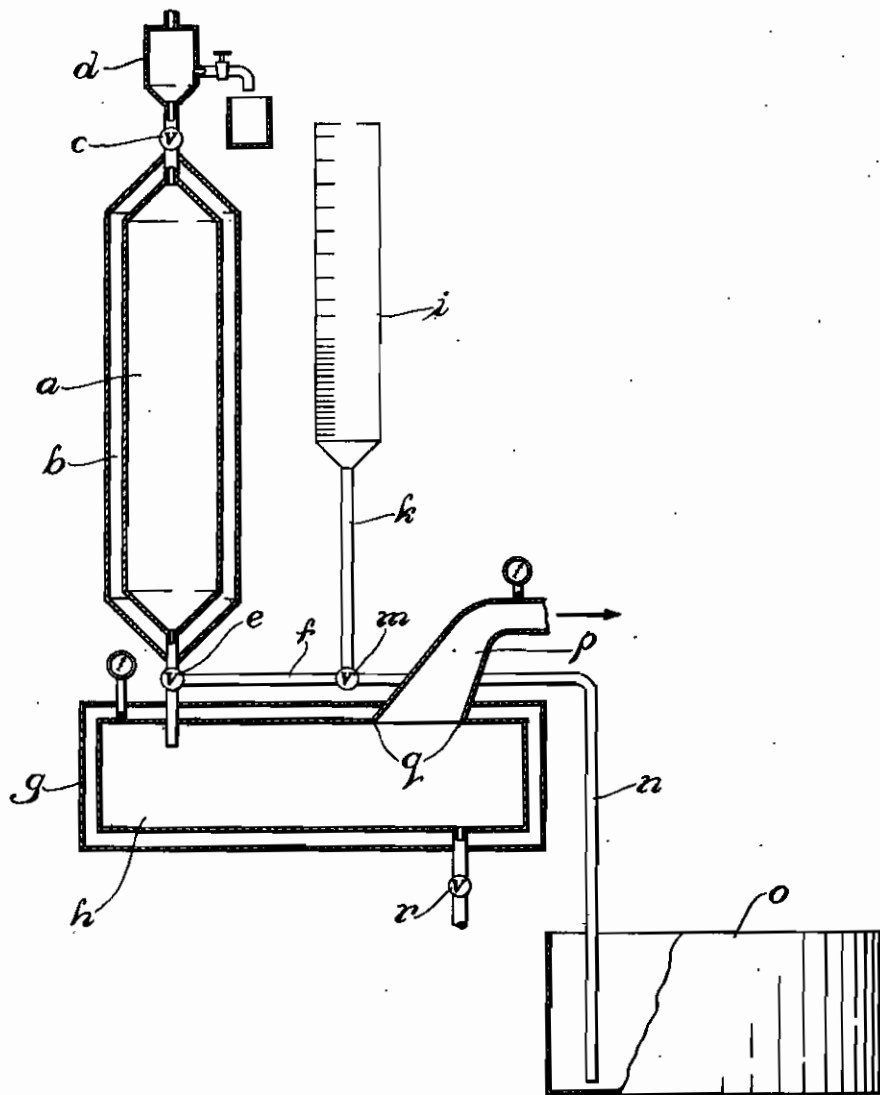


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# ALIEN PROPERTY CUSTODIAN

## PRODUCTION OF LINEAR POLYAMIDES

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The present invention relates to the production of linear polyamides and more specifically to a discontinuous two-phase polymerization of amide-forming reactants.

It has been proposed to convert the reaction mixture in the production of polyamides by heat condensation of polyamide-forming reactants into homogeneous liquids before the conversion temperature is reached by adding such materials which dissolve the reaction mixture, such as phenols, alcohols or water, under pressure. Polyamide-forming reactants are for instance salts of diamines and dicarboxylic acids, amino carboxylic acids or derivatives thereof capable of condensation, such as esters or amides, amide-forming derivatives, having a substituted nitrogen, for instance urethans or formyl compounds of amino acids and diamines, these latter in conjunction with dicarboxylic acids. If the reaction mixture is a homogeneous liquid, the reaction proceeds more smoothly and quickly, since a much better and more uniform heat exchange is attained. The addition of water is generally such, that the reaction mixture contains considerably more water than is freed during the amide condensation itself. Of course the water which is added as well as the water formed during the reaction must be removed during the condensation.

