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Riggert

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[54] **PROCESS FOR THE PRODUCTION OF TECHNICAL ENDLESS FILAMENTS OF HIGH-MOLECULAR WEIGHT LINEAR POLYMERS**

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[51] **Int. Cl.** **B28b 3/20**

[58] **Field of Search** ..... 264/176 F, 169; 18/85 E, 8 SF, 8 P, 125 E, 125 B; 425/207

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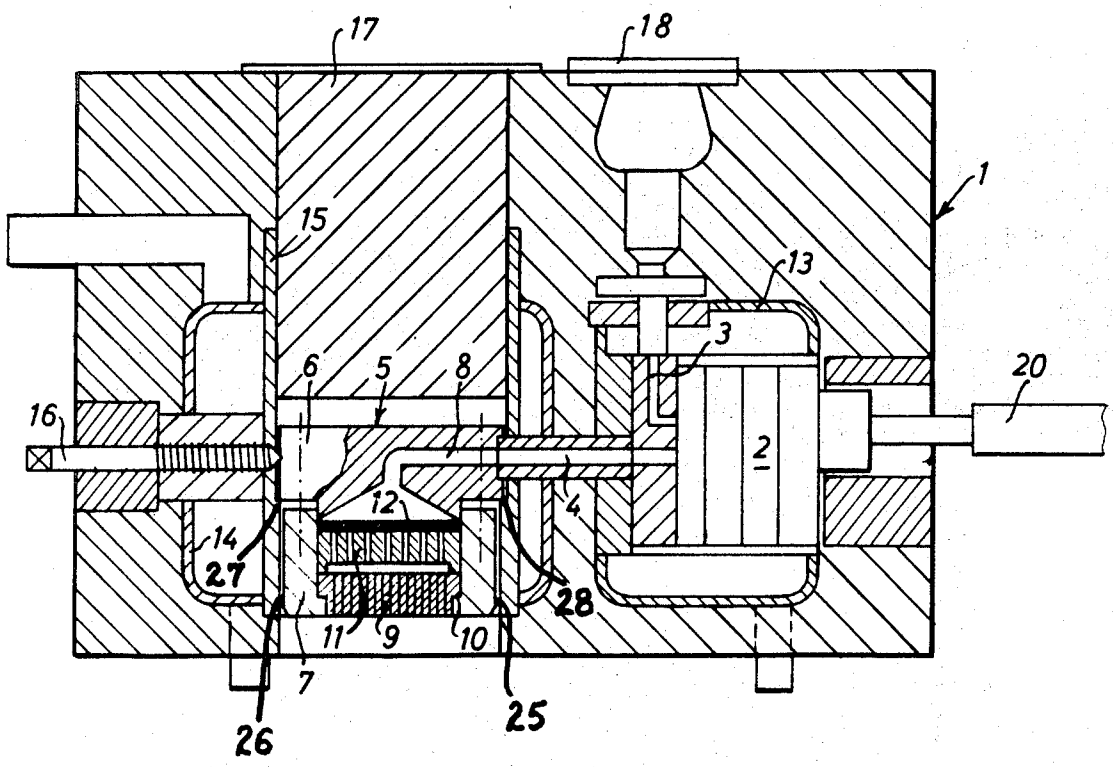
[57] **ABSTRACT**

Process for production of endless filaments from high molecular weight polymers having improved properties of low $\eta_{intr.}$ loss, and few capillary breaks per 10 Km, in a melt spinning process wherein the polymer melt is supplied to a spinning beam at high pressure, the melt is thereafter passed through a flow path constriction which effects a pressure drop of from 150 to 1200 atmospheres and a melt enthalpy increase sufficient to internally heat each of the melt particles uniformly and independently of their position in the melt flow cross section, and thereafter maintaining the increased temperature of the melt by heating all the surfaces thereafter contacted by the melt.

