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(54) Titre : METHODE POUR LA POLYMERISATION HYDROLYTIQUE EN CONTINU DE LAUROLACTAME

(54) Title: PROCESS FOR THE CONTINUOUS HYDROLYTIC POLYMERIZATION OF LAUROLACTAM

(57) **Abrégé/Abstract:**

Continuous hydrolytic polymerization of laurolactam is achieved in a simple and economical manner by a process in which laurolactam and water are metered in via a pump, if desired passed through a reactor having largely ideal backmixing, subsequently reacted in a tube reactor to give a prepolymer which is then depressurized via a depressurization valve into a degassing apparatus from which it is discharged, wherein a) the water content in the prepolymerization is from 7 to 20% by weight, b) the reaction temperature in the prepolymerization is from 280 to 320°C and c) the depressurization valve is regulated in such a way that the working pressure is above the partial pressure of water vapour of the reaction mixture. The polyamide 12 obtained has a low residual monomer content, excellent colour and is free of gel constituents.



Abstract

Continuous hydrolytic polymerization of laurolactam is achieved in a simple and economical manner by a process in which laurolactam and water are metered in via a pump, if desired passed through a reactor having largely ideal backmixing, subsequently reacted in a tube reactor to give a prepolymer which is then depressurized via a depressurization valve into a degassing apparatus from which it is discharged, wherein a) the water content in the prepolymerization is from 7 to 20% by weight, b) the reaction temperature in the prepolymerization is from 280 to 320°C and c) the depressurization valve is regulated in such a way that the working pressure is above the partial pressure of water vapour of the reaction mixture. The polyamide 12 obtained has a low residual monomer content, excellent colour and is free of gel constituents.

The invention relates to a process for the continuous hydrolytic polymerization of laurolactam, in which hydrolytic cleavage is first used to prepare a prepolymer which is subsequently condensed to give a high-molecular-weight product.

Polyamide 12 is conventionally prepared from laurolactam by batchwise hydrolytic polymerization in a stirred reaction vessel, as is described in various published patent applications (see, for example, DE-A 15 70 774, DE-A 21 52 194 and DE-A 36 21 804).

10 This method possesses, inter alia, the following inherent disadvantages:

- The amount of water that can be added is limited by the pressure resistance of the reactor used. Water has a strongly accelerating effect on the ring cleavage and thus on the prepolymerization but also gives high steam pressures at the temperatures required. Since the costs of large, stirred reaction vessels increase greatly with the permissible operating pressure, relatively small amounts of water are usually used. This results in long reaction times and leads to high
20 manufacturing costs.

- The batchwise procedure results in only sequential utilization of individual equipment items such as conveying facilities, discharge filters and granulators. These equipment items therefore have to be designed for throughputs which are much higher than the average throughput of the total plant, which leads to high costs.

- In the batchwise operation of pressure vessels, problems often arise from material which remains in the vessel

when the latter is discharged. In the present case, prolonged residence times result in interfering secondary reactions of the polyamide 12 formed. Product residues in the reactor and in the lines can, for example, lead to gel-like impurities in the next batch.

The disadvantages of a batchwise mode of operation can be avoided by a continuous polymerization process.

Continuous polymerization of caprolactam to give polyamide 6 has been the state of the art for some time, as described in, for example, H. Ludewig, Faserforschung Textiltechn. 2, 341 - 355 (1951). However, the processes described for caprolactam are, without exception, not applicable to laurolactam, since laurolactam behaves completely differently from caprolactam in respect of the polymerization conditions required (water content, pressure, temperature, residence time).

Thus, DE-A 33 06 906 describes a process for the continuous polymerization of caprolactam, in which the lactam containing from 1 to 25% by weight of water is heated to a temperature of from 220 to 280°C in a prepolymerization zone at a pressure of from 1 to 10 bar with simultaneous evaporation of the water over a residence time of from 1 to 10 minutes and is subsequently further polymerized in a polymerization zone with continuous removal of the steam. However, use of laurolactam in place of the lactams having from 7 to 12 ring members described in this document gives virtually no conversion.

