

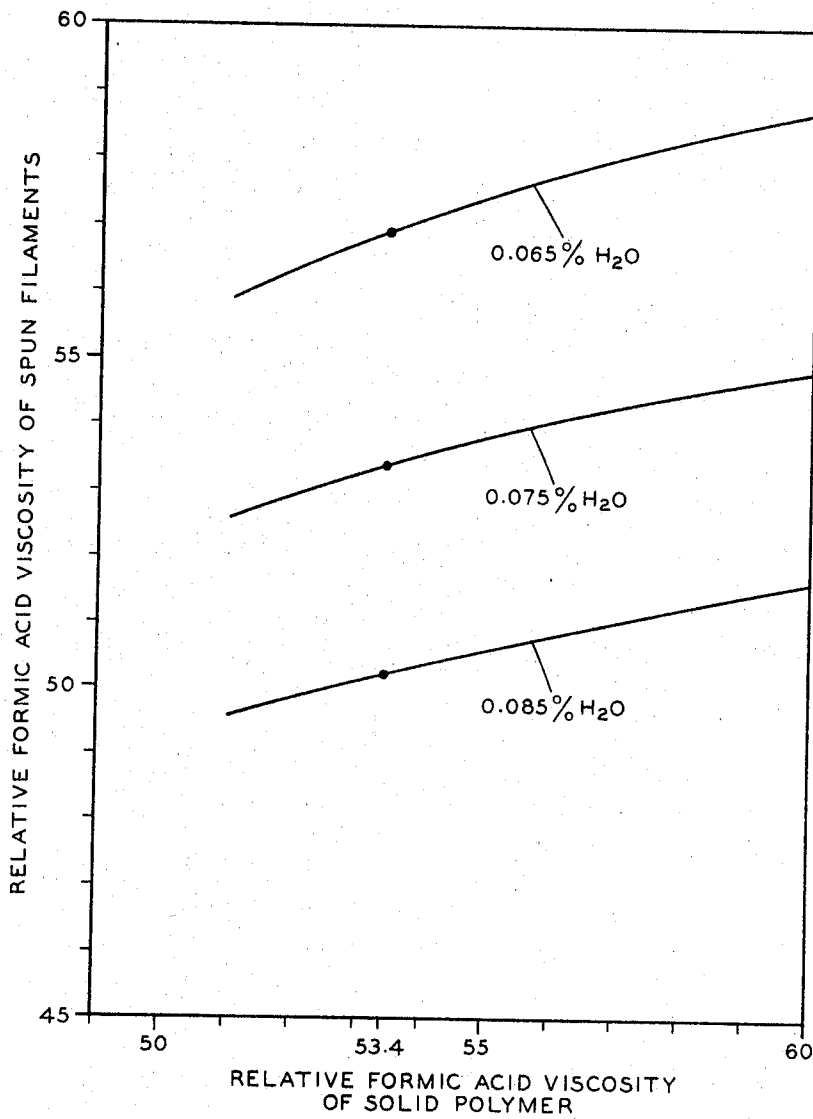
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PRODUCTION OF POLYCAPROAMIDE FILAMENTS OF UNIFORM WATER CONTENT

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PRODUCTION OF POLYCAPROAMIDE FILAMENTS OF UNIFORM WATER CONTENT

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This invention relates to production of filaments from poly-ε-caproamide and more particularly to improvements in handling water-washed polycaproamide pellets preparatory to melt spinning into filaments.

It is known that uniformity of physical properties of a synthetic filament, including dyeability thereof, varies sharply with uniformity of the molecular weight of the synthetic plastic material employed. Since uniformity of physical properties is important technically for the production of high quality textile goods and the like from the synthetic filaments, an important technical problem is to improve the molecular weight uniformity throughout all the filaments produced in a melt spinning process.

In melt spinning of polyamides it has been found that the water content of the melt influences the molecular weight of the polyamide. Accordingly, it has been proposed to control this water content of the melt by maintaining the melt, prior to spinning the same, under a moist atmosphere in equilibrium with the melt. A difficulty in this procedure lies in obtaining equilibrium between the whole viscous melt and the moist atmosphere above it.

