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(54) Title: PROCESS FOR PREPARING PELLETS OF POLY(TRIMETHYLENE TEREPHTHALATE)

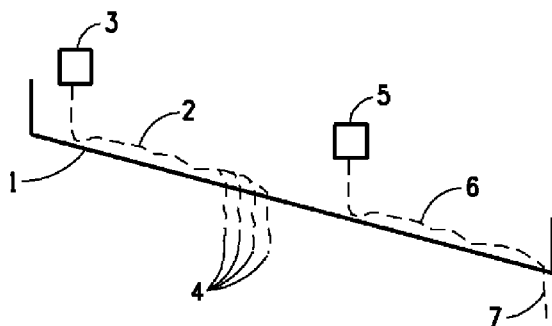


FIG. 1a

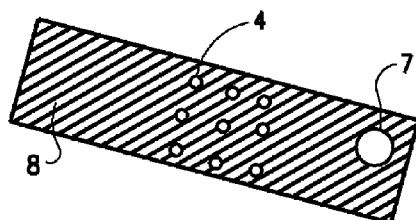


FIG. 1b

(57) Abstract: The process creates a radial temperature gradient in an extruded strand in a direction normal to the direction of motion thereof (that is, normal to the longitudinal direction thereof) so that upon exiting the first quench region the surface of the strand has solidified while at least the preponderant portion of the interior of the strand remains above the cold crystallization temperature, T_{cc} . Then, in the annealing region, heat from the warmer interior will be transferred to the cooler surface, causing the surface to heat up into the range of T_{cc} , thereby inducing the surface to undergo crystallization. Once the surface has undergone crystallization, the strand is thoroughly quenched in a second quench region so that the strand will be ready for pelletization, accumulation or other handling steps.



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PROCESS FOR PREPARING PELLETS OF POLY(TRIMETHYLENE TEREPHTHALATE)

This application claims benefit of U. S. Provisional 61/447,868, filed
5 March 1, 2011, and U. S. Provisional 61/447,875, filed March 1, 2011,
which are herein incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to melt processing of
poly(trimethylene terephthalate) into pellets suitable for future use in fiber
10 production, injection molding, and other fabrication methods.

BACKGROUND OF THE INVENTION

Polytrimethylene terephthalate (PTT) is prepared by the
polycondensation reaction of 1,3-propanediol with terephthalic acid or
terephthalic acid esters. PTT polymer and copolymers thereof are finding
15 ever increasing commercial use in the preparation of fibers, fabrics,
carpets, films, molded parts and the like.

Standard practice in the polymer art is to manufacture thermoplastic
polyesters in a "continuous polymerizer" extruding the produced molten
polymer through an extruder equipped with a so-called "strand die" which is
20 simply a metal plate having one or more about 1/8 - 1/4" circular cross-
section holes in it. A continuous strand, about 1/10 - 1/8" in diameter, of
molten thermoplastic polymer is extruded out of each hole of the strand
die. Immediately upon discharge from the strand die, the hot strand is
usually passed through a water quench region normally consisting of a
25 water quench tank or a water spray chamber. The length of the quench
region is largely dependent upon the linear rate of extrusion of the strand -
- that is, how fast the strand is moving - and the melt temperature of the
strand at the exit of the die. At the end of the quench region, the strand is
separated from the water, and is directed to a cutter that cuts the strand
30 into pellets about 1/8" long.

This practice, developed for poly(ethylene terephthalate) (PET), has been applied to poly(trimethylene terephthalate) (PTT). Because of the rapid quenching of the strand, the resulting pellets tend to exhibit amorphous (that is, non-crystalline) surfaces. This is not a problem in PET because the glass transition temperature is sufficiently high that the amorphous surfaces remain solid until the pellet is further melt processed. PTT exhibits a glass transition temperature (T_g) of about 45 °C -- much lower than that of PET and other well-known polyesters such as PBT or PEN. It has been found that when PTT pellets prepared by the process described supra are stored where the ambient temperature reaches about 40 °C, some degree of surface polymer flow may occur on a microscopic scale, thereby causing stored pellets to stick together, forming aggregates that hinder the smooth flow of pellets during processing. By inducing surface crystallization, pellets can be produced that exhibit greatly reduced sticking and aggregation when subject to relatively high storage temperatures.