There have hitherto been few developments specifically for the continuous hydrolytic polymerization of laurolactam. All the inventions published in this field have considerable

disadvantages which greatly limit the economics or the product properties.

Thus, SU-A 12 08 044 requires the use of phosphoric acid as catalysts; the lauro lactam conversion reaches only 99%. The remaining residual monomer content of 1% causes problems in processing and use of the product. Commercial use of this product would require a preceding, complicated removal of monomer. In addition, the use of such a strongly acid catalyst has the disadvantage that the polylauro lactam thus prepared
10 experiences increased hydrolytic degradation in its processing or in use at elevated temperature; in addition, the polymerization reactors and the processing machines are subjected to increased corrosion.

JP-A 60 041 647 covers only the region of very high temperatures and pressures as process parameters. However, under these conditions there is more formation of gel particles and the colour is impaired. Furthermore, only oligomers can be obtained at first, and the further polycondensation of these oligomers requires, e.g. as described in JP-A 61 166 833,
20 complicated techniques and equipment items such as degassing screw machines.

The process described in JP-A 49 021 313 leads to reaction times which give no substantial advantages in comparison with non-continuous batch procedures (residence time a total of 13 hours). The procedure described leads to gelling of the product in the second reactor.

In GB-A 1 468 653, phosphoric acid has, according to the invention, to be present as catalyst; the depressurization

process is carried out isothermally at great expense; furthermore, it has been found that the monomer removal described cannot be carried out in practice. US-A 4 077 946 suffers from the same disadvantages and can be evaluated similarly.

EP-A 0 530 592 describes a continuous polymerization process in a complicated multi-path reactor which has to be kept under a temperature gradient. To prepare the finished polymer, a condensation facility with stirrers is required. The water
10 contents given in the polymerization (from 1 to 10%) lie outside the values for a maximum space-time yield. As a result, the residence times of from 7 to 8 hours required for the prepolymerization offer no advantage in comparison with the batchwise process.

It is therefore an object of the present invention to design an economical process which is simple in terms of apparatus. In addition, there should be no need for any catalysts which remain in the product at the end, although use of a catalyst is not excluded from the invention. The residual
20 monomer content of the polymer obtained should correspond to that of the materials produced by batchwise methods or be even lower. Finally, the product should be of very good quality in respect of colour and gel content.

These objects are achieved by a process for the continuous hydrolytic polymerization of laurolactam, in which laurolactam and water are metered in, for example, via a pump, if desired passed through a reactor having largely ideal backmixing, subsequently react in a tube reactor to give a

prepolymer which is then depressurized via a depressurization valve into a degassing apparatus from which it is discharged, wherein

- a) the water content in the prepolymerization is from 7 to 20% by weight,
- b) the reaction temperature in the prepolymerization is from 280 to 320°C and
- c) the depressurization valve is regulated in such a way that the working pressure is above the partial pressure of water vapour of the reaction mixture.

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Lauro lactam and water are preferably conveyed separately using a pump for each, with preference being given to using reciprocating pumps or reciprocating diaphragm pumps.

In the optional subsequent reactor having largely ideal

backmixing, the material streams are mixed and gently brought to the reaction temperature. For this purpose, use can be made of, for example, a suitably constructed stirred reactor, but preferably a loop reactor. The loop
5 reactor contains a pump which circulates the fed-in material at preferably from 10 to 100 times the flow rate of the feed stream.

The mean residence time of the reactive material in the tube reactor is preferably from 0.5 to 6 hours and
10 particularly preferably from 1.5 to 4 hours. To narrow the residence time distribution, the tube can be, if desired, completely or partially fitted with static mixer elements.

By means of regulation of the depressurization valve, a
15 definite, freely selectable process pressure in the interior of the reactor can be maintained. The set pressure is selected in such a way that any formation of steam bubbles in the tube reactor is prevented.

