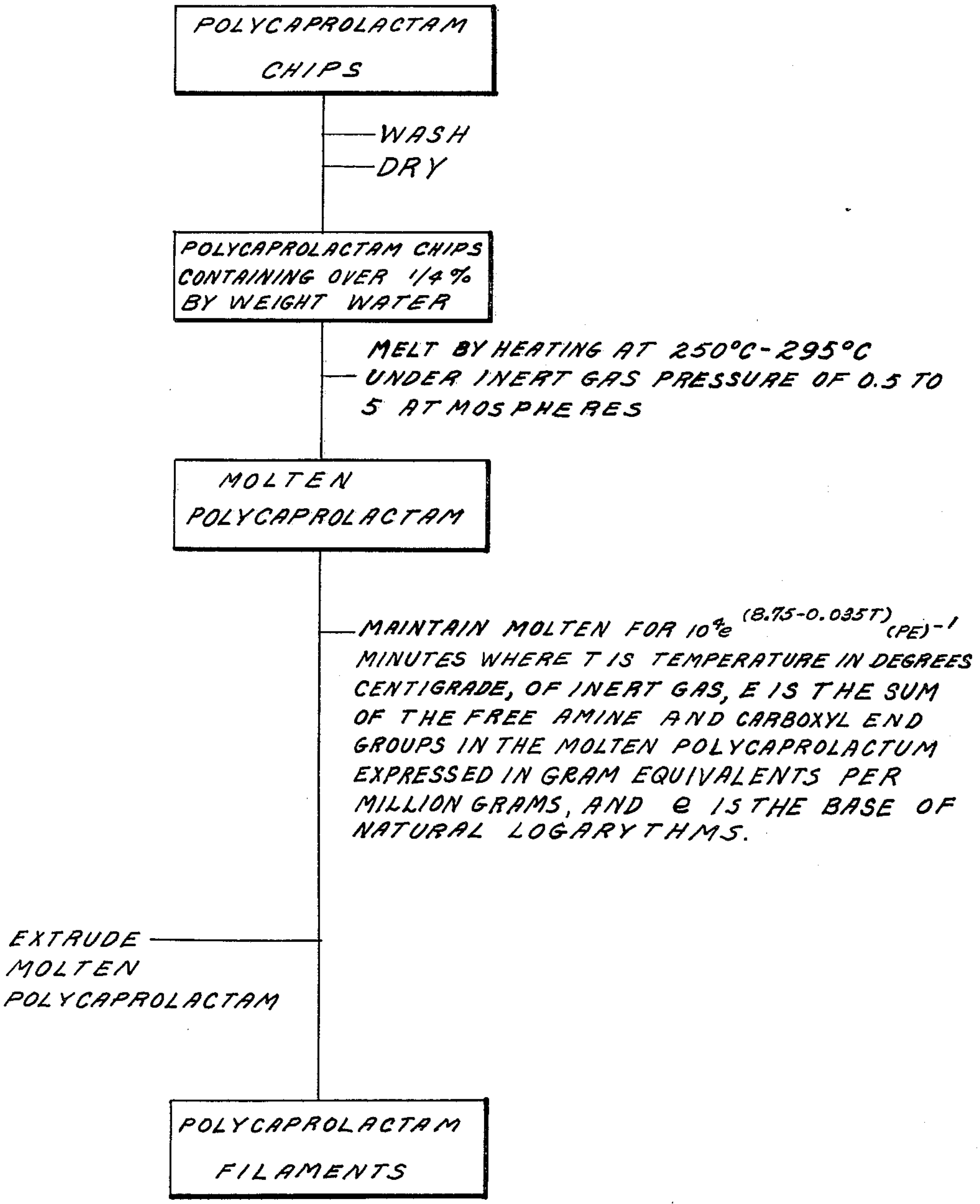
June 11, 1963 R. F. J. FREEMAN 3,093,445