Hanniman et al., US2009/0057935, discloses a process for producing a non-adhering granule from a polyester above T_g by introducing a granulated material into cooling water at 80-110 °C, where the granulated material is prepared from a melt and fed to an underwater melt cutter.

Duh et al., US 6,297,315, discloses a process for crystallizing PTT before pelletizing by immersing the quenched strand into a water batch heated to 60-100 °C. Duh teaches that best results are obtained by crystallization after pelletization. Further, according to Duh, a water temperature of 60 °C requires a 20 minute crystallization time to achieve satisfactory results. This is because, as Duh shows, 60 °C is below the crystallization temperature of about 69 °C.

Nishiyama et al, JP7223221 (A) (abstract only), discloses a process suitable for use with a polyester having a T_g less than 40 °C in which a molten strand is quenched, then subject to stretching to induce crystallization therein, followed by pelletization.

Shelby et al., US 6,159,406, discloses a process for crystallizing difficult to crystallize polyester melts before pelletizing by quenching the strand, and then stretching the strand by winding on two sets of godets separated by a hot water bath set above T_g through which the strand
5 passes.

SUMMARY OF THE INVENTION

In one aspect, the invention provides a process comprising:

- 10 (a) preparing a molten strand of a poly(trimethylene terephthalate) composition wherein the strand has a surface and an interior;
- (b) contacting the molten strand with water in a first quench region for a sufficient period of time so that the surface of the molten strand solidifies and at least a preponderant portion of the interior remains above the cold
15 crystallization temperature of the poly(trimethylene terephthalate) composition, thereby preparing a surface-solidified strand;
- (c) separating the surface-solidified strand from the water;
- (d) exposing the surface-solidified strand to ambient air in
20 an annealing region for a sufficient period of time to induce cold crystallization on the surface of the strand producing a surface-crystallized strand;
- and
- (e) contacting the surface-crystallized strand with water in a
25 second quench region for a sufficient period of time to solidify the interior of the strand.

In another aspect, the invention provides an apparatus comprising
-- an extrusion means for extruding a molten polymer strand;
-- a pelletizer; and,
30 -- a trough disposed to convey a polymer strand from the extrusion means to the pelletizer; the trough comprising
-- an interior bottom surface;

- a water dispensing means disposed to provide a layer of water on a first portion of the interior bottom surface that is proximate to the extrusion means;
- a mesh or perforated surface disposed in the trough downstream from the water dispensing means, disposed to permit the separation of water from a water-immersed strand incident upon it;
- and,
- a second portion of the interior bottom surface downstream from that mesh or perforated surface, disposed to contain a layer of water.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a illustrates a side longitudinal cross-sectional view of a trough in an embodiment of the invention wherein the trough comprises a plurality of perforations in the interior bottom surface thereof.

Figure 1b illustrates a bottom view of the trough shown in Figure 1a, showing the plurality of perforations downstream from the first portion, and a large drainage hole in the furthest downstream portion.

Figure 2 illustrates a side longitudinal cross-sectional view of the trough in an embodiment of the invention wherein the trough interior bottom does not have perforations downstream from the first portion of the trough so that water introduced at the portion closest to the strand die can flow unimpeded to the drainage hole at the end of the trough. Instead, in this embodiment, the trough is provided with a raised wire mesh portion that is disposed just above the water.

Figure 3 illustrates a representation of an embodiment of the apparatus and process of the invention that was employed in the Examples, *infra*.

DETAILED DESCRIPTION OF THE INVENTION

When a range of numerical values is provided herein, it is intended to encompass the end-points of the range unless specifically stated

otherwise. Numerical values used herein have the precision of the number of significant figures provided, following the standard protocol in chemistry for significant figures as outlined in ASTM E29-08 Section 6.