I have found that in the melt spinning of poly-ε-caproamide, the viscosity of the spun polymer can be controlled within very acceptable limits by closely controlling the moisture content throughout the whole of the solid polymer which is to be melted for spinning into filaments. The polymer for spinning is usually obtained by polymerizing the monomer to about 90% of completion, extruding the polymer as a melt, pelleting, and then water washing to remove the low molecular weight ingredients such as caprolactam monomer and cyclic dimers and trimers of caprolactam. These water-extractibles are usually reduced to not above about 5% by weight and preferably to not above about 3% by weight. In the usual operations, the resulting water-washed granules or pellets are intensively dried, usually to a level not above about 0.1%

(B)

moisture content. Every effort is made to obtain dry granules of constant, uniform molecular weight; and then every effort is made to protect these granules from exposure to moisture during the subsequent storage and handling thereof.

In accordance with my invention, I dry the water-washed solid polycaproamide to a low and closely defined average level of moisture content, and I additionally subject the resulting dried solid polymer to conditioning as by prolonged contact with inert gas having substantially constant temperature and having substantially constant water vapor pressure at the level required for equilibrium with said dried granules. By the conditioning operation of my invention the moisture content of the solid polymer is brought to a definite low average value which is substantially uniform value throughout the whole of the product. When this solid polymer of definite and uniform moisture content is then stored, handled and melted for spinning in conventional manner for polycaproamide, the resulting filaments as spun, I find, have defi-

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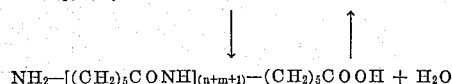
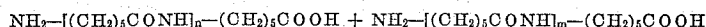
nately improved molecular weight uniformity over that obtained by similarly handling and spinning the dried polymer but without the above-cited conditioning operation of my invention. Specifically, by my invention molecular weight of spun filaments as indicated by the usual relative viscosity measurement at 10% concentration in aqueous 90% formic acid solution at 25° C. (ASTM D-789-59T) can be controlled to desired values within a standard deviation of about 2% of the desired value and better.

In particular when the desired relative formic acid viscosity of the spun filaments is to be in the range of about 40 to about 80, the polymer to be spun is brought to relative formic acid viscosity (measured on water-washed, dried polymer) in the said range and the polymer is water-washed to bring the water-extractible content to not above about 5% by weight, preferably not above 3% by weight. The average water content of this solid water-washed polymer is then brought to a prescribed weight percent value ± 0.01 , this value being within the range from about 0.035% by weight to about 0.115% in accordance with my invention; and uniformity of the value for water content in random small samples of this solid polymer is brought within a standard deviation not above about 0.003% by weight based on weight of the polymer. This solid polymer to be spun is suitably in a granular form such as pellets, chips, flakes, beads or the like. A particularly desirable range of relative formic acid viscosities of my solid polymer is from about 45 to about 65 with standard deviation not above about 0.6. Correspondingly the average water content in this solid polymer composition of my invention will be from about 0.050% to about 0.095%, correlated with relative viscosity as explained below.

The following equations can be used in the practice of my invention to determine the proper level of water content of solid polymer for producing a predetermined relative formic acid viscosity:

$$(A) \quad Z = \frac{(-\text{CONH}-)(\text{H}_2\text{O})}{(-\text{NH}_2)(-\text{COOH})}$$

The parentheses indicate concentrations of the designated groups in the polycaproamide, and concentration of water present therein, expressed in mol units, e.g. gram-equivalents per kilogram of polymer. Z is the equilibrium constant for the condensation-hydrolysis reaction:



$$(1) \quad \text{Log}_{10} Z = 1495/T - 0.261$$

where T is in degrees absolute.

