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VACUUM-THERMAL TREATMENT OF POLYMERIZED CAPROLACTAM TO REDUCE THE CONTENT OF LOW MOLECULAR WEIGHT CONSTITUENTS THEREIN

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The present invention relates to the production of filaments of polymerized caprolactam and more particularly to the treatment of polymerized caprolactam to reduce the content of low molecular weight constituents therein whereby a more efficient spinning may take place leading to the formation of filaments and threads of textile quality.

Caprolactam may be continuously polymerized by the addition of small quantities of water and acid in accordance with conventional techniques. Solid caprolactam polymerizate in the form of powder or chips may be continuously melted and spun to form shaped structures. While it is desirable for reasons of economy to carry out the continuous polymerization of caprolactam followed immediately by the spinning of the polymer formed, heretofore, the combined polymerization and spinning operations could not be applied with respect to the production of endless textile threads. This is due to the fact that the polymerizate which is spun contains too large a quantity of low molecular weight materials which exude or perspire from the spun thread even after conventional drawing procedures.

Technologically, in order to obtain a high grade product, the portion of these low-molecular weight materials must be considerably decreased after the polymerization. The content of the low molecular weight compounds is present in the so-called water-soluble extract. The water-soluble portion of the polymerizate amounts to about 10% by weight and consists of about 60% by weight monomer caprolactam and about 40% by weight of oligomers of caprolactam, i.e. dimer, trimer, tetramer, etc. Due to the temperature-dependent equilibrium between the high- and low-molecular weight constituents in polyamide melts, based upon caprolactam, the low molecular weight compounds, even after their removal are always reproduced in the polymerized caprolactam material.

In order to obtain serviceable threads and filaments from polymerized caprolactam having favorable tensile strength and elasticity values, the portion of low molecular weight constituents in the spun fiber must not amount to more than about 2% by weight. Thus, it is known to extract the polymerizate in finely divided form to reduce the content of low molecular weight constituents. Generally, the polymerizate in the form of chips is treated with water to extract the low molecular weight constituents therefrom.

Alternatively, the low molecular weight materials may be distilled off from the polymerizate by subjecting the melt to vacuum distillation, in the presence of inert gases such as nitrogen, carbon dioxide, water vapor and the like if necessary.

Where the polymerized caprolactam which has been extracted in chip form is thereafter melted and where a melt which has been extracted in the foregoing manner is exposed to higher temperatures, such as those temperatures used in the spinning operation, the equilibrium between the high and low molecular weight materials in

the melt is reestablished after a short time and accordingly the extract content increases once more. In the past, therefore, it has always been considered extremely important to maintain the time of stay of the extracted polymerizate as short as possible in the spinning head by appropriately constructing the spinning heat wherein the melt is subjected to higher temperatures.

In accordance with conventional procedures, it has only been possible to produce endless threads or filaments of textile quality having comparatively low viscosity and low tensile strength values. Besides this, the finished fiber material must still be washed before the final processing to the desired finished products in order to once more decrease the portion of disturbing low molecular weight constituents to an acceptable extent.

This is also the case with respect to a known process in which the polymerizate is preliminarily evacuated to remove the low molecular weight constituents and/or polymerizate chips are extracted by washing, and thereafter stored in molten state for a predetermined period at a temperature maintained just above the melting point of the product, such that the melt is only brought to the required spinning temperature in the last stages of the spinning device.

It has become evident that in the vacuum extraction of polymerized caprolactam, a different ratio of monomers to oligomers is found in the extract portion. During the vacuum extraction treatment, the monomers preponderantly distill off so that the oligomers preponderantly remain behind in the melt. This disturbed ratio of the extract constituents to one another acts unfavorably on the threads which are subsequently spun from the melt since the preponderant oligomer portion remaining in the melt causes the spun threads and filaments to have brittle properties as well as poor drawing characteristics.

It is an object of the present invention to overcome the foregoing drawbacks and to provide a process for the production of polymerized caprolactam having a reduced content of low molecular weight constituents, such that in the subsequent spinning operation, threads and filaments of favorable textile quality will be formed.

It is another object of the invention to provide for the continuous polymerization of caprolactam which, upon vacuum and thermal treatment, may be immediately passed to the spinning step in one over-all operation.

Other and further objects of the invention will become apparent from a study of the within specification and accompanying examples.