In the polymerization of lactams which leads to nearly the identical polyamides as the condensation of the corresponding amino acids the addition of water to the reaction mixture is not necessary for the uniform progress of the reaction throughout the reaction mass, since the lactams usually melt without decomposition far below the reaction temperature and the melting point of the polyamides from amino carboxylic acids generally does not considerably exceed the reaction temperature. The usual addition of water or of reactants which set free water has the object to catalyze and accelerate the reaction by forming reactive amino acid molecules. In the process of polymerizing lactams therefore there is no distinct upper or lower limit for the water content of the reaction mass. Unless very little water is added, the steam formed during the lactam polymerization when working in a closed vessel must be driven off after the equilibrium is reached, whereafter the mass is heated while removing volatile reaction products, until no further splitting off of water by condensation occurs. For practical reasons the water content will only be made high enough to procure a satisfactory acceleration of reaction, especially since

a more liberal addition of water seems to lower somewhat the degree of polymerization of the final product, even though water is incapable of forming stable reaction terminating end-groups.

Such stable end-groups, however, are obtained by reactants which form heat-stable salts with reactive end-groups, for instance when alkalies are added which react with the carboxylic acid groups and on the other hand, if acids are added (such as hydrochloric acid, phosphoric acid, toluenesulfonic acid, and salts thereof with amino carboxylic acids or amines, preferably amines which can be acetylated or which are volatile) which react with the amino groups of the polyamides and prevent further condensation. By adding mono-functional reactants to the reaction mixture which react with the amino groups or carboxylic acid groups, for instance monocarboxylic acids or monoamines, it is also possible to form stable end-groups. It is, moreover, important to exclude oxygen from the reaction. By this means it is avoided that the quality of the polyamide articles obtained is impaired and disturbing resinous oxidation products are formed on the walls of the reaction vessel.

My present invention has as an object a new and improved discontinuous two-phase process for the preparation of linear polyamides from polyamide-forming reactants liquified below the reaction temperature, especially mixtures containing polymerizable lactams. Other objects will appear more in detail hereinafter.

Reference is made to the accompanying drawing which is a schematic view showing an apparatus for carrying out the process of my invention.

The object is accomplished by carrying out the first stage of the invention in the heated pressure vessel completely or nearly completely charged with the reactants, until the desired degree of reaction is reached. The pressure vessel preferably has a relatively small diameter, in order to attain a more uniform heat exchange. In the second stage of the process the liquid reaction mass is discharged into a relatively large receiver without previously removing the volatile products. In this receiver the heat treatment is continued and finished. Towards the end of the polymerization it is of advantage to heat the mixture under reduced pressure.

My present invention is a valuable improvement in this art, since it provides a process superior to the methods hitherto practised. By my process the duration of reaction in the pressure vessel can be considerably shortened, especially

when the vessel is heated during charging. The space available in the autoclave can also be utilized much better than in the processes hitherto known, since the valves are not clogged up when the pressure is decreased owing to the complete charging in contrast with the usual methods. Furthermore the overheating and resinification of the reactants on the walls of the vessel are avoided by the substantially complete charging with the reaction mixture. The residues of the batch are dissolved by the next batch. It is therefore hardly necessary to clean the vessel with special means. The receiver can easily be arranged so that its interior is accessible through holes or by detachable front walls. Finally it is more easily and simply possible in the practice of my process than in the known processes to exclude the atmospheric oxygen especially damaging in the first step.

