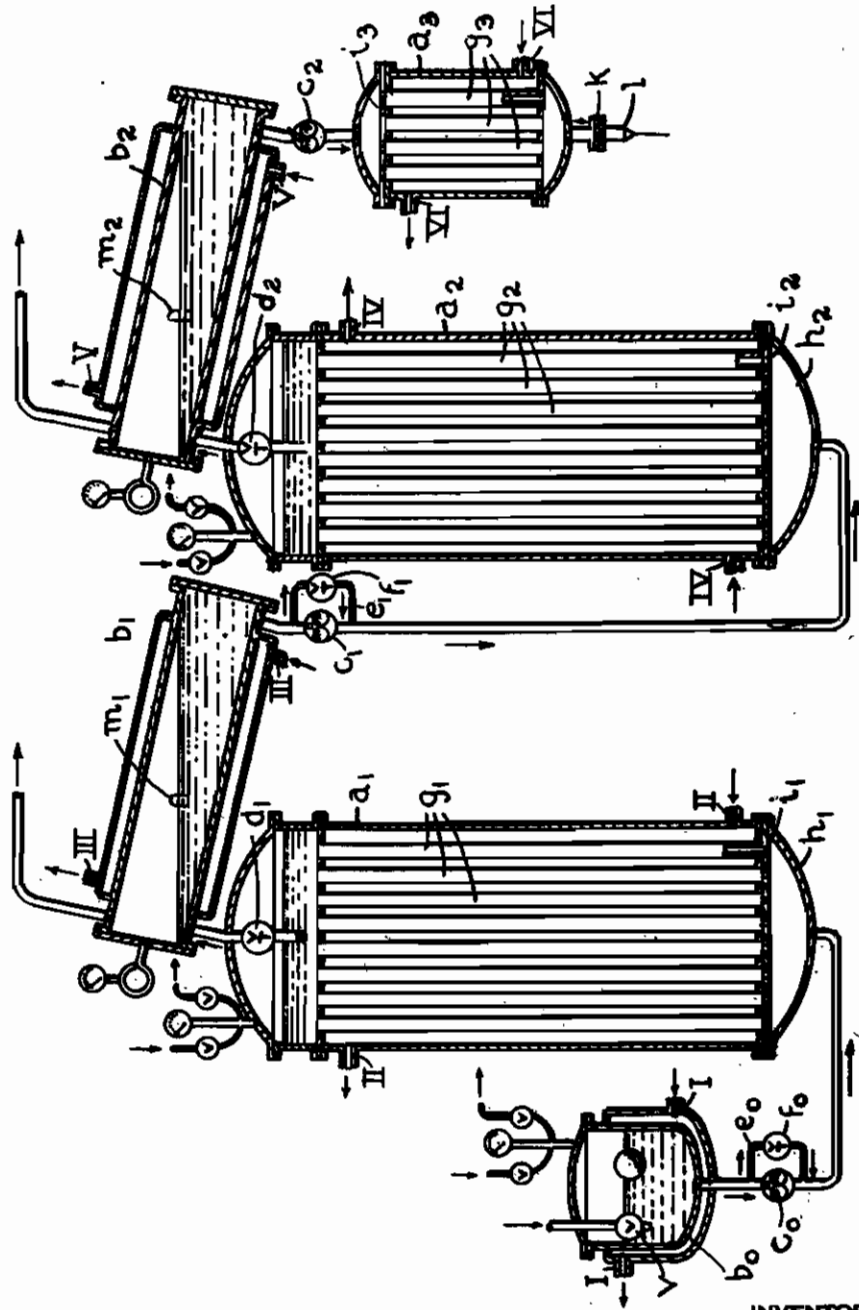


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 METHOD AND APPARATUS FOR PRODUCING  
 LINEAR POLYMERS  
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# ALIEN PROPERTY CUSTODIAN

## METHOD AND APPARATUS FOR PRODUCING LINEAR POLYMERS

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This invention relates to the production of synthetic linear polymers.

In the production of linear fusible condensation polymers, especially polyamides, such as condensation products of  $\omega$ -aminocarboxylic acids with 5 or more chain-members between the amino- and the carboxylic acid groups, of condensation products from  $\omega\omega$ -diamines and  $\omega\omega$ -dicarboxylic acids or functional derivatives thereof, or of polymerizates of lactams according to the U. S. Patent Application Ser. No. 220,266 filed July 20, 1938, it has proved advantageous, to work under pressure in the first step and then to finish off the reaction at reduced pressure, for instance at atmospheric pressure and in vacuo. The greater pressure in the first step accelerates the reaction, since the formation of the polymers is followed by a contraction in volume. In the second step with lower pressure or with sub-atmospheric pressure the volatile reaction products, solvents or unreacted starting materials (monomers) and volatile accelerators are intended to be removed. Treatment under pressure during the first step is especially advantageous if it is desired to accelerate the reaction, for instance the polymerization of a lactam by volatile compounds capable of being acylated, such as alcohols, water, ammonia, amines. In this case already a comparatively small amount, for instance 1/80 to 1/6 mol of these compounds calculated on 1 mol lactam causes the time of reaction to be substantially shortened as against the time required by working at atmospheric pressure.