For example, the number 40 encompasses a range from 35.0 to 44.9, whereas the number 40.0 encompasses a range from 39.50 to 40.49. In one aspect the present invention provides a process comprising:

- (a) preparing a molten strand of a poly(trimethylene terephthalate) composition wherein the strand has a surface and an interior;
- (b) contacting the molten strand with water in a first quench region for a sufficient period of time so that the surface of the molten strand solidifies and falls below the cold crystallization temperature while at least a preponderant portion of the interior remains above the cold crystallization temperature of the poly(trimethylene terephthalate) composition, thereby preparing a surface-solidified strand;
- (c) separating the surface-solidified strand from the water;
- (d) exposing the surface-solidified strand to ambient air in an annealing region for a sufficient period of time to induce cold crystallization on the surface of the strand producing a surface-crystallized strand;
- and
- (e) contacting the surface-crystallized strand with water in a second quench region for a sufficient period of time to solidify the interior of the strand.

The object of the process hereof is to create a radial temperature gradient in the extruded strand in a direction normal to the direction of motion thereof (that is, normal to the longitudinal direction thereof) so that upon exiting the first quench region the surface of the strand has solidified while at least the preponderant portion of the interior of the strand remains above the cold crystallization temperature, T_{cc} "Preponderant portion"

shall mean at least 50% of the interior of the strand. Then, in the annealing region, heat from the warmer interior will be transferred to the cooler surface, causing the surface to undergo crystallization. Once the surface has undergone crystallization, the still warm strand can then be thoroughly quenched in the second quench region so that the strand will be ready for pelletization, accumulation or other handling step.

In the art of thermal analysis, T_g and T_{cc} refer to specific temperatures determined according to specified methods from, for example, differential scanning calorimetry data. However, the average practitioner of the art understands that these temperatures so determined lie within a range of several degrees that define the transition to which they refer. Thus, for example, cold crystallization will occur over a range of several degrees, but the rate, under one set of standard test conditions, reaches a maximum at T_{cc} .

The critical temperatures referred to, namely the glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) are known to shift somewhat depending upon the specific components of the PTT composition hereof. For example, T_g and T_{cc} are both known to vary depending upon the type and concentration of comonomer in the polymer.

While T_g and T_{cc} have clear and precise scientific definitions, they are defined phenomenologically for the purposes of the present invention, without reference to an actual temperature reading. T_g is defined for the purposes of the present invention as that temperature above which polymer molecules exhibit sufficient mobility so that pellet sticking behavior can occur. T_{cc} is defined for the purposes of the present invention as that temperature at which the surface of the strand undergoes crystallization at a maximum rate while in the annealing region.

It is not necessary to actually measure T_g and T_{cc} as herein defined. When the molten polymer strand is extruded, it is, by definition, above both T_g , T_{cc} , and the crystalline melting point of the polymeric composition. When the molten strand exits the first quench region according to the process hereof, it is clear to the practitioner hereof that the surface has

solidified and is no longer molten. Moreover, the surface-hardened strand must have sufficient strength to resist breakage under tension.

On the other hand, if the surface of the strand has not become at least partially crystallized upon exiting the annealing region, a practitioner
5 can conclude that the residence time in the first quench region was too long, so that the temperature of a preponderant portion of the interior had been reduced to below T_{cc} .

Suitable for the practice of the present invention are homopolymers of PTT and copolymers thereof comprising at least 70 % of monomer units
10 of trimethylene terephthalate. Polymers suitable for the practice of the present invention can contain up to 25 % by weight of various additives as are commonly incorporated into polymers to impart additional functionality. Such additives include but are not limited to UV stabilizers, inorganic fillers, antistats, pigments, and flame retardants. Any suitable PTT
15 composition must exhibit cold crystallization in order to be operable in the process hereof.

In one embodiment, the PTT composition comprises PTT homopolymer.

The strand according to the invention is a moving strand. That is,
20 any arbitrarily selected point on the strand undergoes continuous translation away from the strand die in a direction parallel to the longitudinal axis of the strand. Taken in its entirety at any given moment in time, the strand extends from the die to the pelletizer. However, for the purposes of the present invention the term "strand" shall also be
25 understood to refer to any appropriate segment of the extruded strand, of any length. For example, when the text refers to contacting the strand with water, it shall be understood that at any given moment in time, a segment of the strand, shorter in length than the entire strand, is undergoing water contact.

30 For the purposes of the present invention, the term "residence time" shall refer to that period of time in which an arbitrarily selected point along the strand spends traversing a particular region as defined herein. The

term "the residence time of the strand" shall be understood to mean the residence time of an arbitrary point along the strand.