In a given solid polycaproamide the average $(-\text{COOH})$ end group concentration in gram-equivalents per kilogram can be determined as say y; and the average water content can be determined as say W in weight percent; which can be converted to gram-mols per kilogram by multiplying by the factor 0.555. When this solid polymer is melted, in general the water content will not be that required for equilibrium of reaction (B) above at the melt temperature, T. Accordingly condensation or hydrolysis will occur, changing the concentration of the $(-\text{COOH})$ end groups from y to $y+x$, and correspondingly changing the water content of the melt.

At the high molecular weights which are of interest, the proportionate change in concentration of



groups, as equilibrium is attained, is negligible compared to the proportionate change in end group concen-

tration and water content; hence the ($-\text{CONH}-$) concentration can be regarded as a constant, C . Moreover the concentration of ($-\text{NH}_2$) groups is equal to that of ($-\text{COOH}$) groups, less the concentration a of any monobasic acid such as acetic acid which may be present as viscosity stabilizer; i.e. ($-\text{NH}_2$) = ($y - a + x$). Accordingly the following equation may be written relating initial end group concentration, y ; initial water content, W ; and x , the change in end group concentration due to establishment of condensation-hydrolysis equilibrium at the melt temperature:

$$(2) \quad Z = C(0.555W - x) / (y - a + x)(y + x)$$

Furthermore I find the following equation expresses relation between relative formic acid viscosity, V , of polycaproatamide (measured by ASTM test D-789-59T), and end group concentration in equivalents per kilogram, q :

$$(3) \quad V = -285.209 + 2164.33q + 11.7188/q$$

The use of the equations is as follows. From the relative viscosity V , of a solid polycaproatamide using Equation 3, or by end group analysis, a value y for initial ($-\text{COOH}$) end group concentration is found. Then using Equation 3, the end group concentration is found corresponding to the relative viscosity, V_m , desired to be reached by the polycaproatamide before it is spun from the melt. This new end group concentration will be ($y + x$) of Equation 2. Z in Equation 2 can be found for given T of the melt by use of Equation 1. Using the resulting values of x and Z and the known values of y , C and a , Equation 2 can be solved for W , the weight percent water required in the solid polymer to produce the desired relative viscosity, V_m , when equilibrium is attained in the melt.

Equally well, Equations 1, 2 and 3 can be used to build a table of the relative viscosities, V_m , which will be reached when starting with solid polymer of given relative viscosities and given water contents, upon its reaching equilibrium in a melt at temperatures T . For this purpose, x is calculated using Equation 2 in the form:

$$(2') \quad x = \frac{1}{2} [a - 2y - C/Z + \sqrt{(a - 2y - C/Z)^2 - 4(y^2 - ay - 0.555WC/Z)}]$$

and V_m is then calculated using $q = y + x$ in Equation 3.

It will be appreciated that the nearer the initial solid polymer is to the desired final end group concentration and corresponding equilibrium water content, the better is the assurance that equilibrium will be closely approached in the polymer melt. Accordingly I bring the average water content, in the drying operations, within about 0.01%, based on weight of the polymer, of the final desired water content. But this alone is not enough to achieve my results, since the slowness of attaining a uniform distribution of water throughout the melt, I have found, causes irregularities in water content from one small portion of my polymer to another to persist, with consequent irregularity in molecular weight in successive portions of the polymer as spun from the melt. A critical feature of my process is accordingly the conditioning step above outlined whereby I bring the uniformity of water content of the solid polymer within a standard deviation not above about 0.003% by weight of the polymer, in random small samples of the solid polymer.

The water content desired in my process can be determined in accordance with the foregoing, by putting $x = 0$ in the above Equation 2, which then becomes:

$$(2'') \quad Z = C(0.555W') / (y - a)y$$

W' in this equation is the water content which will be in equilibrium at temperature T with polymer of initial ($-\text{COOH}$) end group concentration y , so that in this polymer there is no change in average relative viscosity or free water content or end group concentration when it is brought to equilibrium in the melt at the temperature T corresponding per Equation 1 to Z of Equation 2".

