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Title: REDUCING GEL FORMATION IN POLYAMIDE MANUFACTURING PROCESSES

Abstract: Described herein are methods of preparing high molecular weight polyamides which reduce or eliminate the production of unwanted gels during the production process. These methods reduce the formation of undesired polyamide gel by polishing the internal surfaces of the production equipment, thereby providing surfaces with smaller surface roughness values.

FIG. 1
before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
REDUCING GEL FORMATION IN POLYAMIDE MANUFACTURING PROCESSES

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 61/817,963, filed May 1, 2013, the disclosure of which is incorporated herein in its entirety by reference.

BACKGROUND

[0002] Nylon is a linear aliphatic polyamide having at least 85% aliphatic linkages between repeating amide units. The term "polyamide" widely in use today indicates a polymer containing a plurality of amide linkages. The term "linear" refers to polyamides obtainable from bifunctional reactants where the structural units are linked end-to-end and in chain-like fashion. As such, this term is intended to exclude three-dimensional polymeric structures that might be present in polymers derived from triamines or from tribasic acids.

[0003] The aliphatic polyamides are derivable from dibasic carboxylic acids and other amide-forming derivatives of dibasic carboxylic acids (e.g., anhydrides, amides, acid halides, half esters, and diesters) when reacted with a primary or secondary amine. The formation of substantially all aliphatic polyamides polymers, from monomers consisting of dicarboxylic acids and diamines, is accomplished by reacting a primary or secondary diamine (diamines having at least one hydrogen attached to each nitrogen) and either a dicarboxylic acid or an amide-forming derivative of a dibasic carboxylic acid.

\[
\text{HOOC-R-COOH} + \text{H}_2\text{N-R'-NH}_2 \rightarrow \text{[NH-R'-NH-CO-R-CO]}_m^- + \text{nH}_2\text{O}
\]

The indicated formula, in which R and R' represent divalent hydrocarbon radicals, represents the product as being composed of long chains built up from a series of identical units of:

\[-\text{NH-R'-NH-CO-R-CO-}\]

where water is a co-product of polymer formation.

[0004] Polyamides can be prepared by continuously passing an aqueous solution of a diamine-dibasic carboxylic acid salt at super-atmospheric pressure
through a continuous reaction zone. The concentrated aqueous solution of amide-
forming reactants (e.g. the diamine-dicarboxylic acid salt) is supplied continuously
to a reaction zone wherein the temperature-pressure conditions are such that
formation of steam is prevented and a major portion of the salt is converted to
polymer. Polymerization is complete when the desired degree of polymerization is
achieved. The degree of polymerization is indirectly expressed in terms of polymer
viscosity. The degree of polymerization, often measured as relative viscosity or
RV, is a proxy measurement for viscosity and molecular weight in turn.

[0005] At elevated temperatures, the degree of polymerization is a function
of and is limited by the amount of water present, by virtue of the dynamic
equilibrium involving polymer and water on the one hand, and depolymerized
polymer or even the reactants on the other. Polyamides having an RV considerably
higher than that attainable through equilibration with steam at atmospheric pressure
are often desirable. The down side of such a process is that the increased time
necessary to produce high viscosity polymer often leads to gelled or otherwise
degraded polymer.

[0006] Undesirable side reactions, such as thermal degradation and
discoloration of polymers in polymerization equipment can occur in the preparation
of polyamides. Such side reactions are recognized in the field of polymer
processing. Prior apparatus means to prevent side reactions are known from U.S.
Patent No. 3,361,537 to Ferrante and U.S. Patent No. 4,134,736 to Hammond; see
also United States Patent No. 3,717,330 to Pinney.

[0007] Gel refers to very high molecular weight, branched or cross-linked
degraded polymer which forms in a nylon polymer melt. The gel is essentially insoluble and
collects in the product and on equipment walls in contact with the molten polymer.
The presence of gelled polymer in the process equipment potentially leads to a host
of manufacturing defects in the finished products. Gel particles break away from
the interior surfaces of the process equipment and damage equipment further
downstream. Further, the gel particles can become incorporated into the final
products, leading to reduced quality and coloration problems. Often, gel can only
be removed from the equipment using extreme measures such as by burning off the gel.

A need exists for improved methods, articles, and systems that reduce the formation of gel during polyamide production processes.

SUMMARY

The present subject matter relates to methods for producing polyamides. More particularly, the present subject matter relates to processes of mixing and staging dicarboxylic acids with diamines and to the preparation of high molecular weight polyamides having a reduced tendency to form unwanted gel. These methods reduce the formation of undesired polyamide gel during the production process. Polyamide polymers are suitable for use in fibers, molded articles, films, and articles containing the same.

The present subject matter relates to methods, articles, and systems for reducing formation of polymer gel during a polyamide production process. The present subject matter reduces the formation of polymer gel by reducing the surface roughness on interior surfaces of processing equipment to reduce the production and stagnation of gel during the production process.

The present subject matter can include a method of reducing formation of polymer gel during a production process of a polyamide, the method including directing a molten polyamide mixture through portions of a polyamide manufacturing system and contacting an inner surface of the system with a molten polyamide mixture, subjecting the inner surface to a surface treatment to produce a treated inner surface, and contacting the treated inner surface with the molten polyamide mixture. The molten polyamide can have a gel time of greater than 15 hours when maintained at a temperature of between 280°C and 295°C in steam at one atmosphere of pressure. The treated inner surface can have an average surface roughness of no greater than 6.00 μη or an average surface roughness of between 1.00 μη and 6.00 μη. The surface treatment can include an abrasive flow machining process.
BRIEF DESCRIPTION OF THE FIGURES

[0012] The drawings, which are not necessarily drawn to scale, illustrate generally, by way of example, but not by way of limitation, the present invention.

