Aug. 31, 1954 R. GABLER 2,687,552

PROCESS AND APPARATUS FOR DIRECT SPINNING OF POLYAMIDES

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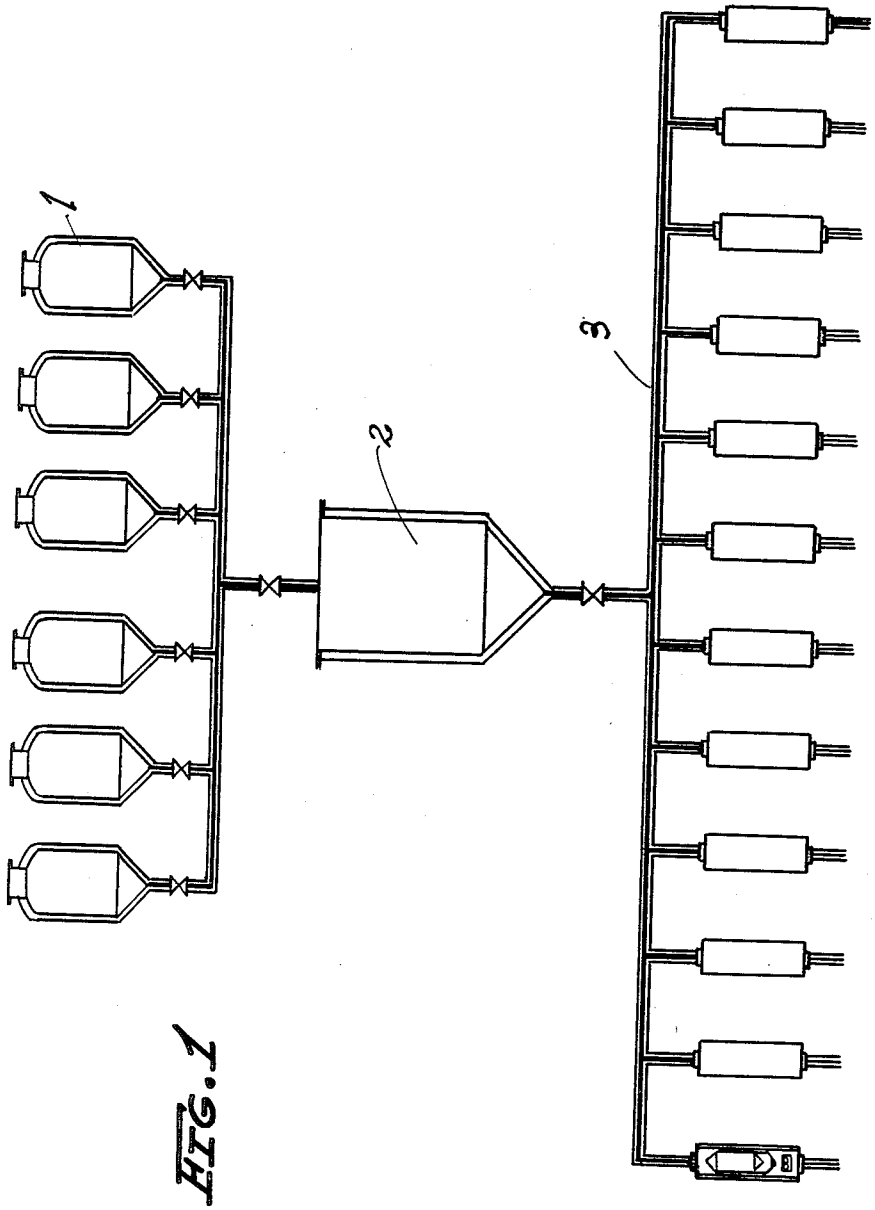