MANUFACTURE OF POLYAMIDE FILAMENTS

Filed July 17, 1961



INVENTOR.
RONALD FRANK JAMES FREEMAN
BY
Cushman, Darby & Cushman
ATTORNEYS

United States Patent Office

3,093,445
Patented June 11, 1963

3,093,445

MANUFACTURE OF POLYAMIDE FILAMENTS

Ronald Frank James Freeman, Abergavenny, England, assignor to British Nylon Spinners Limited, Pontypool, Monmouthshire, England

Filed July 17, 1961, Ser. No. 124,394
Claims priority, application Great Britain Aug. 23, 1960
6 Claims. (Cl. 18—54)

This invention relates to improvements in or relating to the manufacture of polyamide filaments and more particularly to the melt-spinning of high molecular weight polycaprolactam into filaments. The invention is illustrated by the flow diagram in the drawing.

By the term high molecular weight polycaprolactam is meant, more accurately, poly-epsilon-caprolactam of sufficiently high molecular weight to be melt-spinnable into filaments. This polyamide, the preparation of which by the polymerization of the lactam is described in United States Patent No. 2,241,321 (Schlack), was manufactured already during the second World War in Germany (under the trademark "Perlon") and is now made also in Italy, U.S.A. and many other countries. The properties of polycaprolactam are generally similar to those of polyhexamethylene adipamide (described in United States specification No. 2,130,523 of Carothers) and both polyamides are melt-spun into filaments suitable for textile uses on a very large scale, the melting being effected under an inert gas to avoid oxidation. There is, however, an important difference in chemical behaviour inasmuch as the former polyamide gradually reverts to the monomeric lactam and some low polymers when maintained in the molten condition. After the molten polycaprolactam has reached equilibrium with these low molecular weight constituents, the proportion of the latter may amount to 10% by weight or more. This low molecular weight material renders the polycaprolactam filaments unfit for textile purposes and must consequently be removed or at least reduced to about two percent by weight. This operation is advisedly effected before melt-spinning the polymer into filaments because not only is the presence of the low molecular weight material during melt-spinning undesirable but also its removal from the filaments is inconvenient. However, about two percent of low molecular weight material are normally formed when pure polycaprolactam is melt-spun, or even more if the time during which the polymer remains molten is prolonged. The polymer must therefore be purified so that it is practically free of said material before the melt-spinning. This purification may be carried out by various means, especially vaporisation in vacuum or extraction or both but for complete removal of the low molecular weight material extraction is often recommended, with or without a preceding vacuum treatment. The usual procedure is accordingly to extract the polycaprolactam in the form of chips with hot water and dry it before melt-spinning it into filaments, as described in French specification No. 882,461, bearing German priority dates of June 18, 1941, and February 24, 1942. Aqueous solutions may also be employed for the extraction; thus the earlier stages thereof may be effected with aqueous solutions of caprolactam, the final stage being carried out with pure water.

In view of the great commercial importance of polycaprolactam much investigational work has been carried out on the polymerisation of the monomeric lactam and on the depolymerisation of the resulting polymer. This work has shown that the proportion of low molecular weight material contained in molten polycaprolactam at equilibrium becomes larger both as the temperature rises and as the water content increases. The presence of water moreover accelerates the reformation of the low molecular weight material (see, for example: Recueil des Travaux Chimiques des Pays-Bay, 1955, vol. 74, p. 1376, and Zeszyty Naukowe Politechniki Lodzkiej No. 9, Chemia, 1955, No. 3, p. 17, also Journal of Polymer Science, vol. 30, issue No. 121, July 1958, p. 459.)