The degassing apparatus used can be, for example, a screw
20 machine, a thin-layer evaporator, a filmtruder or a flash vessel. Particularly suitable is a flash vessel whose internal pressure can be regulated by means of a regulating valve in the outgoing vapour line. Since the melt cools as a result of the evaporation process, it can be
25 advantageous, depending on the water content used, to pass the fed-in melt after depressurization as a film over the internal wall of a heated vertical tube, so as to be able to supply a small amount of heat. The mean residence time of the melt in the flash vessel is advan-
30 tageously from 1 to 3 hours.

If desired, the plant can possess a further degassing stage which can comprise the same equipment items as the first degassing stage. Here too, a flash vessel can be used with particular advantage. In this case, it should
35 be possible to apply reduced pressure. Another preferred

possibility is the use of a degassing screw machine.

In the upstream reactor having a largely ideal backmixing or, if such a reactor is not installed, in the first sections of the tube reactor, the hydraulic cleavage of the lauro lactam commences. If, for example, a loop reactor is used, the cleavage process takes place there up to a conversion of from about 30 to 40%. In the further course of the reaction, the cleavage is completed up to a residual of lauro lactam of about 0.3 % by weight. At the same time, the polycondensation proceeds up to a number average degree of polymerization (depending on the water content) of from 10 to 20.

The major part of the water is removed in the first depressurization process, the further condensation then commences. In the depressurization vessel, a definite level of polymer melt is preferably maintained, so that the material has available sufficient residence time for the condensation.

The product largely free of water in the degassing apparatus is preferably discharged via a pump, particularly preferably a gear pump.

In the second degassing apparatus present if desired, a further depressurization process is carried out. In this way, even higher molecular weights can be achieved.

Additives such as, for example, molecular-weight regulators (such as lauric acid or dodecanedioic acid), copolymers such as caprolactam, ω -aminoundecanoic acid or AH salt solution or, if desired, catalysts such as phosphoric acid or hypophosphorous acid can also be fed in at any desired point of the plant. It is also possible to feed in stabilizers.

The process of the invention has, in particular, the following advantages:

- under the conditions indicated, a mean residence time in the tube reactor of from 0.5 to 6 hours (depending on the temperature selected and the water content) suffices for a virtually complete conversion. This leads to a high space-time yield.

- The depressurization process proceeds in a controllable manner without problem, despite the extreme pressure drop.

10 - Contrary to expert opinion hitherto, use of a flash vessel as depressurization apparatus results in no caking, not even after very long operating times, although the flash vessel has to possess neither a stirrer nor other means for cleaning the surfaces.

- The polyamide 12 obtained has a low residual monomer content, excellent colour and is free of gel constituents.

The invention is further illustrated with reference to the accompanying drawing showing, by way of example and in schematic form, embodiments of the invention. The invention is also illustrated in the following Examples.

20 Figure 1 shows schematically a continuous plant for the continuous hydrolytic polymerization of laurolactam. The plant comprises the following components:

- 1 a reciprocating pump each for laurolactam and water,
- 2 a circulation reactor having a total volume of 17 l and fitted with circulating pump,
- 3 a tube reactor having an internal diameter of 100 mm and a total length of 27 m, with sets of static mixers situated 6 m apart,

- 4 a pressure holding valve,
- 5a a depressurization vessel having a volume of 150 l and fitted with a pressure-regulated depressurization unit,
- 6a a gear discharge pump and
- 7 a discharge unit for extrusion, cooling and granulation.

In one embodiment of the invention there is provided a further depressurization vessel 5b and a further gear discharge pump 6b.

Example 1

Polyamide 12 was prepared according to the invention in the apparatus of Figure 1, but without the further depressurization vessel 5b and further gear discharge pump 6b, under the following conditions:

Wall temperature in plant items 2 to 6a:	290°C
Wall temperature in plant item 7:	270°C
Pressure in plant items 2 to 4:	80 bar
Pressure in plant item 5a:	1.5 bar
Mean residence time in plant item 5a:	2 h
Mass flow of laurolactam:	42 kg/h
Mass flow of water:	8 kg/h

The product obtained has a light colour and possesses a molecular weight (number average from terminal group determination) of 14,500. The residual content of laurolactam is less than 0.3%. The product is free of gel constituents.