For the particular calculations on which the accompanying figure is based, the following values of the above noted quantities used in the equations were employed:

Relative viscosity, V , of starting polymer = about 51-60;

T of melt = about 265°C. or $538^\circ \text{ absolute};$

C for ($-\text{CONH}-$) groups = 8.730 eq./kg.

a for monobasic acid concentration = 0.0304 eq./kg.

The accompanying figure is a graph drawn in accordance with the above equations showing plots of formic acid viscosity of solid, dried polymer-formic acid viscosity of filaments melt spun from this polymer at temperature of 265°C. , the solid polymer having water content at three different levels, namely 0.065%, 0.075%, and 0.085% corresponding to the three lines shown in the graph. It will be appreciated from the graph that when water content of the solid polymer to be spun is allowed to vary by as little as 0.01% the resulting variation in relative formic acid viscosity of the spun polymer filaments will be as great as ± 3 or 4 units, even if the polymer started at a constant viscosity. Thus for instance, according to the graph, if polymer granules employed for spinning have relative formic acid viscosity of 53.4, the filaments resulting from spinning thereof also show viscosity of 53.4 provided the granules employed were uniformly at moisture content of 0.075%; but the resulting filaments show viscosity of 57, whenever the moisture content of the granules drops to 0.065% and the resulting filaments show viscosity of 50.2 whenever the moisture content of the granules employed for these filaments rises to 0.085%.

Various methods can be used to effectuate the polymer conditioning, i.e. the uniform distribution of water content throughout the solid polymer required in my process. In particular, individual particles such as granules or powder are contacted with an inert gas having a substantially constant temperature in the range between about 30°C. and about 120°C. and having a substantially constant water vapor partial pressure in the range between about 0.001 and about 10 mm. of mercury; said contact being maintained substantially continuously for at least about two days. Particularly preferred temperatures for these conditioning operations are at least about 30°C. , to assure a sufficient rate of equilibration of moisture content among the granules but not above about 50°C. , to minimize effects of cooling during subsequent handling and storage. Water vapor partial pressure to be maintained in gas of this temperature will generally be in the range between about 0.1 mm. of Hg and about 1 mm. of Hg. The inert gas employed in these operations desirably is under moderate superatmospheric pressure to assure that atmospheric oxygen will be excluded from contact with the granules during the period of conditioning. Examples of suitable inert gases are nitrogen, carbon oxides, hydrogen, and mixtures thereof.

Various types of apparatus for mixing solids with gases can be used to contact the polymer granules with the conditioning gas in accordance with the foregoing. Among such suitable types of apparatus is, for example, the circulating type, wherein solids are fed to the top of a large vertical, gas-filled tank and fall through the gas atmosphere in the tank by gravity; then are rapidly conveyed outside the tank to the top for recirculation. Another suitable type is the tumbling type such as a tumbling barrel wherein solids are carried up the sides of a horizontally rotating tank, e.g. by flights along the sides, and are allowed to drop through a gas atmosphere in the tank. A third suitable type is the rake mixer (Herreshoff furnace) wherein the solids are supported on trays in a tank containing the conditioning gas, and the solids are turned over and contacted with the gas by rotating rakes or the like. Modifications and combinations of the foregoing are also suitable and will be obvious to those skilled in the art of solid/gas mixing.

Suitable apparatus for conditioning polymer granules in accordance with my invention also includes apparatus

of types used for drying solids. In particular, the so-called "through circulation dryers" can be used, wherein the granules to be dried are supported on screens through which the conditioning gas is circulated upward or downward. Pneumatic conveying dryers can also be used, and rotary dryers similar to the tumbling barrel mixers above referred to. Screw conveyor dryers and vibrating conveyor dryers with provision to maintain the conditioning gas therein can also be used, either for the entire conditioning or for finishing the conditioning and conveying the resulting polymer to storage or to the melting operation.

Other methods of producing my conditioned solid polymer include drying solid polymer in finely divided form to the prescribed average moisture content; and thereafter thoroughly blending the resulting particles while maintaining a constant total moisture content.