For many years it has thus been held necessary thoroughly to dry the polycaprolactam chips after they have been washed. In Germany during the war, for example (see "Synthetic Fiber Developments in Germany," published in 1946 by Textile Research Institute, Inc., page 466) the chips are said to have been dried down to 0.15% moisture. British specification No. 676,585 of Inventa A.G. fuer Forschung und Patentverwertung dating from 1949, for instance, refers to complete removal of water and British specification No. 747,913 of VEB. Thueringisches Kunstfaserwerk "Wilhelm Pieck" Schwarza, dating from 1953 to "elaborate drying." Although according to the invention described in British specification No. 813,527 of Farbenfabriken Bayer, moist chips with a water content up to 10% by weight can be used, this is apparently because they are dried whilst being melted by means of a stream of gas so that a dry melt is obtained (see especially lines 34 to 36 of page 2 of said specification).

The present invention is based on the startling discovery that, provided certain conditions are observed during melt-spinning, the drying of the wet chip can be dispensed with. It is necessary to restrict the time during which the polycaprolactam remains molten in a manner depending on the temperature. The maximum permissible time during which the polymer may remain molten has also been found to depend on the pressure of the inert gas, under which the polycaprolactam is melted, and on the total number of free carboxyl and amine end groups in the polycaprolactam. Under these conditions, which will be defined below, the proportion of low molecular weight material in the resulting melt-spun filaments is found to be acceptable for textile purposes. Since drying is an expensive process, the omission of the drying stage constitutes an important economic advantage.

It is, however, well known that, when a substance is being dried, the removal of water becomes more difficult and costly as the quantity of water remaining diminishes. The removal of the last small residue of water thus causes the most trouble. For instance, it is frequently found that although the water content of polyamide chips can be reduced to about ¼% by means of a hot air drier, further removal of water is not feasible owing to the length of time taken and the likelihood of deterioration of the polymer by oxidation, without the employment of other means, e.g. a vacuum drier. It is accordingly in respect of the last small residue of water that the advantages of the present invention particularly apply. The invention consequently contemplates also the melt-spinning of partially dried polycaprolactam chips which contain over ¼% water.

If in the course of industrial manufacture polycaprolactam chips are washed with hot water and allowed to drain freely they may contain from 10% to 25% of water, or even as little as 3–4% if they are allowed to dry for a very long time. When too wet, the chips tend to cake together or form a paste and cannot be poured or conveniently moved from one vessel to another, and it is often desirable to dry the chips sufficiently to avoid this difficulty. It may be necessary for this purpose to reduce the water content to 7–12% but it will be understood that all the figures quoted in this paragraph are approximate and liable to considerable variation because they depend very much on the size and geometrical shape of the chips.

As already pointed out the time, during which the polycaprolactam remains molten in the present process of melt-spinning, is restricted in a manner depending on the temperature of melt-spinning, on the pressure of the inert gas present and on the total number of free carboxyl and amine end groups in the polycaprolactam, and numerous experiments have shown that the said time can be defined by the following expression:

$$t=10^4.e^{(8.75-0.035T)}.(P.E)^{-1}$$

in which

t=maximum permissible time in minutes during which the polycaprolactam is maintained in a molten condition.

e=the base of the natural logarithms.

T=temperature in degrees centigrade (ranging from 250 to 295° C.)

P=pressure in atmospheres of inert gas (ranging from 0.5 to 5 atmospheres.)

E=sum of the free amine and carboxyl end groups in the molten polycaprolactam expressed in gram equivalents per million grams.

N.B.—The free amine and carboxyl ends contained by the polycaprolactam are determined by appropriate titration methods. The determination may be carried out on a sample of polymer taken from the melt pool or on a sample of the extruded filaments. It may be pointed out, however, that the values for the amine and carboxyl ends found in the polycaprolactam chips are usually suitable for insertion in the above expression because, except in the case of polymers for which the sum of the amine and carboxyl ends is less than 80, the change in the values occasioned by melting can be neglected.

Accordingly the present invention relates to a process for the manufacture of polyamide filaments by melting high molecular weight polycaprolactam chips at a temperature from 250° to 295° C. under an inert gas at a pressure from 0.5 to 5 atmospheres and extruding the molten polyamide in the form of filaments, characterised in that the polycaprolactam chips have been washed with water but not dried or only incompletely dried and contain over ¼% by weight of water and that the polyamide is maintained in a molten condition for a period not exceeding in minutes the value of the expression:

$$10^4.e^{(8.75-0.035T)}(P.E)^{-1}$$

whereof the symbols are as hereinbefore defined.

