Abstract:
The present invention relates to a process for making a hydrophilic polyamide without excessive foaming by delaying the introduction of the hydrophilic monomer. The hydrophilic monomer may be added to the polymerization process after at least a portion of the water has been removed from the process.
PROCESS OF MAKING HYDROPHILIC POLYAMIDE WITHOUT EXCESSIVE FOAMING

FIELD OF THE INVENTION

[0001] The present invention is directed to a polyamide synthesis process without excessive foaming. In particular, the present invention is directed to a polyamide synthesis process comprising adding a polyetheramine during the polymerization process to reduce foaming.

BACKGROUND OF THE INVENTION

[0002] In the conventional polyamide synthesis process, the means of incorporating a desired functionality into the polyamide copolymer has been to add the monomer at the first cycle, known as the salt stage, together with all other additives at the beginning of the polymerization process. The polymerization process then continues in multiple cycles where the pressure and temperature conditions are carefully adjusted to effectively remove the water (as steam), the poly-condensation byproduct. The initial cycles in the process contain the highest water content and consequently have a high rate of steam release. As the process continues, the water content is reduced to the residual level in the polymer melt.

[0003] Any level of foaming is a nuisance to deal with in any chemical synthesis process. Steady foam develops with rigid gas-liquid cell interfaces and rapidly grows in process equipment and lines, especially in high-water containing environments and/or under vacuum conditions. In the polyamide synthesis, the rising polymer melt viscosity further complicates the water bubble formation, migration to the melt surface and steam disengagement from the melt surface which also contributes to excessive foaming. In processes involving severe foaming, the process vacuum lines were observed to be blocked as a result of polymer entrainment from rising foam in the lines. Undesired blockages in the process vacuum lines by solidified polymer lead to process and controls instabilities which result in inferior polymer quality, not to mention process disruptions with significant cost penalties.

[0004] WO2014/057363 teaches a method for introducing hydrophilic functionality into the polyamide copolymer, by reactive incorporation of hydrophilic additive such as up to 15 wt.% of a hydrophilic polyetherdiamine. Examples of such additives include Elastamine® RE 2000 monomer and Jeffamine® ED-2003. Scale-up tests have revealed that the initial polymerization cycles may trigger severe foaming from the increased steam release under certain process
conditions. Thus it would be desirable to provide a commercially acceptable process wherein excessive foam/froth could be managed while still including a hydrophilic additive.

SUMMARY OF THE INVENTION

[0005] In a first embodiment, the present invention is directed to a process for making polyamide comprising: (a) heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide; (b) removing water from the aqueous solution of (a) to at least partially concentrate the aqueous solution; (c) adding polyetheramine to the at least partially concentrated aqueous solution of (b); and (d) heating the solution of (c) to further polymerize the diacid, diamine and polyetheramine and to remove water from the solution. The partially concentrated solution of step (b) may contain less than 70 wt.% water, preferably less than 60 wt.% water, more preferably less than 50 wt.% water. The polyetheramine may be present in an amount ranging from 1 wt.% to 20 wt.% of the polyamide, preferably from 5 to 15 wt.%, more preferably from 10 to 15 wt.%. In some aspects, the diacid is selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, pimelic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, maleic acid, glutaric acid, traumatic acid, and muconic acid, 1,2- or 1,3-cyclohexane dicarboxylic acids, 1,2- or 1,3-phenylenedicarboxylic acids, 1,2- or 1,3-cyclohexane diacetic acids, isophthalic acid, terephthalic acid, 4,4'-oxybisbenzoic acid, 4,4-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, p-t-butyl isophthalic acid and 2,5-furandicarboxylic acid, and mixtures thereof and the diamine is selected from the group consisting of ethanol diamine, trimethylene diamine, putrescine, cadaverine, hexamethylene diamine, 2-methyl pentamethylene diamine, heptamethylene diamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,2-dimethyl pentamethylene diamine, octamethylene diamine, 2,5-dimethyl hexamethylene diamine, nonamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, decamethylene diamine, 5-methylnonane diamine, isophorone diamine, undecamethylene diamine, dodecamethylene diamine, 2,2,7,7-tetramethyl octamethylene diamine, bis(p-aminocyclohexyl)methane, bis(aminomethyl)norbornane, C2-C16 aliphatic diamine optionally substituted with one or more C1 to C4 alkyl groups, aliphatic polyether diamines and furanic diamines, such as 2,5-bis(aminomethyl)furan, and mixtures thereof. The aqueous solution may further comprises a catalyst. The polyetheramine may be a polyetherdiamine. The
polyetheramine may have a weight average molecular weight of at least 1500. The solution in step (a) may be heated to a temperature from 190 to 230°C. The solution in step (d) may be heated to a temperature from 240 to 320°C. No polyetheramine is added during step (a) or step (b). The polyamide may have a moisture regain from 10 to 30%, preferably from 10 to 25%, and more preferably from 15 to 25%.

