



- (51) **International Patent Classification:**
C07D 223/10 (2006.01) *C07D 201/04* (2006.01)
- (21) **International Application Number:**
PCT/EP2014/064517
- (22) **International Filing Date:**
8 July 2014 (08.07.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
201310320035.9 26 July 2013 (26.07.2013) CN
- (71) **Applicant:** DSM IP ASSETS B.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).
- (72) **Inventors:** CUIPER, Anna Dite; P.O. Box 4, NL-6100 AA Echt (NL). KNAAP, VAN DER, Theodorus Albertus; P.O. Box 4, NL-6100 AA Echt (NL). TINGE, Johan Thomas; P.O. Box 4, NL-6100 AA Echt (NL).
- (74) **Agent:** DUFFY, Jim; P.O. Box 4, NL-6100 AA Echt (NL).
- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** CONTINUOUS PROCESS FOR RECOVERY OF CAPROLACTAM AND CRYSTALLINE AMMONIUM SULFATE

(57) **Abstract:** Present application discloses an industrial scale continuous process for recovery of caprolactam and crystalline ammonium sulfate. By controlling the weight ratio of the amount of aqueous ammonium sulfate solution being recycled to the amount of Beckmann rearrangement mixture charged into the neutralization section within the range of more than 0.001 and less than 1, the productivity of the crystalline ammonium sulfate is increased, however neither the color of the crystalline ammonium sulfate nor the quality of the produced pure caprolactam is unduly influenced.



CONTINUOUS PROCESS FOR RECOVERY OF CAPROLACTAM AND
CRYSTALLINE AMMONIUM SULFATE

5 The present invention relates to an improvement in continuous processes for recovery of caprolactam and crystalline ammonium sulfate.

 It is known that cyclohexanone oxime can be produced according to various technologies, like ammoximation technology, from HSO technology, NO reduction technology and HPO[®] technology. In general, the produced cyclohexanone
10 oxime can be converted into caprolactam, with the use of an acid. This reaction is known as Beckmann rearrangement and is applied on commercial scale. In these processes in general sulfuric acid or oleum (also called fuming sulfuric acid) are used as an acid source. The resulting reaction mixtures of such Beckmann rearrangements contain mainly caprolactam and sulfuric acid. Subsequently, these rearrangement
15 mixtures are in general neutralized by ammonia in the presence of water, whereby two phases are formed. One phase is a crude caprolactam phase and the other phase is an aqueous ammonium sulfate phase. Both phases can be worked-up to produce the products caprolactam and ammonium sulfate, respectively.

 CN103012273A discloses neutralized crystallization system and
20 method of preparing caprolactam through caprolactam rearrangement solution. The neutralized crystallization system is characterized in that a feeding mixer is connected with an inlet in the upper part of a neutralized crystallization reactor, an upper-layer organic phase outlet of the neutralized crystallization reactor is connected with an inlet of a caprolactam oil layer separator, a lower-layer heavy organic phase outlet of the
25 neutralized crystallization reactor is connected with an inlet of an ammonium sulfate centrifugal machine, an outlet at one end of the caprolactam oil layer separator is connected with a caprolactam collecting tank, an outlet at the other end of the caprolactam oil layer separator is connected with an ammonium sulfate mother liquor collection tank, an outlet at the lower end of the ammonium sulfate centrifugal machine
30 is connected with an ammonium sulfate washing dryer, an outlet at the upper end of the ammonium sulfate centrifugal machine is connected with the ammonium sulfate mother liquor collection tank which is connected with the neutralized crystallization reactor through a mother liquor circulating pump.

GB996,322 discloses a process for the simultaneous recovery of ammonium sulfate and pure lactams from mixtures which have been obtained by Beckmann rearrangement of cycloalkanone oximes with sulfuric acid or oleum. The mixtures have been neutralized by contacting with ammonium sulfate solution and ammonia so that no solid ammonium sulfate is precipitated during neutralization. The ammonium sulfate crystals are obtained by evaporating the water of the ammonium sulfate solution obtained after the separation of the crude lactam. The crystallized ammonium sulfate is separated and the resultant mother liquor is after dilution with water returned to the neutralization zone. Claim 2 of GB996,322 claims a process wherein ammonium sulfate mother liquor in an amount of five to fifty times of the amount of rearrangement mixture is returned to the neutralization zone. In example 1 of GB996,322 the amount of mother liquor, before dilution with water, is about 32 times the amount of the rearrangement mixture.

