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PROCESS FOR PRECONCENTRATING LACTAM OILS

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This invention relates to lactams and more particularly to a process for preconcentrating lactam oils obtained by the Beckmann rearrangement of the oximes of cyclic ketones and subsequent neutralization.

It is an object of this invention to provide a process for the preconcentration of water-containing lactam oils, wherein a preconcentrated lactam oil is obtained which may be extracted without the formation of emulsions.

A further object of the invention is to provide a process for the preparation of preconcentrated lactam oils from crude lactam oils which yield lactams in high yield and of very good quality.

Still another object of the invention is the provision of a process for the preparation of preconcentrated lactam oils which enables the employment of multi-step extractors for the extraction of the preconcentrated lactam oils without formation of emulsions.

Finally, it is an object of the invention generally to improve on processes for the preconcentration of crude lactam oils as now customarily practised.

Other objects of the invention will become apparent from the following description.

As the result of the Beckmann rearrangement of the oximes of cyclic ketones with fuming sulfuric acid or sulfuric acid proper, the corresponding lactams are first obtained in solution of concentrated sulfuric acid. For the purpose of isolating these lactams, the sulfuric acid is commonly neutralized in technical processes with ammonia water. In this manner an ammonium sulfate liquor is obtained on which the lactams separate as so-called "lactam oil." Depending on the nature of the lactam and the particular process and working conditions, this lactam oil has about the following composition:

66–68% of the particular lactam
28–31% of water
1.4–2% of ammonium sulfate
0.2–0.4% of ammonia and
0.1–0.3% of the corresponding ketone

In case it is desired to obtain lactams of high quality and in high yield from these lactam oils, then the latter cannot be distilled in vacuo directly, but have first to be subjected to an extracting procedure. It is common practice to employ chlorinated hydrocarbons as extracting agents in the extracting procedure referred to. However, the use of such chlorinated hydrocarbons results in the disadvantage that emulsions are frequently formed in the lactam-poor stages of the extraction, that is after the major portion of the lactam has already been extracted from the oil.

It has been observed that the formation of emulsions can be entirely avoided by removing from the lactam oil prior to the extraction a part of the water and at the same time the ammonia and ketone contained therein. With a view to producing the desired effect referred to, it is sufficient to remove a quantity of water so that the lactam content in the oil increases to about 72–78%. It is not advisable to extend this preconcentration so as to obtain

a lactam content above 80% since in this case disturbing separation of ammonium sulfate from the oil may easily occur.

In accordance with this invention the preconcentration of the lactam oil referred to is effected by passing a gas through the lactam oil in fine distribution and at elevated temperature. In this manner lactams of excellent quality are then subsequently obtained. Nitrogen or advantageously air may be used as the gas referred to. In case air is employed, impurities contained in the lactam oil are oxidized by the air which results in an increased purity of the final product.

According to a further feature of the inventive process the oxidizing effect and thus the purifying effect may be enhanced still further by adding to the lactam oil small amounts of catalytically active metal salts, such as for example manganese acetate or cobalt acetate. The lactams proper are not attacked or otherwise affected by the presence of such metal salts. The inventive process may be performed batchwise or continuously.

The inventive process has many advantages besides the fact that the quality of the lactams subsequently obtained is considerably improved. For example, the process requires for its performance very simple and inexpensive apparatus only and is easily carried out. In addition to the fact that the pre-concentration of the lactam oil avoids the formation of emulsions during the subsequent extraction, a considerable purifying effect is obtained.

The process of the invention will now be described by several examples, but it should be understood that these examples are given by way of illustration rather than by way of limitation, and that many variations may be made in for example amounts, temperature and process conditions in general, without departing in any way from the spirit and scope of the invention.

Example 1

The process to be described was carried out in a relatively wide reaction tube which along its entire length was heated to about 100° C. by a hot water jacket surrounding the tube. 1000 parts by weight of a methyllactam oil were placed into the reaction tube. The methyllactam was obtained by the Beckmann rearrangement of the oxime of o-methylcyclohexanone and subsequent neutralization. It contained 68% of methyllactam, 28% of water, 1.1% of o-methylcyclohexanone, 1.4% of ammonium-sulfate, and 0.2% of ammonia. Nitrogen was blown through the lactam oil within the tube in fine distribution. The rate of nitrogen blown through the tube was about one hundred times the volume of the lactam oil per hour. After three hours an amount of water had distilled off which corresponded to a lactam increase in the oil of 9% so that the oil then contained 77% of lactam. The oil was then also entirely devoid of o-methylcyclohexanone and ammonia.