8 Claims, 2 Drawing Figures



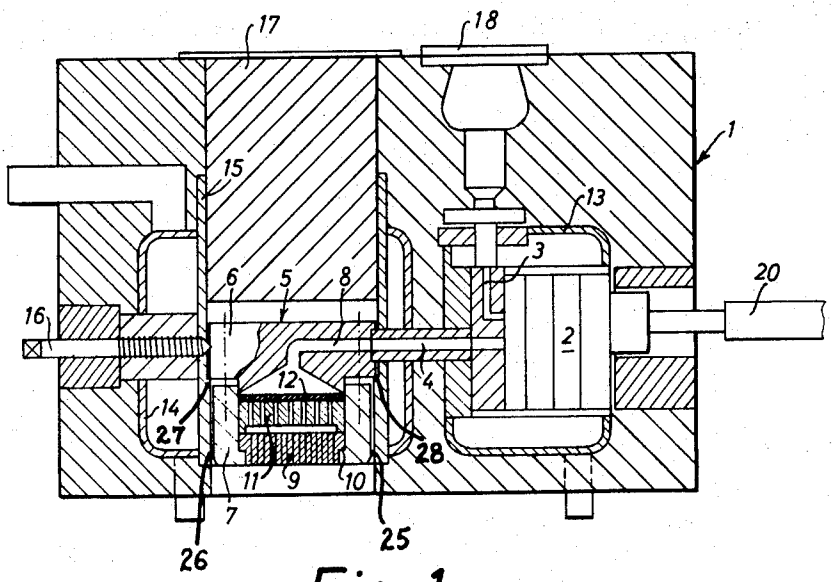


Fig. 1

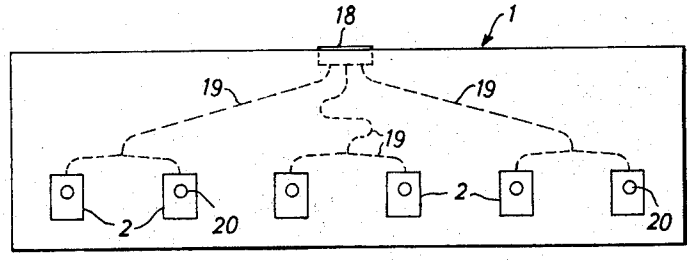


Fig. 2

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PROCESS FOR THE PRODUCTION OF TECHNICAL ENDLESS FILAMENTS OF HIGH-MOLECULAR WEIGHT LINEAR POLYMERS

BACKGROUND OF THE INVENTION

The invention relates to a process for the production of so-called "technical" filaments and threads (yarns) of high-molecular weight linear polymers, in particular polyesters, according to an improved melt-spinning process.

An important area of use of such technical endless filaments is the production of tire cord. A number of high polymers are well suited for this utility, especially polyesters, polyamides, and their well known modifications. Such high polymers behave similarly with respect to the considerations with which this invention is concerned, i.e., at spinning temperature these polymers tend either to a state of decomposition or to after-polymerization. The processing of any high polymers exhibiting such tendencies into technical endless filaments therefore lies generally within the scope of the present invention, although in the following description reference will be made particularly to filaments of polyethylene terephthalate.

Since tire cord and the inlays formed of it are among the essential construction elements for the safety and useful life of a tire, high quality requirements are naturally placed on such endless filaments. In view of the alternating stretching and compression stresses which tires in operation experience, a necessary precondition for the use of synthetic filaments for tire cord is an adequate fatigue resistance of the filaments. As is well known, the fatigue resistance increases with the mean molecular weight of the polymer. From this, it is desirable to produce filaments with as high as possible molecular weight.