GB1,353,448 discloses a process wherein the reaction mixture that has been obtained by subjecting a cyclic ketoxime to the Beckmann rearrangement in the presence of sulfuric acid or oleum is neutralized with ammonia or an ammonium base. A concentrated aqueous phase is obtained after extraction of a lactam layer with a solvent. Mother liquor is obtained in the ammonium sulfate crystallization step. The mother liquor together with the concentrated aqueous phase is purified by extraction with lactam. The thus obtained purified aqueous ammonium sulfate solution might be recycled to the crystallization stage or the neutralization stage.

US4,138,472 describes a process for obtaining crystalline ammonium sulfate from reaction mixtures which have been obtained by Beckmann rearrangement of cyclohexanone oxime with sulfuric acid or oleum. The mixtures are neutralized with ammonia and the recycled ammonium sulfate mother liquor at temperatures from 80 °C to 115 °C. During the neutralization no solid ammonium sulfate precipitates. Ammonium sulfate crystals are obtained by evaporating the water of the ammonium sulfate solution under reduced pressure, followed by separating off the crystallized ammonium sulfate and recycling the mother liquor to the neutralization stage. In example 1 of US4,138,472 the amount of mother liquor, before dilution with water, is about 32 times the amount of the mixture from the rearrangement section. In the description of US4,138,472 it is mentioned that the ratio of the amount of mother liquor to the amount of the mixture from the rearrangement is from about 5 to 50.

US4,806,638 presents a process in which reaction mixtures obtained by Beckmann rearrangement of cyclohexanone oxime with sulfuric acid or oleum are neutralized by gaseous ammonia. The reaction mixture is mixed with recycled ammonium sulfate mother liquor on condition that no solid ammonium sulfate is precipitated during the neutralization. Thus, crystalline ammonium sulfate is obtained by evaporation of the water in the ammonium sulfate solution under reduced pressure. The crystalline ammonium sulfate is separated from the ammonium sulfate mother liquor. Claim 2 of US4,806,638 claims a process in which the reaction mixture obtained by Beckmann rearrangement reaction of cyclohexanone oxime with sulfuric acid (or oleum) is mixed with the recycled ammonium sulfate mother liquor. The amount of mother liquor is in the range from 5 to 50 times of the amount of the reaction mixture. In example 1 of US4,806,638 the amount of mother liquor, before dilution with water, is about 16 times the amount of the mixture from the rearrangement section.

US3,937,789 discloses a process for the neutralization of a solution of ϵ -caprolactam in sulfuric acid with ammonia in the presence of water at a temperature of about 40 °C to 50 °C under sub-atmospheric pressure. In the reaction vessel, ammonium sulfate crystals are formed and the heat evolved by the exothermic reaction between sulfuric acid and ammonia is utilized to evaporate a substantial portion of the water. Mother liquor obtained by separating off the ammonium sulfate is recycled to the reaction vessel. Examples 2 and 3 of US3,937,789 describe the neutralization of Beckmann rearrangement mixture with ammonia whereby ammonium sulfate is produced. In both examples, the ammonium sulfate is separated by centrifugation and the ammonium sulfate containing mother liquor is recycled to the neutralization vessel. In example 2 the amount of ammonium sulfate containing mother liquor recycled to the neutralization vessel is more than 3.3 times the amount of Beckmann rearrangement mixture charged to the neutralization vessel. In example 3, it is more than 11.3 times.

In the prior art, a large amount of mother liquor has been recycled to the neutralization section. As it is well known that the mother liquor of the crystallization of ammonium sulfate contains higher content of organic impurities such as octahydrophenazine. It is well known that even a very low concentration of octahydrophenazine will result in a very negative impact on the quality of the final caprolactam. Therefore, the recycling of large amounts of mother liquor to the neutralization section results also in the recycling of large amounts of organic impurities

to the neutralization section. This will decrease the quality and productivity of the caprolactam.