The methyllactam oil thus obtained may be extracted in an extractor comprising for example 5 steps without any formation of emulsions. The yield of pure methyllactam amounted to 96%. The methyllactam exhibited after distillation in vacuo a permanganate number of 520 seconds. In contrast thereto methyllactam which has not been subjected to the treatment described forms milky emulsions in the fourth and fifth steps of the extractor.

For the purpose of establishing the advantages obtained by the inventive process, water was distilled off at atmospheric pressure from a lactam oil of the same composition as used in this example, until the methyllactam content in the oil had increased to 76%. The thus pretreated oil was readily extracted in a 5-step extractor. The methyllactam was obtained in a yield of 93% only. After distillation in vacuo the methyllactam thus obtained exhibited a permanganate number of only 340 seconds.

Example 2

The process to be described was performed in a relatively wide reaction tube which was steam-heated along its entire length by steam of 0.1 atmosphere excess pressure. The discharge end of the tube was provided with an overflow pipe. A 6-step extractor was operatively connected with the overflow pipe. 1000 parts by weight per hour of a lactam oil were introduced from above into the reaction tube. The lactam oil was obtained by the Beckmann rearrangement of cyclohexanone oxime and subsequent neutralization and had the following composition:

	Percent
Caprolactam	66
Water	30.4
Ammonium sulfate	2.1
Ammonia	0.4
Cyclohexanone	0.3

Air, preheated to about 100° C., was passed through the reaction tube. The rate of the hot air through the lactam oil was about one hundred times the volume of the lactam oil per hour. During its passage through the reaction tube the caprolactam content of the lactam oil increased to 75–76% and the oil was entirely freed from ammonia and cyclohexanone. The thus concentrated lactam oil left the reaction tube through the overflow pipe at the bottom end of the reaction tube and was directly introduced into the 6-step extractor. During the extraction in the extractor no emulsions were formed. The caprolactam thus obtained in a yield of 98–99% had—after distillation in vacuo a permanganate number of 940 seconds.

For the purpose of establishing the advantages obtained by the inventive process, a lactam oil of the same composition as used in this example was distilled at reduced pressure until the caprolactam content in the oil had increased to 76%. This concentrated oil was likewise extracted in a 6-step extractor. The yield, however, was only 97% while the permanganate number of the caprolactam—after vacuum distillation—was 500 seconds.

Further, a lactam oil of identical composition which has not been subjected to any preconcentration whatsoever cannot successfully be extracted in a 6-step extractor since formation of emulsions will occur already in the fourth step. For this reason, only a 3-step extractor can be employed. The yield in this case amounts to 93–95% only. The caprolactam obtained after distillation had a permanganate number of 550 seconds.

Example 3

1000 parts by weight of a lactam oil of the same composition as that employed in Example 2 was treated in the same manner as described in Example 2. However, 0.02% of an aqueous solution of manganese acetate of 50% concentration were added to the lactam oil prior to the gas treatment. No emulsion formation occurred during extraction. The caprolactam was obtained in a yield of 98–99% and had a permanganate number of 1500 seconds and more. Moreover, the caprolactam exhibited an excellent stability to light.

What I claim is:

1. A process for the preconcentration of water-containing lactam oil obtained by the Beckmann rearrangement of oximes of cyclic ketones and subsequent neutralization, comprising the step of passing a stream of air through said water-containing oil at elevated temperature until the water content of said oil has been reduced to a predetermined value.

2. A process as claimed in claim 1, wherein a catalytically active metal salt is added to said water-containing lactam oil prior to passing said air through said lactam oil, said metal salt being a salt of the group of salts consisting of manganese acetate and cobalt acetate.

3. A process for the preconcentration of a liquid containing about 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% of ammonia and 0.1–0.3% of a ketone, comprising the step of reducing the content of said water and substantially removing said ammonia and said ketone by passing a gas selected from the class consisting of molecular oxygen containing gas and nitrogen through said liquid at elevated temperature until the content of said lactam in said liquid has risen to above 72 but below 80%.