In one embodiment, the extrudate consists of a single strand. In an alternative embodiment, the extrudate comprises a plurality of strands.

5 According to the present invention, the residence time of the strand in the first quench region is sufficient to reduce the temperature of the surface to a temperature where the surface is solid and has sufficient strength to resist breakage upon tension, but insufficient to cause at least a preponderant portion of the interior to fall below the cold crystallization
10 temperature of the poly(trimethylene terephthalate) composition. In one embodiment, the residence time of the strand in the first quench region lies in the range of 0.2 to 2 sec. In a further embodiment, the residence time of the strand in the first quench region lies in the range of 0.3 to 1.0 sec.

15 Further according to the invention, the strand exits the first quench region and enters the annealing region where the surface undergoes reheating at least to T_{cc} by the latent heat remaining in the interior of the strand. According to the invention, the residence time of the strand in the annealing region is sufficient to induce crystallization on the surface of the
20 strand. In one embodiment, the residence time of the strand in the annealing region lies in the range of 0.3 to 5 sec. In a further embodiment, the residence time of the strand in the annealing region lies in the range of 0.5 to 2.5 sec.

 Further according to the invention, following the annealing region,
25 the strand is passed through a second water quench region for a period of time sufficient to further solidify the interior of the strand. In one embodiment, the residence time in the second quench region lies in the range of 1 to 10 sec. In a further embodiment the residence time in the second quench region lies in the range of 1.5 to 3.5 sec.

30 In one embodiment, the water temperature, T_w , in the first and second quench regions is, independently, in the range of $0\text{ }^{\circ}\text{C} < T_w < 60\text{ }^{\circ}\text{C}$. In a further embodiment, $20\text{ }^{\circ}\text{C} \leq T_w \leq 50\text{ }^{\circ}\text{C}$. In a still further embodiment, $35\text{ }^{\circ}\text{C} \leq T_w \leq 45\text{ }^{\circ}\text{C}$.

The water quench may be effected by any means known to be acceptable in the art. In one embodiment, water quenching is effected by immersing the strand in a water bath. In an alternative embodiment, the water quenching is effected by passing the strand through a water spray.

- 5 In one embodiment of the process hereof, the water quench is effected by same means in both the first and second quench regions. In an alternative embodiment, the water quench is effected by different means in the first and second quench regions.

- 10 As the strand exits the first quench region and enters the annealing region, it must be separated from residual quench water residing on or entrained with the strand surface. Any convenient means for so separating is satisfactory, including air jet drying, draining through drain holes, passing over a dessicant bed, and the like. While it is not necessary for the strand to be bone dry, it is necessary for the proper
15 crystallization of the surface to replace the high heat capacity liquid water on the strand surface with low heat capacity air.

- Following quenching in the second quench region, the strand can be further processed. In an embodiment, the strand is fed to a pelletizer for cutting into pellets that are well-suited for production of fiber, film, and
20 injection molded parts, among other uses. In an alternative embodiment, the strand itself may be collected in bulk.

An apparatus is described for use with the present process wherein the apparatus comprises

- an extrusion means for extruding a molten polymer strand;
- 25 -- a pelletizer; and,
- a trough disposed to convey a polymer strand from the extrusion means to the pelletizer; the trough comprising
 - an interior bottom surface;
 - a water dispensing means disposed to provide a layer of
30 water on a first portion of the interior bottom surface that is proximate to the extrusion means;
 - a mesh or perforated surface disposed in the trough downstream from the water dispensing means, disposed to

permit the separation of water from a water-immersed strand incident upon it;

and,

- 5 -- a second portion of the interior bottom surface downstream from that mesh or perforated surface, disposed to contain a layer of water.

The extrusion means is not critical so long as it results in the extrusion of a molten strand. Suitable means include screw-type extruders, Farrell continuous mixers, gear pumps, so-called continuous
10 polymerizers, screw pumps, hydraulic pumps and the like. Any of these extrusion means is employed herein to feed a strand die from which can be extruded a molten strand, according to the invention.

Any pelletizer designed for pelletizing polymer strands is suitable for use in the present invention. Pelletizers are well known in the art, and
15 are widely available commercially from many sources.