The present application provides an industrial scale continuous process for the recovery of caprolactam and crystalline ammonium sulfate comprising
5 the following steps:

I) charging of

i) a cyclohexanone oxime Beckmann rearrangement mixture;

ii) an aqueous solution; and

iii) ammonia

10 to a neutralization section;

whereby a crude caprolactam phase and an aqueous ammonium sulfate phase are formed;

II) separating the crude caprolactam phase from the aqueous ammonium sulfate phase formed in step I);

15 III) evaporating water from the aqueous ammonium sulfate phase separated in step II) to form crystalline ammonium sulfate and condensing the evaporated water into a condensed water phase;

IV) recovering crystalline ammonium sulfate obtained in step III), whereby an aqueous ammonium sulfate solution is obtained;

20 V) recycling at least part of the aqueous ammonium sulfate solution obtained in step IV) to step I);

characterized in that

- a. the weight ratio of the amount of aqueous ammonium sulfate solution being recycled to the amount of Beckmann rearrangement mixture charged in step I) is
25 more than 0.001 and less than 1; and
- b. wherein the cyclohexanone oxime Beckmann rearrangement mixture comprises caprolactam and sulfuric acid.

In this application, industrial scale means that the productive capacity of crystalline ammonia sulfate is more than 1000 kg/hr.

In an embodiment of the invention, the three streams i) a cyclohexanone oxime Beckmann rearrangement mixture ii) an aqueous solution and iii) ammonia are fed to the neutralization section simultaneously.

In another embodiment of the invention stream i) and stream ii) are
5 introduced into the neutralization section at any sequence before stream iii) is introduced.

Alternatively, stream ii) and stream iii) may be introduced into the neutralization section at any sequence and then introducing stream i).

The cyclohexanone oxime Beckmann rearrangement mixture
10 introduced into the neutralization process further comprises caprolactam and sulfuric acid. The cyclohexanone oxime that is used for the production of a cyclohexanone oxime Beckmann rearrangement mixture may be the cyclohexanone oxime originating from ammoximation technology, from HSO technology or from HPO[®] technology. In a preferred embodiment the cyclohexanone oxime Beckmann rearrangement reaction is
15 a 2-stage or a 3-stage reaction. In a more preferred embodiment the cyclohexanone oxime Beckmann rearrangement reaction is a 2-stage reaction.

The ammonia used to neutralize the cyclohexanone oxime Beckmann rearrangement mixture charged in step I) is either in the form of ammonia gas or in the form of ammonia water. Preferably, the ammonia water contains about 25 wt.%
20 ammonia.

Preferably, the neutralization process is carried out at a temperature ranging from 45 °C to 75 °C and at atmospheric pressure.

The neutralization process is an exothermal process and the heat released from the neutralization process is removed by heat exchangers. In one
25 preferred embodiment, the heat released from the neutralization process is utilized for the evaporation of water in the ammonium sulfate crystallization process.

In the neutralization process, after neutralizing the cyclohexanone oxime Beckmann rearrangement mixture with the ammonia, a crude caprolactam phase and an aqueous ammonium sulfate phase are formed. The light phase is the
30 crude caprolactam phase and the heavy phase is the aqueous ammonium sulfate phase. In a preferred embodiment, the concentration of the ammonium sulfate of the

aqueous ammonium sulfate phase ranges from 30 to 50 wt.%, more preferably from 38 to 48 wt.% and most preferably about 44 wt.%.

An aqueous solution is introduced into the neutralization section. The objective of introducing the aqueous solution is to dilute the concentration of sulfuric acid of the cyclohexanone oxime Beckmann rearrangement mixture so that no solid ammonium sulfate is precipitated when the neutralization process is carried out. "No solid ammonium sulfate is precipitated" is defined as less than 0.1 wt.% of ammonium sulfate is precipitated when the neutralization process is carried out.

In one preferred embodiment, the aqueous solution introduced into the neutralization section comprises fresh water, condensed water of the ammonium sulfate crystallization process (step III)), optionally water from a process for the polymerization of caprolactam to nylon-6, and optionally, an aqueous solution obtained from the purification of caprolactam process.