FIG. 1

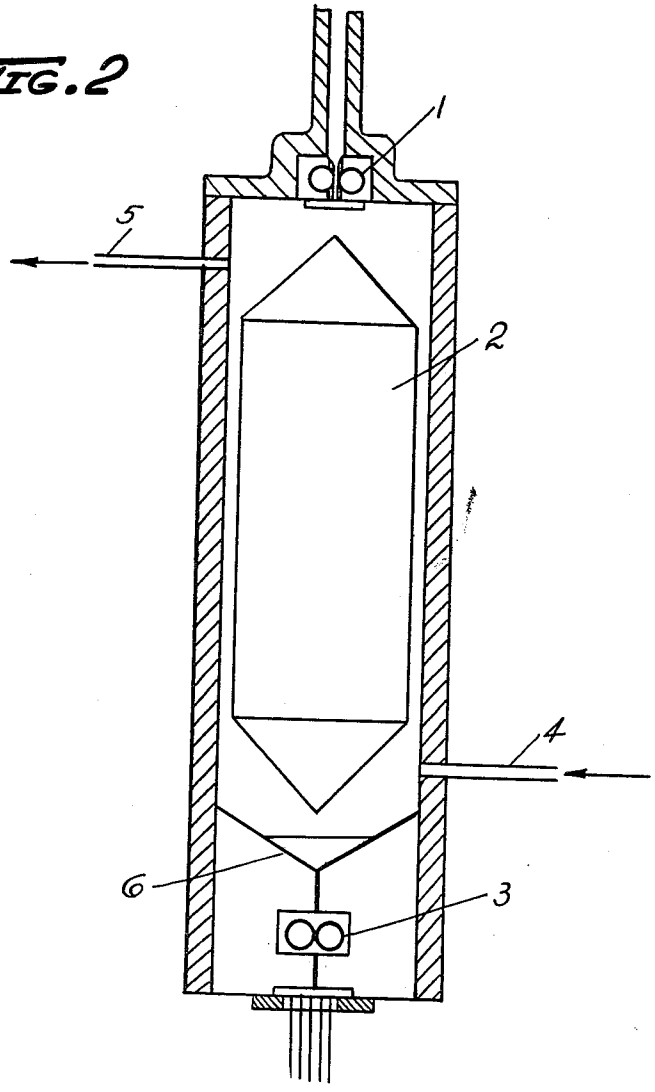
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FIG. 2



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PROCESS AND APPARATUS FOR DIRECT SPINNING OF POLYAMIDES

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5 Claims. (Cl. 18—8)

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This invention relates to improvements in the spinning of polyamide melts from ω-amino-carboxylic acids.

Polyamides on the basis of ω-amino-carboxylic acids, formed from free ω-amino-carbonic acids or their polyamide forming derivatives, e. g. the esters or lactams, by themselves or mixed with other polyamide forming materials such as diamines and dicarboxylic acids, mostly still contain certain quantities of unchanged monomer components or low molecular condensation products.

These low molecular components disturb the subsequent process stages considerably. Quite aside from the bothersome development of vapors at the spinning nozzles, the strength of the formed structures, in particular of spun threads, is so extensively reduced that the subsequent cold stretching process can be carried out only with greatly reduced ratio of stretch and under greatest difficulties.

It has furthermore been observed that the low-molecular portions bloom on the surface when the formed material is stored and there form irregular, unsightly and sticky coverings which make further processing, in particular dyeing, practically impossible.

The quantity of the low-molecular portions contained in these polyamides depends almost exclusively on the temperature used in condensation and amounts in general to 8–15%, for instance in the polymerization of ε-caprolactam at 250° C. to 10–11%.

Practical experience has shown that, in the individual processing stages of a polyamide structure on the basis of an ω-amino-carboxylic acid or of a polyamide forming derivative, certain amounts of low-molecular portions must not be exceeded if most favorable working conditions and best characteristics of the polyamide compound produced are to be achieved.

