 nm according to ISO 7059. The origin of the turbidity is found in the presence of different mixtures of non-nylon-6 material/compounds present in the carpet (waste), for example lubricants, anti-statics, dye stuffs, anti-stain compounds, flame retardants and backing material. Because some carpets give rise to this turbidity and others do not, and because it is desirable to process all post consumer nylon-6 containing carpets with one process, the turbidity problem may arise randomly when purifying ϵ -caprolactam obtained from these nylon-6 containing carpets. This turbidity problem does not occur when the ϵ -caprolactam is hydrogenated according to the invention (a water clear solution is obtained). Thus with the process according to the invention all nylon-6 containing carpets can be used as nylon-6 source without such a turbidity problem.

It is known per se to purify mixtures containing water and ϵ -caprolactam by means of hydrogenation. EP-A-411455, CS-A-160312 and J-Stresinka and J. Mokry, PetraChemia, 20 No. 5-6, 171-177 (1970), describe for instance a purification by means of hydrogenation of an ϵ -caprolactam/water mixture. The ϵ -caprolactam as described in these references is however obtained via the Beckmann rearrangement of cyclohexanone oxime in fuming sulphonic acid (hereafter called "rearrangement" ϵ -caprolactam).

Hydrogenation as a purification method of ϵ -caprolactam obtained by depolymerization of nylon-6 fibres was never considered as a suitable method for purification. This consideration was based on the fact that this ϵ -caprolactam will contain another kind of contamination due to the additives present in nylon-6 fibers (such as the earlier mentioned lubricants, anti-statics, anti-stain compounds, dye stuffs and flame

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retardants) as, for example, described in JP-A-52108991. Another reason why more contamination is present in ϵ -caprolactam obtained by depolymerization compared to "rearrangement" ϵ -caprolactam is because the

5 depolymerization is, as a rule, conducted at higher temperatures compared to the temperature of the rearrangement reaction. Higher temperature results in more side reactions of the ϵ -caprolactam resulting in a higher degree of contamination. Especially "carpet" ϵ -caprolactam

10 will contain even more contaminants due to the non-nylon-6 materials (additives and backing) and dirt present in the, as a rule used, carpets. Because of the presence of these contaminations until now "carpet" ϵ -caprolactam is purified with an oxidizing agent, preferable with KMnO_4 , a

15 purification method described for example in JP-A-52108991 and JP-A-52111585 for ϵ -caprolactam from nylon-6. This is also clear from DE-C-851195, which teaches that ϵ -caprolactam obtained from heavily contaminated nylon-6 sources will have to be purified with KMnO_4 . It is

20 therefore surprising that hydrogenation can be used advantageously as described above for treating "carpet" caprolactam.

The hydrogenation by the method according to the invention can be carried out in any way known to the

25 person skilled in the art. As a rule the hydrogenation is carried out in the presence of a heterogeneous hydrogenation catalyst. The heterogeneous catalyst can be contacted with the hydrogen-containing reaction mixture in various ways. Hydrogenation may for example take place in

30 a stirred tank in which the catalyst particles are suspended in the mixture to be purified (slurry phase process). A drawback of the slurry phase process is that the catalyst particles and the purified mixture must be separated in an additional process step after the

35 hydrogenation reaction. Such a separation step, for example by means of filtration, is cumbersome. Therefore, the hydrogenation is more preferably effected in a fixed-



bed reactor with the catalyst being fixed in the reactor, so that the additional step for separation of the catalyst and reaction mixture can be dispensed with. An example of a possible fixed-bed reactor is the trickle-phase reactor.

5 The hydrogenation catalyst may be any known heterogeneous hydrogenation catalyst. Examples of such catalysts are ruthenium on aluminium oxide, rhodium on aluminum oxide, platinum on carbon, palladium ob carbon, Raney nickel or nickel on silicone oxide. Preferably, the
10 hydrogenation catalyst contains nickel.

 Suitable nickel catalysts with a support usually have a nickel content between 5 and 80 wt.%. The catalyst may contain in addition to nickel some activators such as Zr, Mn, Cu or Cr. The activator content is generally
15 between 1 and 20 wt.%.

 If palladium-containing heterogeneous catalysts are used, the palladium content will generally be between 0.01 and 10 wt.%.

 If a fixed-bed reactor is used, catalysts are
20 employed in which an active metal is on the external surface of a support. Such catalysts can be prepared using the method in which a pre-formed support (for instance pellets, spheres or ribbons) is contacted with an aqueous solution of a metal salt (for example the metal nitrate)
25 dried, and subsequently calcined.

 The size of the pre-formed support that is chosen will be as small as possible without the pressure drop across the fixed bed becoming unacceptable. For example the average particle diameter of pellets for a
30 support is usually between 1 and 5 mm.

 Catalyst activation, if applied, can be effected in any known manner. In Example 3 of EP-A-411455, for instance, the catalyst is activated by passing gaseous hydrogen over the catalyst for 8 hours while increasing
35 the temperature stepwise from 80 to 200°C. The activation can also be carried out in situ at a temperature of 70-100°C in which the catalyst is contacted with water (or a



water/ ϵ -caprolactam mixture) in which hydrogen is dissolved. The activation pressure may be between 0.1 and 10 MPa.

5 The hydrogenation residence time depends on the method that is chosen for contacting the heterogeneous catalyst with hydrogen and the water- ϵ -caprolactam mixture. If a reactor is chosen in which the catalyst is fixed in the reactor (fixed-bed reactor), the residence time is generally more than 10 seconds, and in particular
10 more than 30 seconds, and in general the residence time is less than 10 minutes and in particular less than 7 minutes.

The required amount of heterogeneous hydrogenation catalyst in case a slurry phase process is
15 used can easily be determined by the person skilled in the art and is as a rule between 0.01 and 5% by weight of the total reaction mixture.

The amount of ϵ -caprolactam in the mixture to be purified may vary between 10 and 95% by weight.
20 Preferably, this concentration is between 30 and 75% by weight of the constituents of depolymerised material.

During the hydrogenation, the hydrogen pressure is between 0.1 and 10 MPa and is preferably between 0.2 and 2 MPa. During the hydrogenation, the temperature is as
25 a rule between 20 and 160°C.

Optionally, the mixture could be hydrogenated by first saturating the mixture with hydrogen and then bringing the saturated mixture into contact with the hydrogenation catalyst under hydrogenation conditions. The
30 catalyst is preferably a metal on a heterogeneous support as described above. The reactor is preferably a packed-bed reactor over which continuously the with hydrogen saturated ϵ -caprolactam/water mixture is led. Under reaction conditions the degree to which the hydrogenation
35 reaction mixture is saturated with hydrogen is generally 50-100%. Preferably, the degree of saturation of the reaction mixture is 80-100%.

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The nylon-6 containing carpet waste used in the process according to the invention is normally composed of nylon-6 tuft on a backing of for example jute, polypropylene, latex or nylon-6 and fillers like calcium carbonate, clay and hydrated aluminum oxide. The nylon-6 carpet waste may be industrial nylon-6 carpet waste obtained as waste in the production of the nylon-6 containing carpets. The process according to the invention is particularly suitable for post consumer nylon-6 carpet waste as explained above. Mixture of industrial- and post consumer nylon-6 containing carpet waste may be used. The mixture of carpet waste may also contain small amounts of polyethylene terephthalate (PET), nylon-6.6, wool, cotton and other materials which are used for face fibre applications in carpets due to imperfection of the sorting procedure when collecting post consumer carpets.

The carpets can be pretreated mechanically reducing the carpet to a smaller size. A large portion of any non-nylon-6 materials, including the above mentioned backing materials, may be removed in a separator. Examples of suitable mechanical separators are supplied by the Schirp Corporation as Type 75, Type 38CIII, Type 58, Type 38CII, Type 66, Type 71, Type 66-L, Type 57, Type 67S600, Type 64 and Type 62C. After this pretreatment, the fraction mainly containing nylon-6 material can be fed to the depolymerization.

The depolymerization reaction can be carried out with or without a catalyst. In JP-A-53143585, for example, an uncatalysed depolymerisation is described, in which nylon-6 is depolymerised in the presence of superheated steam. As a rule, the depolymerisation is carried out in the presence of a catalyst. Examples of catalysed depolymerisations are also described in JP-A-53132585. Suitable catalysts are for example inorganic acids for example phosphoric acid and boric acid or organic acids for example benzenesulphonic acid, phthalic acid, adipic acid, and acetic acid. Phosphoric acid is in practice the



most preferred.

The depolymerisation is as a rule carried out at a temperature of 230-325°C and preferably between 250-280°C. The superheated steam is preferably fed to the reactor at a temperature of 250-500°C. The steam is preferably supplied from the beginning of the depolymerisation in order to take up the volatile ϵ -caprolactam formed so as to obtain a condensate containing from 1 to 40% by weight of ϵ -caprolactam. The content of phosphoric acid in the depolymerisation reactor is as a rule between 0.1-10 wt.% and, preferably, between 2-7 wt.%, based on the total nylon-6 fed to the reactor.

The mixture of water and crude ϵ -caprolactam, obtained after the depolymerisation, can be submitted immediately to the hydrogenation step. According to the invention, preferably one or more additional purification steps are carried out before or after the crude water- ϵ -caprolactam mixture is purified by hydrogenation. A possible additional purification step which can be carried out before the hydrogenation is a distillation in which by-products released or formed during the depolymerisation can be removed, as is described in US-A-5169870. Another additional purification step is a purification via an ion exchanger, as for example described in JP-A-52108991 and by J. Stresinka and J. Mokry, PetraChemia, 20 No. 5-6, 171-177 (1970). Other purification steps known to the person skilled in the art, such as, for example, extraction and/or absorption over active carbon can also be applied.