Example 2:

This is carried out in the same way as Example 1,

except that here the circulation reactor is omitted. The properties of the product remain unchanged, except that the residual monomer content rises to 0.5%.

Example 3:

This is carried out in the same way as Example 1, but with an amount of hypophosphorous acid (H_3PO_2) being added to the water fed in in such a way that the total amount, based on laurolactam fed in, is 60 ppm.

10 A high-quality product corresponding to that of Example 1 is obtained, but the molecular weight is 19,400.

Example 4:

This example is carried out in apparatus that includes, in addition to the depressurization vessel 5a as described in Example 1, a further depressurization vessel 5b and also an additional gear discharge pump 6b are used, as shown in Figure 1.

The process parameters are:

Pressure in plant item 5a:	2.0 bar
Pressure in plant item 5b:	0.5 bar
20 Mean residence time in plant item 5b:	2 h

Otherwise, the parameters correspond to those in Example 1. The product obtained has a light colour and is free of gel constituents. The residual content of laurolactam is less than 0.3%. The molecular weight is 18,700.

23443-533

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CLAIMS:

1. A process for a continuous hydrolytic polymerization of laurolactam, comprises:

metering in laurolactam and water, if desired passed
5 through a reactor having largely ideal backmixing;

subsequently reacting laurolactam and water in a tube reactor to give a prepolymer;

then depressurizing the prepolymer via a depressurization valve into a degassing apparatus; and

10 discharging produced polyamide 12 from the degassing apparatus, wherein:

a) in the prepolymerization, water is contained at a concentration of from 7 to 20% by weight,

b) the prepolymerization is conducted at a
15 temperature of from 280 to 320°C, and

c) the depressurization valve is regulated in such a way that a working pressure is above a partial pressure of water vapour of a reaction mixture.

2. A process for a continuous hydrolytic polymerization
20 of laurolactam to form polyamide 12, which process comprises:

continuously supplying water and laurolactam to a tube reactor for prepolymerization in the tube reactor, and

passing material exiting from the tube reactor via a depressurization valve into a degassing apparatus from which
25 polyamide 12 is discharged, wherein:

a) in the prepolymerization, water is contained at a concentration of from 7 to 20% by weight,

23443-533

11

b) the prepolymerization is conducted at a temperature of from 280° to 320°C, and

c) the tube reactor is maintained at a pressure above a partial pressure of water in a reaction mixture.

- 5 3. The process according to claim 1 or 2, wherein the water and laurolactam are fed to the tube reactor via a reactor having largely ideal backmixing.
4. The process according to claim 3, wherein the reactor having largely ideal backmixing is a loop reactor.
- 10 5. The process according to any one of claims 1 to 4, wherein the degassing apparatus is a flash vessel.
6. The process according to claim 5, wherein molten materials are passed as film over an internal wall of a heated vertical tube in an inflow region of the flash vessel.
- 15 7. The process according to any one of claims 1 to 6, wherein a mean residence time in the tube reactor is from 0.5 to 6 hours.
8. The process according to any one of claims 1 to 6, wherein a mean residence time in the tube reactor is from 1.5
20 to 4 hours.
9. The process according to any one of claims 1 to 8, wherein the tube reactor is fitted with static mixer elements situated at intervals or extending completely along its length.
10. The process according to claim 5, wherein a mean
25 residence time in the flash vessel is from 1 to 3 hours.
11. The process according to any one of claims 1 to 10, wherein the degassing is carried out in two stages.

23443-533

12

12. The process according to claim 11, wherein a second degassing stage is carried out in a flash vessel or a degassing screw machine.

13. The process according to any one of claims 1 to 12,
5 wherein additives are fed in at any desired point of the process.