The washing of the polycaprolactam chips with water, referred to in the above paragraph, is intended to include the use of aqueous solutions for this purpose; thus, for example, an aqueous solution of caprolactam is often employed in the earlier stages of the washing which is completed with the aid of pure water. The time during which the polyamide is maintained in a molten condition is advantageously not more than 80% of the period specified in the above paragraph, because, as already explained, the shorter the period in question, the smaller the proportion of low molecular material in the resulting filaments and it is preferred that the proportion of this low molecular material be below 2.0% by weight.

Examples of inert gases which prevent oxidation of the polyamide are: nitrogen, steam, helium and hydrogen. The inert gas is preferably at or near atmospheric pressure, but it may be above or below atmospheric pressure. It is preferred that the inert gas be steam at a pressure which is atmospheric or within 3% of the existing atmospheric pressure. Even when the atmosphere of inert gas provided is other than steam, e.g. nitrogen, steam will in fact be present owing to its evolution when the undried or incompletely dried polycaprolactam is melted.

The process of the present invention may very desirably comprise melting high molecular weight polycaprolactam chips containing over 3½% water under steam at atmospheric pressure or within 3% thereof at between 265° C. and 280° C.

The polycaprolactam chips employed in carrying out the process of the present invention may contain much more water than ¼% and it is frequently convenient to use without further drying polycaprolactam chips having a water content upwards of 3½% or 7% when such chips become available in the course of industrial manufacture. Particularly is it desirable to make use of polyamide chips containing over 3½% water but insufficient to cause them to cake together or form a paste.

The polycaprolactam chips employed in accordance with the invention may contain conventional adjuvants such as delustrants, dyes, pigments and stabilisers.

The following examples, in which the percentages are by weight, are by way of illustrating not limiting the invention.

Example 1

Polycaprolactam containing 0.15% of acetic acid and 0.4% of titania and having a relative viscosity of 2.63 as determined by the method quoted below, is extruded through a die and quenched in water to form bristles of ¾ mm. diameter. These bristles are cut by means of a rotary cutter into chips ¾ mm. long. The low molecular weight material contained in the chips amounts, as estimated by aqueous extraction, to 9.1%

The relative viscosity of the polycaprolactam is determined by dividing the viscosity of a 1% solution of the polymer in 96% aqueous sulphuric acid at 25° C. by the viscosity of the said aqueous sulphuric acid at the same temperature.

The polycaprolactam chips are washed in their own weight of water at 90° C. for 1 hour, and the said washing repeated a further five times with fresh water whereby the proportion of low molecular weight material is reduced to 0.2% (calculated on the dry polymer). The resulting chips are at 90° C. After most of the adherent water has been allowed to drain away, the chips are found to contain 14% of water. On analysis the polyamide is found to contain 40 gram equivalents of amine ends and 65 gram equivalents of carboxy ends per 10^6 grams.

To avoid discoloration during storage the chips are cooled to 35° C. by a blast of cold air. The chips then contain 9% of water and flow freely if poured. After being pneumatically transported to a storage bunker the chips have a water content of 7%. The polycaprolactam chips are melted under steam at atmospheric pressure at a temperature of 270° C. in an apparatus similar to that illustrated in British specification No. 653,757. The molten polyamide is extruded in the form of filaments at such a speed that the period during which the polyamide remains molten is 30 minutes. The resulting filaments are found to posses a relative viscosity of 2.64 and to contain 1.5% of material which is extractable by water. After being stretched by known methods these filaments prove to be eminently suitable for textile purposes.