As a final purification step, the ϵ -caprolactam is recovered by separating it from the water, the final, purified ϵ -caprolactam being obtained. This separation can be carried out in any way known to the person skilled in the art. The ϵ -caprolactam may, for example, be recovered by means of crystallisation or hot melt crystallisation. Another known method is distillation or concentration by evaporation, optionally in the presence of a small amount



of sodium hydroxide solution.

It has been found that a purification which includes (1) an extraction with an organic solvent, (2) a hydrogenation according to the invention, (3) an ion
5 exchange treatment and (4) a final distillation will result in ϵ -caprolactam which can be directly reused in making nylon-6 suitable for making carpet fibres or any other application. Preferably the purification is conducted in the above given sequence.

10 The extraction can be conducted in the same manner as in the purification for "rearrangement ϵ -caprolactam". Suitable extraction organic solvents are practically immiscible with water. Examples of these solvents are ethers, for example ethyl-, n-propyl-,
15 butylether, dioxane; aromatic solvents for example benzene, toluene, xylene, cumene and ethylbenzene; aliphatic solvents for example cyclohexane, isopropylcyclohexane and ethylcyclohexane; chloroalkanes, for example chloroform, mono-, di-, tri-, tetrachloro-
20 ethane.

The ion exchange treatment can be conducted in the same manner as in the purification for "rearrangement" ϵ -caprolactam as described in for example the above mentioned references. Preferably first a cationic ion
25 exchanger is used and subsequently an anionic ion exchanger is used.

The final distillation can be conducted in the same manner as in the purification for "rearrangement" ϵ -caprolactam.

30 The invention is explained further by reference to the following, non-restrictive examples.

The 'permanganate number' (=PM number) is defined as the number of seconds elapsing after the addition of 1.00 ml of potassium permanganate 0.0020 Mol/l
35 to 100 ml of caprolactam solution (3.00 g/100 ml) of 293 K (=20°C) until the moment at which the colour of this solution becomes equal to the colour of a standard



5 solution. The standard solution consists of 3000 mg of cobaltnitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 12 mg of potassium dichromate in 1 l water. The PN number may only be used for comparison purposes of the Experiments and Examples as described below.

Example I

10 A mixture of 570 g of nylon-6 fibre and 30 g non-nylon-6 carpet waste, mechanically separated from industrial carpet waste (carpet waste: nylon-6 face fibre, latex adhesive, polypropylene backing and CaCO_3), were depolymerised in a Hastalloy C steel reactor in the presence of 21 ml of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 120
15 min and the temperature was held at 280-290°C during the reaction. 3800 g of distillate were collected and were composed of 15% by weight of ϵ -caprolactam, most of the remainder being composed of water. The mixture was concentrated by evaporation to a lactam concentration of
20 30%.

300 g of this concentrated mixture (the mixture to be purified) were introduced into a 0.5 l stirred autoclave together with 0.4 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was
25 hydrogenated for 1 hour under a hydrogen pressure of 0.5 MPa at 90°C and 900 rpm.

Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a
30 fluted filter.

5 ml of 50% by weight sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately
35 0.13-0.2 Kpa. The specifications of the distilled ϵ -caprolactam are reported in Table 1.

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Comparative experiment A

The mixture to be purified from Example I was diluted to a 15% by weight solution. 333 g of this mixture were stirred for 30 min together with 33.6 g of 3% by weight potassium permanganate solution at 40°C and a pH of 7.0. The pH was adjusted to a pH of 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO₂) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 35 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 1.7 g.

The ε-caprolactam-containing mixture was then distilled in the same way as described in Example 1. The specifications of the ε-caprolactam formed in this way are reported in Table 1.

Comparative experiment B

333 g of the mixture to be purified from Example I were immediately distilled in the same way as in Example I. The specifications of the ε-caprolactam purified in this way are reported in Table 1.

TABLE 1

	<u>I</u>	<u>A</u>	<u>B</u>
° Hazen ⁽¹⁾			
(ISO 8112)	1	1	26
PM number ⁽²⁾	>10,000	>10,000	177
Abs 290 ⁽³⁾			
(ISO 7059)	0.04	0.51	3.32
Alkalinity ⁽⁴⁾	0.01	0.04	0.50
Vl bases ⁽⁵⁾	0.08	0.38	0.61
(ISO 8661)			

⁽¹⁾ ° Hazen is a measure of the colour; a lower number implies a better product.



- (2) PM number (permanganate number) is a measure of the oxidizability. A higher number indicates that less oxidizable contamination is present.
- (3) Abs 290 is the absorbance at 290 nm of a 50%-strength solution in a 4 cm cuvette; a lower number implies a better product.
- (4) Alkalinity/acidity: (meq/kg) measured by titration.
- (5) V1 bases: volatile bases (meq/kg) [volatile components which can be liberated with hydroxide solution].

Example II

400 g of nylon-6 industrial carpet fibre waste were depolymerised in a Hastalloy C steel reactor in the presence of 14.7 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 155 min and the temperature was held at 280-295°C during the reaction. 4360 g of distillate were collected. The distillate was composed of 8% by weight of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated by evaporation to a lactam concentration of 33 wt.%. (The mixture to be purified.)

300 g of this concentrated mixture were introduced into a 0.5 l stirred reactor together with 1.0 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was hydrogenated for 1 hour under a hydrogen pressure of 0.1 MPa at 90°C and 900 rpm.

Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a fluted filter.

5 ml of 1.5 N sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 0.13-0.2 KPa. The specifications of the distilled ϵ -caprolactam are

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reported in Table 2.

Comparative experiment C

The mixture to be purified from Example II was concentrated by evaporation to a 70 wt.% solution. 140 g of this mixture were stirred for 15 min together with 13.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO₂) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 2 g.

The ε-caprolactam-containing mixture was then distilled in the same way as described in Example 1. The specifications of the ε-caprolactam formed in this way are reported in Table 2.

TABLE 2

	<u>II</u>	<u>C</u>
° Hazen (ISO 8112)	4	53
PM number	2700	900
Abs 290		
(ISO 7059)	0.98	n.m. ⁽²⁾
PAN (ISO 8660) ⁽¹⁾	8.3	9.5
Turbidity ⁽³⁾	no	yes
⁽¹⁾	PAN number is a measure for the amount of oxidizable contamination in the ε-caprolactam. A low number indicates a low amount of these contamination	
⁽²⁾	n.m. = not measurable due to turbidity according to ISO 7059	
⁽³⁾	measured by visual observation	

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Example III

400 g (of which 32 g non-nylon-6 material) of nylon-6 fibre (post consumer nylon-6 containing carpet waste originating from latex-jute, polypropylene containing
5 carpets) mechanically separated as well as possible from carpet waste, were depolymerised in a Hastalloy C steel reactor in the presence of 15.2 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 170 min and the temperature was held at 280-
10 300°C during the reaction. 5060 g of distillate were collected. The distillate was composed of 6 wt.% of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated to a ϵ -caprolactam concentration of 33 wt.%. (The mixture to be purified.)

15 300 g of this concentrated mixture was introduced into a 1.0 l stirred reactor together with 150 g benzene. The resulting mixture was stirred for 15 minutes and subsequently two phases, a "water-phase" and a "benzene phase" formed, which were separated by phase
20 separation.

The water-phase was again introduced in the reactor together with fresh benzene (50 g benzene/100 g water-phase). The mixture was again stirred for 15 minutes and subsequently separated into two phases.
25 This extraction with benzene was repeated another two times. The resulting "four benzene phases" were mixed with fresh water (25 g/100 g benzene phase). This mixture was stirred for 15 minutes and subsequently separated into two phases.

30 This water extraction was repeated another two times. The resulting water-phases from the benzene extraction and the water-phases obtained from the water extraction were mixed together. The resulting mixture was concentrated by evaporation to a lactam concentration of
35 33 wt.%.

This resulting mixture was hydrogenated in the same manner as described in Example I. After the



separation of the hydrogenation catalyst the mixture was contacted with a cationic ion exchanger (DOWEX 50) and subsequently with an anionic ion exchanger (DOWEX 21K), 1 ml of ion exchanger per 10 ml water/ ϵ -caprolactam mixture is used. The ion exchanger was placed in a column and the water/ ϵ -caprolactam mixture was passed over this packed-bed.

The resulting mixture was distilled in the same manner as described in Example I. The specifications of the distilled ϵ -caprolactam are reported in Table 3. The ϵ -caprolactam was of a quality that it could be reused directly in the manufacture of nylon-6 fibers or other nylon-6 products in which it was not needed to blend the ϵ -caprolactam thus obtained with virgin ϵ -caprolactam obtained by a beckmann rearrangement or any other known synthetic method of preparation.

Comparative Experiment D

The mixture to be purified from Example III was concentrated by evaporation to a lactam concentration of 70 wt. %.

70 g of this mixture was stirred for 15 min together with 9.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO_2) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The filter cake, composed of dry manganese dioxide, weighed 1.7 g.

3.5 ml of 1.5 N aqueous sodium hydroxide solution was then added to the mixture. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 1-1.5 mm Hg. The specifications of the distilled ϵ -caprolactam are reported in Table 3.