The following example sets forth a specific embodiment of my invention, illustrative of my invention and of the best mode of carrying it out contemplated by me; but the invention is not to be interpreted as limited to all details of this example.

Example

Poly-e-caproamide cylindrical pellets ($\frac{1}{10}$ inch x $\frac{1}{10}$ inch) were withdrawn from a dryer at average moisture content of 0.0787% by weight of the polymer. They contained acetic acid chain terminator in concentration of about 0.03 gram-equivalent per kilogram of polymer. The observed standard deviation of the moisture content in these pellets was 0.004% by weight of the polymer as measured on 119 random samples of 10 grams each. These pellets had average relative formic acid viscosity of 54.61 and an observed standard deviation of viscosity of 0.523 as measured on 119 random samples of 11 grams each.

These pellets were supplied to a circulating type mixing apparatus wherein a pneumatic conveyor carried the solids from the conical base of a large vertical cylindrical mixing tank up to the feed inlet at the top of the tank. The cylindrical body of the tank was about 11.5 ft. x 30 ft. and the conical base had a depth of about 10 feet. Finished product was drawn off by diverting the solids from the pneumatic conveyor to a forward feed conveyor. The tank was provided with a central bottom outlet and additionally with a circle of open ended standing pipes rising to different heights within the tank and feeding to the pneumatic conveying system, whereby the mixing of solids in the tank was promoted. The tank capacity was 120,000 lbs. of pellets.

The tank was maintained under superatmospheric pressure of about 1.5 atmospheres absolute by nitrogen gas having dew point at 1 atmosphere pressure of -37° C. i.e. providing a water vapor partial pressure of about 0.2 mm. of Hg at 1 atmosphere pressure, and about 0.3 mm. of Hg at the operating pressure of 1.5 atmospheres.

The pneumatic conveyor for the above conditioning apparatus utilized the nitrogen gas withdrawn from the bottom of the tank as the conveying gas. After compression of the nitrogen used for conveying to 1.5 atmospheres for use in the tank, the nitrogen was passed through a heat exchanger to maintain its temperature at about 38° C. and was then introduced together with the pellets being conveyed thereby into the top of the tank.

This conditioning apparatus was operated with residence time of about 6 days, and the pellets thus conditioned were then forwarded to storage tanks wherein they were maintained at about room temperature under nitrogen gas of the same dew point as used in the conditioning apparatus and at pressure of about 2.3 atmospheres absolute.

From the storage tanks the pellets were supplied to the hopper of a melt spinning apparatus under the nitrogen atmosphere from the storage tanks. From this hopper the pellets descended to heated coils which melted the pellets; the melt collected in a pool from which the melt

was pumped at constant delivery rate through the usual spinning apparatus. The residence time of the melt in the pool was of the order of $\frac{1}{2}$ -1 hour, more or less. Tests upon the nitrogen atmosphere of this melt spinning apparatus indicated no significant transfer of moisture between this atmosphere and the polymer in this apparatus.

Moisture content was determined on the pellets coming from the conditioner by the same procedure as used on the pellets from the dryer. They had slightly greater moisture content than the pellets from the dryer, namely 0.0807%. These conditioned pellets showed a lowering of 25% had been effected in observed standard deviation in moisture content, namely from 0.004% to 0.003% by weight of the polymer. Their average relative formic acid viscosity, measured as before, was 54.61 with observed standard deviation of 0.516.

Upon measuring the relative formic acid viscosity of the yarn collected below the spinneret, produced by the operation of this example, viscosity of 55.82 was found and the observed standard deviation in this viscosity was 0.61 as measured on 597 random samples of 5.5 grams each.

By way of comparison, a yarn was produced by the above outlined procedure except that the pellets were taken from the dryer without being subjected to the above outlined conditioning operation. The pellets from the dryer had moisture content of 0.0804% with observed standard deviation of 0.004% by weight of the polymer, and had average relative formic acid viscosity of 55.27 with observed standard deviation of 0.485, both measured as above except using 101 samples. The resulting yarn collected below the spinneret showed relative formic acid viscosity of 56.23 with observed standard deviation of 0.87, measured as above except using 222 samples.