Polyamide threads of finer titre, in particular silks with individual thread titres of 1–3 den., react particularly sensitively to overstepping of the permissible amounts of low-molecular portions, whereas coarse threads, as for instance bristles and wires, are less senitive and can easily be spun with a monomer content of 8–15% corresponding to the polymerization equilibrium.

In the case of polyamide silks on the basis of ω-amino-carboxylic acids or their lactams, on the other hand, disturbances already arise, if, before spinning, the content of low-molecular components in the melt exceeds 6–7%. Smooth stretching with maximum stretch ratio on the other

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hand already necessitates a limitation of the monomer content to 3–4%. The unavoidable low-molecular portions content in the polymer melts of ω-amino-carboxylic acids or their lactams and polyamide-forming derivatives made it hitherto impossible to spin such melts in an uninterrupted flow to polyamide silks of fine titre.

As already mentioned, there exists a process for the direct spinning of polyamide melts on the basis of ω-amino-carboxylic acids to threads of coarse titre such as are required for the production of bristles, wires, etc. In the case of these relatively thick threads, a content of low-molecular portions of 8–15% has proven bearable. It is different, however, in the case of threads of fine title, for example the silks such as are required for the production of stockings and other textile weaves and knits. Here, removal of the low-molecular portions is indispensable. The elimination of these disturbing portions took place hitherto by extraction. To this end the polymer melt had to be shaped into a ribbon, cooled off, and reduced to small pieces and after the extraction the wet material had to be dried again till practically free of water. It was also attempted to avoid these circumstantial and time-consuming working stages by removing the monomer portions out of the polymerization vessel or out of a stock pot by means of vacuum distillation.

One was, however, in this manner only able to reduce the monomer content to about 4–5%. Moreover, the success of the evacuation was almost completely vitiated by the re-formation, due to equilibrium, of a further 2–3% of monomers, corresponding to the relatively long period the melt remains in the pipes from the polymerization vessel or evacuated intermediary vessel to the spinning heads and in these themselves. Thus the low molecular portions again rose to a percentage which led to severe disturbances when spinning and subsequently stretching.

This invention relates to a process which eliminates the low-molecular portions to such an extent that it is now possible to spin polyamide melts on the basis of ω-amino-carboxylic acids and/or their lactams directly, i. e. maintaining the fluid condition, to threads of all thicknesses down to the finest so far usual stocking silk titres. The removal of the monomers is hereby so extensive that the subsequent stretching process also is not detrimentally affected.

The removal of the low-molecular portions takes place, according to the invention, by thin-film evaporation, whereby the use of a vacuum is not absolutely necessary. Decisive was the

realization that the elimination of the volatile portions is fully effective only if undertaken directly before the spinning nozzle, i. e. in the spinning head itself in order to leave the melt a minimum of time for the re-formation of monomer components.

The comparatively quick speed of re-formation of the low-molecular portions of the temperatures of 250–280° C. usually obtained in the spinning pump aggregate requires special measures in order to have the evaporation of the low-molecular portions take place quicker than their re-formation from the polymerizate.

This is achieved according to this invention by thin film evaporation.

As is well known, the speed of evaporation of a liquid can be considerably increased by distributing the matter in a thin film over a large heated surface. In the present case we have to deal with no simple liquid but with a complicated system of a plurality of substances in which a relatively small amount of volatile components is dissolved in a large excess of non-volatile viscous polyamide flux. In such cases complications arise as a rule in that the speed of evaporation is influenced in an unclear manner by complicated diffusion processes as well as by cohesion and border surface effects.

All the more astonishing was the discovery that, by extensive spreading of the polyamide melt to be treated in the form of a thin film on a heated surface, the evaporation of the low-molecular components can be so accelerated that their re-formation from the polymers during the stay on the thin-film evaporator may be practically disregarded.

In the accompanying drawing:

Fig. 1 shows schematically a combination of devices adapted for carrying out my new direct spinning process.

Fig. 2 is a vertical section through a thin film evaporator according to the invention.