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TABLE 3

	III	D
	2	5
5 ° Hazen (ISO 8112)		
PM number	> 10.000	2000
Abs 290 (ISO 7059)	0.16	2.5
Alkalinity	0.04	-
Vl bases (ISO 8661)	0.38	-
PAN (ISO 8660)	3.6	8.5
10		

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C L A I M S

1. Method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam is obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.
2. Method according to claim 1, characterized in that the amount of ϵ -caprolactam in the mixture is between 10 and 95% by weight.
3. Method according to any one of claims 1-2, characterized in that the mixture is first saturated with hydrogen and subsequently contacted with a heterogeneous hydrogenation catalyst.
4. Method of purifying contaminated ϵ -caprolactam dissolved in water obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the purification includes the following purification steps: an extraction with an organic solvent, a hydrogenation according to any one of claims 1-3, an ion exchange treatment and a final distillation.
5. Method of reclaiming ϵ -caprolactam from nylon-6 containing carpet, characterized in that the nylon-6 material is mechanically separated from a large portion of the non-nylon-6 material, the nylon-6 is depolymerized, the ϵ -caprolactam obtained is dissolved in water and purified according to a method according to any one of claims 1-4.
6. Method according to claim 5, characterized in that the depolymerisation of nylon-6 is carried out in the presence of phosphoric acid.
7. Method according to any one of claims 5 and 6, characterized in that the nylon-6 containing carpet is post consumer nylon-6 containing carpet.



A B S T R A C T

The invention relates to a method of preparing ϵ -caprolactam by depolymerisation of nylon-6 originating
5 from carpet waste wherein the mixture of ϵ -caprolactam and water is hydrogenated in the presence of hydrogen and a hydrogenation catalyst. The amount of ϵ -caprolactam in the mixture can be between 10 and 95% by weight.

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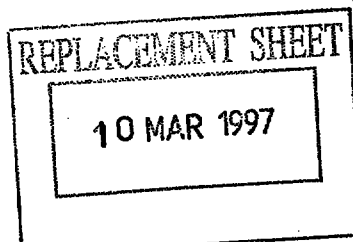
RECLAIMING ε-CAPROLACTAM FROM CARPET WASTE

The invention relates to the reclamation of ε-caprolactam from carpet waste, and more particularly to a method of purifying contaminated ε-caprolactam dissolved in water, in which the contaminated ε-caprolactam has been obtained by means of depolymerisation of nylon-6 originating from carpet waste.

Such a method is disclosed in US-A-5169870. Said patent specification describes a method in which nylon-6 from carpet made from nylon-6 fibers is depolymerised in the presence of phosphoric acid and steam. The phosphoric acid serves as depolymerisation catalyst. The carpet is traditionally composed of nylon-6 tufts and of a, for example, jute, polypropylene or latex backing. Also, the latex may contain fillers. The post-consumer carpet will also contain various sorts of dirt. These materials are present during depolymerization, due to the difficulty of fully separating the nylon-6 from the non-nylon-6 material, according to US-A-5169870. This non-nylon-6 material will result in impurities which have to be removed from the ε-caprolactam in order to obtain ε-caprolactam reusable for making nylon-6. According to US-A-5169870 this so-called "carpet" ε-caprolactam should be purified in the following manner. The volatile components and added steam, which are released during depolymerisation, are condensed and fractionated to separate some non-aqueous contamination from this crude mixture containing water and ε-caprolactam. This crude water-ε-caprolactam mixture is then further purified by adding potassium permanganate for an oxidative treatment in order to oxidize the impurities which are not removed by the fractionation.

The addition of potassium permanganate is disadvantageous because solid manganese dioxide (MnO₂) is

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produced during the purification. This solid manganese dioxide has to be removed by means of, for example, filtration. The removal of manganese dioxide is troublesome, particularly in a continuous process. A further disadvantage is that manganese dioxide is a valueless by-product which causes environmental pollution.

The object of this invention is to provide a method of purifying contaminated ϵ -caprolactam obtained from carpet waste in which the quality of the final product, ϵ -caprolactam, is at least as good as that of the ϵ -caprolactam obtained by the known method described above but which method does not result in the production of solid manganese dioxide.

This object is achieved in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.

It has been found that, if the contaminated ϵ -caprolactam is purified by the method according to the invention, the final product has the same or better quality features as ϵ -caprolactam obtained by the method described in US-A-5169870. These quality features are for example °Hazen (ISO 8112), PM number, Abs 290 (ISO 7059), Alkalinity VI bases (ISO 8661) and PAN (ISO 8660).

An additional advantage of the process according to the invention is that hydrogen is easier to obtain and to process than potassium permanganate. The method according to the invention therefore also offers an economically and also environmentally attractive process for reclaiming ϵ -caprolactam from carpet waste.

Another advantage of the process according to the invention will be elucidated below. When starting from different types of nylon-6 containing carpets, it appeared that ϵ -caprolactam obtained from some carpets and purified with KMnO_4 according to US-A-5169870 shows a visual turbidity (hazy shine in contrast with the normally observed water clear solution) when dissolved in water.

REPLACEMENT SHEET

10 MAR 1997

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10 MAR 1997

- 3 -

This turbidity indicates impurities which make the ϵ -caprolactam not suitable for further reuse in making nylon-6 fibres. The turbidity makes it for example impossible to measure the extinction at 290 nm according to ISO 7059. The origin of the turbidity is found in the presence of different mixtures of non-nylon-6 material/compounds present in the carpet (waste), for example lubricants, anti-statics, dye stuffs, anti-stain compounds, flame retardants and backing material. Because some carpets give rise to this turbidity and others do not, and because it is desirable to process all post consumer nylon-6 containing carpets with one process, the turbidity problem may arise randomly when purifying ϵ -caprolactam obtained from these nylon-6 containing carpets. This turbidity problem does not occur when the ϵ -caprolactam is hydrogenated according to the invention (a water clear solution is obtained). Thus with the process according to the invention all nylon-6 containing carpets can be used as nylon-6 source without such a turbidity problem.

It is known per se to purify mixtures containing water and ϵ -caprolactam by means of hydrogenation. EP-A-411455, CS-A-160312 and J-Stresinka and J. Mokry, PetraChemia, 20 No. 5-6, 171-177 (1970), describe for instance a purification by means of hydrogenation of an ϵ -caprolactam/water mixture. The ϵ -caprolactam as described in these references is however obtained via the Beckmann rearrangement of cyclohexanone oxime in fuming sulphonic acid (hereafter called "rearrangement" ϵ -caprolactam).

Hydrogenation as a purification method of ϵ -caprolactam obtained by depolymerization of nylon-6 fibres was never considered as a suitable method for purification. This consideration was based on the fact that this ϵ -caprolactam will contain another kind of contamination due to the additives present in nylon-6 fibers (such as the earlier mentioned lubricants, anti-statics, anti-stain compounds, dye stuffs and flame

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10 MAR 1997

retardants) as, for example, described in JP-A-52108991. Another reason why more contamination is present in ϵ -caprolactam obtained by depolymerization compared to "rearrangement" ϵ -caprolactam is because the depolymerization is, as a rule, conducted at higher temperatures compared to the temperature of the rearrangement reaction. Higher temperature results in more side reactions of the ϵ -caprolactam resulting in a higher degree of contamination. Especially "carpet" ϵ -caprolactam will contain even more contaminants due to the non-nylon-6 materials (additives and backing) and dirt present in the, as a rule used, carpets. Because of the presence of these contaminations until now "carpet" ϵ -caprolactam is purified with an oxidizing agent, preferable with KMnO_4 , a purification method described for example in JP-A-52108991 and JP-A-52111585 for ϵ -caprolactam from nylon-6. This is also clear from DE-C-851195, which teaches that ϵ -caprolactam obtained from heavily contaminated nylon-6 sources will have to be purified with KMnO_4 . It is therefore surprising that hydrogenation can be used advantageously as described above for treating "carpet" caprolactam.

The hydrogenation by the method according to the invention can be carried out in any way known to the person skilled in the art. As a rule the hydrogenation is carried out in the presence of a heterogeneous hydrogenation catalyst. The heterogeneous catalyst can be contacted with the hydrogen-containing reaction mixture in various ways. Hydrogenation may for example take place in a stirred tank in which the catalyst particles are suspended in the mixture to be purified (slurry phase process). A drawback of the slurry phase process is that the catalyst particles and the purified mixture must be separated in an additional process step after the hydrogenation reaction. Such a separation step, for example by means of filtration, is cumbersome. Therefore, the hydrogenation is more preferably effected in a fixed-

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bed reactor with the catalyst being fixed in the reactor, so that the additional step for separation of the catalyst and reaction mixture can be dispensed with. An example of a possible fixed-bed reactor is the trickle-phase reactor.

The hydrogenation catalyst may be any known heterogeneous hydrogenation catalyst. Examples of such catalysts are ruthenium on aluminium oxide, rhodium on aluminum oxide, platinum on carbon, palladium on carbon, Raney nickel or nickel on silicone oxide. Preferably, the hydrogenation catalyst contains nickel.

Suitable nickel catalysts with a support usually have a nickel content between 5 and 80 wt.%. The catalyst may contain in addition to nickel some activators such as Zr, Mn, Cu or Cr. The activator content is generally between 1 and 20 wt.%.

If palladium-containing heterogeneous catalysts are used, the palladium content will generally be between 0.01 and 10 wt.%.