The condensed water of the ammonium sulfate crystallization process is almost pure water. Preferably, at least 25 wt.%, preferably at least 50 wt.%, more preferably at least 75 wt.% of the condensed water is recycled to the neutralization section.

The aqueous solution obtained in the caprolactam purification process is the aqueous phase obtained by extracting the crude caprolactam with an organic solvent, and/or the condensed water obtained in the distillation section. This aqueous solution contains up to 5 wt.% ammonium sulfate. In a preferred embodiment the aqueous phase obtained by extracting the crude caprolactam with the organic solvent is then stripped by steam. Optionally, the stripped aqueous phase is introduced to the neutralization section. Preferably, at least 10 wt.%, more preferably at least 15 wt.%, even more preferably at least 20 wt.% of the aqueous phase obtained by extracting the crude caprolactam with an organic solvent is introduced to the neutralization section.

An aqueous ammonium sulfate solution obtained in step IV) after recovery of the crystalline ammonium sulfate in the crystallization process is recycled to the neutralization section (step I)).

In one preferred embodiment, at least 10 wt.%, preferably at least 20 wt.%, of the total amount of the aqueous solution introduced into the neutralization section originates from the process for the polymerization of caprolactam to nylon-6.

The total amount of the aqueous solution herewith is the amount of aqueous solution introduced into the neutralization section plus the amount of the recycled aqueous ammonium sulfate solution charged to the neutralization section.

5 The weight ratio of the amount of ammonium sulfate solutions obtained in step IV) and recycled to the neutralization section to the amount of cyclohexanone oxime Beckmann rearrangement mixture charged in step I) is more than 0.001 and less than 1, preferably more than 0.01 and less than 0.25, and even more preferably more than 0.02 and less than 0.1.

10 The aqueous ammonium sulfate solution that is obtained after recovery of the crystalline ammonium sulfate in step IV), comprises mother liquor obtained during the separation of crystalline ammonium sulfate in e.g. a centrifuge, and/or washing liquor obtained by washing the crystalline ammonium sulfate in e.g. a centrifuge, and/or aqueous solution separated from an ammonium sulfate crystallizer. This aqueous ammonium sulfate solution that is obtained after recovery of the
15 crystalline ammonium sulfate in step IV) contains ammonium sulfate and organic impurities. The concentration of ammonium sulfate of the aqueous ammonium sulfate solution is more than 30 wt.%, preferably more than 40 wt.%. Most of the organic impurities result from the Beckmann rearrangement reaction, while the others result from the impurities in the feeds to the Beckmann rearrangement section. It is not
20 desirable to introduce these impurities into the neutralization reaction since it will reduce the purity of obtained caprolactam.

By controlling the weight ratio of the amount of recycled ammonium sulfate solution to the amount of Beckmann rearrangement mixture in the range of 0.001 to 1, the organic impurities in the caprolactam can be controlled within an
25 acceptable scope.

In one preferred embodiment, the aqueous ammonium sulfate solution obtained in step IV) is recycled to the neutralization section directly. To be specific, the aqueous ammonium sulfate solution is not purified prior to being recycled.

30 The pH value of the aqueous ammonium sulfate phase formed in the neutralization section is preferably kept in the range between 3 and 8, more preferably between 4 and 6 and most preferably about 5 (determined at a temperature of 25°C).

The present application further provides a method for obtaining high purity caprolactam.

In a preferred embodiment, the aqueous ammonium sulfate phase separated in step II) is extracted with a solvent to remove dissolved caprolactam. Then the dissolved solvent is removed from the resulting extracted aqueous ammonium sulfate phase. The extracted aqueous ammonium sulfate phase is subjected to a
5 crystallization process by evaporating the water from the aqueous ammonium sulfate phase to form crystalline ammonium sulfate. The solvent used to extract the ammonium sulfate is one or more selected from benzene, toluene or xylene.