The trough is disposed to define a path between the strand die and the pelletizer, conveying the strand from strand die to pelletizer. For the purposes herein, the term "downstream" refers to the relative position with respect to the path from the strand die to the pelletizer. For example, a
20 second position along the path is further downstream than a first position if the second position is further from the strand die and closer to the pelletizer than is the first position. The trough provides the means for quenching the strand according to the process of the invention.

A suitable trough can be made of any water impermeable material, including but not limited to metal, ceramic, or plastic. In a typical
25 embodiment hereof, the trough is made from metal, typically stainless steel or aluminum. The trough is designed to hold a layer of water, into which the strand is immersed according to the process of the invention.

The trough comprises a water dispensing means that is disposed to
30 dispense water into a first portion of the interior bottom surface of the trough where that first portion is proximate to, and generally as close as possible, to the strand die so that the molten strands can be immersed in as short a time as possible after exiting the strand die. Suitable water

dispensing means can be any that are known in the art. Suitable water dispensing means can be water sprays, water pumps, hoses or tubes any of which can be connected to a water tap or reservoir.

The trough further comprises a mesh or perforated surface
5 downstream from the first portion of the trough, the mesh or perforated surface disposed to separate the water from a water immersed strand that is exiting the first portion of the trough, according to the process hereof. In one embodiment, the mesh can be any material that forms a mesh, grid, or netting that allows water to pass through. It is typically made of a non-
10 water absorbing material such as metal, ceramic, or plastic.

In an alternative embodiment, the perforated surface comprises a plurality of perforations in the interior bottom surface of the trough itself. In a further embodiment, the trough further comprises a series of cover plates that can be used to cover the perforations on the exterior bottom
15 surface of the trough, thereby adjusting the length of the perforated surface.

In either embodiment, the water entrained by the strand in the process is able to drain off through the perforations or mesh, allowing the segment of the strand traversing this portion to undergo annealing in air
20 according to the process hereof.

The trough further comprises a second portion of the interior bottom surface that is disposed to contain a layer of water, this for the final quench in the process hereof. In one embodiment, wherein the mesh or perforated surface comprises a raised structure that resides above the
25 water level, only a single water dispensing means is necessary since the water can flow freely underneath the elevated mesh or perforated surface. In an alternative embodiment, wherein the perforated surface is a portion of the interior bottom surface itself, the water input in the first portion proximate to the strand die will drain out the holes in the bottom of the
30 trough, unless it is saved by inserting a system of baffles and gutters to direct the water to the second portion, downstream from the mesh or perforated surface. Alternatively, the water required for the second portion

can be supplied by a second water dispensing means that can be any of those suitable for the first water dispensing means.

Figure 1a is a side longitudinal cross-sectional schematic view of an embodiment wherein the trough comprises a plurality of perforations in the interior bottom surface thereof. The metal trough, **1**, is disposed so that water, **2**, dispensed from a first dispensing means, **3**, forms a layer flowing downstream, and then draining through a plurality of drainholes, **4**, on the interior bottom surface of the trough (not seen in this view). A second water dispensing means, **5**, is disposed to dispense water, **6**, to form a second water layer flowing downstream to a drainage hole, **7**, (not seen in this view) in the downstream end of the trough.

Figure 1b is a view of the exterior bottom, **8**, of the trough shown in Figure 1a, showing the plurality of perforations, **4**, downstream from the first portion, and the larger drainage hole, **7**, in the furthest downstream portion.

Figure 2 is a side longitudinal cross-sectional schematic view of the trough, **21**, in an embodiment wherein the trough interior bottom does not have perforations downstream from the first portion of the trough so that water, **22**, dispensed by a water dispensing means, **23**, introduced at the portion closest to the strand die can flow unimpeded to the drainage hole, **24**, at the end of the trough. Instead, in this embodiment, the trough is provided with a raised wire mesh portion, **25**, that is disposed just above the water.

The invention is further described in but not limited to the following specific embodiments.