Polyethylene terephthalate has come into strong prominence in the last few years for use in tire cord production. Polyethylene terephthalate unfortunately undergoes a considerable thermal decomposition between the conclusion of the production of the spinning raw material (raw polymer melt) and its subsequent shaping into threads. This thermal decomposition increases appreciably as the molar weight of the spinning raw material rises, and — in the case of filament formation from polymer chips — cannot be prevented even by an intensive drying of the spinning raw material. Because of the thermal decomposition problem, the increase in the molecular weight of the spinning raw material which is entirely possible with polymerforming processes of today can only in part be passed on to the spun filaments or thread formed therefrom. This thermal decomposition can be reduced, to be sure, if the molten spinning raw material is maintained for as short a time and as low a temperature as possible. However, the residence time of the spinning melt in the spinning apparatus is unfortunately prescribed by the dimensions of the apparatus, and the lower limit of the spinning temperature is determined by the highly undesirable condition of melt fracture. Where melt fracture occurs, the spun, unstretched filaments do not have a smooth or even surface, and exhibit fluctuations in diameter which are unacceptable for use as technical yarn, like tire cord.

It is evident from this that the spinning requirements are diametrically opposed. On the one hand, low melting temperature is required in the interest of a low decomposition, and on the other hand, high spinning temperature is required for trouble-free spinning. The solution of these problems was attempted by the proposal described in German published application 1,292,306. There the melt was supplied at a temperature below the spinning temperature, and then the melt was heated to the spinning temperature before the filament formation. This was sought to be achieved by an arrangement in which the heating box of the melt- spinning device is subdivided into two heating sections by a partition provided between the spinning pump block and the spinning head, with the heating medium being separately supplied to each section. To be sure, this proposal permits in theory separate, differentiated temperature conduction within the spinning apparatus. However, due to the relatively short residence time of the melt in the higher temperature zone and the unavoidable laminarity of flow of the highly viscous melt, the melt is not uniformly heated to the spinning temperature over the flow cross section. The undesirable consequence is inhomogeneity of the filaments over the cross section of the spinning nozzle plate, especially where the nozzle plate has a relatively large number of holes.

It is among the objects of the present invention to avoid these disadvantages, and in particular, to attain a rapid, uniform heating of the melt over the flow cross section before the spinning. In general terms, it is another object of the present invention to keep the loss of the high molecular weight achieved by a progressive polymer-formation process as low as possible in the case of rapidly decomposing high polymers. It is another object to pass the high molecular weight on to the filaments without spinning difficulties, or in the case of strongly after-polymerizing high polymers, to keep the rise in the molecular weight as low as possible.

The process of the invention solves the above problems by heating the melt prior to spinning by pressure decrease by means of a flow path construction, and then maintaining the melt temperature level by corresponding heating of all the surfaces touched by the melt before the final spinning.

The process of this invention results in an ideally uniform temperature increase over the full flow cross section by energy transformation at the choke point during the pressure decrease, in which each melt particle undergoes an equally great enthalpy increase, or "tempering," independently of its position in the flow cross section. According to the invention it is assured that this "tempering" state cannot be lost through heat lead-off by providing a simultaneous, corresponding heating of the spinning apparatus surfaces contacted by the melt. Characteristic of this invention is that heating by means of an external heat supply is obviated. In other words, what is characteristic of this invention is the utilization of an energy transformation for the direct, brief, and uniform internal heating of the melt, in which the amount of heat required for that purpose arises within the melt itself. This requires a higher spinning pump pressure to establish the required pressure gradient, which is built up and absorbed without difficulty by a suitable dimensioning of the spinning apparatus. In the process according to this invention about a 4° C. temperature increase per 100 atmospheres of pressure gradient is obtained in the spining processing of polyethylene terephthalate.

The threads of yarns produced according to the invention consist of filaments which are distinguished by a low scatter of both the diameter and the double refraction as measured over the thread cross section, i.e., low variation in these values from filament to filament. As a result, further processing propertires are excellent. Thus, by means of a one-stage or several-stage stretching process, there can be achieved yarns or threads of high tensile strength having a low filament capillary breakage number. Furthermore, the filaments show only a relatively slight decrease in the molecular weight as compared to the spinning raw material.