In a preferred embodiment, the crude caprolactam phase separated in step II) is subjected to a caprolactam purification process such as being extracted
10 with a solvent such as benzene, toluene or xylene. Accordingly an organic caprolactam comprising phase and an aqueous ammonium sulfate comprising phase are formed. In a preferred embodiment, the aqueous ammonium sulfate comprising phase is stripped in order to recover organic solvent and is then discharged. Optionally, a fraction of the obtained aqueous ammonium sulfate comprising phase and/or the stripped aqueous
15 phase is introduced to the neutralization section. Additionally, the organic caprolactam comprising phase is worked-up to produce pure caprolactam. In an embodiment the organic caprolactam comprising phase is back-extracted with water whereby an aqueous caprolactam phase and an organic phase are formed. The obtained aqueous caprolactam phase is further purified to produce pure caprolactam by ion exchange
20 treatment (both anionic and cationic ion exchangers), hydrogenation, removal of water and other components with a boiling point below that of caprolactam via distillation and overhead distillation of caprolactam. A fraction of the water that is removed via distillation is after condensation introduced to the neutralization section.

In an embodiment of present invention, the resultant pure
25 caprolactam preferably has a permanganate absorption number (PAN) with a maximum value of 4.0; a volatile base level with a maximum value of 0.50 mmol/kg and an E290 with a maximum value of 0.05 (ISO 7059 determination).

The present application also provides a process for preparing a high grade crystalline ammonium sulfate and this process has also a high recovery yield for
30 crystalline ammonium sulfate.

The crystallization process is carried out by evaporating water from the aqueous ammonium sulfate phase separated in step II) to form crystalline ammonium sulfate and condensing the water evaporated into condensed water. The crystallization process is carried out in crystallizers. In one preferred embodiment, there

are 4 to 6 crystallizers in-effect. Generally, the first crystallizer is operated at pressure of higher than 100kPa. Accordingly, at least 16 wt.% of the aqueous ammonium sulfate is crystallized at pressure of higher than 100 kPa.

5 The crystalline ammonium sulfate is removed and mother liquor is obtained. In one preferred embodiment, the obtained crystalline ammonium sulfate is washed with an aqueous phase. Preferably the aqueous phase is water or an aqueous ammonium sulfate containing solution.

10 A fraction of the mother liquor and/or washing liquor obtained by washing the crystalline ammonium sulfate might be recycled to the neutralization section. The remainder of the mother liquor and washing liquor obtained by washing the crystalline ammonium sulfate is purged and/or recycled to crystallizers. In a preferred option no mother liquor and no washing liquor obtained by washing the crystalline ammonium sulfate is purged. Accordingly, all the mother liquor and/or washing liquor obtained by washing the crystalline ammonium sulfate are recycled to
15 the neutralization section and/or are recycled to crystallizers.

In a preferred embodiment of present invention an aqueous solution separated from an ammonium sulfate crystallizer is recycled to the neutralization section.

20 In another preferred option a mixture comprising mother liquor obtained during the separation of crystalline ammonium sulfate and/or washing liquor obtained by washing the crystalline ammonium sulfate and/or aqueous solution separated from an ammonium sulfate crystallizer is recycled to the neutralization section.

25 In yet another preferred option the fraction of the aqueous ammonium sulfate solution that is obtained after recovery of the crystalline ammonium sulfate in step IV) and recycled to step I) is the only purge of the crystallization section.

30 Preferably the weight ratio of the amount of the recycled ammonium sulfate solution to the amount of Beckmann rearrangement mixture charged in step I) is more than 0.001, more preferably more than 0.005, most preferably more than 0.01 and less than 1, more preferably less than 0.3 and most preferably less than 0.1.

Accordingly, the recovery yield of crystalline ammonium sulfate is higher than 75 wt.%, more preferably, higher than 90 wt%, and even more preferably

more than 95 wt.% relative to the amount of ammonium sulfate present in the aqueous ammonium sulfate phase separated in step II).

The present application provides a simple process for recovery of the crystalline ammonium sulfate, because it does not need a separate work-up unit for the aqueous ammonium sulfate solution that is recycled to the neutralization section.

The present application also provides a process that requires low investment, because no special work-up unit is needed and the amount of ammonium sulfate solution recycled back to the neutralization section is rather small.