As the further condensation is carried out in the independent receiver the reaction duration in the pressure vessel can be reduced to a minimum. The receiver can be constructed considerably lighter and therefore also more spacious, since it need only stand a good vacuum or at most a moderately high pressure up to about 5 atm. It is also possible to combine several batches in the receiver and to improve the uniform quality of the end product by stirring, if necessary by means of a stirring mechanism or by pressing an inert gas, for instance nitrogen. Receivers with flat bottom and elliptical cross section are preferred when monomeric substances, such as monomeric lactam in polymerizing  $\epsilon$ -caprolactam, are to be removed in vacuo.

It is also possible to convert the polymer chemically in the receiver without any difficulty, as for instance by other polyamide-forming substances, especially such as do not contain lactam-forming reactants, as for instance salts from diamines and dicarboxylic acids, furthermore substances capable of controlling the degree of polymerization or inactivating catalysts, as for instance strong acids and derivatives thereof. These last-named substances for instance include alkaline reacting agents, such as potassium hydroxide, potassium acetate, potassium oleate, magnesium stearate, lithium-phenolate and sodium amino caprolactam. The substances can be introduced directly into the receiver by a pressure sluice or incorporated into the mass on its way from the polymerization vessel to the receiver. The boiling up of the mass in the receiver effects a homogeneous distribution of said substances. Inactivating agents added in excess can also be adapted to serve as stabilizers at the same time.

Physically reacting substances can likewise be added to the mixture in the receiver, such as pigments, resins, filling agents and preformed polyamides.

The process of this invention is applicable to liquified mixtures of polyamides, as for instance condensable salts dissolved in water, such as hexamethylene-diammonium adipate, pentamethylene-diammonium sebacate or *s*-dimethyl-hexamethylenediammonium adipate. The process is, however, of greatest value in using batches containing lactams and, if required, volatile reaction accelerators and/or polyamide-forming substances capable of producing volatile accelerators especially water or alcohols in the heat, such as amino carboxylic acids and amino carboxylic acid esters, salts from diamines and dicarboxylic acids and, if desired, further substances capable of accelerating or regulating the

reaction or suitable for stabilization, as for instance acids as hydrofluoric acid, hydrochloric acid, phosphoric acid, benzenesulfonic acid or salts thereof with amines or amino carboxylic acids and monofunctional substances capable of forming stable end-groups, such as monocarboxylic acids, amines with one amide-forming amino group, and alcohols having a higher molecular weight.

In many cases the water content of the reaction mixture may be low. The mixture conventionally contains less than one mol of water for each amide group in the polymer, for instance  $1/100$ – $1/2$  mol. It is evident that the process is also adapted to carry out the reaction in the absence of water or compounds containing hydroxyl groups, for instance in the alkaline polymerization of lactams with sodium amide or organic alkali metal amides.

The less volatile substances are present or are formed during the reaction the more the space available in the autoclave can be utilized. It is advantageous to heat only such amounts of reaction mixture in the vessel that the pressure does not exceed 30 atm. However, the process is not limited to determinate pressures. In vessels having very strong walls it is also possible to carry out the reaction under higher pressures than mentioned above, for instance when methanol is present.

The pressure brought about by the reaction in the vessel may be partially compensated by allowing a portion of the reaction mixture to flow into an expansion vessel likewise heated to reaction temperature. Such an expansion vessel may, for instance, consist of a cylinder with a displacing piston or of an elastic member similar to high-pressure membrane pumps.

It is of advantage to fill the autoclave completely with the reaction mixture and then to press back a part of the mixture into the feed pipe by means of an inert gas (free from oxygen). The pressing back may also be effected by the pressure of the steam formed.

Instead of the usual manometer mounted at the upper end of the autoclave an opening closed by a resistant membrane is arranged at the lower part of the autoclave. When the pressure is too high, the membrane is torn and the mixture flows into an adjacent container.