4. A process for the preconcentration of a liquid containing about 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% of ammonia and 0.3% of a ketone which comprises adding to said liquid a small amount of a catalytically active metal salt selected from the class consisting of manganese acetate and cobalt acetate, reducing the content of said water and substantially removing said ammonia and said ketone by passing air through said liquid at elevated temperature until the content of said lactam in said liquid has risen to above 72% but below 80%.

5. A process as claimed in claim 3 wherein said gas is nitrogen.

6. A process for the preconcentration of a liquid containing about 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% of ammonia and 0.1–0.3% of a ketone, comprising the steps of introducing said liquid into a reaction tube heated to about 100° C., and passing a gas selected from the class consisting of molecular oxygen containing gas and nitrogen through said reaction tube at a rate of about one hundred times the volume of said liquid per hour, until said ammonia and said ketone are removed and the content of said lactam in said liquid is above 72% but below 80%.

7. A process for the preconcentration of a liquid containing 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% ammonia and 0.1–0.3% of a ketone, comprising mixing said liquid with an aqueous solution of a metal salt selected from the group consisting of manganese acetate and cobalt acetate, introducing the liquid so formed into a reaction tube heated to about 100° C., and passing air through said reaction tube at a rate of about 100 times the volume of said liquid per hour, until said ammonia and said ketone are removed and the content of said lactam in said liquid is above 72% but below 80%.

8. A process as claimed in claim 6, wherein said gas is preheated prior to being passed through said reaction tube.

9. A process of preconcentrating a methyllactam oil containing about 68% of a methyllactam, 28% of water, 0.2% of ammonia, 1.4% of ammonium sulfate and 1.1% of o-methylcyclohexanone which methyllactam oil is obtained by the Beckmann rearrangement of o-methylcyclohexanone oxime and subsequent neutralization, said process comprising the steps of introducing said methyllactam oil into a reaction tube heated to about 100° C., and passing nitrogen through said reaction tube at a rate of about one hundred times the volume of said methyllactam oil per hour until said ammonia, said o-methylcyclohexanone and a portion of said water have been removed and said methyllactam comprises about 77% of said methyllactam oil.

10. A process of preconcentrating a caprolactam oil containing about 66% of caprolactam, 30.4% of water, 2.1% of ammonium sulfate, 0.4% of ammonia and 0.3% of cyclohexanone which caprolactam oil is obtained by the Beckmann rearrangement of cyclohexanone oxime and subsequent neutralization, said process comprising the steps of introducing said caprolactam oil into a heated reaction tube, and passing air heated to about 110° C. and at a rate of about one hundred times

the volume of said caprolactam oil through said reaction tube until said cyclohexanone, said ammonia and a portion of said water have been removed and said caprolactam comprises 75–76% of said caprolactam oil.

11. In a process as claimed in claim 10, wherein about 0.02% of an aqueous solution of manganese acetate of about 50% strength is added to said caprolactam oil prior to passing said hot air through said reaction tube.

12. A process for the preconcentration of a liquid containing about 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% of ammonia and 0.1–0.3% of a ketone, comprising the step of reducing the content of said water and substantially removing said ammonia and said ketone by passing air through said liquid at elevated temperature until the content of said lactam in said liquid has risen to above 72% but below 80%.

13. A process for the preconcentration of a liquid containing about 66–68% of a lactam, 28–31% of water, 1.4–2% of ammonium sulfate, 0.2–0.4% of ammonia and 0.1–0.3% of a ketone, comprising the steps of introducing said liquid into a reaction tube heated to about 100° C., and passing air through said reaction tube at a rate of about 100 times the volume of said liquid per hour, until said ammonia and said ketone are removed and the content of said lactam in said liquid is above 72% but below 80%.

14. A process for recovering a lactam from a water-containing lactam oil obtained by the Beckmann rearrangement of an oxime of a cyclic ketone, the subsequent neutralization and the extraction of said water containing lactam oil with a chlorinated hydrocarbon solvent, the improvement which comprises passing a stream of a gas selected from the class consisting of a molecular oxygen containing gas and nitrogen through said water containing lactam oil at elevated temperatures until the water content thereof is reduced to a predetermined value, the treatment with said gas stream being effected prior to the extraction with said chlorinated hydrocarbon, whereby the formation of emulsions during said extraction step is avoided and the permanganate number of said lactam is raised to a relatively high value.

15. A process according to claim 14 wherein said gas is nitrogen.

16. A process according to claim 14 wherein the temperature is kept at about 100–110° C.

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