[0013] FIG. 1 is a schematic flow diagram of one example system for the production of a polyamide.


DETAILED DESCRIPTION

[0015] Throughout the following description, specific details are set forth in order to provide a more thorough understanding of the invention. However, the present subject matter may be practiced without these particulars. In other instances, well known elements have not been shown in the figures or described in detail in order to preserve clarity. These embodiments may be combined, other elements may be utilized or structural or logical changes may be made without departing from the scope of the present subject matter. Accordingly, the specification is to be regarded in an illustrative, rather than a restrictive, sense.

[0016] As used herein, the terms "gelation time," "gel time," or the like refer to the time required for making a polymer insoluble in 98-100% formic acid when heated to a certain temperature under a stream of steam at one atmosphere. Nylon 6,6 (sometimes abbreviated "N66"), for example, can be heated to a temperature of between 280°C to 295°C. The insolubilization of the polymer in formic acid can be confirmed in the following manner: The polymer is crushed into powders of 10 to 20 mesh, the powder (0.1 g) is charged in a flask and 98-100% formic acid (20 mL) is added thereto; the flask is allowed to stand for four hours at which point the state of the polymer is observed. When the polymer does not contain any gel, it is completely dissolved in solvent in four hours. On the other hand, when the polymer contains any gel, the particles are only dampened and expanded with the solvent and a uniform formic acid solution is not obtained after four hours. By the presence of this dampened and expanded polymer, the gelation of the polymer is confirmed.
[0017] In one example, the gelation time is measurable as the time required to show an inflection in a graph of viscosity versus the heating time for a polymer sample maintained at a constant temperature and constant steam pressure. This measurement typically results in a time substantially comparable to the gelation time obtained by measuring insolubility as described above.

[0018] As used herein, the term "relative viscosity" (RV) refers to the ratio of solution and solvent viscosities measured in a capillary viscometer at 25°C. RV by ASTM D789-06 is the basis for one test procedure and is the ratio of viscosity in centipoise at 25°C of an 8.4 wt % solution of polyamide in 90% formic acid (i.e., a solution of nine parts by weight formic acid and one part by weight water) to the viscosity in centipoise at 25°C of 90% formic acid alone.

[0019] As used herein, the term "surface texture" refers to the typical surface including geometric irregularities (e.g., roughness, waviness, and grain). Surface texture is quantifiable by the vertical measure of deviation for a real surface from that of an idealized surface. Large vertical deviations indicate a rough surface, while small deviations indicate smoothness or a more highly polished surface. Roughness is a high frequency (sort wavelength) component of the surface measured by standard means.

[0020] The term "roughness average" (Rₐ) is the measured average from the surface peaks and valleys of those irregularities and expressed in micrometers (µm) and in micro-inches (µi). Surface texture measurement is known to those of ordinary skill in the art and employs a surface profile instrument. A known surface profiler instrument is available from TAYLOR-HOBSON, a company of AMETEK, INC., 1100 Cassatt Road, P.O. Box 1764, Berwyn, Pennsylvania, 19312 USA.

[0021] The specification of roughness for a manufactured part is often expressed as an upper limit and related to the frictional properties of the surface. A roughness average for a surface can be improved by techniques such as bead blasting, turning, or electro-polishing. Polishing with grit is used to obtain a Rₐ of 1.00 to 6.00 µm, which is also called a No. 3 finish or "semi-polished." Similar polishing means can be used to obtain a Rₐ of 0.9 to 1.50 µm, also known as a No. 4 finish, or a Rₐ of 0.60 to 1.00 µm, also known as a No. 4A finish. No. 4 and 4A...
finishes are bright and still have a visible grain, but are not specular in reflective character. The No. 4A finish is often used where food contact is expected. A satin polished finish is also called a No. 5 finish and it has a Rₐ of no greater than 0.5 μm. A bright polished surface is non-directional with high image clarity and a Rₐ of no greater than 0.10 μm. Nonconventional polishing techniques, such as electro-polishing, have the potential to achieve a Rₐ of 0.10 to 0.80 μm. Grit polishing can achieve a No. 7 finish with the use of 600 grit powders (e.g., SiC powder) or a No. 5 finish with the use of 320 grit powders.

The present subject matter relates to methods of reducing formation of polymer gel during a polyamide production process, such as nylon production processes (e.g., production processes for nylon 6, nylon 7, nylon 11, nylon 12, nylon 6,6, nylon 6,9; nylon 6,10, nylon 6,12, or copolymers thereof). The present subject matter can reduce the tendency of nylon 6,6 polymer to gel by reducing the stagnation zones available to the polymer in the process equipment. A stagnation zone can include substantially any of those through which molten nylon 6,6 polymer is conducted for any period of time at the temperature of processing (e.g., 260°C to 290°C). This reduction in flow stagnation is achieved by a process of polishing the surfaces that are in contact with molten polymer, as a rough inner surface can promote stagnation. Surfaces in contact with molten nylon 6,6 polymer are substantially internal surfaces and can include surfaces of mixing devices (e.g., in-line static mixers) placed within conduits conducting the polymer; surfaces that would typically be difficult to access with conventional polishing techniques.