[0006] In a second embodiment, the present invention is directed to a process for making polyamide comprising delaying introduction of a monomer providing hydrophilic functionality for incorporation into the polymer to a location in the process where water content is reduced. Making the polyamide may comprise four heating cycles, wherein an aqueous solution of diacid and diamine are added in a first heating cycle to convert at least a portion of the diacid and diamine to polyamide; and further wherein the monomer is added in a second, third or fourth heating cycle. Water may be removed from the aqueous solution prior to adding the monomer to form an at least partially concentrated aqueous solution. The at least partially concentrated aqueous solution may contain less than 70 wt.% water after the water is removed, preferably less than 60 wt.%, more preferably less than 50 wt.%. The polyamide may have a moisture regain from 10 to 30%, preferably from 10 to 25%, and more preferably from 15 to 25%.

[0007] In a third embodiment, the present invention is directed to a process for making polyamide comprising: (a) heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide and to remove water from the aqueous solution; and (b) injecting a hydrophilic additive to the partially concentrated aqueous solution of (a) to incorporate hydrophilic functionality into a resulting polyamide copolymer at an injection rate sufficient to provide a predetermined desired water regain while suppressing foaming of the at least partially concentrated aqueous solution by delayed introduction of the hydrophilic additive. Heating step (a) may be preceded by at least one step of heating and removing water. The process may further comprise controlling the injection rate of the hydrophilic additive to provide water regain from 10 and 30 wt.%, preferably from 10 to 25 wt.%, more preferably from 15 to 25 wt.%. The partially concentrated aqueous solution may comprise less than 70 wt.% water, preferably less than 60 wt.%, more preferably less than 50 wt.%.
DETAILED DESCRIPTION

Introduction

[0008] The present invention is directed to a process for making polyamide, the process comprising heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide; removing water from the aqueous solution to at least partially concentrate the aqueous solution sufficiently to reduce the propensity of the aqueous solution to form a stable foam layer; adding polyetheramine to the at least partially concentrated aqueous solution; and heating the solution to further polymerize the diacid, diamine and polyetheramine and to remove water from the solution. The disclosed process addresses the problem of severe foaming by selectively delaying the hydrophilic additive, e.g., polyetheramine, introduction into the polymerization process, until there is reduced water content and thus the rate of steam evolution is comparatively low and hence the propensity to foam is substantially reduced. The improvement comes in not having to deal with the buildup of foam in process equipment and vacuum lines where the entrained polymer solidifies with partial or complete line blockage.

[0009] The hydrophilic polyetheramine, e.g., a polyetherdiamine, is added to improve moisture regain properties. From a reaction engineering standpoint, it would be desirable to introduce the hydrophilic polyetherdiamine at the beginning of the polymerization cycle to maximize the opportunity for incorporation into the finished polymer. However, the disclosed process takes a counterintuitive approach by intentionally foregoing a portion of the available reaction time by introducing the hydrophilic polyetherdiamine later in the process. Surprisingly, the addition of hydrophilic functionality later in the process, e.g., after the aqueous solution is at least partially concentrated, produces the finished hydrophilic polyamide with equally acceptable water regain properties. In a conventional process, the additives are typically mixed in at the beginning of the process so they may be properly incorporated into the polymer matrix. The conventional polyamide synthesis is faced with excessive foaming as the polymerization continues in multiple cycles where the pressure and temperature conditions are carefully adjusted in a stepwise manner for the water removal as the poly-condensation byproduct.

[0010] The disclosed process improves the process of polyamide synthesis, especially in the presence of hydrophilic additives, by minimizing the foaming problem. Thus the problem of unacceptably excessive foaming during the multi-cycle synthesis of polyamides, when reactively incorporated with functional hydrophilic linkages, is solved by selectively delaying the
hydrophilic additive introduction into the polymerization process, for example, in the later stages of the process as against in the beginning of the polymerization process.

Definitions

[0011] Although the following detailed description contains many specifics for the purpose of illustration, a person of ordinary skill in the art will appreciate that many variations and alterations to the following details are within the scope of the herein disclosed embodiments. Accordingly, the following embodiments are set forth without any loss of generality to, and without imposing limitations upon any claimed invention. Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as this may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs.

[0012] As used in this specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a polyamide" includes a plurality of polyamides.