Referring to the accompanying drawing, *a* is a cylindrical autoclave which has a relatively small diameter, consists of non-rusting refined steel (V4A) and tapers at its upper and lower ends. The autoclave is provided with a heating jacket *b* and connected at its upper part by a cock *c* with an over-flow container *d* which can electrically be heated to a temperature high enough to prevent the reaction mass from becoming solid. In its lower part said autoclave is connected by a three-way-cock *e* on the one hand with a—if required—heated pipe *f* and on the other hand with a container *h* having a flat, for instance elliptical cross section and being provided with a heating jacket *g*. *i* designates a graduated vessel connected with the cock *e* by pipes *k* and *l* separated by a three-way-cock *m*. Said cock *m* is furthermore connected by a piping *n* with a store tank *o* for the liquid starting material. Attached to the top of the container *h* is a fractionating column *p*, the lower part of which is protected from spraying substances by plates *q*. The container *h* can be emptied by a cock *r*. This apparatus works as follows.

The starting mixture kept in the liquid con-

dition in the heated container *o* and consisting, for instance, of  $\epsilon$ -caprolactam and water or a substance capable of splitting off water at raised temperatures, such as amino undecolic acid, hexamethylenediammonium sebacate or hexamethylenediammonium adipate is pressed after the cocks *c* and *e* have been opened through pipes *n* and *f* into the autoclave *a* heated to 100° C. until the liquid has entered the over-flow-container *d* through the cock *c*. Said cock *c* is then shut off and the cock *m* turned so as to connect the autoclave with the graduated vessel *i*. Subsequently the autoclave is heated in such an extent, that a part of the liquid is pressed into the vessel *i*. When the cock *e* is shut off a maximum pressure of 20–25 atm. in the autoclave shall not be exceeded at the reaction temperature of 240° C. The portion pressed into the pipe *f* and the graduated vessel *i* is caused to flow back into the store tank *o*. For this reason it is preferred to give the pipe *f* a slightly inclined position. When the desired reaction degree has been reached, the autoclave *a* is connected with the container *h* by opening the cock *e*. Thus the reaction mixture is pressed into the container *h* by the pressure of the vapors in the autoclave. In the container *h* there is only a small pressure, for instance about 1–5 atm. adjusted by an exhaust steam valve. If necessary, the velocity of flow of the reaction mixture can also be increased by pressing an inert gas, such as nitrogen, carbon-dioxide or superheated steam through the valve *c*.

In the container *h* which, for instance, in polymerizing  $\epsilon$ -caprolactam can be heated to 250–260° C the mass is after-condensed at atmospheric pressure for one to three hours. The volatile products as, for instance, monomeric lactam, are removed by reducing the pressure to 2–10 mm. The time required for this vacuum distillation depends upon the ratio of surface to quantity of the molten mass and amounts to about 15 minutes to

two hours and more. In the container *h* the reaction mass may be mixed with stirring. This means is of advantage when substances are added in this second phase of the process which, for instance, regulate the final degree of polymerization or inactivate a catalyst or the like, such as the anion of a mineral acid. The molten polyamide is then fed to spinning machines or cast into films or worked up into rods and ribbons.

The molten final product can also be fed to a receiver in which several batches are mixed and from there to the working machines.

#### Example

A molten mixture of 100 mols of  $\epsilon$ -caprolactam, 10 mols of water and 0.5 mol of  $\epsilon$ -aminocaproic acid hydrochloride is pressed from below into the autoclave heated to 100° C until it is completely filled with the liquid. By pressing back a certain part of the batch, as described above, such an amount of polyamide-forming reactants is adjusted in the autoclave, that the pressure produced by this amount when heated to 240° C would not exceed 20–25 atms. The mixture is then heated to 240° C and kept at this temperature for 2.5 hours, whereafter it is pressed into a horizontal flat container which is under a blow-off pressure of 5 atm. In this container the mass is further heated to 250° C while the pressure is gradually reduced to atmospheric pressure. When the mixture has been after-heated at 250° C and 760 mm for 1.5 hours, the pressure in this container is gradually reduced to 3 mm, whereby the greatest part of the lactam not having reacted with the other substances is distilled off. After heating the mass at 250° C and 3 mm for one hour the molten polyamide is pressed by nitrogen pressure with the aid of a measuring pump to a spinneret to be worked up into bristles.

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