The thin-film evaporator can be constructed in various forms.

In the embodiment shown in Figure 2, **1** is the supply pump to the thin-film evaporator, **2** the heated surface of the thin-film evaporator and **3** the supply pump to the nozzle block. At **4** inert gas enters the evaporator head and at **5** the low-molecular portions are removed from the apparatus. The conical upper part has proved especially good in this form for the purpose of distributing the melt uniformly and in a thin layer over the entire surface.

Of course, the present application is not restricted to the indicated form of the invention. It is intended to cover all devices suitable to subjecting a polyamide melt in finely distributed form to an evaporation process on a heated surface, whereby volatile components escape from the polymer melt. Thus the thin-film evaporator can also take the form, for example, of concentric pipes, a ball, a simple cone, a double cone, etc. For the uniform distribution of the melt a multi-aperture nozzle, a ring-slit or a rotating disc which spreads the product on the inner side of a heated pipe can be used. Chrome-plated or non-rusting steel, glass or ceramic material may be employed as material for the heated surface. It is appropriate to work the surface of the thin-film evaporator as smooth as possible, e. g. polishing metal surfaces in order to permit smooth flowing of the film of the melt.

The heating of thin-film evaporator may be effected directly with electricity, by means of a heating fluid or steam or by means of induction heating, etc.

One may also renounce heating the surface of the thin-film evaporator and heat the film of the melt directly by means of high-frequency or ultra-red heating.

In order to assure sufficient elimination of the volatile components and, on the other hand, not to leave the polyamide melt unnecessarily long on the thin-film evaporator, whereby the melt might possibly be injured, it is necessary to adjust the time of stay of the melt and the conditions of pressure and temperature exactly to the surface conditions of the evaporator. The following numerical examples will serve to explain this:

On a thin-film evaporator of the form corresponding to Fig. 2 with an effective surface of 1500 sq. cm. a polyamide melt with 10.5% low-molecular parts was spread with various speeds and treated with a pre-heated nitrogen stream at atmospheric pressure. The monomer content of the spun silk amounted, at a speed of

3 g./min. to 2.8%
10 g./min. to 3.7%
30 g./min. to 7.4%

The thin-film evaporation may be conducted at any pressure. It is particularly simple to work at atmospheric pressure or slightly in excess thereof whereby an inert stream of gas, which may appropriately be pre-heated, is employed as stirring means for evaporating the low-molecular product. The inert gas, preferably nitrogen, after separating out the volatile portions, is re-introduced into the apparatus in closed circuit. By means of reducing the pressure in the thin-film evaporator the evaporation of the low-molecular components may be considered accelerated so that, with a given output of the pumps the effective surface of the thin-film evaporator may be kept relatively small to achieve the same output as a normal pressure evaporator. At pressures greater than .1 mm. Hg it is recommended, even when working in vacuum, to use an inert protective gas to avoid injury of the melt by oxidation. At still lower pressures such a measure is not necessary.

A further very effective arrangement was found to be a second surface arranged parallel or concentric with the thin-film evaporator at a small distance of a few mm. This second surface may be heated or cooled but not below the melting-point of the low-molecular components as these would otherwise be deposited there and clog the narrow slit. Working with cooled counter-surface proved particularly effective when working at low pressures of 10^{-1} to 10^{-3} mm. Hg. Under such extreme conditions, however, changes easily occur in the polyamide melt, such as formation of foam or increases in viscosity which may imperil the spinnability of the melt.

At normal working with the thin-film evaporator, i. e. at normal pressure or slight vacuum no disturbing formation of foam or bubbles occurs and the increase of the viscosities of the melt and of the solution of the polyamide, though always occurring, remain within limits which in no way prevent further processing. Normally, the true viscosity (I. V.) of a polyamide which enters the thin-film evaporator with an I. V. of 1.0 increases to 1.05–1.10 on emergence from the nozzle. The viscosity of the polyamide melt changes by an amount which is percentually about equal.