Typically, a continuous polymerization processes includes, in sequence: a reactor stage, a flasher stage, a steam/polymer separator stage, and a finishing stage. FIG. 1 illustrates such a process in the form of example system 10 for producing nylon 6,6.

System 10 includes reservoir 12 that contains an aqueous solution of a dicarboxylic acid, a diamine, and a solvent (e.g., water) in a liquid or substantially liquid phase. The dicarboxylic acid and the diamine can form an ammonium carboxylate salt. In an example, where system 10 is configured for nylon 6,6 production, reservoir 12 can include hexamethylene diammonium adipate salt.
(nylon 6,6 salt), which can be dissolved in water in reservoir 12. Reservoir 12 can be used to mix, store, or heat the aqueous solution of the ammonium carboxylate salt.

In one example, evaporator 14 is used to increase the concentration of the ammonium carboxylate salt solution to, for example, about 72 wt% salt in water. To do so, the solution in reservoir 12 is transferred to evaporator 14 via conduit 16. Evaporator 14 is configured to convert a portion of the water in the aqueous solution from a substantially liquid phase to a substantially gaseous phase in the form of a water vapor stream 18. Evaporator 14 may do so by heating the solution. In an example, the concentration of the ammonium carboxylate salt solution exiting the reservoir 12 and being fed into the evaporator 14 is from about 35 wt% to about 65 wt% salt in water or from about 52 wt% to about 65 wt% salt in water.

The reaction mixture from evaporator 14 can be directed into reactor 20 via conduit 22. Within the reactor 20, unreacted dicarboxylic acid and diamine can react with each other, or with the polyamide prepolymer, or both, to form a first polyamide polymer. The temperature in the reactor 20 can be further increased beyond that in the evaporator 14 to remove additional water. Reactor 20 can be equipped with rectifying column 24 that is in fluid communication with reactor 20, such as via conduit 26. Rectifying column 24 can be, in turn, in fluid communication with vent line 28.

The polyamide polymer formed in reactor 20, along with unreacted dicarboxylic acid and diamine, can be transferred from reactor 20 to flasher 30 via conduit 32 by use of pump 38. Within flasher 30, the temperature of the reaction mixture of the polyamide polymer and the unreacted dicarboxylic acid and diamine is increased. At an inlet of the flasher 30, the pressure of the reaction mixture is relatively high, such as from about 1.9 MPa to about 2.1 MPa. This pressure can gradually decrease as the reaction mixture travels through flasher 30 so that at the outlet of flasher 30, the pressure is relatively low, in some cases being nearly a vacuum of from about 25 KPa to about 50 KPa. At the temperature within flasher 30, the gradually reducing pressure exerted on the reaction mixture as it passes
through flasher 30 results in further removal of water from the reaction mixture in the form of flashed-off steam. As the steam flashes off from the reaction mixture, the polyamide polymer can undergo further polymerization. At an outlet end of flasher 30, a two phase mixture of gaseous steam and a liquid mixture of the polyamide polymer and unreacted dicarboxylic acid and diamine can be formed. The steam can be released from flasher 30, such as through vent holes in the flasher 30 (not shown), or with the product stream leaving flasher 30 via outlet conduit 34. The effluent from the flasher stage (which is also referred to as the "secondary reactor") includes polyamide pre-polymer, typically with an RV of 9 to 20 or a water content of less than about 2-3 wt %, or about 1 wt % or less.

Flasher 30 can include at least one relatively long tube that winds through flasher 30, also referred to as the coil of flasher 30. The tube can carry the reaction mixture from an inlet of flasher 30 to an outlet. The tube can start with a small cross-sectional area, e.g., a small diameter, at the inlet and can expand along the length of the tube until it has a relative larger cross-sectional area, e.g., a relatively large diameter, at the outlet. The increase in cross-sectional area from the inlet to the outlet can provide for the decrease in pressure from the inlet of flasher 30 to the outlet, as described above.

A catalyst can be added to the reaction mixture to help facilitate the condensation reaction that form the polyamides described herein. In an example, the catalyst can be added to the reaction mixture at evaporator 14 (e.g., into an inlet of evaporator 14), at reactor 20 (e.g., into an inlet of reactor 20), or at flasher 30 (e.g., into an inlet of flasher 30). Although a catalyst can be added, it is not necessary for the polyamide polymerization reactions to occur. In an example, the catalyst can comprise at least one of sodium hypophosphite, manganese hypophosphite, or phenyl phosphinic acid.

The polyamide polymer formed in flasher 30 and unreacted dicarboxylic acid and diamine can be transferred from flasher 30 to finisher 36 via conduit 34 by use of pump 44.

Finisher 36 can provide for further removal of water so that the polyamide polymer undergoes further polymerization. Control variables (e.g.,
temperature, pressure and hold-up volume) in the finishing apparatus can be adjusted to produce a final polymer having a desired RV, typically in the range of 30 to 100. Temperature in the finishing apparatus is typically maintained in the range of 270°C to 290°C, while pressure is typically maintained at 250 to 640 millibars and hold-up volumes are typically about 20 to 40 minutes.