If a fixed-bed reactor is used, catalysts are employed in which an active metal is on the external surface of a support. Such catalysts can be prepared using the method in which a pre-formed support (for instance pellets, spheres or ribbons) is contacted with an aqueous solution of a metal salt (for example the metal nitrate) dried, and subsequently calcined.

The size of the pre-formed support that is chosen will be as small as possible without the pressure drop across the fixed bed becoming unacceptable. For example the average particle diameter of pellets for a support is usually between 1 and 5 mm.

Catalyst activation, if applied, can be effected in any known manner. In Example 3 of EP-A-411455, for instance, the catalyst is activated by passing gaseous hydrogen over the catalyst for 8 hours while increasing the temperature stepwise from 80 to 200°C. The activation can also be carried out in situ at a temperature of 70-100°C in which the catalyst is contacted with water (or a



10 MAR 1997

- 6 -

water/ ϵ -caprolactam mixture) in which hydrogen is dissolved. The activation pressure may be between 0.1 and 10 MPa.

The hydrogenation residence time depends on the method that is chosen for contacting the heterogeneous catalyst with hydrogen and the water- ϵ -caprolactam mixture. If a reactor is chosen in which the catalyst is fixed in the reactor (fixed-bed reactor), the residence time is generally more than 10 seconds, and in particular more than 30 seconds, and in general the residence time is less than 10 minutes and in particular less than 7 minutes.

The required amount of heterogeneous hydrogenation catalyst in case a slurry phase process is used can easily be determined by the person skilled in the art and is as a rule between 0.01 and 5% by weight of the total reaction mixture.

The amount of ϵ -caprolactam in the mixture to be purified may vary between 10 and 95% by weight. Preferably, this concentration is between 30 and 75% by weight of the constituents of depolymerised material.

During the hydrogenation, the hydrogen pressure is between 0.1 and 10 MPa and is preferably between 0.2 and 2 MPa. During the hydrogenation, the temperature is as a rule between 20 and 160°C.

Optionally, the mixture could be hydrogenated by first saturating the mixture with hydrogen and then bringing the saturated mixture into contact with the hydrogenation catalyst under hydrogenation conditions. The catalyst is preferably a metal on a heterogeneous support as described above. The reactor is preferably a packed-bed reactor over which continuously the with hydrogen saturated ϵ -caprolactam/water mixture is led. Under reaction conditions the degree to which the hydrogenation reaction mixture is saturated with hydrogen is generally 50-100%. Preferably, the degree of saturation of the reaction mixture is 80-100%.

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The nylon-6 containing carpet waste used in the process according to the invention is normally composed of nylon-6 tuft on a backing of for example jute, polypropylene, latex or nylon-6 and fillers like calcium carbonate, clay and hydrated aluminum oxide. The nylon-6 carpet waste may be industrial nylon-6 carpet waste obtained as waste in the production of the nylon-6 containing carpets. The process according to the invention is particularly suitable for post consumer nylon-6 carpet waste as explained above. Mixture of industrial- and post consumer nylon-6 containing carpet waste may be used. The mixture of carpet waste may also contain small amounts of polyethylene terephthalate (PET), nylon-6.6, wool, cotton and other materials which are used for face fibre applications in carpets due to imperfection of the sorting procedure when collecting post consumer carpets.

The carpets can be pretreated mechanically reducing the carpet to a smaller size. A large portion of any non-nylon-6 materials, including the above mentioned backing materials, may be removed in a separator. Examples of suitable mechanical separators are supplied by the Schirp Corporation as Type 75, Type 38CIII, Type 58, Type 38CII, Type 66, Type 71, Type 66-L, Type 57, Type 67S600, Type 64 and Type 62C. After this pretreatment, the fraction mainly containing nylon-6 material can be fed to the depolymerization.

The depolymerization reaction can be carried out with or without a catalyst. In JP-A-53143585, for example, an uncatalysed depolymerisation is described, in which nylon-6 is depolymerised in the presence of superheated steam. As a rule, the depolymerisation is carried out in the presence of a catalyst. Examples of catalysed depolymerisations are also described in JP-A-53132585. Suitable catalysts are for example inorganic acids for example phosphoric acid and boric acid or organic acids for example benzenesulphonic acid, phthalic acid, adipic acid, and acetic acid. Phosphoric acid is in practice the



10 MAR 1997

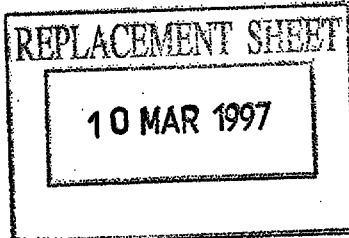
most preferred.

The depolymerisation is as a rule carried out at a temperature of 230-325°C and preferably between 250-280°C. The superheated steam is preferably fed to the reactor at a temperature of 250-500°C. The steam is preferably supplied from the beginning of the depolymerisation in order to take up the volatile ϵ -caprolactam formed so as to obtain a condensate containing from 1 to 40% by weight of ϵ -caprolactam. The content of phosphoric acid in the depolymerisation reactor is as a rule between 0.1-10 wt.% and, preferably, between 2-7 wt.%, based on the total nylon-6 fed to the reactor.

The mixture of water and crude ϵ -caprolactam, obtained after the depolymerisation, can be submitted immediately to the hydrogenation step. According to the invention, preferably one or more additional purification steps are carried out before or after the crude water- ϵ -caprolactam mixture is purified by hydrogenation. A possible additional purification step which can be carried out before the hydrogenation is a distillation in which by-products released or formed during the depolymerisation can be removed, as is described in US-A-5169870. Another additional purification step is a purification via an ion exchanger, as for example described in JP-A-52108991 and by J. Stresinka and J. Mokry, PetraChemia, 20 No. 5-6, 171-177 (1970). Other purification steps known to the person skilled in the art, such as, for example, extraction and/or absorption over active carbon can also be applied.

As a final purification step, the ϵ -caprolactam is recovered by separating it from the water, the final, purified ϵ -caprolactam being obtained. This separation can be carried out in any way known to the person skilled in the art. The ϵ -caprolactam may, for example, be recovered by means of crystallisation or hot melt crystallisation. Another known method is distillation or concentration by evaporation, optionally in the presence of a small amount





of sodium hydroxide solution.

It has been found that a purification which includes (1) an extraction with an organic solvent, (2) a hydrogenation according to the invention, (3) an ion exchange treatment and (4) a final distillation will result in ϵ -caprolactam which can be directly reused in making nylon-6 suitable for making carpet fibres or any other application. Preferably the purification is conducted in the above given sequence.

The extraction can be conducted in the same manner as in the purification for "rearrangement ϵ -caprolactam". Suitable extraction organic solvents are practically immiscible with water. Examples of these solvents are ethers, for example ethyl-, n-propyl-, butylether, dioxane; aromatic solvents for example benzene, toluene, xylene, cumene and ethylbenzene; aliphatic solvents for example cyclohexane, isopropylcyclohexane and ethylcyclohexane; chloroalkanes, for example chloroform, mono-, di-, tri-, tetrachloro-ethane.

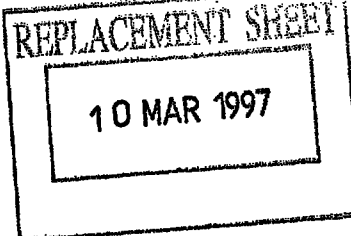
The ion exchange treatment can be conducted in the same manner as in the purification for "rearrangement ϵ -caprolactam" as described in for example the above mentioned references. Preferably first a cationic ion exchanger is used and subsequently an anionic ion exchanger is used.

The final distillation can be conducted in the same manner as in the purification for "rearrangement ϵ -caprolactam".

The invention is explained further by reference to the following, non-restrictive examples.

The 'permanganate number' (=PM number) is defined as the number of seconds elapsing after the addition of 1.00 ml of potassium permanganate 0.0020 Mol/l to 100 ml of caprolactam solution (3.00 g/100 ml) of 293 K (=20°C) until the moment at which the colour of this solution becomes equal to the colour of a standard





solution. The standard solution consists of 3000 mg of cobaltnitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 12 mg of potassium dichromate in 1 l water. The PN number may only be used for comparison purposes of the Experiments and Examples as described below.

Example I

A mixture of 570 g of nylon-6 fibre and 30 g non-nylon-6 carpet waste, mechanically separated from industrial carpet waste (carpet waste: nylon-6 face fibre, latex adhesive, polypropylene backing and CaCO_3), were depolymerised in a Hastalloy C steel reactor in the presence of 21 ml of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 120 min and the temperature was held at 280-290°C during the reaction. 3800 g of distillate were collected and were composed of 15% by weight of ϵ -caprolactam, most of the remainder being composed of water. The mixture was concentrated by evaporation to a lactam concentration of 30%.

300 g of this concentrated mixture (the mixture to be purified) were introduced into a 0.5 l stirred autoclave together with 0.4 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was hydrogenated for 1 hour under a hydrogen pressure of 0.5 MPa at 90°C and 900 rpm.

Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a fluted filter.

5 ml of 50% by weight sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 0.13-0.2 Kpa. The specifications of the distilled ϵ -caprolactam are reported in Table 1.

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10 MAR 1997

- 11 -

Comparative experiment A

The mixture to be purified from Example I was diluted to a 15% by weight solution. 333 g of this mixture were stirred for 30 min together with 33.6 g of 3% by weight potassium permanganate solution at 40°C and a pH of 7.0. The pH was adjusted to a pH of 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO₂) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 35 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 1.7 g.