The vapors of the low-molecular components

removed from the thin-film evaporator by the inert stirring gas or the vacuum pump are condensed in a cooler and recovered in such a pure form that they can be directly re-employed for polymerization purposes.

The carrying out of the new direct spinning process takes place as shown in Fig. 1 in such a manner that the polymer melt including 8–15% low-molecular components as it arises according to one of the well-known processes from an ω-amino-carboxylic acid or one of its polyamide-forming derivatives is blown off from one or more autoclaves 1 in Fig. 1 or from a pipe for continuous polymerization into an equalization vessel 2 and from there is led to the spinning heads 4 via distributor conduits 3 corresponding in number to the number of spinning-points. In the distributor conduits to the spinning heads, which are heated to a temperature slightly above the melting-point of the polyamide used, the melt flows down-grade into the supply pump of the thin-film evaporator. It has proven to be a particularly favorable working method to supply the stock-vessel 2 with melt by means of a larger number of small autoclaves, for instance six, which are emptied in regular 4 hour periods.

One thus obtains products more uniform as regards degree of polymerization and low-molecular component content, whereby the operation of the thin-film evaporator and spinning reliability is considerably improved.

The temperature of the thin-film evaporator is preferably adjusted at 30° C. above the melting-point of the polyamide to be spun, but not in excess of 280° C. as above this temperature injurious decomposition phenomena set in. The supply quantity corresponding to the spinning titre is set at the pumps 1 and 3 in Fig. 2, whereby with a given surface of the thin-film evaporator the time of stay of the melt is determined. The elimination of the volatile components to the desired degree is adjusted by regulation of the speed of flow of the stirring gas and/or the pressure when working with vacuum. After leaving the thin-film evaporator, the melt collects in the funnel-shaped space 6 in Fig. 2 about the spinning pump. The amount of melt collecting there is restricted to a minimum and should preferably not contain more than half an hour's spinning supply.

With the process as invented, it is possible to remove the volatile components from polyamide melts on the basis of ω-amino-carbonic acids to such an extent that it is possible to spin even fine-titred polyamide silks such as stocking silk, weaving silk, and tire-cord silk directly from the melt of the polymerization vessel under avoidance of any solid intermediary condition.

The process may be made fully continuous by feeding the direct spinning apparatus so much monomeric raw material that the continuous spinning process is not interrupted for a moment. In this operation, the adjustment of the speed of polymerization to the capacity of the spinning machine is purely a question of the dimensions of the apparatus. As an important advantage of the process as invented is to be regarded, in addition to the simplification of the technological process, above all the fact that the relatively unsensitive monomeric raw material is introduced into the closed direct spinning apparatus and leaves it only as a finally formed structure and up to that point has no opportunity to come in contact with atmospheric air, dust or other sources of dirt. Through this isolation of the process and the already mentioned continuity of the process the path is opened to more uniform polyamide fibres of better quality for textile purposes.

Example 1

In a reaction tube heated to 250° C. a mixture of 90% ε caprolactam and 10% water to which is added 0.4% sebazinic acid, as means for breaking up the chains, is continuously fed by means of a pump. The reaction is carried out under exclusion of oxygen and controlled in such a manner that the melt remains 15 hours in the reaction tube. From the lower part of the tube the polymer melt, which still contains 12–15% of low-molecular components, is pumped into an intermediary vessel which is heated to 240° C., and from there distributed to 12 spinning heads of a spinning machine. As shown in Fig. 2, the spinning heads are equipped with thin-film evaporators of 1500 sq. mm. surface each and heated to 250° C. The feed pump and spinning pump are adjusted to an output of 11 g./min. At a pressure of 15 cm. column of water the volatile components are driven off with nitrogen pre-heated to 250° C. The silk spun at the 12 spinning heads with an unstretched titre of 105 den. exhibited a content of between 3 and 4% low-molecular components and was subsequently stretched in a ratio of 1:3.5.