EXAMPLES

Figure 3 is a schematic depiction of the apparatus in the Examples hereof. A K-Tron® Loss in Weight feeder, **31**, was used to feed pellets, **32**, of DuPont Sorona® J1141 (1.02 dL/g IV, available from the DuPont Company) to the feed throat, **33**, of a 40 mm Werner and Pfleiderer co-rotating twin screw extruder, **34**, at a rate of 296 lbs/hour. In the extruder the pellets were melted and the resulting melt conveyed to an 8-hole

strand die, **35**, from which 8 strands, **36**, were extruded (only one shown), moving at 93 cm/sec. The 40 mm extruder was characterized by a barrel length of 1780 mm and L/D = 45. The extrusion conditions are shown in Table 1:

Table 1		
	Set Point	Actual
Feed Barrel 1	Cold water	
Barrell 2	220 °C	221 °C
Barrell 3	220 °C	221 °C
Barrell 4	220 °C	244 °C
Barrell 5	220 °C	233 °C
Barrell 6	220 °C	238 °C
Barrell 7	220 °C	240 °C
Barrell 8	220 °C	258 °C
Barrell 9	220 °C	254 °C
Barrell 10	220 °C	255 °C
Barrell 11	220 °C	219 °C
Die	220 °C	227 °C
Screw speed		395 RPM
Die Pressure		290 psi
Vacuum		25.0 in. H ₂ O
Feeder speed		293 lb/hr
Extrudate melt		269 °C

5

Within about 3 inches from exiting the die, **35**, the molten strand, **36**, was directed using guides (not shown) through the first quench region, **37**, by immersion in 11 °C water, **38**, dispensed from a water shower, **39**, contained in a 12 foot long water trough, **310**. The strand exited the first quench region, **37**, into the annealing region, **311**, and was conveyed over a wire mesh, **312**, elevated above the water, **38**. Following the annealing region, **311**, the strand was passed into the second quench region, **313**, using guides (not shown) from which the quenched strand, **314**, was fed to a pelletizer, **315**, while the water drained out by a drain hole, **316** (not shown). The pelletizer, **315**, chopped the strand into pellets, **317**, about 1/8 inch in length, and were collected in a collection can, **318**.

15

The residence time of the strand in the annealing region was varied by making small adjustments in the length of the wire mesh, **312**. The residence time was calculated from the calculated rate of speed of the strand based on mass flow, pellet diameter and density and the actual distance traversed by the strand.

20

The densities of the pellets prepared under each set of conditions were determined from He pycnometry.

A 23 g aliquot of pellets from each test condition was placed in a 7 cm diameter aluminum pan. A sheet of aluminum foil was placed over the pan, and the thus covered pan was placed in a temperature-controlled hydraulic press at 40 °C and 18.5 kPa for 24 hours. After 24 hours, the pan was removed and the pellets that had aggregated to one another were removed by hand, and weighed. The percentage of the weight of the original 23 g aliquot that had aggregated was recorded as the “% sticking.”

Comparative Example A represents the standard practice in the art adapted from the process for pelletizing PET.

Comparative Example B represents a condition in which the residence time in the annealing region was insufficient.

Table 2				
Residence Times (sec)				
	First Quench Region	Annealing Region	Density (g/cc)	Sticking (%)
CE A	all underwater	0	1.308	42
CE B	0.35	1.08	1.310	43
Ex 1	0.35	1.22	1.312	17
Ex 2	0.35	2.19	1.314	2
Ex 3	0.35	2.51	1.337	0

CLAIMS

We claim:

1. A process comprising:
 - 5 (a) preparing a molten strand of a poly(trimethylene terephthalate) composition wherein the strand has a surface and an interior;
 - (b) contacting the molten strand with water in a first quench region for a sufficient period of time so that the surface of the molten strand solidifies and at least a preponderant
10 portion of the interior remains above the cold crystallization temperature of the poly(trimethylene terephthalate) composition, thereby preparing a surface-solidified strand;
 - (c) separating the surface-solidified strand from the water;
 - 15 (d) exposing the surface-solidified strand to ambient air in an annealing region for a sufficient period of time to induce cold crystallization on the surface of the strand producing a surface-crystallized strand;
and
 - 20 (e) contacting the surface-crystallized strand with water in a second quench region for a sufficient period of time to solidify the interior of the strand.
2. The process of Claim 1 further comprising pelletizing the strand after it exits the second quench region.
- 25 3. The process of Claim 1 wherein the period of time in the first quench region lies in the range of 0.2 to 2 seconds.
4. The process of Claim 3 wherein the period of time in the first quench region lies in the range of 0.3 to 1.0 second.
5. The process of Claim 1 wherein the period of time in the annealing
30 region lies in the range of 0.3 to 5 seconds.
6. The process of Claim 5 wherein the period of time in the annealing region lies in the range of 0.5 to 2.5 seconds.