The ε-caprolactam-containing mixture was then distilled in the same way as described in Example 1. The specifications of the ε-caprolactam formed in this way are reported in Table 1.

Comparative experiment B

333 g of the mixture to be purified from Example I were immediately distilled in the same way as in Example I. The specifications of the ε-caprolactam purified in this way are reported in Table 1.

TABLE 1

	<u>I</u>	<u>A</u>	<u>B</u>
° Hazen ⁽¹⁾			
(ISO 8112)	1	1	26
PM number ⁽²⁾	>10,000	>10,000	177
Abs 290 ⁽³⁾			
(ISO 7059)	0.04	0.51	3.32
Alkalinity ⁽⁴⁾	0.01	0.04	0.50
Vl bases ⁽⁵⁾	0.08	0.38	0.61
(ISO 8661)			

⁽¹⁾ ° Hazen is a measure of the colour; a lower number implies a better product.

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- (2) PM number (permanganate number) is a measure of the oxidizability. A higher number indicates that less oxidizable contamination is present.
- (3) Abs 290 is the absorbance at 290 nm of a 50%-strength solution in a 4 cm cuvette; a lower number implies a better product.
- (4) Alkalinity/acidity: (meq/kg) measured by titration.
- (5) V1 bases: volatile bases (meq/kg) [volatile components which can be liberated with hydroxide solution].

Example II

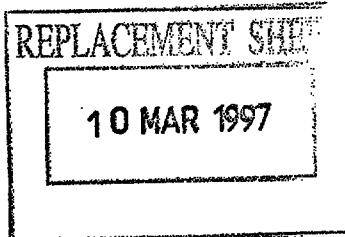
400 g of nylon-6 industrial carpet fibre waste were depolymerised in a Hastalloy C steel reactor in the presence of 14.7 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 155 min and the temperature was held at 280-295°C during the reaction. 4360 g of distillate were collected. The distillate was composed of 8% by weight of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated by evaporation to a lactam concentration of 33 wt.%. (The mixture to be purified.)

300 g of this concentrated mixture were introduced into a 0.5 l stirred reactor together with 1.0 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was hydrogenated for 1 hour under a hydrogen pressure of 0.1 MPa at 90°C and 900 rpm.

Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a fluted filter.

5 ml of 1.5 N sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 0.13-0.2 KPa. The specifications of the distilled ϵ -caprolactam are





reported in Table 2.

Comparative experiment C

The mixture to be purified from Example II was concentrated by evaporation to a 70 wt.% solution. 140 g of this mixture were stirred for 15 min together with 13.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO₂) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 2 g.

The ε-caprolactam-containing mixture was then distilled in the same way as described in Example 1. The specifications of the ε-caprolactam formed in this way are reported in Table 2.

TABLE 2

	<u>II</u>	<u>C</u>
° Hazen (ISO 8112)	4	53
PM number	2700	900
Abs 290		
(ISO 7059)	0.98	n.m. ⁽²⁾
PAN (ISO 8660) ⁽¹⁾	8.3	9.5
Turbidity ⁽³⁾	no	yes

(1) PAN number is a measure for the amount of oxidizable contamination in the ε-caprolactam. A low number indicates a low amount of these contamination

(2) n.m. = not measurable due to turbidity according to ISO 7059

(3) measured by visual observation

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10 MAR 1997

Example III

400 g (of which 32 g non-nylon-6 material) of nylon-6 fibre (post consumer nylon-6 containing carpet waste originating from latex-jute, polypropylene containing carpets) mechanically separated as well as possible from carpet waste, were depolymerised in a Hastalloy C steel reactor in the presence of 15.2 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 170 min and the temperature was held at 280-300°C during the reaction. 5060 g of distillate were collected. The distillate was composed of 6 wt.% of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated to a ϵ -caprolactam concentration of 33 wt.%. (The mixture to be purified.)

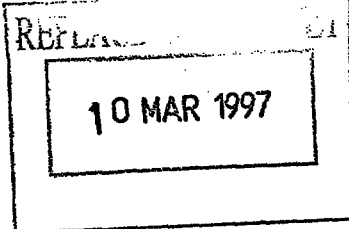
300 g of this concentrated mixture was introduced into a 1.0 l stirred reactor together with 150 g benzene. The resulting mixture was stirred for 15 minutes and subsequently two phases, a "water-phase" and a "benzene phase" formed, which were separated by phase separation.

The water-phase was again introduced in the reactor together with fresh benzene (50 g benzene/100 g water-phase). The mixture was again stirred for 15 minutes and subsequently separated into two phases. This extraction with benzene was repeated another two times. The resulting "four benzene phases" were mixed with fresh water (25 g/100 g benzene phase). This mixture was stirred for 15 minutes and subsequently separated into two phases.

This water extraction was repeated another two times. The resulting water-phases from the benzene extraction and the water-phases obtained from the water extraction were mixed together. The resulting mixture was concentrated by evaporation to a lactam concentration of 33 wt.%.

This resulting mixture was hydrogenated in the same manner as described in Example I. After the





separation of the hydrogenation catalyst the mixture was contacted with a cationic ion exchanger (DOWEX 50) and subsequently with an anionic ion exchanger (DOWEX 21K), 1 ml of ion exchanger per 10 ml water/ ϵ -caprolactam mixture is used. The ion exchanger was placed in a column and the water/ ϵ -caprolactam mixture was passed over this packed-bed.

The resulting mixture was distilled in the same manner as described in Example I. The specifications of the distilled ϵ -caprolactam are reported in Table 3. The ϵ -caprolactam was of a quality that it could be reused directly in the manufacture of nylon-6 fibers or other nylon-6 products in which it was not needed to blend the ϵ -caprolactam thus obtained with virgin ϵ -caprolactam obtained by a beckmann rearrangement or any other known synthetic method of preparation.

Comparative Experiment D

The mixture to be purified from Example III was concentrated by evaporation to a lactam concentration of 70 wt.%.

70 g of this mixture was stirred for 15 min together with 9.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO_2) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The filter cake, composed of dry manganese dioxide, weighed 1.7 g.

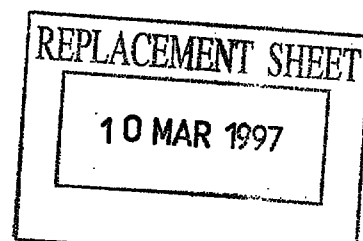
3.5 ml of 1.5 N aqueous sodium hydroxide solution was then added to the mixture. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 1-1.5 mm Hg. The specifications of the distilled ϵ -caprolactam are reported in Table 3.

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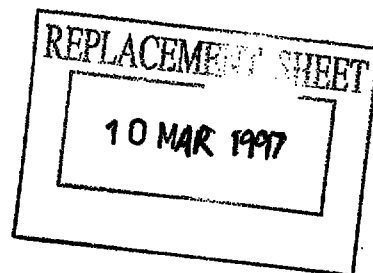
TABLE 3

	III	D
° Hazen (ISO 8112)	2	5
PM number	> 10.000	2000
Abs 290 (ISO 7059)	0.16	2.5
Alkalinity	0.04	-
Vl bases (ISO 8661)	0.38	-
PAN (ISO 8660)	3.6	8.5



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C L A I M S

Method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam is obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst. Method according to claim 1, characterized in that the amount of ϵ -caprolactam in the mixture is between 10 and 95% by weight.

Method according to any one of claims 1-2, characterized in that the mixture is first saturated with hydrogen and subsequently contacted with a heterogeneous hydrogenation catalyst.

Method of purifying contaminated ϵ -caprolactam dissolved in water obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the purification includes the following purification steps: an extraction with an organic solvent, a hydrogenation according to any one of claims 1-3, an ion exchange treatment and a final distillation.

Method of reclaiming ϵ -caprolactam from nylon-6 containing carpet, characterized in that the nylon-6 material is mechanically separated from a large portion of the non-nylon-6 material, the nylon-6 is depolymerized, the ϵ -caprolactam obtained is dissolved in water and purified according to a method according to any one of claims 1-4.

Method according to claim 5, characterized in that the depolymerisation of nylon-6 is carried out in the presence of phosphoric acid.

Method according to any one of claims 5 and 6, characterized in that the nylon-6 containing carpet is post consumer nylon-6 containing carpet.

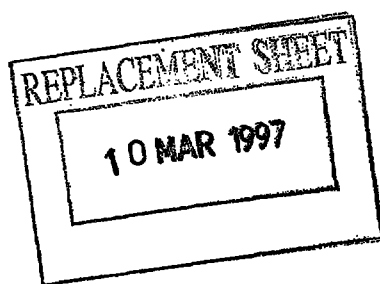
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RECLAIMING ϵ -CAPROLACTAM FROM CARPET WASTE

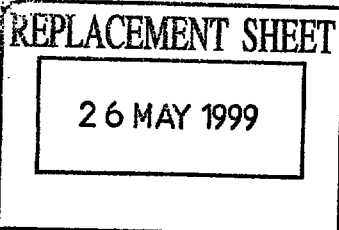
A B S T R A C T

The invention relates to a method of preparing ϵ -caprolactam by depolymerisation of nylon-6 originating from carpet waste wherein the mixture of ϵ -caprolactam and water is hydrogenated in the presence of hydrogen and a hydrogenation catalyst. The amount of ϵ -caprolactam in the mixture can be between 10 and 95% by weight.