[0013] In this disclosure, "comprises," "comprising," "containing" and "having" and the like may have the meaning ascribed to them in U.S. Patent law and may mean "includes," "including," and the like, and are generally interpreted to be open ended terms. The term "consisting of" is a closed term, and includes only the components, structures, steps, or the like specifically listed, and that which is in accordance with U.S. Patent law. "Consisting essentially of" or "consists essentially of" or the like, when applied to methods and compositions encompassed by the present disclosure refers to compositions like those disclosed herein, but which may contain additional structural groups, composition components or method steps. Such additional structural groups, composition components or method steps, etc., however, do not materially affect the basic and novel characteristic(s) of the compositions or methods, compared to those of the corresponding compositions or methods disclosed herein. In further detail, "consisting essentially of" or "consists essentially of" or the like, when applied to methods and compositions encompassed by the present disclosure have the meaning ascribed in U.S. Patent
law and the term is open-ended, allowing for the presence of more than that which is recited (e.g., trace contaminants, components not reactive with the polymer or components reacted to form the polymer, and the like) so long as basic or novel characteristics of that which is recited is not changed by the presence of more than that which is recited, but excludes prior art embodiments.

[0014] When using an open ended term, like "comprising" or "including," it is understood that direct support should be afforded also to "consisting essentially of" language as well as "consisting of" language as if stated explicitly.

[0015] The term "Amine Hydrogen Equivalent Weight" (AHEW) is defined as the molecular weight of the polyetheramine divided by the number of active amine hydrogens per molecule. For illustration, an idealized polyetherdiamine having a number average molecular weight of 2000 and where all the ends of the polyether were amine ends, hence contributing 4.0 active amine hydrogens per molecule, would have an AHEW of 500 g per equivalent. If, for comparison, 10 percent of the ends were in fact hydroxyl rather than amine, then there would be only 3.6 active amine hydrogens per molecule and the polyetheramine would have an AHEW of 556 g per equivalent. The number of active amine hydrogen per molecule, and therefore the AHEW, of a given polyetheramine may be calculated according to known and conventional techniques in the art, however it is preferably calculated by determining the amine group nitrogen content using the procedure described in ISO 9702.

[0016] The term "aliphatic group" refers to a saturated or unsaturated linear or branched hydrocarbon group and encompasses alkyl, alkenyl, and alkynyl groups, for example.

[0017] The terms "alk" or "alkyl" refer to straight or branched chain hydrocarbon groups having 1 to 12 carbon atoms, for example 1 to 8 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, pentyl, hexyl, heptyl, n-octyl, dodecyl, octadecyl, amyl, 2-ethylhexyl, and the like. An alkyl group is optionally substituted, unless stated otherwise, with one or more groups, selected from aryl (optionally substituted), heterocyclo (optionally substituted), carbocyclo (optionally substituted), halo, hydroxy, protected hydroxy, alkoxy (e.g., C1 to C7) (optionally substituted), acyl (e.g., C1 to C7), aryloxy (e.g., C1 to C7) (optionally substituted), alkylester (optionally substituted), acrylester (optionally substituted), alkanoyl (optionally substituted), aroyl (optionally substituted), carboxy, protected carboxy, cyano, nitro,
amino, substituted amino, (monosubstituted)amino, (disubstituted)amino, protected amino, amido, lactam, urea, urethane, sulfonyl, and the like.

[0018] The term "alkenyT refers to straight or branched chain hydrocarbon groups having 2 to 12 carbon atoms, for example 2 to 4 carbon atoms, and at least one double carbon to carbon bond (either cis or trans), such as ethenyl. An alkenyl group is optionally substituted, unless stated otherwise, with one or more groups, selected from aryl (including substituted aryl), heterocyclo (including substituted heterocyclo), carbocyclo (including substituted carbocyclo), halo, hydroxy, alkoxy (optionally substituted), aryloxy (optionally substituted), alkyiester (optionally substituted), arylester (optionally substituted), alkanoyl (optionally substituted), aroyl (optionally substituted), cyano, nitro, amino, substituted amino, amido, lactam, urea, urethane, sulfonyl, and the like.

[0019] The term "alkynyl" refers to straight or branched chain hydrocarbon groups having 2 to 12 carbon atoms, for example 2 to 4 carbon atoms, and at least one triple carbon to carbon bond, such as ethynyl. An alkynyl group is optionally substituted, unless stated otherwise, with one or more groups, selected from aryl (including substituted aryl), heterocyclo (including substituted heterocyclo), carbocyclo (including substituted carbocyclo), halo, hydroxy, alkoxy (optionally substituted), aryloxy (optionally substituted), alkyiester (optionally substituted), arylester (optionally substituted), alkanoyl (optionally substituted), aroyl (optionally substituted), cyano, nitro, amino, substituted amino, amido, lactam, urea, urethane, sulfonyl, and the like.