7. The process of Claim 1 wherein the period of time in the second quench region lies in the range of 1 to 10 seconds.
8. The process of Claim 7 wherein the period of time in the second quench region lies in the range of 1.5 to 3.5 seconds.
- 5 9. The process of Claim 1 wherein the water has a temperature of greater than 0 °C but less than 60 °C.
10. The process of Claim 9 wherein the water has a temperature within the range of 35 to 45 °C.
11. The process of Claim 1 wherein the period of time in the first
- 10 quench region lies in the range of 0.3 to 1.0 second; the period of time in the annealing region lies in the range of 0.5 to 2.5 seconds; the period of time in the second quench region lies in the range of 1.5 to 3.5 seconds; the water has a temperature in the region of 35 to 45 °C.

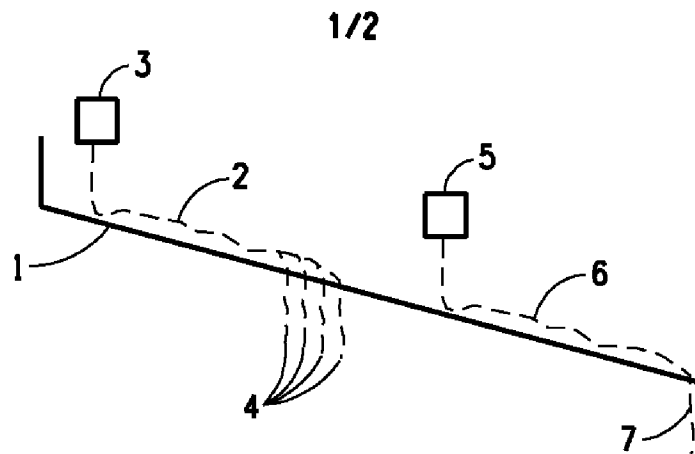


FIG. 1a

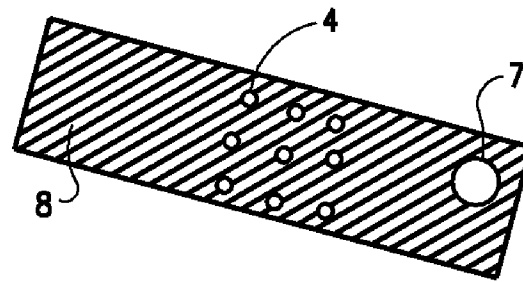


FIG. 1b

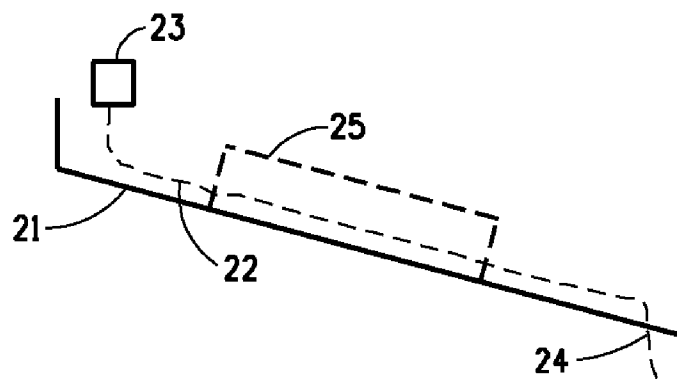
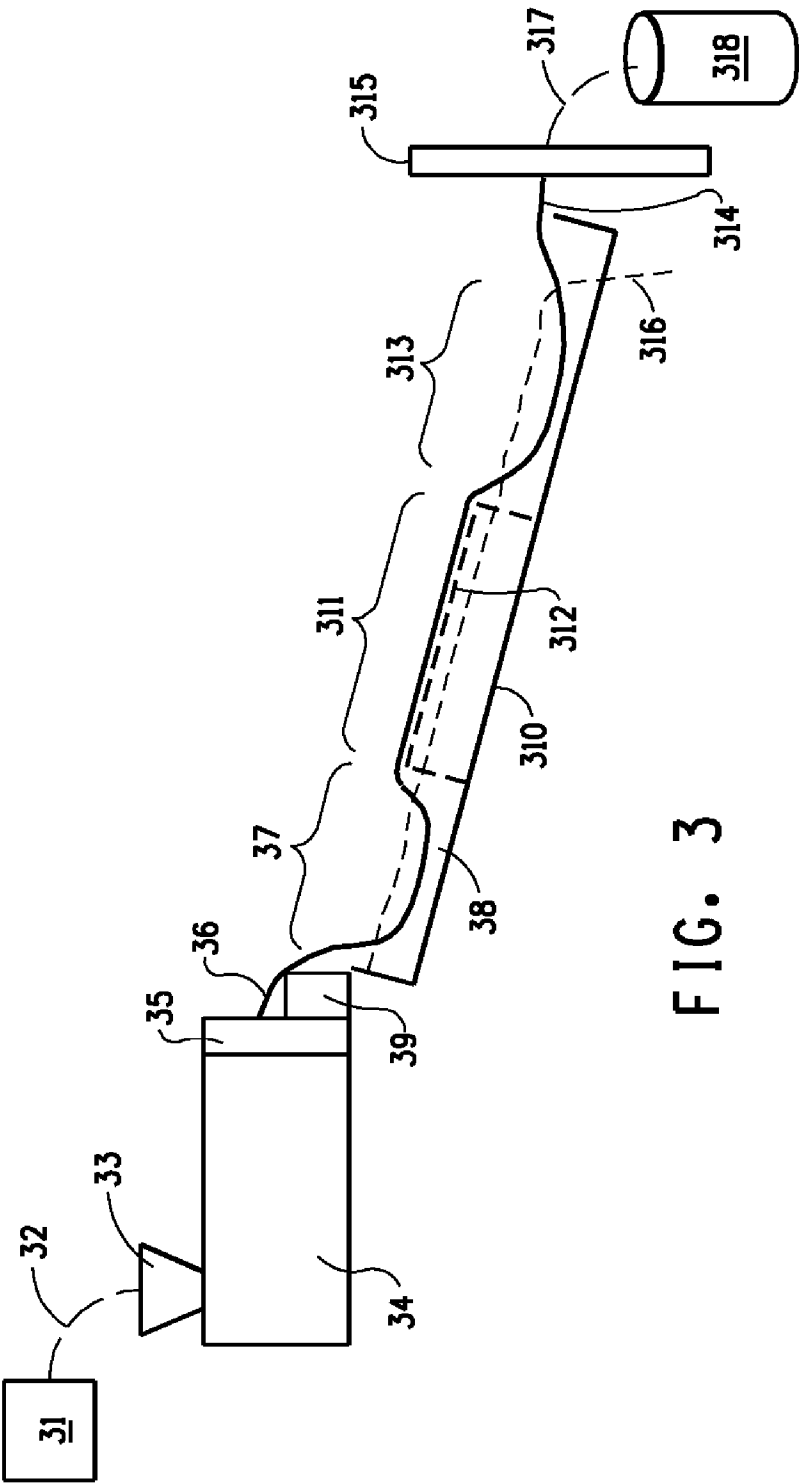


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/027212

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29B9/06 C08J3/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 6 159 406 A (SHELBY MARCUS DAVID [US] ET AL) 12 December 2000 (2000-12-12) cited in the application column 1, line 12 - column 2, line 10 column 4, line 8 - line 18 figure 1 -----	1-11
A	US 2003/092874 A1 (OKAJIMA SHINICHI [JP] ET AL) 15 May 2003 (2003-05-15) paragraph [0002] paragraph [0079] - paragraph [0085] ----- -/--	1

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

6 June 2012

Date of mailing of the international search report

14/06/2012

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European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Fageot, Philippe

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/027212

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 242 289 A (FORGASH ANTHONY R [US] ET AL) 7 September 1993 (1993-09-07) column 1, line 6 - line 24 column 2, line 50 - column 4, line 17 figures 1-3	1

INTERNATIONAL SEARCH REPORT

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International application No

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