In the production of technical endless filaments of polyethylene terephthalate, it has been found especially advantageous if the following conditions are met: 1) the high molecular weight melt is supplied at a temperature T_1 between 280° and 330° C., and 2) is exposed to a pressure drop or pressure gradient, Δp, between 150 and 1200 atmospheres, at the earliest after 50 percent of its residence time between melt generation and spinning, and 3) the surface temperature, T_2, of all the surfaces contacted by the melt after the pressure drop is maintained within the following limits:

$$\frac{T_1^2}{T_1-[17\times10^{-3}\Delta p]}\leqq T_2\leqq\frac{T_1^2}{T_1-\left[10\left(\frac{\Delta p}{100}\right)^{2/3}\right]}$$

As the above limit formulas make clear, T_2 depends on the height of the pressure gradient (drop) and the temperature T_1 of the melt before the pressure drop. Preferably, the polyethylene terephthalate melt is supplied at a temperature T_1 between 285° and 310° C., and is exposed to a pressure drop (gradient) Δp between 200 and 800 atmospheres.

It is advantageous if the pressure decrease is carried out in the flow path between spinning pump and spinning nozzle plate. Good results are achieved in the finished filaments or threads especially when the pressure drop is located in the vicinity of the spinning nozzle plate. An especially simple and effective manner of carrying out the process of this invention is in providing that the pressure drop takes place substantially at the spinning filter, which in spinning devices in general is placed in the upper part of the so-called spinning nozzle pack. Metal sieves having 10,000 to 50,000 meshes/cm² are well suited as spinning filter material for this purpose. Such sieves can be stratified in several layers one over another and are suitably supported against the high spinning pump pressure. Sintered metal filters have also proved usable for this purpose.

In principle, the pressure decrease can be carried out according to three methods or combinations thereof in the spinning apparatus. Besides the use of spinning filter as the main choke zone for achieving the pressure drop, there can be used secondly, if need be, also the filter supporting plate, or, third, the nozzle plate bores. In the case of the supporting plate and/or nozzle bores, bores with a large length/diameter ratio, l/d, are required to achieve the pressure drop required in this invention. However, unlimited l/d ratios are not possible, at least for the nozzle bores, principally for reasons of manufacturing technology. For example, diameters of less than 1mm, very common for this spinning technology, cannot be manufactured with adequate precision where the l/d ratio is above 20. In addition, large l/d ratios are expensive to manufacture. Therefore, according to the process of this invention, the pressure is brought down preferably and largely at the spinning filter. Letting pressure down at the spinning filter is also preferable because there the temperature distribution in the melt is more uniform.

In the execution of the process of the invention, it is possible to proceed both from polymer chips, which, in a known manner, are melted up on grids or by means of extruder devices, and also directly from a polymer melt obtained directly after the conclusion of the polymerization or polycondensation. In either case, short feed paths between melt discharge and spinning device are recommended. The process of the invention is particularly adapted to the processing of polymers having spinning melt solution viscosities, $\omega_{intr.}$, equal or greater than 0.85, and preferably equal to or greater than 0.92.

In the drawings there is shown a spinning apparatus example suited for the process of the invention, in two schematic representations.

FIG. 1 represents a section through a spinning position of a spinning beam.

FIG. 2 shows a six-position beam in a rear view.

Referring now to FIG. 1, within the self-supporting and thermally insulating beam body 1 (which is cross-hatched), there are provided for each spinning position a high-pressure spinning pump 2, normally a gear wheel type metering pump, having product inlet line 3 and product outlet line 4, as well as a spinning head, generally designated as 5. The spinning head 5, in the present example, being substantially rotationally symmetrical, consists of a feed plate 6 and a spinning nozzle pack holder 7 screwed together with it from above (not shown). The feed plate 6 has a radially-outward directed product inlet line 8 aligned with the product outlet line 4, which product inlet line 8 expands conically downward to about the diameter of the spinning nozzle pack. The spinning nozzle pack comprises:

a. the spinning nozzle plate 9 provided with a large number of nozzle bores, which plate is seated on an inwardly-directed ring shoulder 10 of the holder 7, b. a filter support plate 11 resting on the plate 9, and c. the filter 12 sandwiched between supporting plate 11 and feed plate 6. The filter in this embodiment consists of a plurality of edge-framed wire gauze layers. The filter 12 has a double function: On the one hand it filters the spinning melt in a known manner, and on the other hand, with respect to its flow resistance, it is dimensioned in such a way that it brings about the main proportion of the desired pressure drop.