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- 17 -

C L A I M STHIS SHEET HAS BEEN
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1. Method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam is obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.
2. Method according to claim 1, characterized in that the amount of ϵ -caprolactam in the mixture is between 10 and 95% by weight.
3. Method according to any one of claims 1-2, characterized in that the mixture is first saturated with hydrogen and subsequently contacted with a heterogeneous hydrogenation catalyst.
4. Method of purifying contaminated ϵ -caprolactam dissolved in water obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the purification includes the following purification steps: an extraction with an organic solvent, a hydrogenation according to any one of claims 1-3, an ion exchange treatment and a final distillation.
5. Method of reclaiming ϵ -caprolactam from nylon-6 containing carpet, characterized in that the nylon-6 material is mechanically separated from a large portion of the non-nylon-6 material, the nylon-6 is depolymerized, the ϵ -caprolactam obtained is dissolved in water and purified according to a method according to any one of claims 1-4.
6. Method according to claim 5, characterized in that the depolymerisation of nylon-6 is carried out in the presence of phosphoric acid.
7. Method according to any one of claims 5 and 6, characterized in that the nylon-6 containing carpet is post consumer nylon-6 containing carpet.

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RECLAIMING EPSILON-CAPROLACTAM FROM CARPET WASTE

Description

[0001] The invention relates to the reclamation of ϵ -caprolactam from carpet waste, and more particularly to a method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam has been obtained by means of depolymerisation of nylon-6 originating from carpet waste.

[0002] Such a method is disclosed in US-A-5169870. Said patent specification describes a method in which nylon-6 from carpet made from nylon-6 fibers is depolymerised in the presence of phosphoric acid and steam. The phosphoric acid serves as depolymerisation catalyst. The carpet is traditionally composed of nylon-6 tufts and of a, for example, jute, polypropylene or latex backing. Also, the latex may contain fillers. The post-consumer carpet will also contain various sorts of dirt. These materials are present during depolymerization, due to the difficulty of fully separating the nylon-6 from the non-nylon-6 material, according to US-A-5169870. This non-nylon-6 material will result in impurities which have to be removed from the ϵ -caprolactam in order to obtain ϵ -caprolactam reusable for making nylon-6. According to US-A-5169870 this so-called "carpet" ϵ -caprolactam should be purified in the following manner. The volatile components and added steam, which are released during depolymerisation, are condensed and fractionated to separate some non-aqueous contamination from this crude mixture containing water and ϵ -caprolactam. This crude water- ϵ -caprolactam mixture is then further purified by adding potassium permanganate for an oxidative treatment in order to oxidize the impurities which are not removed by the fractionation.

[0003] The addition of potassium permanganate is disadvantageous because solid manganese dioxide (MnO_2) is produced during the purification. This solid manganese dioxide has to be removed by means of, for example, filtration. The removal of manganese dioxide is troublesome, particularly in a continuous process. A further disadvantage is that manganese dioxide is a valueless by-product which causes environmental pollution.

[0004] In *Chemiefasern/Textilindustrie* 42, 497 (1992) depolymerization of nylon-6 containing carpets has been disclosed. Purification of the ϵ -caprolactam is done by means of oxidation.

[0005] The object of this invention is to provide a method of purifying contaminated ϵ -caprolactam obtained from carpet waste in which the quality of the final product, ϵ -caprolactam, is at least as good as that of the ϵ -caprolactam obtained by the known method described above but which method does not result in the production of solid manganese dioxide.

[0006] This object is achieved in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.

[0007] It has been found that, if the contaminated ϵ -caprolactam is purified by the method according to the invention, the final product has the same or better quality features as ϵ -caprolactam obtained by the method described in US-A-5169870. These quality features are for example °Hazen (ISO 8112), FM number, Abs 290 (ISO 7059), Alkalinity VI bases (ISO 8661) and PAN (ISO 8660).

[0008] An additional advantage of the process according to the invention is that hydrogen is easier to obtain and to process than potassium permanganate. The method according to the invention therefore also offers an economically and also environmentally attractive process for reclaiming ϵ -caprolactam from carpet waste.

[0009] Another advantage of the process according to the invention will be elucidated below. When starting from different types of nylon-6 containing carpets, it appeared that ϵ -caprolactam obtained from some carpets and purified with $KMnO_4$ according to US-A-5169870 shows a visual turbidity (hazy shine in contrast with the normally observed water clear solution) when dissolved in water. This turbidity indicates impurities which make the ϵ -caprolactam not suitable for further reuse in making nylon-6 fibres. The turbidity makes it for example impossible to measure the extinction at 290 nm according to ISO 7059. The origin of the turbidity is found in the presence of different mixtures of non-nylon-6 material/compounds present in the carpet (waste), for example lubricants, anti-statics, dye stuffs, anti-stain compounds, flame retardants and backing material. Because some carpets give rise to this turbidity and others do not, and because it is desirable to process all post consumer nylon-6 containing carpets with one process, the turbidity problem may arise randomly when purifying ϵ -caprolactam obtained from these nylon-6 containing carpets. This turbidity problem does not occur when the ϵ -caprolactam is hydrogenated according to the invention (a water clear solution is obtained). Thus with the process according to the invention all nylon-6 containing carpets can be used as nylon-6 source without such a turbidity problem.

[0010] It is known per se to purify mixtures containing water and ϵ -caprolactam by means of hydrogenation. EP-A-411455, EP-A-138241, JP-B-42011958, DE-B-1253716, Can. J. Chem. Engineer 60, 319 (1982), CS-A-160312 and J-Stresinka and J. Mokry, *PetraChemia*, 20, 5-6, 171-177 (1970), describe for instance a purification by means of hydrogenation of an ϵ -caprolactam/water mixture. The ϵ -caprolactam as described in these references is however obtained via the Beckmann rearrangement of cyclohexanone oxime in fuming sulphonic acid (hereafter called "rearrangement" ϵ -caprolactam).

[0011] Hydrogenation as a purification method of ϵ -caprolactam obtained by depolymerization of nylon-6 fibres was never considered as a suitable method for purification. This consideration was based on the fact that this ϵ -caprolactam will contain another kind of contamination, namely the residual monomer present in nylon-6 fibres (such as the earlier mentioned

REPLACEMENT SHEET

02 OCT 1999

- ☒ Description : paged ... to paged
☒ Claim(s) : paged ... to paged
☐ Drawing(s) : paged to paged
☒ Abstract : paged ... to paged

DATE OF RECEIPT 2/10/99

lubricants, antistatics, anti-stain compounds, dye stuffs and flame retardants) as, for example, described in JP-A-52108991. Depolymerization of nylon-6 fibers, textiles, solid nylon-6 waste is also known from DE-A-1945956, DE-A-2440243, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A5, VCH Weinheim, p. 42-43, (1986), JP-A-50059382, Int. Polymer Science and Technol. 1, (1974) & Chem. Prumysl. 24, 394 (1974), CS-A-143252 & C.A. 77:1272216 (1972). None of these documents describes hydrogenation as purification method. Another reason why more contamination is present in ϵ -caprolactam obtained by depolymerization compared to "rearrangement" ϵ -caprolactam is because the depolymerization is, as a rule, conducted at higher temperatures compared to the temperature of the rearrangement reaction. Higher temperature results in more side reactions of the ϵ -caprolactam resulting in a higher degree of contamination. Fibre Chemistry 1986, 229-241 describes hydrogenation as a purification method. There is no indication however that hydrogenation would be a suitable method to purify "carpet" ϵ -caprolactam. Especially "carpet" ϵ -caprolactam will contain even more contaminants due to the non-nylon-6 materials (additives and backing) and dirt present in the, as a rule used, carpets. Because of the presence of these contaminations until now "carpet" ϵ -caprolactam is purified with an oxidizing agent, preferable with KMnO_4 , a purification method described for example in JP-A-52108991 and JP-A-52111585 for ϵ -caprolactam from nylon-6. This is also clear from DE-C-851195, which teaches that ϵ -caprolactam obtained from heavily contaminated nylon-6 sources will have to be purified with KMnO_4 . It is therefore surprising that hydrogenation can be used advantageously as described above for treating "carpet" caprolactam.

[0012] The hydrogenation by the method according to the invention can be carried out in any way known to the person skilled in the art. As a rule the hydrogenation is carried out in the presence of a heterogeneous hydrogenation catalyst. The heterogeneous catalyst can be contacted with the hydrogen-containing reaction mixture in various ways. Hydrogenation may for example take place in a stirred tank in which the catalyst particles are suspended in the mixture to be purified (slurry phase process). A drawback of the slurry phase process is that the catalyst particles and the purified mixture must be separated in an additional process step after the hydrogenation reaction. Such a separation step, for example by means of filtration, is cumbersome. Therefore, the hydrogenation is more preferably effected in a fixed-bed reactor with the catalyst being fixed in the reactor, so that the additional step for separation of the catalyst and reaction mixture can be dispensed with. An example of a possible fixed-bed reactor is the trickle-phase reactor.

[0013] The hydrogenation catalyst may be any known heterogeneous hydrogenation catalyst. Examples of such catalysts are ruthenium on aluminium oxide, rhodium on aluminium oxide, platinum on carbon, palladium on carbon, Raney nickel or nickel on silicone oxide. Preferably, the hydrogenation catalyst contains nickel.