[0032] The finished polymer is then conveyed from a finisher 36 to one or more polymer transfer lines 40 and on to several downstream processes represented in FIG. 1 as final processing system 42. Transfer lines 40 can feed into final processing system 42 via pump 46 where the final polyamide polymer can undergo further mechanical processing, such as one or more of spinning, extrusion, and pelletization. For example, the final polyamide polymer can be extruded through a die having a plurality of small capillaries to continuously produce a plurality of polyamide strands. The stands can be cut into polyamide pellets in a pelletizer.

[0033] Polymer gel builds up on the internal surfaces of the system contacting the molten polymer (e.g., on the internal surfaces of the various components of system 10). For example, the various conduits or transfer lines of system 10 are typically stainless steel piping that will accumulate polymer gel on an internal surface which must then be periodically removed from the process for maintenance. The maintenance can include subjecting the removed pipe to high temperatures in order to burn away the polymer gel from the inner surfaces. After cleaning in this manner, the pipe can be returned to service in the system. However, such burned pipe usually has a shorter gel time as compared to new pipe. For example, burned pipe typically is expected to have a gel time of substantially less than 15 hours or less than 10 hours.

[0034] New, unused pipe has can have a No. 3 finish internally and, in some cases, a No.4 finish having a $R_a$ of 0.90 to 1.50 $\mu m$. During use, contact with molten polymer causes the inner surfaces to wear and become pitted. Such wear texturing, pitting in particular, has been discovered to provide zones for flow stagnation and eventual gel formation. It has been realized that recovery of the internal surface texture to that of the as-received pipe is desirable and leads to reduced gel formation.
The present subject matter includes methods of reducing formation of polymer gel during a production process of a polyamide. FIG. 2 illustrates method 100 of the invention for reducing formation of polymer gel during such a production process. At 102, method 100 includes a molten polyamide mixture directed through portions of a polyamide manufacturing system, wherein the molten polyamide mixture contacts an inner surface of the manufacturing system and the molten polyamide has a gel time of greater than 15 hours when maintained at a temperature of between 280°C and 295°C in steam at one atmosphere of pressure. At 102, a polymer gel can build up on the inner surfaces of the system.

At 104, method 100 includes subjecting an inner surface of the system to a surface treatment to produce a treated inner surface, wherein the treated inner surface has an average surface roughness of no greater than 6.00 µm, of between 1.00 µm and 6.00 µm, of between 0.90 µm and 1.50 µm, of between 0.60 µm and 1.00 µm, of no greater than 0.5 µm, of no greater than 0.10 µm, or of between 0.10 µm and 0.80 µm.

To subject the inner surface to the surface treatment, the component may be removed from the system in order to undergo an abrasive flow machining (AFM) process. AFM processes that can be used include procedures similar to those described in U.S. Patents 3,521,412 to McCarty; 3,634,973 to McCarty; 3,819,343 to Rhoades; 4,936,057 to Rhoades; 5,070,652 to Rhoades, et al.; 5,367,833 to Rhoades, et al; and 5,788,558 to Klein. A long length of polymer transfer piping (which may include a tortuous path) can be processed with AFM to machine the internal surface of the piping to a polished finish that is the same or better than new piping. An AFM process entails passing a viscous mixture containing a grinding agent through a lumen of the process equipment. As the mixture passes through the equipment, the internal surfaces are brought into abrading contact with the grinding agent. Multiple mixtures can be serially passed through the equipment, each with a finer grinding agent, thereby further polishing the inner surfaces.

The AFM process can include contacting the inner surface with a first mixture of a first silicon polymer (e.g., polyborosiloxane or silicone putty SS-
91) and a first grinding agent. The first mixture can include a plasticizer (e.g., isopropyl stearate) or a lubricant (e.g., a silicone grease). The first grinding agent can include particles of silica, alumina, garnet, tungsten, carbide, silicon carbide (e.g., silicon carbide #120), diamond, or boron carbide. The first grinding agent can form between 2 and 15 parts by weight of the first mixture. The first grinding agent can have a mean particle size range of from 0.005 mm to 1.5 mm, a mean particle size range of less than 16.0 \( \mu \text{m} \), or a mean particle size of less than 36.0 \( \mu \text{m} \).

The AFM process can include contacting the inner surface with additional mixtures of polymer and grinding agents. For example, the AFM process can include contacting the inner surface with a second mixture of a second silicon polymer and a second grinding agent after contacting the inner surface with the first mixture. The second silicon polymer can be the same or different than the first silicon polymer. The second grinding agent can be the same or different from the first grinding agent. For example, the second grinding agent can have a mean particle size that is smaller than the mean particle size of the first grinding agent so as to produce a more polished inner surface.

The surface treatment can also include heating the inner surface to burn away polymer gel residue. Heating can be applied before or after the AFM process.

At 106, method 100 provides that the surface treatment procedures are complete and the treated inner surface is installed in the polymer manufacturing system. The treated inner surface remains substantially free of gelling for more than 15 hours or more than 30 hours. Hence, the treated inner surface may not need to undergo additional surface treatments (e.g., a second surface treatment) for at least 15 hours or for at least 30 hours after receiving the first surface treatment.