It is an object of this invention to provide a continuous process of producing linear synthetic polymers.

A further object of the invention consists in the provision of suitable apparatus' by which the process can be carried into effect.

Still further objects reside in details of the construction of the said apparatus as will be more fully understood with reference to the accompanying drawing.

Figure 1 is a diagrammatic cross sectional view of an apparatus suitable for the continuous production of linear superpolymers.

Before dealing specifically with the single Figure it appears necessary to explain the principle of the invention.

We have found that the production of polyamides can be carried out with great advantage continuously even under conditions which necessitate the removal of volatile by-products by feeding the liquid or liquified starting material by means of suitable feeding means in practically uniform amount calculated on the end products continuously in several different pressure steps through the apparatus wherein each step of high pressure is followed by a step of lower pressure.

The reaction mixture may contain all necessary additions before it is fed to the apparatus. A process of this kind in which any desired number of double steps may be employed has proved especially valuable if during the reaction substantial amounts of volatile compounds, for instance water or alcohol must be added in order to accelerate the reaction. And furthermore if compounds are added during the reaction which improve the products or which form interpolymeric modifications with these compounds, reacting with a renewed formation of volatile compounds, or if substantial amounts of volatile compounds are gradually set free during the polyamide-formation, for instance if acids are split off from esters, alcohols, phenols or acyl compounds.

Organic polymers of the kind described especially fusible polyamides serve very often for the production of shaped articles of uniform diameter which are formed either in the plastic or fused state by extrusion from a mouth piece or from the openings of, for instance a spinneret. In the first case the production of rods or tubes of all kinds, in the second case the production of threads, bristles, horse-hair etc. is concerned. Hitherto it has been usual to solidify the final product of the polymerization from the melt in the form of rods, blocks, ribbons etc. or to lead the same from openings into water whereby cable or ribbon-like irregular articles are obtained. These products were then again melted at a suitable temperature and pressed through openings in the manner described above.

We have found further, that the above described process for the production of the polymerizate may be combined with great advantage with the known process for the production of shaped articles from the melt. According to the invention the throughput through the polymerization apparatus is so adjusted that the amount of material which is subjected to treatment, i. e. including any additions made during the reaction, corresponds at all times with the amount of material which is mechanically shaped. In this manner the amount of polymerizate which is continuously produced leaves the apparatus after it has been mechanically shaped without any interruption of the process. It is evident that this last step which no longer effects any chemical change but is subject only to the laws of physics will usually require other conditions of pressure and temperature as the preceding steps of polymerization or condensation. According to this invention therefore the process is further so developed that polymerization or condensation and the shaping are carried out under different conditions of pressure and temperature adjustable at will.

Since uniform pressure does not prevail in

the different steps of the process, the pressure rising and falling all the time, it is of course necessary to provide several pumps for increasing the pressure, for instance worm pumps or gear pumps which feed the material under treatment on after the pressure has been released, under the pressure prevailing in the next step. A suitable apparatus for carrying the process into effect is shown diagrammatically in the single Figure of the drawing. Each double step of the polymerization apparatus consists of two containers in different pressure which are mounted one after the other. Two of such steps are shown in the drawing, they can, however, if necessary, be increased in number. A feeding pump is arranged between the container of lower pressure  $b_0, b_1, b_2$  and the subsequent containers of higher pressure  $a_1, a_2, a_3$ . The feeding pump may be a gear pump  $c_0, c_1, c_2$ , the sucking side of the pump being connected with the container of lower pressure, the pressing side with the subsequent container of higher pressure. This pump does not only separate the two containers but also adjusts the pressure prevailing in any of the containers. The container of higher pressure is advantageously arranged as a heating pipe system with pipes  $g_1, g_2, g_3$  which are surrounded by a heating liquid from without. The heating pipe system and the expansion vessel are separated by throttle valves  $d_1, d_2$  by means of which the surplus pressure in the heating pipe system is adjusted.

The amount of material used up during the continuous process must be continuously substituted. A float chamber  $b_0$  the content of which is continuously refilled from a container, serves this purpose. The refilling is controlled by the float valve  $v$ . From this float chamber the first pump  $c_0$  feeds the liquid starting material, for instance  $\epsilon$ -caprolactam with a certain water content and with a content of substances which control the polymerization such as  $\epsilon$ -aminocaproic acid hydrochloride before polymerization. The material is fed under pressure into the first heating pipe container  $a_1$ . The partly polymerized material is fed to the sucking side of pump  $c_1$  after it has been led through the throttle valve  $d_1$  into the vessel  $b_1$  where the pressure is released. The material leaves pump  $c_1$  again under high pressure. It is led into the heating pipe system  $a_2$  for its second polymerization step and this is repeated as often as is necessary under the special conditions of the polymerization.