The present application also provides a process that increases the yield of crystalline ammonium sulfate, because besides purging aqueous ammonium sulfate solution to step I) no additional purge of aqueous ammonium sulfate solution is needed.

EXAMPLES

Analytical methods:

PAN number (permanganate absorption number) ISO 8660 - Plastics - Determination of permanganate index of caprolactam - Spectrometric method.

Volatile bases (VB) ISO 8661 - Caprolactam for industrial use - Determination of volatile bases content – Titrimetric method after distillation.

E290: ISO 7059 - Caprolactam for industrial use - Determination of absorbance at a wave length of 290 nm.

COD (chemical oxygen demand) content, which is a measure for the concentration organic impurities, refers to values as determined according to ASTM D 1252-95 (dichromate method).

COMPARATIVE EXAMPLE

This comparative Example was performed in a commercial caprolactam plant that was operated in a continuous mode and consisted of a 2-stage Beckmann rearrangement reaction section (hereafter refer to as reaction section), a Beckmann rearrangement mixture neutralization section (hereafter refer to as neutralization section), a caprolactam purification section and an ammonium sulfate crystallization section.

In the reaction section cyclohexanone oxime was reacted with oleum and a Beckmann rearrangement mixture was obtained. In the first stage of the reaction section (hereafter referred to as a first stage) both cyclohexanone oxime and oleum were fed, while a Beckmann rearrangement mixture from the first stage was discharged. This Beckmann rearrangement mixture was charged to the second stage of the reaction section (hereafter refer to as a second stage). Additionally, fresh cyclohexanone oxime was fed to the second stage. Beckmann rearrangement mixture produced in the second stage was discharged and was fed to a neutralization section. The amount of Beckmann rearrangement mixture that was fed to the neutralization section was approximately 37 ton per hour.

In the neutralization section the Beckmann rearrangement mixture produced in the second stage was neutralized with aqueous ammonia. This neutralization section was also fed with fresh filtered water and condensed water recovered from the caprolactam purification section. During the neutralization a 2-phase system was formed: a crude caprolactam phase and an aqueous ammonium sulfate phase. Subsequently, these two phases were separated in a phase separator by gravity due to a density difference of both phases. The crude caprolactam phase was fed to the caprolactam purification section and the aqueous ammonium sulfate phase was sent after pre-treatment to the ammonium sulfate crystallization section.

In the caprolactam purification section the crude caprolactam was first extracted with benzene, whereby a benzenic caprolactam phase and an aqueous ammonium sulfate consisting phase were formed. This aqueous ammonium sulfate consisting phase was stripped in order to recover benzene and was then discharged. The benzenic caprolactam phase was back-extracted with water whereby an aqueous caprolactam phase and a benzenic phase were formed. The obtained aqueous caprolactam phase was further purified to produce pure caprolactam by ion exchange treatment (both anionic and cationic ion exchangers), hydrogenation, removal of water and other components with a boiling point below that of caprolactam via distillation and overhead distillation of caprolactam. A fraction of the water that was removed via distillation is after condensation reused in the neutralization section. About 18 ton of pure caprolactam per hour was obtained after condensation of the overhead distilled caprolactam.

The aqueous ammonium sulfate phase obtained after phase separation after neutralization with ammonia had a pH value of approximately 5

(determined at a temperature of 25 °C). This aqueous ammonium sulfate phase was first extracted with benzene in order to recover dissolved caprolactam from this aqueous ammonium sulfate phase. Then the extracted aqueous ammonium sulfate phase was steam stripped in order to recover dissolved benzene. The obtained
5 stripped aqueous ammonium sulfate phase had an ammonium sulfate content of approximately 44 % by weight and was fed to the ammonium sulfate crystallization section.

The ammonium sulfate crystallization section consisted of 4 evaporative type crystallizers that were arranged in 2 series of 2 crystallizers. Each
10 series of crystallizers were heat integrated by in-effect evaporation: fresh steam was used to drive the first crystallizers and the vapors generated in these crystallizers drive the second crystallizers. From all crystallizers aqueous ammonium sulfate slurries were discharged and via centrifugation separated into wet ammonium sulfate crystals and mother liquor. After a washing step with water the obtained washed wet ammonium
15 sulfate crystals were dried. The average production of dried ammonium sulfate crystals was almost 24.8 ton per hour. The dried ammonium sulfate crystals were white colored. From each crystallizer a flow of aqueous ammonium sulfate solution was purged in order to prevent brown coloring of the produced ammonium sulfate crystals. The total purge amounted about 1.7 ton aqueous ammonium sulfate solution per hour and was
20 not recycled back into the process. The ammonium sulfate content in this aqueous ammonium sulfate solution was about 45 % by weight.