After receiving the first surface treatment, or after receiving additional supplemental surface treatments, the treated inner surface can have any suitable gel time, such as about 15 hours to about 20 years, about 30 hours to about 10 years, or about 15 hours or less, or about 20 hours, 36 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 1.5 weeks, 2 weeks, 3 weeks, 1 month, 2 months, 3 months, 4 months, 5 months, 6 months, 8 months, 10 months, 1 year, 1.5 years, 2
years, 3 years, 5 years, 10 years, or about 20 years or more. After receiving the first surface treatment, or after receiving additional supplemental surface treatments, during use the formation of gel on the treated inner surface can occur at any suitable rate, such that an average thickness of gel of about 1 mm is formed on the treated surface in about 15 hours to about 20 years, about 30 hours to about 10 years, or about 15 hours or less, or about 20 hours, 36 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 1.5 weeks, 2 weeks, 3 weeks, 1 month, 2 months, 3 months, 4 months, 5 months, 6 months, 8 months, 10 months, 1 year, 1.5 years, 2 years, 3 years, 5 years, 10 years, or about 20 years or more. After receiving the first surface treatment, or after receiving additional supplemental surface treatments, during use the treated inner surface can remain substantially free of gel for any suitable period of time, such as about 15 hours to about 20 years, about 30 hours to about 10 years, or about 15 hours or less, or about 20 hours, 36 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 1.5 weeks, 2 weeks, 3 weeks, 1 month, 2 months, 3 months, 4 months, 5 months, 6 months, 8 months, 10 months, 1 year, 1.5 years, 2 years, 3 years, 5 years, 10 years, or about 20 years or more.

At 106, method 100 can include contacting the treated inner surface with the molten polyamide mixture. The molten polyamide can include nylon (e.g., nylon 6,6). The molten polyamide mixture that contacts the inner surface can be at a temperature in the range of between 260°C and 290°C.

The production process may be a continuous polyamide production process (e.g., a continuous nylon production process). The inner surface can include a portion of an in-line static mixer.

The molten polyamide mixture that contacts the inner surface can include water in an amount of between 0.1 weight percent to 28 weight percent, or between 0.1 weight percent to 10 weight percent, or between 0.1 weight percent to 1 weight percent, or in an amount of 0.1 weight percent.

The present subject matter also includes products that include a polyamide produced by the above described methods.
EXAMPLES

[0047] General System for Examples. In a continuous nylon 6,6 manufacturing process, adipic acid and hexamethylenediamine are combined in an approximately equimolar ratio in water to form an aqueous mixture containing nylon 6,6 salt and having about 50 wt% water. The aqueous salt is transferred to an evaporator at approximately 105 L/min. The evaporator heats the aqueous salt to about 125-135 °C (130 °C) and removes water from the heated aqueous salt, bringing the water concentration to about 30 wt%. The evaporated salt mixture is transferred to a tubular reactor at approximately 75 L/min. The reactor raises the temperature of the evaporated salt mixture to about 218-250 °C (235 °C), allowing the reactor to further remove water from the heated evaporated salt mixture, bringing the water concentration to about 10 wt%, and causing the salt to further polymerize. The reacted mixture is transferred to a flasher at approximately 60 L/min. The flasher heats the reacted mixture to about 270-290 °C (285 °C) to further remove water from the reacted mixture, bringing the water concentration to about 0.5 wt%, and causing the reacted mixture to further polymerize. The flashed mixture, having a relative viscosity of about 13, is transferred to a finisher at approximately 54 L/min. In the transfer piping between the flasher and the finisher, the polymer mixture maintains a temperature of about 285 °C. The transfer piping between the flasher and the finisher has a diameter of about 0.5 meters, and a length of about 20 meters. The finisher subjects the polymeric mixture to a vacuum to further remove water, bringing the water concentration to about 0.1 wt% and the relative viscosity to about 60, such that the polyamide achieves a suitable final range of degree of polymerization before transferring the finished polymeric mixture to an extruder and a pelletizer at about 54 L/min.

[0048] In the Examples, the gelation time is determined by measuring the time the transfer piping is used in the system prior to exhibiting the property of forming gel when a gel-free nylon 6,6 polymer is contacted to the inner surface of the transfer piping at 1 atm and at about 285 °C, flowing at about 59 L/min. The presence of gel is determined in the following manner: A cooled sample of the polymer mixture that emerges from the transfer piping is crushed into powders of
about 15 mesh; the powder (0.1 g) is charged into a flask and 98-100% formic acid (20 mL) is added thereto; the flask is allowed to stand for four hours at which point the state of the polymer is observed. When the polymer does not contain any gel, it is completely dissolved in solvent in four hours. On the other hand, when the polymer contains any visually detectable gel, the gel particles are only dampened and expanded with the solvent and a uniform formic acid solution is not obtained after four hours.

[0049] The abrasive flow machining treatments are conducted with one or more treatments using a mixture of a silicone and a grinding agent.

[0050] General method for determination of gelation rate. Each gelation rate described in the Examples is determined by taking an average of the gelation rate as determined by two methods. In the first method, while the reaction mixture is still hot the system is drained of the liquid reaction mixture, the system is cooled, disassembled, and visually inspected to estimate the volume of gel therein. In the second method, while the reaction mixture is still hot the system is drained of liquid reaction mixture, cooled, filled with water, and drained of the water. The volume of water drained from the system is subtracted from the gel-free volume of the system to determine the volume of gel in the system. For determination of gelation rates in one or more specific pieces of equipment or downstream of a particular location, only the specific pieces of equipment or the system downstream of the particular location is filled with water. In both methods, the density of the gel is estimated at 0.9 g/cm³.