[0014] Suitable nickel catalysts with a support usually have a nickel content between 5 and 80 wt.%. The catalyst may contain in addition to nickel some activators such as Zr, Mn, Cu or Cr. The activator content is generally between 1 and 20 wt.%.

[0015] If palladium-containing heterogeneous catalysts are used, the palladium content will generally be between 0.01 and 10 wt.%.

[0016] If a fixed-bed reactor is used, catalysts are employed in which an active metal is on the external surface of a support. Such catalysts can be prepared using the method in which a pre-formed support (for instance pellets, spheres or ribbons) is contacted with an aqueous solution of a metal salt (for example the metal nitrate) dried, and subsequently calcined.

[0017] The size of the pre-formed support that is chosen will be as small as possible without the pressure drop across the fixed bed becoming unacceptable. For example the average particle diameter of pellets for a support is usually between 1 and 5 mm.

[0018] Catalyst activation, if applied, can be effected in any known manner. In Example 3 of EP-A-411455, for instance, the catalyst is activated by passing gaseous hydrogen over the catalyst for 8 hours while increasing the temperature stepwise from 80 to 200°C. The activation can also be carried out in situ at a temperature of 70-100°C in which the catalyst is contacted with water (or a water/ ϵ -caprolactam mixture) in which hydrogen is dissolved. The activation pressure may be between 0.1 and 10 MPa.

[0019] The hydrogenation residence time depends on the method that is chosen for contacting the heterogeneous catalyst with hydrogen and the water- ϵ -caprolactam mixture. If a reactor is chosen in which the catalyst is fixed in the reactor (fixed-bed reactor), the residence time is generally more than 10 seconds, and in particular more than 30 seconds; and in general the residence time is less than 10 minutes and in particular less than 7 minutes.

[0020] The required amount of heterogeneous hydrogenation catalyst in case a slurry phase process is used can easily be determined by the person skilled in the art and is as a rule between 0.01 and 5% by weight of the total reaction mixture.

[0021] The amount of ϵ -caprolactam in the mixture to be purified may vary between 10 and 95% by weight. Preferably, this concentration is between 30 and 75% by weight of the constituents of depolymerised material.

[0022] During the hydrogenation, the hydrogen pressure is between 0.1 and 10 MPa and is preferably between 0.2 and 2 MPa. During the hydrogenation, the temperature is as a rule between 20 and 160°C.

[0023] Optionally, the mixture could be hydrogenated by first saturating the mixture with hydrogen and then bringing the saturated mixture into contact with the hydrogenation catalyst under hydrogenation conditions. The catalyst is

REPLACEMENT SHEET

02 OCT 1999

preferably a metal on a heterogeneous support as described above. The reactor is preferably a packed-bed reactor over which continuously the with hydrogen saturated ϵ -caprolactam/water mixture is led. Under reaction conditions the degree to which the hydrogenation reaction mixture is saturated with hydrogen is generally 50-100%. Preferably, the degree of saturation of the reaction mixture is 80-100%.

[0024] The nylon-6 containing carpet waste used in the process according to the invention is normally composed of nylon-6 tuft on a backing of for example jute, polypropylene, latex or nylon-6 and fillers like calcium carbonate, clay and hydrated aluminum oxide. The nylon-6 carpet waste may be industrial nylon-6 carpet waste obtained as waste in the production of the nylon-6 containing carpets. The process according to the invention is particularly suitable for post consumer nylon-6 carpet waste as explained above. Mixture of industrial- and post consumer nylon-6 containing carpet waste may be used. The mixture of carpet waste may also contain small amounts of polyethylene terephthalate (PET), nylon-6.6, wool, cotton and other materials which are used for face fibre applications in carpets due to imperfection of the sorting procedure when collecting post consumer carpets.

[0025] The carpets can be pretreated mechanically reducing the carpet to a smaller size. A large portion of any non-nylon-6 materials, including the above mentioned backing materials, may be removed in a separator. Examples of suitable mechanical separators are supplied by the Schirp Corporation as Type 75, Type 38CIII, Type 58, Type 38CII, Type 66, Type 71, Type 66-L, Type 57, Type 67S600, Type 64 and Type 62C. After this pretreatment, the fraction mainly containing nylon-6 material can be fed to the depolymerization.

[0026] The depolymerization reaction can be carried out with or without a catalyst. In JP-A-53143585, for example, an uncatalysed depolymerisation is described, in which nylon-6 is depolymerised in the presence of superheated steam. As a rule, the depolymerisation is carried out in the presence of a catalyst. Examples of catalysed depolymerisations are also described in JP-A-53132585. Suitable catalysts are for example inorganic acids for example phosphoric acid and boric acid or organic acids for example benzenesulphonic acid, phthalic acid, adipic acid, and acetic acid. Phosphoric acid is in practice the most preferred.

[0027] The depolymerisation is as a rule carried out at a temperature of 230-325°C and preferably between 250-280°C. The superheated steam is preferably fed to the reactor at a temperature of 250-500°C. The steam is preferably supplied from the beginning of the depolymerisation in order to take up the volatile ϵ -caprolactam formed so as to obtain a condensate containing from 1 to 40% by weight of ϵ -caprolactam. The content of phosphoric acid in the depolymerisation reactor is as a rule between 0.1-10 wt.% and, preferably, between 2-7 wt.%, based on the total nylon-6 fed to the reactor.

[0028] The mixture of water and crude ϵ -caprolactam, obtained after the depolymerisation, can be submitted immediately to the hydrogenation step. According to the invention, preferably one or more additional purification steps are carried out before or after the crude water- ϵ -caprolactam mixture is purified by hydrogenation. A possible additional purification step which can be carried out before the hydrogenation is a distillation in which by-products released or formed during the depolymerisation can be removed, as is described in US-A-5169870. Another additional purification step is a purification via an ion exchanger, as for example described in JP-A-52108991 and by J. Stresinka and J. Mokry, *PetraChemia*, 20 No. 5-6, 171-177 (1970). Other purification steps known to the person skilled in the art, such as, for example, extraction and/or absorption over active carbon can also be applied.

[0029] As a final purification step, the ϵ -caprolactam is recovered by separating it from the water, the final, purified ϵ -caprolactam being obtained. This separation can be carried out in any way known to the person skilled in the art. The ϵ -caprolactam may, for example, be recovered by means of crystallisation or hot melt crystallisation. Another known method is distillation or concentration by evaporation, optionally in the presence of a small amount of sodium hydroxide solution.

[0030] It has been found that a purification which includes (1) an extraction with an organic solvent, (2) a hydrogenation according to the invention, (3) an ion exchange treatment and (4) a final distillation will result in ϵ -caprolactam which can be directly reused in making nylon-6 suitable for making carpet fibres or any other application. Preferably the purification is conducted in the above given sequence.

[0031] The extraction can be conducted in the same manner as in the purification for "rearrangement ϵ -caprolactam". Suitable extraction organic solvents are practically immiscible with water. Examples of these solvents are ethers, for example ethyl-, n-propyl-, butylether, dioxane; aromatic solvents for example benzene, toluene, xylene, cumene and ethylbenzene; aliphatic solvents for example cyclohexane, isopropylcyclohexane and ethylcyclohexane; chloroalkanes, for example chloroform, mono-, di-, tri-, tetrachloroethane.

[0032] The ion exchange treatment can be conducted in the same manner as in the purification for "rearrangement" ϵ -caprolactam as described in for example the above mentioned references. Preferably first a cationic ion exchanger is used and subsequently an anionic ion exchanger is used.

[0033] The final distillation can be conducted in the same manner as in the purification for "rearrangement" ϵ -caprolactam.

[0034] The invention is explained further by reference to the following, non-restrictive examples.

[0035] The 'permanganate number' (=PM number) is defined as the number of seconds elapsing after the addition

REPLACEMENT SHEET

02 OCT 1999

of 1.00 ml of potassium permanganate 0.0020 Mol/l to 100 ml of caprolactam solution (3.00 g/100 ml) of 293 K ($\approx 20^\circ\text{C}$) until the moment at which the colour of this solution becomes equal to the colour of a standard solution. The standard solution consists of 3000 mg of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 12 mg of potassium dichromate in 1 l water. The PM number may only be used for comparison purposes of the Experiments and Examples as described below.

Example I

[0036] A mixture of 570 g of nylon-6 fibre and 30 g non-nylon-6 carpet waste, mechanically separated from industrial carpet waste (carpet waste: nylon-6 face fibre, latex adhesive, polypropylene backing and CaCO_3), were depolymerised in a Hastalloy C steel reactor in the presence of 21 ml of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 120 min and the temperature was held at $280\text{--}290^\circ\text{C}$ during the reaction. 3800 g of distillate were collected and were composed of 15% by weight of ϵ -caprolactam, most of the remainder being composed of water. The mixture was concentrated by evaporation to a lactam concentration of 30%.

[0037] 300 g of this concentrated mixture (the mixture to be purified) were introduced into a 0.5 l stirred autoclave together with 0.4 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was hydrogenated for 1 hour under a hydrogen pressure of 0.5 MPa at 90°C and 900 rpm.

[0038] Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a fluted filter.

[0039] 5 ml of 50% by weight sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 0.13-0.2 Kpa. The specifications of the distilled ϵ -caprolactam are reported in Table 1.

Comparative experiment A

[0040] The mixture to be purified from Example I was diluted to a 15% by weight solution. 333 g of this mixture were stirred for 30 min together with 33.6 g of 3% by weight potassium permanganate solution at 40°C and a pH of 7.0. The pH was adjusted to a pH of 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO_2) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 35 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 1.7 g.