Example 2

In a closed pressure vessel 80 parts of ε-caprolactam and 20 parts of sebazinic acid hexamethylene-diamine are heated for 12 hours to 250°–255° C. under exclusion of oxygen. Di-polymer melt was pressed every four hours by means of nitrogen from the autoclaves into the equalization vessel from where the melt flowed to the spinning heads of a twelve-fold spinning machine. The melt, which still contained 9–11% low-molecular components, was distributed by means of the feed pump at a speed of 56 g./min. to a thin-film evaporator consisting of concentric pipes of 450 sq. cm. surface each. Both pipes were heated to 245°–250°. At a pressure of 10^{-2} mm. Hg the low-molecular components were removed from the melt to such an extent that, maintaining a sump of 150–180 g., a silk of 1200 den., unstretched, with a content of 1.5–2.5% low-molecular components could be spun.

Example 3

In an apparatus according to Fig. 1 a mixture consisting of 60 parts of ε-caprolactam, 30 parts of endomethylene lactam, 10 parts of water and 0.4 part of sebazinic acid were polymerized for 10 hours at 250–255° C. under exclusion of oxygen, the melt being subsequently pressed into a heated equalization vessel. From there the melt was fed to the spinning heads of a twelve-fold spinning machine through tubes heated to 240° C. The spinning heads were equipped with thin-film evaporators according to Fig. 2 of 800 sq. cm. each, over which the material to be spun was uniformly spread by means of a feed pump and distributor nozzle. With an output of 11 g./min. the melt remained 15–18 min. in the thin-film evaporator. At a pressure of 300 mm. Hg under nitrogen rinsing at 260° C. the volatile components were distilled off to such an extent that the spun silk contained an average amount of 2.2–2.8% of these components.

I claim:

1. A process for direct spinning of polyamides produced from a material selected from the group

consisting of omega-amino carboxylic acids, esters of omega-amino carboxylic acids, the lactams of omega-amino carboxylic acids, comprising accumulating a mass of molten polyamide containing about 8–15% of unpolymerized monomer, passing said molten polyamide in the form of a thin liquid film over a surface to reduce the monomer content to at most 4% by evaporation, and spinning said molten polyamide shortly after de-monomerizing before the monomer can re-form above 4% in amount, said spinning being conducted below the decomposition temperature of said polyamide at about 240–260° C.

2. A process according to claim 1, wherein said surface has an area of about 450–1500 square centimeters and the thin liquid film of polyamide traverses said surface in about 15 to 18 minutes, said evaporation being effected through heating of said surface.

3. A process according to claim 1, wherein the evaporation of monomer from said thin liquid film of polyamide is effected in a stream of nitrogen.

4. An apparatus for the direct spinning of liquid polyamides of omega-amino carboxylic acids containing about 8–15% of unpolymerized monomer, comprising a substantially vertical heating chamber, first pump means discharging into said heating chamber near its upper end, exhaust means connected to said heating chamber near its upper end, a conical spreading surface positioned within said heating chamber with its apex adjacent said first pump means and its base

remote from said first pump means, heating means positioned beneath said conical surface, exit means connected to said chamber near its lower end, second pump means having an inlet line and an outlet line, said exit means connected to said inlet line of said second pump means, and spinning means connected to said outlet line of said second pump means, whereby upon passage of a stream of molten polyamide through said first pump means into said chamber said liquid passes over said conical surface in the form of a thin film and out by said exit means into said spinning means through said second pump means, the monomer being evaporated from said thin film and passing out said exhaust means as a vapor.

5. An apparatus according to claim 4 including a polymerization vessel discharging into said first pump means, said exhaust means leading into said polymerization vessel, whereby monomer evaporated from said thin film is returned to said polymerization vessel for conversion to polyamide.

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