Example 1a, comparative example. New pipe.

[0051] The transfer piping between the flasher and the finisher is new pipe having an inner surface with a No. 4 finish and an Rₐ of 1 μη. The transfer piping has a gelation time of 5.4 months, and remains substantially gel free for about 5.4 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 10.8 months. Prior to 5.4 months, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after 5.4 months.
Example lb, comparative example. Pitted pipe with no treatment.

[0052] The transfer piping between the flasher and the finisher is pipe that has been used in the system for about 5 years. The inner surface of the pipe is clean and has an $R_a$ of about 0.5 mm. The transfer piping has a gelation time of 5 hours, and remains substantially gel free for about 5 hours. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1 month. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example lc, comparative example. Pipe with gelation and burning treatment, 0.5 mm roughness after treatment.

[0053] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, to give a cleaned transfer pipe having an $R_a$ of about 0.5 mm. The transfer piping has a gelation time of about 5 hours, and remains substantially gel free for about 5 hours. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1 month. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example Id comparative example. Pipe with gelation and burning treatment, 100 $\mu$m roughness after treatment.

[0054] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, to give a cleaned transfer pipe having an $R_a$ of about 100 $\mu$m. The transfer piping has a gelation time of about 10 hours, and remains substantially gel free for about 10 hours. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1 month. Prior to the gelation time being reached, the total gel accumulation
downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 1. Comparative example. Pipe with gelation and burning treatment. 10 μm roughness after treatment.

[0055] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, to give a cleaned transfer pipe having an $R_a$ of about 10 μm. The transfer piping has a gelation time of about 13 h, and remains substantially gel free for about 13 h. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1 month. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 2. Comparative example. Pipe with gelation and burning treatment, 6 μm roughness after treatment.

[0056] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, to give a cleaned transfer pipe having an $R_a$ of about 6 μm. The transfer piping has a gelation time of about 14 h, and remains substantially gel free for about 14 h. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1 month. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 2. Pipe with gelation, burning treatment, and abrasive flow machining, 5.9 μm roughness after treatment.

[0057] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, which is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an $R_a$ of about 5.9 μm. The transfer piping has a gelation time
of about 16 hours, and remains substantially gel free for about 16 hours. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 1.5 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 3. Pipe with gelation, burning treatment, and abrasive flow machining, 5.5 μm roughness after treatment.

[0058] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an Rₜ of about 5.5 μm. The transfer piping has a gelation time of about 72 hours, and remains substantially gel free for about 72 hours. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 2 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 4. Pipe with gelation, burning treatment, and abrasive flow machining, 4 μm roughness after treatment.

[0059] The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an Rₜ of about 4 μm. The transfer piping has a gelation time of about 2 weeks, and remains substantially gel free for about 2 weeks. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 3 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.
Example 5. Pipe with gelation, burning treatment, and abrasive flow machining, 3 µm roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an $R_s$ of about 3 µm. The transfer piping has a gelation time of about 1 month, and remains substantially gel free for about 1 month. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 4 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.


The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an $R_s$ of about 2 µm. The transfer piping has a gelation time of about 3 months, and remains substantially gel free for about 3 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 6 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 7. Pipe with gelation, burning treatment, and abrasive flow machining, 1 µm roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an $R_s$ of about 1 µm. The transfer piping has a gelation time of about 5.4 months, and remains substantially gel free for about 5.4 months. An
approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 11 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 8. Pipe with gelation, burning treatment, and abrasive flow machining, 0.5 μm roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an Ra of about 0.5 μm. The transfer piping has a gelation time of about 5.8 months, and remains substantially gel free for about 5.8 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 11.5 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 9. Pipe with gelation, burning treatment, and abrasive flow machining, 0.1 μm roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an Ra of about 0.1 μm. The transfer piping has a gelation time of about 6 months, and remains substantially gel free for about 6 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 12 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.
Example 10. Pipe with gelation, burning treatment, and abrasive flow machining, 0.09 µη roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an R_s of about 0.09 µη. The transfer piping has a gelation time of about 6 months, and remains substantially gel free for about 6 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 12 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 11. Pipe with gelation, burning treatment, and abrasive flow machining, 0.06 µη roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an R_s of about 0.06 µη. The transfer piping has a gelation time of about 6 months, and remains substantially gel free for about 6 months. An approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 12 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

Example 12. Pipe with gelation, burning treatment, and abrasive flow machining, 0.02 µη roughness after treatment.

The transfer pipe between the flasher and the finisher is subjected to a burning treatment to remove a coating of gel therein, and is subsequently subjected to an abrasive flow machining treatment to polish the inner surface of the pipe such that it has an R_s of about 0.02µη. The transfer piping has a gelation time of about 6 months, and remains substantially gel free for about 6 months. An
approximately 1 mm average thickness of gel forms on the inner surface of the piping in about 12 months. Prior to the gelation time being reached, the total gel accumulation downstream of the transfer piping is about 0.5 Kg/day, which increases to about 0.6 Kg/day after the gelation time has passed.