The spinning pump 2 is surrounded by a heating jacket 13, which is heated by any convenient heat transfer medium, for example the mixture of diphenyl and diphenyl oxide, while the spinning head 5 is arranged separately within its own heat transfer medium in heating vessel 14. The heating systems 13 and 14 are maintained at different temperatures, so that heating jacket 13 brings about in the supplied melt the temperature T_1 and heating vessel 14 maintains the temperature T_2.

As FIG. 1 makes clear, the spinning head 5 is inserted from above in a receiving tube 15 of the heating vessel 14 and pressed tightly by a radially acting pressure screw 16 against the product outlet line 4. The receiving tube 15 is closed by an insulating plug 17. Prefera-

bly, the heating jacket **13** and the heating vessel **14** are each continuous for all the spinning positions of a beam, or alternatively may be constructed to communicate with one another by means of pipelines.

It should be noted that an air gap **25, 26** surrounds the spinning head **5** between it and the receiving tube **15,** and the only contact point therebetween is at the radial shoulder **27, 28.** The gap may range from about **1** to 3mm in width, to ensure even heat transfer from vessel **14** to the head by radiation and convection.

FIG. **2** shows that the product lines **19** are adapted to have equal length between a central supply place **18** and the individual spinning pumps **2,** so that the melt has a uniform residence time for all the spinning positions. The reference number **20** designates the spinning pump drive shafts.

The process of the invention is explained in detail in the following with the aid of seven examples, of which the Example **1** describes a conventional technique not according to this invention, operating without appreciable pressure drop and without temperature rise before the spinning.

Examples **2, 5** and **7** relate to the process of this invention and clearly show its advantages.

Examples **3, 4** and **6** relate to processes in which not all the features of this invention are present simultaneously, or the work is done according to the state of technology. The solution viscosity is given in the examples as the measure for the mean molecular weight, which was determined as the $\omega_{intr.}$ value by standard procedures. The concentration of the measuring solution amounted to 0.5 *g*/100 ml., the solvent is a phenol-tetrachloroethane mixture (60 : 40) and the measuring temperature was 25° C. In the examples, the diameter fluctuations along an unstretched thread filament serve as the measure of the melt fracture. The diameter fluctuations are recorded as the variation coefficient (CV_D value) in percentages. In some examples also the variation coefficient of the double refraction (CV_n value) is given in percentages.

EXAMPLE I

(Conventional Technique)

A. A melt of polyethylene terephthalate having a solution viscosity of $\omega_{intr.} = 1.04$ was supplied at a temperature T_1 of 310° C. to a six-position spinning beam. All the product lines, including spinning pump and spinning nozzle pack, were heated to $T_2 = 310°$ C. The pressure drop in the spinning nozzle filter amounted to 80 atmospheres. From a spinning nozzle plate having 200 holes, each of 0.4 mm diameter, there was generated a thread with a spinning denier of 5900 den. at a draw-off speed of 400 m/min. The solidification of the spun thread was delayed in known manner by an afterheater, in order to preclude any undesirably great molecular pre-orientation. The mean CV_D value of the unstretched thread filaments was found to be 4.8 percent, which indicates a spinning free of melt-fracture. After stretching the resultant cord base thread in a ratio of 1 : 6.1, there was found to be 20 capillary breaks per 10,000 meters and a tensile strength of 9.0 *g*/den. Of great disadvantage was the severe drop of the solution viscosity of the thread, which was found to be $\omega_{intr.} = 0.86$. B. In an otherwise corresponding test where the melt temperature was 282° C. instead of 310° C., the thread material obtained was no longer faultlessly spinnable and stretchable because of setting in of melt fracture. In this case, the mean CV_D value of the thread filaments rose to 17 percent, while the solution viscosity in the thread was $\omega_{intr.} = 0.95$.