Of course, it cannot be expected that all pumps  $c_1, c_2, c_3$  which work under different conditions of temperature and pressure feed exactly the same amount of material even if they are of even size and run the same revolutions per minute. According to the invention the pumps at the beginning of the working step are given a certain overfeed and a bypass tube  $e_0, e_1$  is arranged which leads from the pressure side to the sucking side of the pump and which incorporates a throttle valve  $f_0, f_1$ . In this manner an adjustment of the throttle valves enable the amount fed by the previous pump to be brought into an agreement with the amount fed by the subsequent pump. The inspection glasses  $m_0, m_1$  on the containers  $b_0, b_1$  aid in controlling the surface of the liquid in the containers and enable the surface to be kept constantly on the same level. For the polymerization preferably heating pipe systems  $a_1, a_2, a_3$  are employed, the material under treatment following slowly through the tubes  $g_1, g_2, g_3$ . Since the speed of flow in these tubes is com-

paratively small, owing to the long time of polymerization, there is a certain danger of the individual tubes being unevenly flown through. Each heating pipe system is therefore closed on its entrance side by a perforated nozzle plate  $i, i_1, i_2$  through which the entering material has to pass. The resistance of the narrow orifices of this perforated plate is so selected that the resistance of flow of the tubes can be neglected. In this manner the same amount of liquid per time unit flows through each of the tubes. The perforated nozzle plate may also be arranged at the exit side, where it may simultaneously act to stow the pressure in the tubes. Under certain circumstances they may substitute the throttle valves  $d_1, d_2$ . As a rule, however, it is more advantageous to employ the perforated plate only for the division of each pressure step. If the perforated plate is mounted in the upper end of the heating pipe system it is sometimes necessary to provide an outlet from the upper end to the vessels  $b_1, b_2$  by means of a special pipe.

If the material is to be formed without intermediate solidification immediately following the polymerization an apparatus is employed which is connected to the last container of the polymerization reaction without any intermediate tubings etc. In this case one of the known devices for the production of pressure, for instance a gear pump, is employed furthermore a heat exchange system in order to the exactly control the temperatures necessary for shaping, a filtering arrangement, for instance the metal screen  $k$  and immediately connected therewith a die mould for the production of profiled rods, tubes etc. or a spinneret or a number of spinnerets arranged in parallel position for the spinning of fibers, monofil, bristles, horse-hair etc. All these parts are mounted together as narrowly as possible to form a single complete apparatus without any pipe line connections, in order to provide the shortest route from the end from the final phase of the polymerization of the spinnable melt to the mouth piece  $l$  of the shaping device.

If it is desired to change the throughput per time unit corresponding with different diameters or different shaping speeds at the exit of mouth piece  $l$ , the amount fed by the different pumps  $c_1, c_2, c_3$  is made to correspond with the changing speed by changing the amount of revolutions of the pumps per minute, if the chemical reaction, as in the case of the polymerization of  $\epsilon$ -caprolactam in the presence of an agent controlling the polymerization such as  $\epsilon$ -aminocaproic acid hydrochloride, permits. This measure is also selected if a change in the duration of the polymerization is necessary owing to the changing conditions of the chemical reaction.

The process which is carried out in different vessels and pipe systems under varying pressures also necessitates different reaction temperatures. In order to provide for these varying temperatures a number of heating zones, for instance circuits 1 to 6 are arranged which can partly be interconnected. It is not difficult to keep the temperature of the heating agent in these circuits at an even level. In this manner it is possible to graduate the reaction and working temperatures in the different vessels  $a_1, a_2$  and  $b_1, b_2$  according to the necessities of the chemical or physical process.

The introduction of additional reaction components is carried out after the first pressure heating, if several double steps are employed advantageously after the first double step before the

pressure pump which in this case acts at the same time as a pump and as a homogenizer. Naturally additional homogenizing devices may be installed.

If larger amounts of volatile products are formed during the reaction or if volatile products, for instance water or alcohol are added in larger amounts from the start it may be of advantage to employ a horizontal tube in the pressure phase, the cross section of which is only partly filled up by the flowing mass. The surface in which the melt and the vapors contact may be enlarged by arranging walls which may be disposed one from the top and one from the bottom or by moving parts, for instance flat feeding worms.

The following examples illustrate the invention:

#### Example 1

The mixture of 100 parts of  $\epsilon$ -caprolactam, 0.75 parts of  $\epsilon$ -aminocaproic acid hydrochloride and 4 parts of water are pressed through a heating apparatus as described in the drawing. The apparatus being so arranged that the mass is left for 4 hours in the first heating zone, kept at 220° C, then flows through the first pressure release vessel heated to 230° C in the course of 2 hours.