In accordance with the present invention, it has been found that polymerized caprolactam may be treated to reduce the content of low molecular weight constituents therein by subjecting the polymerized caprolactam to vacuum treatment followed by thermal treatment above the melting point of the caprolactam and repeating the vacuum treatment, followed by thermal treatment at least one more time. In this manner the polymerized caprolactam after the last thermal treatment may be immediately spun to form a shaped structure as desired.

In consequence of the present invention, the direct spinning of continuously polymerized caprolactam is made possible and it is no longer necessary to produce polymerized caprolactam in the form of chips, to thereafter wash the chips, dry the same, and finally remelt them for the spinning operation. In accordance with the present invention, a fiber material based upon polymerized caprolactam is advantageously produced which possesses high elasticity and tensile strength values. The filaments, threads, or other fiber material produced in this way may be processed to cord silk form, for use as tire linings. Significantly, the fibers produced in accordance with the process of the invention do not require a rewashing pro-

cedure. Furthermore, the process of the invention may be varied within broad limits so that it is possible to produce textile threads, for example, having characteristics rendering the same versatile and therefore useful for many commercial applications.

Broadly, in accordance with the process of the invention an extract-poor polyamide based on caprolactam having a desirably high ratio of monomers to oligomers in the extract may be produced in a manner that the content of water soluble extract constituents is decreased through repeated evacuation of the melt wherein after each evacuation the disturbed equilibrium ratio of monomers to oligomers in the water-soluble extract of the melt is once more increased by means of a thermal treatment. Surprisingly, it has been discovered that the comparatively high oligomer content in the polymerizate decreases in consequence of the thermal treatment in favor of an increase in the content of monomers. Nevertheless, at the same time, the total content of water extract soluble materials is, including the total of monomers and oligomers, also increased. Additionally, it has been found in accordance with the invention that the viscosity of the polymerized caprolactam extracted by evacuation in vacuum may be still further increased by means of the thermal treatment which follows.

In accordance with the invention, in order to produce the desired fibers, filaments, threads, and the like, having low extract content with less than 2.5% by weight of monomers and oligomers, at least two vacuum treatments in each case followed by an adjoining thermal treatment are required. Upon termination of the last thermal treatment, the melt may be conveniently passed to the spinning operation.

It will be understood that the low molecular weight constituents in the water-soluble extract portion includes monomers as well as oligomers wherein the molecular weight normally does not exceed about 450. About 90% or more of these oligomer portions consists of dimers, whereas the remaining portion consists of trimers and at most traces of oligomers, having more than three monomer groups therein.

Generally, the evacuation, carried out by vacuum treatment of the melt, employs pressure up to about 0.6 torr, and preferably pressures within the range of from about 0.3 to 0.5 torr (i.e. 0.6 mm. Hg). The temperature of the melt during the vacuum treatment is preferably within the range of about 240–270 degrees C., and the vacuum treatment is extended for a period of from about 15 to 100 minutes.

The thermal treatment of the melt, on the other hand, is carried out at a temperature of preferably from about 240 to 300 degrees C. over an extended period of from 1 to 4 hours, i.e., at a pressure above about 0.6 torr (0.6 mm. Hg).

The content of monomers to oligomers in the low molecular weight constituents present after the vacuum and thermal treatments is within the ratio range of from 1:6 to 2:1, wherein the total content of low molecular weight constituents amounts at most to 2.5% by weight.

Specifically, a resinous polymerizate which has been obtained by means of the pressure polymerization of molten caprolactam with small quantities of water and acid during a period of from about 15–25 hours at pressures of from 10–30 and preferably 20 atmospheres, and at a temperature of from 240 to 300 degrees C. generally has a content of about 10% by weight of water-soluble extract materials. These extract materials generally comprise about 70% of the monomers and 30% of oligomers. A polymerizate obtained in the foregoing manner, in accordance with the present invention, is thus subjected to evacuation by vacuum treatment, at a pressure up to about 0.6 torr and preferably 0.3–0.5 torr, and a temperature of from 240 to 270 degrees C. In this way the adhering water and the preponderant portion of the water-soluble extract materials are removed from the polymerizate.

The time of stay in this first vacuum step amounts to about 15–100 minutes.