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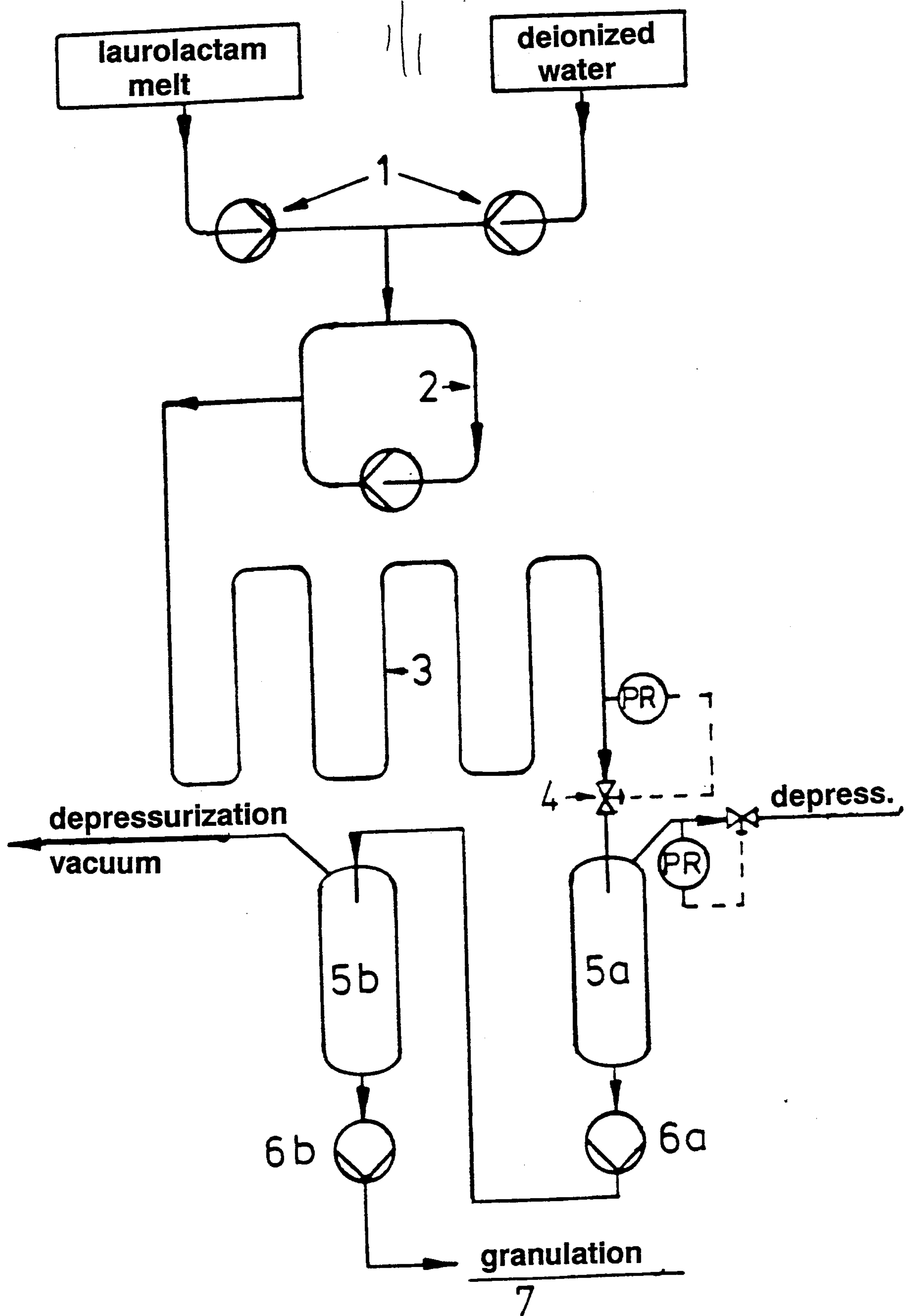


Fig. 1

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