On its way to the second pressure heating system 5 parts of 9-aminononanoic methylester are added to the melt in order to improve the stability of the final product and the mixture is homogenized by the pressure pump. The mixture flows through the second pressure phase in 2 hours at 240 to 250° C and is then kept in the second pressure release vessel for 1 hour at 250° C in order to remove the alcohol formed. From there it flows continuously on to the heat exchange system which feeds the melt to the spinneret at a temperature of 230° C.

#### Example 2

A mixture of 113 parts of  $\epsilon$ -caprolactam, 0.2 parts of ethyl alcohol, 0.6 parts of  $\epsilon$ -aminocaproic acid chloride is pressed in the course of 1.5 hours at 230° C through the first pressure phase of the apparatus illustrated in the drawing. Upon leaving the heating pipe system the pressure in the mass is released and the mass flows at atmospheric pressure through a slightly inclined tube heated to 240° C in the course of 2 hours, in which time the alcohol distills off. After the mass has left the intermediate vessel 20 parts of molten 9-formylaminononanoic acid are introduced therein by means of a gear pump and the mass is homogenized for the second pressure phase by the pressure pump. The melt is pressed through the second pressure phase in an hour at a temperature of 240 to 250° C and reaches a second horizontal vessel kept at a vacuum of 10 mm. The mass flows through this vessel in 2 hours at a temperature of 240 to 250° C. The newly formed volatile components have been distilled off in the second reduced pressure phase. The mass is pressed by means of a gear pump through a heat exchange system having a temperature of 230° C and from there to a series of 5 spinnerets arranged in parallel each having 16 holes of 0.4 mm diameter. The threads leaving the spinnerets are drawn off with a speed of 250 meters per minute. By cold drawing the threads a tensile strength of 4 to 5 grams pro deniers is obtained.

#### Example 3

A mixture of 100 parts of  $\epsilon$ -caprolactam and 10 parts of water flows through the first pressure phase

with a temperature of 230° C in 40 minutes. The pressure is released in the first low pressure phase and the mass is pressed after remaining at atmospheric pressure for 1 hour into a second high pressure phase at a temperature of 255° C. After 2 hours the melt reaches the second horizontal low pressure vessel and passes therethrough in a relatively thin layer of about 4 cm height in 2 hours at a temperature of 250° C. On its way to the spinneret the temperature is finally adjusted at 230° C.

#### Example 4

$\epsilon$ -aminocaproic acid ethylester is pressed in 2 hours through the first pressure phase at 220° C. After the pressure has been released to atmospheric pressure the precondensed mass flows through a horizontal tube at 230° C in 2 hours, the splitting off of alcohol being continued. In the subsequent high pressure phase which is again passed through in 2 hours, the temperature is increased to 250 to 265° C. The pressure is now released and the mass introduced into a flat horizontal tube-shaped vessel maintained under a vacuum of 2 mm Hg. During this stage the  $\epsilon$ -caprolactam formed as a by-product is separated in vapor form. After being kept in the low pressure phase for 2 hours the polyamide melt is shaped into a continuous rod of 8 mm thickness by means of a spinneret.

#### Example 5

A mixture of 8 parts of  $\epsilon$ -caprolactam and 2 parts of 9-aminononanoic acid is pressed inside half an hour through a heating pipe system kept at 210° C and arranged vertically, then fed into a flat tube-shaped vessel, heated to 230° C, the surplus pressure being released. After remaining in the pressureless phase for 3 hours the mass enters a second high pressure heating system kept at 250° C, flows therethrough inside 2 hours and reaches another horizontal tube-shaped vessel evacuated for the purpose of removing volatile components (monomers), the vessel being kept at 250° C and being passed by the melt in 1.5 hours before the melt is shaped by means of a spinneret.

#### Example 6

A mixture of 108 parts of adiponitrile, 116 parts of hexamethylenediamine and 50 parts of water containing  $\frac{1}{10}$  of the amount of hydrogen sulfide necessary for neutralizing the diamine, is led in 5 hours through a flat horizontal pressure tube in which the temperature rises gradually from 200 to 270° C. At the end of the tube ammonia, hydrogen sulfide and steam and the molten polyamide are continuously removed by separate members, the pressure being released to atmospheric. The melt is fed into a second horizontal tube heated to 275° C. After remaining therein for an hour the melt is pressed into a horizontal heating pipe system kept at 280° C. After flowing therethrough for 2 hours the mass again reaches a flat tube-shaped vessel in which it is freed of the remaining volatile compounds in the course of 1.5 hours at 260 to 280° C at a pressure of 2 mm. The finished polyamide is finally continuously pressed through a slot into cold water.

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