In this manner a polymerizate is obtained which has an extract content of only about 1.5% by weight. The extract at this point includes over 90% of oligomers. In the adjoining first thermal treatment, which takes place immediately after the first vacuum treatment, the extract content rises once more to about 3–5% by weight and simultaneously the ratio of monomers to oligomers approaches the equilibrium stage and amounts to about 1:1. In this first thermal treatment, the polymerized caprolactam is subjected to temperatures of from 240 to 300 degrees C. over a period of 1–4 hours and preferably 1.5–3.5 hours.

The thermal treatment may be effected in completely filled conduits or vessels, or in containers under an inert protective gas such as for example nitrogen. The pressure is not critical for the thermal treatment, and accordingly the same may be carried out at decreased pressures as well as at moderately increased pressures. In particular, the thermal treatment may adjoin the preceding vacuum treatment in each case such that the evacuated melt is maintained under the temperature conditions for the required period of thermal treatment while the same remains in the sump of the vacuum evaporator apparatus. In this way, preferably the vacuum treatment and adjoining thermal treatment may be carried out in the same vessel.

The polymerized caprolactam upon completion of the first vacuum treatment and adjoining thermal treatment possesses approximately the desired natural ratio of monomers to oligomers, i.e. about 6:4, although the total portion of these water-soluble extract constituents is still too high for producing threads, filaments, and the like of the desired quality. The polymerizate at this point has an extract content of between 3–5%.

Accordingly, the polymerizate is subjected to vacuum treatment once more under these same conditions as in the first vacuum treatment. In this manner, a practically completely anhydrous extract is obtained having an extract content of about 1% by weight which consists almost completely of oligomers. As a result of this second vacuum treatment, the polymerizate has a relative solution viscosity in sulfuric acid (hereinafter referred to simply as viscosity) which corresponds to a value of 2.5–2.6. This value precisely corresponds to the concentration of the acid added for the stabilization during the polymerization period. The viscosity value remains constant even during the second adjoining thermal treatment.

The second thermal treatment is carried out in the same manner as the first thermal treatment wherein the same conditions are employed.

If desired, the vacuum and thermal treatments may be repeated, but in any case at least two vacuum and adjoining thermal treatments are necessary in accordance with the invention.

Conveniently, the last thermal treatment is suitably connected for the direct spinning of the polymerized caprolactam immediately thereafter. The spinning process may be carried out in accordance with conventional techniques whereby the desired filaments, threads, fibers, and the like may be produced efficiently and without obtaining objectionable exuding and perspiring of low molecular weight constituents.

It will be appreciated that the second and subsequent thermal treatments, if any, may be carried out in the sump of the vacuum extraction apparatus and that during the time of stay under thermal treatment, as well as in the connecting lines to the spinning apparatus and in the spinning head thereof, the polymerizate is exposed for a period of 1–4 hours to temperatures of from 240 to 300 degrees C. By maintaining the polymerized caprolactam at this increased temperature, the very small water content therein increases only slightly. In any case, however, the extract content does not exceed about 2.5% by

weight, i.e. the allowable limit for carrying out the effective spinning of the material. Nevertheless, during this thermal treatment, the content of monomers increases considerably at the cost of the oligomers, whereby the ratio of monomers to oligomers once more approaches the equilibrium ratio desired, i.e. 6:4.

Broadly, the vacuum and thermal treatments which repeatedly follow one another ordinarily, in accordance with the process of the invention, permit the effective reduction of the content of low molecular weight constituents to be carried out and the spinning of the vacuum and thermal-treated material in an over-all continuous manner in the same way as is carried out with the conventional continuous polymerization and spinning of monomer caprolactam. In accordance, with the foregoing, a high grade polymerizate is produced by the process of the invention having a monomer content of 0.5–1.5% by weight and a total extract content of about 2.5% by weight. The spun threads or filaments are extremely well adapted to conventional drawing operations.

Suitably, in accordance with the invention, as noted heretofore, the endless filaments or threads produced do not require additional washing and drying treatments before being further processed, to the desired finished products. Upon the customary textile processing operations, the spun materials may be simply subjected to subsequent work up procedures. Thus, a continuous process from the polymerization to the spinning stages is provided which makes possible the production of high-grade threads and filaments of very uniform quality in a completely automatic manner.

The following examples are set forth for the purpose of illustrating the invention, and it is to be understood that the invention is not to be limited thereto.