EXAMPLE 2

(The Invention)

The initial procedure as in Example **1** was fillowed, but with the modification that the polymer was supplied to the spinning beam, at $T_1 = 292°$ C. instead of at 310° C. The spinning beam, including spinning pump, was likewise heated to $T_1 = 292°$ C. The melt residence time during its conveyance from the place of generation to the spinning beam was the same as in Example **1.** In contrast to Example **1,** the spinning nozzle pack was heated to a temperature of $T_2 = 310°$ C. By use of a spinning nozzle filter consisting of a sieve filter combination of **24** metal screen layers each having 17,000 meshes/cm², the pressure drop, Δp, was 320 atmospheres. The temperature of the spinning nozzle pack was therefore within the temperature range according to the invention. Using the spinning nozzle plate described in Example **1,** a thread having spinning titer of 5900 denier was spun, again at 400 m/min. draw-off speed. The mean CV_D value of the thread filaments was 4.6 percent. In agreement with Example **1,** the thread had 25 breaks per 10,000 m, which is within the measurement error limits. As compared to Example **1,** the molecular decomposition of the polymer was significantly improved, being considerably less under the process parameters of the invention, the thread having a solution viscosity of $\omega_{intr.} = 0.94$.

EXAMPLE 3

(Comparison)

Under the conditions of Example **2,** but with a temperature $T_1 = T_2$ of 292° C. (lying outside the invention), a thread having a CV_n value of 10 percent was obtained. The thread CV_D value was 12 percent exhibiting a poor melt fracture, and the capillary break frequency of 120 breaks per 10,000 *m* was considerably above that of the thread of Examples **1** and **2.** The $\omega_{intr.}$ value of 0.95 showed no demonstrable advantage over that of Example **2.**

EXAMPLE 4

(Comparison)

Initially, the same procedure as in Example **2** was followed, with the modification that the spinning nozzle pack was heated to a temperature T_2 of 325° C. This temperature T_2 lies outside the range according to this invention. The $\omega_{intr.}$ value of the thread was 0.93 which is only a little lower than in Example **2.** Although under these process conditions no melt fracture occurred, the CV_D value was 10 percent, as a result of the temperature inhomogeneity of the melt emerging from the spinning nozzle plate. For the same reason, the CV_n value amounted to 15 percent, and as a consequence the capillary break frequency was considerable. With respect to a thread tensile strength of 9.0 g/den. 100 capillary breaks per 10,000 m were counted.

EXAMPLE 5 (The Invention)	EXAMPLE 6 (Comparison)	EXAMPLE 7 (The Invention)

In the table below is presented data for three further examples. Summarized in the table are the data for the temperatures, the pressure drop, the initial and end vis-

cosities ($\omega_{intr\ A}$ and $\omega_{intr\ E}$), the viscosity decrease ($\Delta\omega_{intr.}$), the CV_D value and, in some cases the CV_n value. The advantages of working with the technique described in the present invention are easily seen by a comparison of the values for the viscosity decrease, and/or for CV_D, and/or for the capillary break numbers. For the sake of better comparison, values for Examples 1 to 4 were also included in the table.

TABLE

	T_1 (° C.)	T_2 (° C.)	Δp (at)	ηintrA	ηintrE	$\Delta\eta$intr.	Capillary break number for 10 Km.	CV_D, percent	CV_n, percent	Corresponding state of technology
Example:										
1a	310	310	80	1.04	0.86	0.18	20	4.8	----------	Prior art.
1b	282	282	80	1.04	0.95	0.09	----------	[1] 17.0	----------	Do.
2	292	310	320	1.04	0.94	0.10	25	4.6	6.8	The invention.
3	292	292	320	1.04	0.95	0.09	120	12.0	10.0	Process not according to the invention.
4	292	325	320	1.04	0.93	0.11	100	10.0	15.0	Do.
5	285	322	760	0.96	0.87	0.09	22	4.7	7.2	The invention.
6	285	285	120	0.96	0.89	0.07	----------	[1] 16.0	----------	Process not according to the invention.
7	300	310	230	1.08	0.95	0.12	27	4.5	7.0	The invention.