Pure caprolactam was produced having the following key measures:

PAN: average about 2
Volatile Base: average about 5
25 E290: average about 0.02

The average COD content in the flows of aqueous ammonium sulfate solutions that were purged from each crystallizer was about 25 gram per kg clear solution.

EXAMPLE OF THE INVENTION

30 This examples performed in the same caprolactam plant that was described in the comparative example and the caprolactam plant was running at the same production rate. So, the amount of Beckmann rearrangement mixture that was

fed to the neutralization section was approximately 37 ton per hour and about 18 ton pure caprolactam per hour was obtained after condensation of the overhead distilled caprolactam.

5 The main difference with the comparative example was that now the total purge of the ammonium sulfate crystallization section, being about 1.7 ton aqueous ammonium sulfate solution per hour, was without any purification charged to the Beckmann rearrangement mixture neutralization section.

10 The impact of recycling the total purge of the ammonium sulfate crystallization section to the neutralization section on the quality of the pure caprolactam can be neglected because all key quality measures PAN, Volatile Base and E290 remained within specifications.

However, the average COD content in the flows of aqueous ammonium sulfate solutions that were purged from each crystallizer was about 40 gram per kg of a clear solution.

15 The average production of dried ammonium sulfate crystal was almost 25.6 ton per hour. This is an increase of about 3% relative to the comparative example. The dried ammonium sulfate crystals were white colored.

20 The weight ratio of the amount of aqueous ammonium sulfate solution being recycled to the Beckmann rearrangement mixture neutralization section to the amount of Beckmann rearrangement mixture charged to the Beckmann rearrangement mixture neutralization section was about 1.7 : 37 (= about 0.046).

25 This example showed that the total purge of the ammonium sulfate crystallization section can be recycled to the Beckmann rearrangement mixture neutralization section resulting in an increase in the production of crystalline ammonium sulfate without unduly influencing the quality of the produced pure caprolactam. Neither the color of the produced ammonium sulfate crystals is unduly influenced.

CLAIMS

1. An industrial scale continuous process for the recovery of caprolactam and crystalline ammonium sulfate comprising the following steps:
- 5 I) charging of
- i) a cyclohexanone oxime Beckmann rearrangement mixture;
- ii) an aqueous solution; and
- iii) ammonia
- to a neutralization section;
- whereby a crude caprolactam phase and an aqueous ammonium
- 10 sulfate phase are formed;
- II) separating the crude caprolactam phase from the aqueous ammonium sulfate phase formed in step I);
- III) evaporating water from the aqueous ammonium sulfate phase separated
- in step II) to form crystalline ammonium sulfate and condensing the
- 15 evaporated water into a condensed water phase;
- IV) recovering crystalline ammonium sulfate obtained in step III), whereby an aqueous ammonium sulfate solution is obtained;
- V) recycling at least part of the aqueous ammonium sulfate solution
- obtained in step IV) to step I);
- 20 characterized in that
- a. the weight ratio of the amount of aqueous ammonium sulfate solution being recycled to the amount of Beckmann rearrangement mixture charged in step I) is more than 0.001 and less than 1; and
- b. wherein the cyclohexanone oxime Beckmann rearrangement mixture
- 25 comprises caprolactam and sulfuric acid.
2. A process according to claim 1, wherein stream i), ii) and iii) are charged simultaneously.
3. A process according to claim 1, wherein the aqueous ammonium sulfate phase formed in step I) has a pH value in the range from 3 to 7 which is
- 30 determined at a temperature of 25 °C.
4. A process according to claim 1, wherein the aqueous ammonium sulfate solution is recycled directly to step I).