[0068] Below are some statements on various aspects of the present invention:

Statement 1: The present subject matter includes a method of reducing formation of polymer gel during production of a polyamide, the method comprising manufacturing the polyamide by directing a molten polyamide mixture through portions of a polyamide manufacturing system, wherein the molten polyamide mixture contacts an inner surface of the manufacturing system and the molten polyamide mixture includes a polymerized polyamide having a gel time of greater than 15 hours when maintained at a temperature of between 280°C and 295°C in steam at one atmosphere of pressure; subjecting the inner surface to a surface treatment to produce a treated inner surface, wherein the treated inner surface has an average surface roughness of less than about 6.00 µm; and continuing the manufacture of the polyamide by contacting the treated inner surface with the molten polyamide mixture.

Statement 2: The method according to statement 1, wherein the treated inner surface has an average surface roughness of between about 0.10 µm and about 6.00 µm.

Statement 3: The method according to statement 1, wherein the treated inner surface has an average surface roughness of between 0.90 µm and 1.50 µm.

Statement 4: The method according to statement 1, wherein the treated inner surface has an average surface roughness of between 0.60 µm and 1.00 µm.

Statement 5: The method according to statement 1, wherein the treated inner surface has an average surface roughness of no greater than 0.5 µm.
Statement 6: The method according to statement 1, wherein the treated inner surface has an average surface roughness of no greater than 0.10 µm.

Statement 7: The method according to statement 1, wherein the treated inner surface has an average surface roughness of between 0.10 µm and 0.80 µm.

Statement 8: The invention according to statement 1, wherein the treated inner surface has an average surface roughness of between 0.90 µm and 1.50 µm.

Statement 9: The method according to any of statements 1-8, wherein the surface treatment includes an abrasive flow machining process.

Statement 10: The method according to any of statements 1-9, wherein the surface treatment includes contacting the inner surface with a first mixture of a first silicon polymer and a first grinding agent.

Statement 11: The method according to statement 10, wherein the silicon polymer is a polyborosiloxane.

Statement 12: The method according to statements 10 or 11, wherein the first mixture includes a plasticizer.

Statement 13: The method according to statement 12, wherein the plasticizer is isopropyl stearate.

Statement 14: The method according to any of statements 10-13, wherein the first mixture includes a lubricant.

Statement 15: The method according to statement 14, wherein the lubricant is silicone grease.

Statement 16: The method according to any of statements 10-15, wherein the first silicon polymer is silicone putty SS-91.

Statement 17: The method according to any of statements 10-16, wherein the first grinding agent includes particles of silica, alumina, garnet, tungsten, carbide, silicon carbide, diamond, or boron carbide.

Statement 18: The method according to statement 17, wherein the first grinding agent includes silicon carbide #120.
Statement 19: The method according to any of statements 10-18, wherein the first grinding agent forms between 2 and 15 parts by weight of the first mixture.

Statement 20: The method according to any of statements 10-19, wherein the first grinding agent has a mean particle size range of from 0.005 mm to 1.5 mm.

Statement 21: The method according to statements 10-19, wherein the first grinding agent has a mean particle size range of less than 16.0 μm.

Statement 22: The method according to any of statements 1-21, wherein the surface treatment includes contacting the inner surface with a second mixture of a second silicon polymer and a second grinding agent after contacting with the first mixture.

Statement 23: The method according to statement 22, wherein the second silicon polymer is the same as the first silicon polymer.

Statement 24: The method according to statements 22 or 23, wherein the second grinding agent has a mean particle size that is smaller than the mean particle size of the first grinding agent.

Statement 25: The method according to any of statements 10-24, wherein the abrasive flow machining process includes the use of an abrasive having a mean particle size of less than 36.0 μm.

Statement 26: The method according to any of statements 1-25, wherein the surface treatment includes heating the inner surface to burn away polymer gel.

Statement 27: The method according to statement 26, wherein the inner surface has an average surface roughness of between 6.00 μm and 0.5 mm after heating to burn away polymer gel.

Statement 28: The method according to any of statements 26 or 27, wherein the surface treatment includes subjecting the inner surface to an abrasive flow machining process after heating the inner surface to burn away polymer gel.

Statement 29: The method according to any of statements 1-28, wherein the molten polyamide includes nylon.
Statement 30: The method according to statement 29, wherein the nylon is nylon 6,6.

Statement 31: The method according to any of statements 1-30, wherein the molten polyamide mixture is at a temperature in the range of between 260°C and 290°C.

Statement 32: The method according to any of statements 1-31, wherein the treated inner surface is subjected to an additional surface treatments no earlier than 15 hours after receiving a first surface treatment.

Statement 33: The method according to statement 32, wherein the treated inner surface is subjected to the additional surface treatments no earlier than 30 hours after receiving the first surface treatment.

Statement 34: The method according to any of statements 1-33, wherein the production process is a continuous polyamide production process.

Statement 35: The method according to statement 34, wherein the continuous polyamide production process is a continuous nylon production process.

Statement 36: The method according to any of statements 1-35, wherein the inner surface is a portion of an in-line static mixer.

Statement 37: The method according to any of statements 1-36, wherein the inner surface is a portion of a static mixer.

Statement 38: The method according to any of statements 1-37, wherein the molten polyamide mixture includes water in an amount of between 0.1 weight percent to 28 weight percent.

Statement 39: The method according to statement 38, wherein the molten polyamide mixture includes water in an amount of between 0.1 weight percent to 10 weight percent.

Statement 40: The method according to statement 38, wherein the molten polyamide mixture includes water in an amount of between 0.1 weight percent to 1 weight percent.