Example 2

Example 1 is repeated except that the rate of extrusion is reduced so that the period during which the polyamide remains molten in 45 minutes. The resulting filaments are found to contain 2.2% of water-extractable material. After being drawn in the solid state to 4.95 times their original length, the filaments possess a denier of 15, a tenacity of 6.6 gm. per denier and an extensibility at break of 25%.

Example 3

Polycaprolactim chips having a relative viscosity of 3.31 and containing 11.5% of low molecular weight material are washed in the same manner as described in Example 1. The washed chips contain 0.3% water extractable material (calculated on the dry polymer).

After draining the chips contain 14% water. The water content is reduced to 12% by centrifuging and, when the chips have been pneumatically transported to a storage bunker, is found further to have fallen to 10%.

The polycaprolactam chips are melted at 270° C. under an atmosphere of steam at a pressure of 2.25 atmospheres.

The molten polycaprolactam contains 40 gram equivalents of amine ends and 40 gram equivalents of carboxyl ends per 10^6 grams. The molten polyamide is spun into filaments through a spinneret with 140 holes, the period during which it remains molten being 23 minutes. The relative viscosity of the filaments is 3.29; they contain 1.9% of low molecular weight material. The extruded filaments are drawn in the solid state over a hot plate at approximately 185° C. to 5.3 times their original length, the final denier being 840. The resulting filaments have a tenacity of 8.5 grams per denier and an extensibility at break of 16%.

Example 4

Example 3 is repeated except that the polycaprolactam chips of 10% water content are further dried until they only contain 0.3% water. The filament obtained exhibit similar good properties.

Example 5

This example is carried out in the same way as Example 3 except that the steam atmosphere employed during the melt-spinning is replaced by an atmosphere of nitrogen at the same pressure, namely 2.25 atmospheres. In this manner polycaprolactam filaments of similar properties are obtained.

What I claim is:

1. A process for the manufacture of polyamide filaments containing not more than 2% of low molecular weight material and suitable for textile purposes which comprises melting high molecular weight polycaprolactam chips which have been washed with water and incompletely dried and contain over ¼% by weight of water by heating said chips at a temperature from 250° C. to 295° C. under an inert gas at a pressure from 0.5 to 5 atmospheres, maintaining the polyamide in a molten condition for a period not exceeding in minutes the value of the following expression:

$$10^4 . e^{(8.75-0.035T)}(P.E)^{-1}$$

wherein e is the base of the natural logarithms, T is the temperature in degrees centigrade, P is the pressure in atmospheres of the inert gas and E is the sum of the free amine and carboxyl end groups in the molten polycaprolactam expressed in gram equivalents per million grams, and extruding the molten polyamide in the form of filaments.

2. A process as claimed in claim 1, wherein the temperature is from 265° C. to 280° C.

3. A process as claimed in claim 1, wherein the polycaprolactam chips contain over 3½% by weight of water but insufficient to cause them to cake together.

4. A process as claimed in claim 1, wherein the polycaprolactam chips contain over 7% by weight of water.

5. A process as claimed in claim 1, wherein the inert gas is steam at a pressure between 0.67 and 1.33 atmosphere.

6. A process for the manufacture of polyamide filaments which comprises melting high molecular weight polycaprolactam chips which have been washed with water and incompletely dried and contain over 3½% by weight of water by heating said chips at a temperature from 265° C. to 280° C. under steam at a pressure of between 0.67 and 1.33 atmosphere, maintaining the polyamide in a molten condition for a period not exceeding in minutes the value of the following expression:

$$10^4 . e^{(8.75-0.035T)}(P.E)^{-1}$$

wherein e is the base of the natural logarithms, T is the temperature in degrees centigrade, P is the pressure in atmospheres of the inert gas and E is the sum of the free amine and carboxyl end groups in the molten polycaprolactam expressed in gram equivalents per million grams, and extruding the molten polyamide in the form of filaments.

References Cited in the file of this patent

UNITED STATES PATENTS

2,571,975 Waltz ---------------- Oct. 16, 1951