5. A process according to claim 1, wherein the aqueous ammonium sulfate phase separated in step II) is extracted with a solvent and the obtained dissolved solvent is removed from the resulting extracted aqueous ammonium sulfate phase prior to being crystallized by evaporation of water from the aqueous ammonium sulfate phase to form crystalline ammonium sulfate.
6. A process according to claim 5, wherein the solvent is one or more selected from benzene, toluene or xylene.
7. A process according to claim 1, wherein the crude caprolactam phase separated in step II) is subjected a purification process such as being extracted with an solvent, whereby an organic caprolactam comprising phase and an aqueous phase comprising ammonium sulfate are formed and the organic caprolactam comprising phase is worked-up to produce a pure caprolactam.
8. A process according to claim 7, wherein the organic caprolactam comprising phase is extracted with water.
9. A process according to claim 1, wherein the weight ratio of the amount of the aqueous ammonium sulfate solution being recycled to the amount of Beckmann rearrangement mixture charged in step I) is more than 0.005 and less than 0.1.
10. A process according to claim 1, wherein the aqueous ammonium sulfate solution being recycled comprises more than 30 wt.% of ammonium sulfate.
11. A process according to claim 1, wherein the neutralization process of step I) is carried out at a temperature in the range from 45 °C to 75 °C under atmospheric pressure.
12. A process according to claim 1, wherein the heat released in neutralization process is removed via heat exchangers.
13. A process according to claim 1, wherein the heat released in neutralization process is utilized for the evaporation of water to form crystalline ammonium sulfate.
14. A process according to claim 1, wherein the aqueous solution of stream ii) comprises condensed water from step III), an aqueous solution obtained during the caprolactam purification process and a water from a process for the polymerization of caprolactam to nylon-6.
15. A process according to claim 1, wherein at least 25 wt.% of the condensed water is charged as aqueous solution to the neutralization section;

16. A process according to claim 1, wherein at least 10 wt.% of the total amount of aqueous solution and the aqueous ammonium sulfate solution charged to the neutralization section originates from the process for the polymerization of caprolactam to nylon-6.
- 5 17. A process according to claim 1, wherein during the neutralization process of step I) less than 0.1 wt.% of solid ammonium sulfate is precipitated.
18. A process according to claim 1, wherein least 16 wt.% of the aqueous ammonium sulfate is crystallized at pressure of higher than 100 kPa.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/064517

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D223/10 C07D201/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data, BIOSIS, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 996 322 A (BASF AG) 23 June 1965 (1965-06-23) cited in the application claims 1, 2; example 1 -----	1-18
X	US 4 806 638 A (BRAND UWE [DE] ET AL) 21 February 1989 (1989-02-21) cited in the application claims 1, 2; example 1 -----	1-18
X	US 3 937 789 A (DONATI IVO ET AL) 10 February 1976 (1976-02-10) cited in the application examples 2, 3 -----	1-18
X	US 2 605 261 A (KAHR KURT ET AL) 29 July 1952 (1952-07-29) claim 1; example 2 ----- -/-	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 September 2014

Date of mailing of the international search report

02/10/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Stroeter, Thomas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/064517

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 353 448 A (STAMICARBON) 15 May 1974 (1974-05-15) claim 3 -----	1-18
X	DE 858 701 C (BASF AG) 8 December 1952 (1952-12-08) claim 1 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/064517

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 996322	A	23-06-1965	CH 415640 A 30-06-1966
			DE 1194863 B 16-06-1965
			GB 996322 A 23-06-1965
			NL 141509 B 15-03-1974
			NL 277685 A 24-09-2014
US 4806638	A	21-02-1989	DE 3635363 A1 21-04-1988
			DE 3767824 D1 07-03-1991
			EP 0264126 A2 20-04-1988
			IN 167450 A1 27-10-1990
			JP H0780836 B2 30-08-1995
			JP S63104956 A 10-05-1988
			US 4806638 A 21-02-1989
US 3937789	A	10-02-1976	NONE
US 2605261	A	29-07-1952	NONE
GB 1353448	A	15-05-1974	GB 1353448 A 15-05-1974
			NL 7106355 A 14-11-1972
DE 858701	C	08-12-1952	NONE