[1] Melt fracture not perfectly spinnable and stretchable.

What is claimed is:

1. In a process for the production of industrial monofilaments from high-molecular weight thermoplastic polymers selected from linear polyester and polyamide polymers by melt-spinning, which high polymers are subject to decomposition or after-polymerization at spinning temperatures, including the steps of supplying a melt of said polymer at a temperature below the spinning temperature, and heating the melt prior to the filament formation, the improvement which comprises:

a. supplying said melt at a temperature T_1, between 280° and 330° C and at high pressure to a spinning unit comprising a spinning pump, a nozzle plate and construction means disposed between said pump and said nozzle plate,

b. passing said melt by means of said spinning pump through a constriction in its flow path said constriction occurring within said constricting means prior to said melt passing through said spinning nozzle plate to effect a pressure drop, Δp, of between 150 and 1200 atmospheres before arrival of said melt at said spinning nozzle, and an increase of the internal energy sufficient to internally heat the melt to a temperature greater than T_1, which increased temperature is uniform and independent of the melt position in the flow cross section under conditions which provide low loss of intrinsic viscosity and does not change the laminarity of melt flow,

c. supplying heat from the exterior to said spinning unit surfaces thereafter contacted by said melt in an amount only sufficient to maintain the increased temperature of said internally heated melt but insufficient to cause substantial thermal degradation or after polymerization, and

d. spinning filaments from said melt, said filaments exhibiting improved properties of low $\omega_{intr.}$ loss, low diameter and double refraction variation coefficients, and few filament breaks per 10 Km. spun thread.

2. A process as in claim 1 wherein said polymer is a polyester.

3. A process as in claim 2 wherein:

a. said polyester is polyethylene terephthalate,

b. said pressure drop is effected at the earliest after 50 percent of the total melt residence time between generation and spinning, and

c. the temperature, T_2, of all of said surfaces touched by said melt after said pressure drop is maintained within the following limits:

$$\frac{T_1^2}{T_1-[(17+10^{-3})(\Delta p)]} \leqq T_2 \leqq \frac{T_1^2}{T_1-\left[10\left(\frac{\Delta p}{100}\right)^{2/3}\right]}$$

4. A process as in Claim 3 wherein said polyethylene terephthalate melt is supplied at a temperature, T_1, between 285 and 310° C., and the pressure drop, Δp, is between 200 and 800 atmospheres.

5. A process as in claim 1 wherein said polymer is supplied at a temperature, T_1, between 285 and 310° C., and the pressure drop, Δ p, is between 200 and 800 atmospheres.

6. A process as in claim 1 wherein:

a. said assembly comprises a spinning pump and a spinning nozzle plate, and

b. said pressure drop is effected in the flow path between said spinning pump and spinning nozzle plate.

7. A process as in claim 6 wherein said assembly includes a spinning filter disposed upstream of said nozzle plate, and said pressure drop is effected principally at said spinning filter.

8. A process as in claim 7 wherein:

a. said polymer is polyethylene terephthalate,

b. said pressure drop is effected at the earliest after 50 percent of the total melt residence time between generation and spinning, and

c. the temperature, T_2, of all of said surfaces touched by said melt after said pressure drop is maintained within the following limits:

$$\frac{T_1^2}{T_1-[(17\times10^{-3})(\Delta p)]} \leqq T_2 \leqq \frac{T_1^2}{T_1-\left[10\left(\frac{\Delta p}{100}\right)^{2/3}\right]}$$

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