Example 1

Caprolactam is melted at 80 degrees C. and while maintained at this temperature is mixed in a mixing device with 0.4% by weight of water and 0.6% by weight of adipic acid. This mixture is continuously forced by a piston pump into a crude coil within which it remains for about 18 hours at a pressure of 20 atmospheres and a temperature of about 256 degrees C. A caprolactam polymerizate is thus formed having a relative solution viscosity in sulfuric acid of 2.0 still containing polymerization water. The reaction mixture includes 90% of polymers and about 6% of monomers and 4% of oligomers (by weight). The polymerization reaction product is fed directly via a worm pump to a thin-layer evaporator maintained under vacuum. In the first vacuum treatment, carried out at an average temperature of 260 degrees C. over a period of 30 minutes, using a vacuum of about 0.4 torr, water, monomers, and some oligomers are distilled off.

In this manner the relative solution viscosity increases to about 2.3. The polymerizate is practically anhydrous, containing 1.8% by weight of extract constituents including about 95% of oligomers. The melt is maintained for a period of four hours in an intermediate vessel heated to 250 to 260 degrees C. Above the level of the melt in the vessel, nitrogen is maintained for rinsing purposes. The nitrogen is flushed through the vessel so as to become loaded with monomer vapors and is conducted from the vessel to a condenser. In this first thermal treatment, the polymerizate material obtained has a relative solution viscosity of 2.5 and an extract content of about 4% by weight including 60% of monomers and 40% of oligomers.

The first thermal treatment is followed by a second vacuum treatment carried out for a period of about 30 minutes at a pressure of 0.3 torr and a temperature of 250–260 degrees C. As a consequence thereof, the extract content is reduced to about 1.5% by weight, and this extract consists almost completely of oligomers. The product is anhydrous. The relative solution viscosity at this point (2.5–2.6) precisely corresponds to the concentration of the stabilizing acid used in the polymerization and remains constant during the second thermal treatment.

The second thermal treatment is carried out for a period of about 1 hour, wherein the polymerizate remains in the conduits and spinning head of the spinning apparatus at a temperature of 260 degrees C. whereupon the same is thereafter spun at this temperature.

Thereafter, the thread spun in this manner has an extract content of 2.1% by weight with a natural ratio of monomers to oligomers (6:4). The polymerizate is particularly homogeneous and has a favorable molecular weight distribution. The threads produced upon spinning the polymerizate treated in the foregoing manner may be effectively drawn in the conventional manner so that a tensile strength of 6.2 g. per den. with 25%–26% elongation before breaking may be obtained. The threads which were spun in accordance with this example were mill threads having a titer of 70/30 den.

Example 2

In order to produce cord silk having highest tensile strength characteristics, by the direct spinning of continuously polymerized caprolactam, treated in accordance with the process of the invention, the procedure of Example 1 is repeated. However, in this case, the polymerization starting material included caprolactam and 0.4% by weight of water and 0.3% by weight of acetic acid. The polymerizate produced in the manner set forth in Example 1 had an extract content of 10% by weight which was of normal composition. The initial relative solution viscosity of 2.8 was increased upon the first vacuum treatment to 3.0 while the extract portion decreased from 10% to 1.8, consisting preponderantly of oligomers. In the first thermal treatment which was carried out for a period of 2 hours, the content of water soluble extract materials increased once more to 3.5% by weight. The extract at this point had the normal composition of 60% by weight monomers and 40% by weight oligomers. After the second vacuum treatment which was carried out, under the same conditions, as in Example 1, the relative solution viscosity reached a stable value of 3.2 wherein the extract content was about 1.5%.

After the second thermal treatment which was operatively connected with the spinning apparatus, an extract poor polymerizate was obtained having about 2% extract content. Upon spinning a very uniform cord silk of 840/140 den. was obtained, which could be very effectively drawn and which possessed the desired textile values of 8.6 g./den. at 14–16% elongation before breaking.