The difference in standard deviation of relative formic acid viscosity above cited, namely 0.61 unit for the product of this example vs. 0.87 unit for the comparison product, represents commercially significant improvement in that the final yarns obtained from this example form higher quality textile products, e.g. in terms of uniformity of dyeing with acid dyes, than do the yarns from the comparison products. The acid-dyed textile goods from the yarns of this example are virtually free of streaks. The improvements observed are quite surprising in view of the apparently small absolute difference in standard deviation of moisture content in the conditioned pellets of this example vs. the same pellets without the conditioning step (0.003 vs. 0.004 weight percent or 0.001% absolute difference).

Comparing the standard deviation in relative formic acid viscosity of the conditioned pellets versus that for the yarn spun therefrom the figures are 0.516 vs. 0.61. The small magnitude of the change, only 0.094 unit or 18% increase, demonstrates the surprising effectiveness of my conditioning treatment in maintaining viscosity uniformity during handling, storage and spinning. By contrast, when my conditioning treatment was omitted in otherwise essentially the same operations, this change was from 0.485 to 0.87, i.e. 0.385 unit or about 80% increase.

In the foregoing discussion and example I have referred only to poly-e-caproamide polymer. It will be recognized that this polymer presents peculiarities in melt spinning e.g. because of its tendency to revert to monomer up to an equilibrium concentration. Accordingly the principles and procedures employed in this invention apply in particular to e-caprolactam homopolymers and other e-caprolactam polymers containing at least about 50 mol percent of e-caprolactam, all of which are included in the term "e-caprolactam polymer" of the appended claims.

I claim:

1. In a process for production of filaments from water-washed e-caprolactam homopolymer by melt spinning, the improvement which comprises, before melt spinning the same, bringing the average water content of solid water-washed particles of said polymer within about 0.01% by weight, based on weight of the polymer, of its ultimate

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level reached in the conditioning below recited, said water content level being in the range from about 0.035% to about 0.115%; then conditioning the resulting polymer particles for spinning by contacting the particles with an inert gas having a substantially constant temperature in the range between about 30° C. and about 120° C. and having a substantially constant water vapor partial pressure in the range between about 0.001 and about 10 mm. of mercury said contact being maintained substantially continuously for at least about 2 days; the ultimate water content of the polymer resulting from said conditioning being in the range from about 0.035% to about 0.115% by weight of the polymer and being at a value $W \pm 0.01$ where W is determined by the following equations in units of weight percent based on polymer:

- (1) $\log_{10} Z = 1495/T - 0.261$, where T is the temperature to be maintained in the melt for spinning, in degrees absolute;
- (2) $V = -285.209 + 2164.33y + 11.7188/y$, where V is the relative viscosity of the polymer;
- (3) $Z = C(0.555W)/(y-a)y$, where Z is defined by Equation 1 above; y is defined by Equation 2 above in units of gram equivalents of COOH end groups per kilogram of polymer; C is the concentration of (—CONH—) groups in the polymer in gram-equivalents per kilogram; and a is the concentration of any monocarboxylic acid incorporated in the polymer, in

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gram-equivalents per kilogram; thereby bringing uniformity of water content of the solid polymer within a standard deviation not above about 0.003% of water by weight based on weight of the polymer; the resulting polymer having relative formic acid viscosity in the range from about 40 to about 80 with standard deviation not above about 0.6 relative formic acid viscosity units, as measured at 10% concentration in aqueous 90% formic acid solution at 25° C.

2. Improvement of claim 1 wherein the gas contacting the solid polymer particles is maintained at temperature in the range between about 30° C. and about 50° C. and the water vapor partial pressure in this gas is maintained in the range between about 0.1 millimeter and about 1 millimeter of mercury.

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