[0041] The ϵ -caprolactam-containing mixture was then distilled in the same way as described in Example I. The specifications of the ϵ -caprolactam formed in this way are reported in Table 1.

Comparative experiment B

[0042] 333 g of the mixture to be purified from Example I were immediately distilled in the same way as in Example I. The specifications of the ϵ -caprolactam purified in this way are reported in Table 1.

TABLE 1

	I	A	B
* Hazen (1) (ISO 8112)	1	1	26
PM number (2)	$\geq 10,000$	$> 10,000$	177
Abs 290 (3) (ISO 7059)	0.04	0.51	3.32
Alkalinity (4)	0.01	0.04	0.50
VI bases (5) (ISO 8661)	0.08	0.38	0.61

(1) * Hazen is a measure of the colour: a lower number implies a better product.

(2) PM number (permanganate number) is a measure of the oxidizability. A higher number indicates that less oxidizable contamination is present.

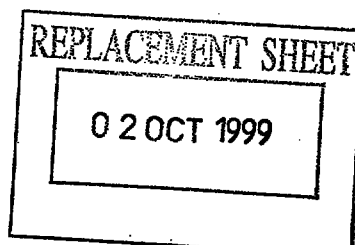
(3) Abs 290 is the absorbance at 290 nm of a 50%-strength solution in a 4 cm cuvette: a lower number implies a better product.

(4) Alkalinity/acidity: (meq/kg) measured by titration.

(5) VI bases: volatile bases (meq/kg) [volatile components which can be liberated with hydroxide solution].

Example II

[0043] 400 g of nylon-6 industrial carpet fibre waste were depolymerised in a Hastalloy C steel reactor in the presence of 14.7 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 155 min and the temperature was held at $280\text{--}295^\circ\text{C}$ during the reaction. 4360 g of distillate were collected. The distillate was composed of 8% by weight of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated by



evaporation to a lactam concentration of 33 wt.%. (The mixture to be purified.)

[0044] 300 g of this concentrated mixture were introduced into a 0.5 l stirred reactor together with 1.0 g of Raney nickel catalyst slurry (50% by weight Raney Ni in water). The mixture was hydrogenated for 1 hour under a hydrogen pressure of 0.1 MPa at 90°C and 900 rpm.

[0045] Most of the catalyst was then removed by means of decantation and the very slight amount of residual catalyst was removed by means of filtration through a fluted filter.

[0046] 5 ml of 1.5 N sodium hydroxide solution was then added to the mixture which had been freed of catalyst. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 0.13-0.2 KPa. The specifications of the distilled ϵ -caprolactam are reported in Table 2.

Comparative experiment C

[0047] The mixture to be purified from Example II was concentrated by evaporation to a 70 wt.% solution. 140 g of this mixture were stirred for 15 min together with 13.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO_2) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The dried filter cake, predominantly composed of manganese dioxide, weighed 2 g.

[0048] The ϵ -caprolactam-containing mixture was then distilled in the same way as described in Example I. The specifications of the ϵ -caprolactam formed in this way are reported in Table 2.

TABLE 2

	II	C
° Hazen (ISO 8112)	4	53
PM number	2700	900
Abs 290 (ISO 7059)	0.98	n.m. (2)
PAN (ISO 8660) (1)	8.3	9.5
Turbidity (3)	no	yes

(1) PAN number is a measure for the amount of oxidizable contamination in the ϵ -caprolactam. A low number indicates a low amount of these contamination

(2) n.m. = not measurable due to turbidity according to ISO 7059

(3) measured by visual observation

Example III

[0049] 400 g (of which 32 g non-nylon-6 material) of nylon-6 fibre (post consumer nylon-6 containing carpet waste originating from latex-jute, polypropylene containing carpets) mechanically separated as well as possible from carpet waste, were depolymerised in a Hastalloy C steel reactor in the presence of 15.2 g of 85 wt.% aqueous phosphoric acid. Superheated steam was passed through the mixture for 170 min and the temperature was held at 280-300°C during the reaction. 5060 g of distillate were collected. The distillate was composed of 6 wt.% of ϵ -caprolactam, most of the remainder being water. The mixture was concentrated to a ϵ -caprolactam concentration of 33 wt.%. (The mixture to be purified.)

[0050] 300 g of this concentrated mixture was introduced into a 1.0 l stirred reactor together with 150 g benzene. The resulting mixture was stirred for 15 minutes and subsequently two phases, a "water-phase" and a "benzene phase" formed, which were separated by phase separation.

[0051] The water-phase was again introduced in the reactor together with fresh benzene (50 g benzene/100 g water-phase). The mixture was again stirred for 15 minutes and subsequently separated into two phases. This extraction with benzene was repeated another two times. The resulting "four benzene phases" were mixed with fresh water (25 g/100 g benzene phase). This mixture was stirred for 15 minutes and subsequently separated into two phases.

[0052] This water extraction was repeated another two times. The resulting water-phases from the benzene extraction and the water-phases obtained from the water extraction were mixed together. The resulting mixture was concentrated by evaporation to a lactam concentration of 33 wt.%.

[0053] This resulting mixture was hydrogenated in the same manner as described in Example I. After the separation of the hydrogenation catalyst the mixture was contacted with a cationic ion exchanger (DOWEX 50) and subsequently with an anionic ion exchanger (DOWEX 21K). 1 ml of ion exchanger per 10 ml water/ ϵ -caprolactam mixture is used. The ion exchanger was placed in a column and the water/ ϵ -caprolactam mixture was passed over this packed-bed.

[0054] The resulting mixture was distilled in the same manner as described in Example I. The specifications of the distilled ϵ -caprolactam are reported in Table 3. The ϵ -caprolactam was of a quality that it could be reused directly in the manufacture of nylon-6 fibers or other nylon-6 products in which it was not needed to blend the ϵ -caprolactam thus obtained with virgin ϵ -caprolactam obtained by a beckmann rearrangement or any other known synthetic method of preparation.

Comparative Experiment D

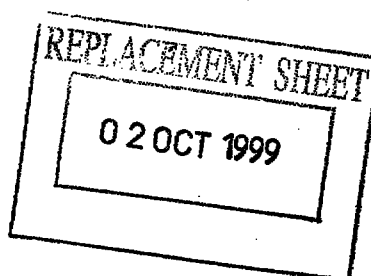
[0055] The mixture to be purified from Example III was concentrated by evaporation to a lactam concentration of 70 wt. %.

[0056] 70 g of this mixture was stirred for 15 min together with 9.3 g of 3% by weight aqueous potassium permanganate solution at 40°C and a pH of 7.0. The pH was kept at 7.0 during the oxidation with the aid of 1.0 N sulphuric acid. The manganese dioxide (MnO_2) formed was then removed from the reaction product by means of a pressure filtration. The filtration time was 60 min. The filter cake, composed of dry manganese dioxide, weighed 1.7 g.

[0057] 3.5 ml of 1.5 N aqueous sodium hydroxide solution was then added to the mixture. This mixture was then distilled by reducing the pressure in steps. Lactam was distilled at approximately 1-1.5 mm Hg. The specifications of the distilled ϵ -caprolactam are reported in Table 3.

TABLE 3

	III	D
* Hazen (ISO 8112)	2	5
PM number	> 10,000	2000
Abs 290 (ISO 7059)	0.16	2.5
Alkalinity	0.04	-
VI bases (ISO 8661)	0.38	-
PAN (ISO 8660)	3.6	8.5





Claims

1. Method of purifying contaminated ϵ -caprolactam dissolved in water, in which the contaminated ϵ -caprolactam is obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the mixture of water and the contaminated ϵ -caprolactam is hydrogenated in the presence of hydrogen and a hydrogenation catalyst.
2. Method according to claim 1, characterized in that the amount of ϵ -caprolactam in the mixture is between 10 and 95% by weight.
3. Method according to any one of claims 1-2, characterized in that the mixture is first saturated with hydrogen and subsequently contacted with a heterogeneous hydrogenation catalyst.
4. Method of purifying contaminated ϵ -caprolactam dissolved in water obtained by means of depolymerisation of nylon-6 originating from carpet waste, characterized in that the purification includes the following purification steps: an extraction with an organic solvent, a hydrogenation according to any one of claims 1-3, an ion exchange treatment and a final distillation.
5. Method of reclaiming ϵ -caprolactam from nylon-6 containing carpet, characterized in that the nylon-6 material is mechanically separated from a large portion of the non-nylon-6 material, the nylon-6 is depolymerized, the ϵ -caprolactam obtained is dissolved in water and purified according to a method according to any one of claims 1-4.
6. Method according to claim 5, characterized in that the depolymerisation of nylon-6 is carried out in the presence of phosphoric acid.
7. Method according to any one of claims 5 and 6, characterized in that the nylon-6 containing carpet is post consumer nylon-6 containing carpet.

REPLACEMENT SHEET

02 OCT 1999

ABSTRACT

RECLAIMING EPSILON-CAPROLACTAM FROM CARPET WASTE

The invention relates to a method of preparing ϵ -caprolactam by depolymerisation of nylon-6 originating from carpet waste wherein the mixture of ϵ -caprolactam and water is hydrogenated in the presence of hydrogen and a hydrogenation catalyst. The amount of ϵ -caprolactam in the mixture can be between 10 and 95% by weight.

REPLACEMENT SHEET

02 OCT 1999