Statement 41: The method according to statement 40, wherein the molten polyamide mixture includes water in an amount of 0.1 weight percent.
[00110] Statement 42: The method according to any of statements 1-41, wherein the inner surface has an average surface roughness of more than 1.50 μη prior to the first surface treatment.

[00111] Statement 43: A product that includes a polyamide produced by any of the methods according to statements 1-42.

[00112] The above description is intended to be illustrative, and not restrictive. Other embodiments can be used, such as by one of ordinary skill in the art upon reviewing the above description. For example, elements of one described embodiment may be used in conjunction with elements from other described embodiments. Also, in the above Detailed Description, various features may be grouped together to streamline the disclosure. This should not be interpreted as intending that an unclaimed disclosed feature is essential to any claim. Rather, inventive subject matter may lie in less than all features of a particular disclosed embodiment. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment. The scope of the invention should be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. As used herein, the terms "including" and "in which" are used as equivalents of the terms "comprising" and "wherein."

[00113] In this document, the terms "a" or "an" are used to include one or more than one, independent of any other instances or usages of "at least one" or "one or more". In this document, the term "or" is used to refer to a nonexclusive or, such that "A, B or C" includes "A only", "B only", "C only", "A and B", "B and C", "A and C", and "A, B and C", unless otherwise indicated. In the appended aspects or claims, the terms "first", "second" and "third", etc. are used merely as labels, and are not intended to impose numerical requirements on their objects. It shall be understood that any numerical ranges explicitly disclosed in this document shall include any subset of the explicitly disclosed range as if such subset ranges were also explicitly disclosed; for example, a disclosed range of 1-100 shall also include the ranges 1-80, 2-76, or any other numerical range that falls between 1 and 100. In
another example, a disclosed range of "1,000 or less" shall also include any range that is less than 1,000, such as 50-100, 25-29, or 200-1,000.

[00114] The Abstract is provided to comply with 37 C.F.R. § 1.72(b), to allow the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims.
CLAIMS

What is claimed is:

1. A method of reducing formation of polymer gel during production of a polyamide, the method comprising:
   manufacturing the polyamide by directing a molten polyamide mixture through portions of a polyamide manufacturing system, wherein the molten polyamide mixture contacts an inner surface of the manufacturing system and the molten polyamide mixture includes a polymerized polyamide having a gel time of greater than 15 hours when maintained at a temperature of between 280°C and 295°C in steam at one atmosphere of pressure;
   subjecting the inner surface to a first surface treatment to produce a treated inner surface, wherein the treated inner surface has an average surface roughness of less than 6.00 µη; and
   continuing the manufacture of the polyamide by contacting the treated inner surface with the molten polyamide mixture.

2. The method of claim 1, wherein the treated inner surface has an average surface roughness of between 0.1 µη and 6.00 µη.

3. The method of any one of claims 1-2, wherein the first surface treatment includes an abrasive flow machining process.

4. The method of claim 3, wherein the first surface treatment includes contacting the inner surface with a first mixture of a first silicon polymer and a first grinding agent.

5. The method of claim 4, wherein the first mixture includes a plasticizer.
6. The method of any one of claims 4-5, wherein the first mixture includes a lubricant.

7. The method of any one of claims 4-6, wherein the first grinding agent includes particles of silica, alumina, garnet, tungsten, carbide, silicon carbide, diamond, or boron carbide.

8. The method of claim 7, wherein the first grinding agent includes silicon carbide #120.

9. The method of any one of claims 4-8, wherein the first grinding agent has a mean particle size range of from 0.005 mm to 1.5 mm.

10. The method of any one of claims 4-9, wherein the first surface treatment includes contacting the inner surface with a second mixture of a second silicon polymer and a second grinding agent after contacting it with the first mixture and wherein the second grinding agent has a mean particle size that is smaller than the mean particle size of the first grinding agent.

11. The method of any one of claims 1-10, wherein the first surface treatment includes subjecting the inner surface to an abrasive flow machining process after heating the inner surface to burn away polymer gel.

12. The method of any one of claims 1-11, wherein the inner surface has an average surface roughness of between 6.00 μm and 0.5 mm after heating to burn away polymer gel.

13. The method of any one of claims 1-12, wherein the molten polyamide includes nylon.
14. The method of any one of claims 1-13, wherein the molten polyamide mixture is at a temperature in the range of between 260°C and 290°C.

15. The method of any one of claims 1-14, wherein the treated inner surface is not subjected to any further surface treatments for a period of at least 15 hours after receiving the first surface treatment.

16. The method of any one of claims 1-15, wherein the polyamide manufacturing system is a continuous nylon production system.

17. The method of any one of claims 1-16, wherein the inner surface is a portion of an in-line static mixer.

18. The method of any one of claims 1-17, wherein the molten polyamide mixture includes water in an amount of between 0.1 weight percent to 28 weight percent.

19. The method of any one of claims 1-18, wherein the inner surface has an average surface roughness of more than 1.50 µm prior to the first surface treatment.

20. A product comprising a polyamide produced by the method of any one of claims 1-19.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G69/28 C08G69/04 B24B31/116

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G B24B

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

Electronic database consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
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Date of the actual completion of the international search: 20 August 2014

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Name and mailing address of the ISA:
European Patent Office, P. B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Barrere, Matthieu

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