What is claimed is:

1. Process for the treatment, prior to spinning, of high molecular weight polymerized caprolactam to reduce the content of low molecular weight monomeric and oligomeric caprolactam constituents therein to at most about 2.5% thereof, which comprises subjecting resinous polymerized caprolactam, containing therein more than 2.5% by weight of low molecular weight monomeric and polymeric caprolactam constituents, at a temperature above the melting point thereof to vacuum treatment at a pressure of up to about 0.6 torr for a period between about 15–100 minutes to remove the volatile constituents present, followed by thermal treatment at a temperature above the melting point of the caprolactam polymer and at a pressure above about 0.6 torr for a period of between about 1–4 hours, to attain an equilibrium ratio of monomeric caprolactam to oligomeric caprolactam in the ratio range of substantially about 60:40 to 70:30, and repeating the vacuum treatment followed by thermal treatment at least one more time, whereby to obtain a total content of monomeric and oligomeric caprolactam constituents of at most about 2.5% by weight of the resinous polymerized caprolactam with the equilibrium ratio of monomeric caprolactam to oligomeric caprolactam

after the last thermal treatment being within the ratio range of substantially about 60:40 to 70:30.

2. Process according to claim 1 wherein the content of low molecular weight constituents including monomeric and oligomeric caprolactam constituents in the vacuum treated and thermally treated polymerized caprolactam obtained is between about 0.5–2.5% by weight thereof.

3. Process for the treatment, prior to spinning, of high molecular weight polymerized caprolactam to reduce the content of low molecular weight monomeric and oligomeric caprolactam constituents therein to at most 2.5% by weight thereof, which comprises subjecting resinous polymerized caprolactam, containing therein more than 2.5% by weight of low molecular weight monomeric and polymeric caprolactam constituents, to a vacuum treatment at a pressure of up to about 0.6 torr and at a temperature of between about 240–270° C. for a period of between about 15–100 minutes, followed by a thermal treatment at a pressure greater than 0.6 torr and a temperature between about 240–300° C. for a period between about 1–4 hours, and repeating the vacuum treatment followed by the thermal treatment each at least one more time, whereby the total content of monomeric and oligomeric caprolactam constituents is reduced to at most about 2.5% by weight of the resinous polymerized caprolactam with the equilibrium ratio of monomeric caprolactam to oligomeric caprolactam being within the percentage range of about 60:40 to 70:30.

4. Process for the production of filaments from high molecular weight resinous water-acid polymerized caprolactam by evacuation and thermal treatment at temperatures above the melting point of the polymerized caprolactam, prior to filament spinning, to reduce the content of low molecular weight monomeric and oligomeric caprolactam constituents therein to at most about 2.5% by weight thereof, which comprises subjecting such resinous polymerized caprolactam, containing therein about 10% by weight of low molecular weight monomeric and polymeric caprolactam constituents, prior to spinning, to evacuation at a temperautre above the melting point thereof and between about 240–270° C. and at a reduced pressure of between about 0.3–0.5 torr for a period of between about 15–100 minutes to remove the volatile constituents present and thus decrease the content of water-soluble extract materials present including monomeric and oligomeric caprolactam constituents from a content of about 10% to at most about 2.5% by weight of the resinous polymerized caprolactam, thereafter subjecting the resulting evacuated polymerized caprolactam to a thermal treatment at a temperature above the melting point thereof and between about 240–300° C. and at a pressure above about 0.6 torr, under an inert protective gas atmosphere for a period of between about 1–4 hours, to adjust the disturbed equilibrium ratio of monomeric caprolactam to oligomeric caprolactam present in the water-soluble extract of the melt and to attain an equilibrium ratio of monomeric caprolactam to oligomeric caprolactam in the ratio range of substantially about 60:40 to 70:30, subjecting the resulting thermally treated polymerized caprolactam to a further evacuation at said temperature of between about 240–270° C. and said reduced pressure of between about 0.3–0.5 torr for a further period of between about 15–100 minutes to remove the further volatile constituents present and thus decrease further the content of water-soluble extract materials present, and thereafter subjecting the resulting further evacuated polymerized caprolactam to a further thermal treatment at said temperature between about 240–300° C. and at a pressure above about 0.6 torr under an inert protective gas atmosphere for a further period of about 1–4 hours, to adjust further said disturbed equilibrium ratio of monomeric caprolactam to oligomeric caprolactam present in the water-soluble extract of the melt, whereby to obtain a total content of monomeric and oligomeric caprolactam constituents of at most about 2.5% by weight of the resinous polymerized caprolactam with the equilibrium ratio of monomeric caprolactam to oligomeric caprolactam after the further thermal treatment being within the ratio range of substantially about 60:40 to 70:30.

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