[0020] Phrases such as "suitable to provide," "sufficient to cause," or "sufficient to yield," or the like, in the context of methods of synthesis, refers to reaction conditions related to time, temperature, solvent, reactant concentrations, and the like, that are within ordinary skill for an experimenter to vary to provide a useful quantity or yield of a reaction product. It is not necessary that the desired reaction product be the only reaction product or that the starting materials be entirely consumed, provided the desired reaction product may be isolated or otherwise further used.

[0021] It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical
value and sub-range includes "'x' to 'y'." To illustrate, a concentration range of "0.1% to 5%" should be interpreted to include not only the explicitly recited concentration of 0.1 wt.% to 5 wt.%, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "" may include traditional rounding according to significant figures of the numerical value. In addition, the phrase "'x' to 'y'" includes "'x' to 'y'.'"

[0022] The term "about" as used herein, when referring to a numerical value or range, allows for a degree of variability in the value or range, for example, within 10%, or, in one aspect within 5%, of a stated value or of a stated limit of a range.

[0023] In addition, where features or aspects of the disclosure are described in terms of a list or a Markush group, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group. For example, if X is described as selected from the group consisting of bromine, chlorine, and iodine, claims for X being bromine and claims for X being bromine and chlorine are fully described as if listed individually. For example, where features or aspects of the disclosure are described in terms of such lists, those skilled in the art will recognize that the disclosure is also thereby described in terms of any combination of individual members or subgroups of members of list or Markush group. Thus, if X is described as selected from the group consisting of bromine, chlorine, and iodine, and Y is described as selected from the group consisting of methyl, ethyl, and propyl, claims for X being bromine and Y being methyl are fully described and supported.

[0024] As used herein, all percent compositions are given as weight-percentages, unless otherwise stated. When solutions of components are referred to, percentages refer to weight-percentages of the composition including solvent (e.g., water) unless otherwise indicated.

[0025] As used herein, all molecular weights (Mw) of polymers are weight-average molecular weights, unless otherwise specified.

[0026] All publications and patents cited in this specification are herein incorporated by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an
admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that may need to be independently confirmed.

[0027] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features that may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method may be carried out in the order of events recited or in any other order that is logically possible.

[0028] Embodiments of the present disclosure employ, unless otherwise indicated, techniques of chemistry, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

Polyamide Polymerization

[0029] The polyamide polymerization process, e.g., for producing nylon, typically consists of a number of stages. In the Evaporative Stage (on a commercial batch plant typically done in a separate vessel, the Evaporator as well known in the art), the salt concentration of the salt solution is increased from about 50% to about 85%, e.g., from 50 to 80 wt.%, by evaporation of much of the water of solution under modest pressure. In Cycle 1 Stage, the vessel is sealed and the temperature of the salt solution increased while the concentration is kept constant. In Cycle 2 Stage, the pressure is controlled while steam is vented off and the temperature increased. This increases the concentration of the mass further while keeping the temperature hot enough to keep the salt and oligomers/polymer being formed as a result of polymerization in solution. In Cycle 3 Stage, a controlled pressure reduction of the steam atmosphere back to atmospheric pressure is performed while again keeping the mixture molten as the temperature increases. In Cycle 4 Stage, the vessel is kept at atmospheric pressure or below (vacuum) allowing for the last stages of water removal and promoting polymerization to useful molecular weight. The temperature increases to its maximum. In Cycle 5 Stage, the vessel is sealed, a slight pressure of nitrogen introduced and the polymer then extruded from the autoclave via a suitable casting outlet, the extruded polymer lace is then typically cooled in water and the cooled lace then chopped into polymer pellets by a cutter. These Stages and the reasons for them are all well known in the art.
See for example Nylon Plastics handbook; Ed. Meivin I Kohan; Hanser/Gardner Publications; ISBN: 1-56990-189-9; Sections 2.3 and 13.2.3.2.

[0030] The polymer synthesis may first comprise heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide. The diacid may be a dicarboxylic acid and may be selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, pimelic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, maleic acid, glutaconic acid, traumatic acid, and muconic acid, 1,2- or 1,3-cyclohexane dicarboxylic acids, 1,2- or 1,3-phenylendiacetic acids, 1,2- or 1,3-cyclohexane diacetic acids, isophthaic acid, terephthalic acid, 4,4'-oxybisbenzoic acid, 4,4-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, p-t-butyl isophthaic acid and 2,5-furandicarboxylic acid, and mixtures thereof. The diamine may be selected from the group consisting of ethanol diamine, trimethylene diamine, putrescine, cadaverine, hexamethylene diamine, 2-methyl pentamethylene diamine, heptamethylene diamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,2-dimethyl pentamethylene diamine, octamethylene diamine, 2,5-dimethyl hexamethylene diamine, nonamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, decamethylene diamine, 5-methylnonane diamine, isophorone diamine, undecamethylene diamine, dodecamethylene diamine, 2,2,7,7-tetramethyl octamethylene diamine, bis(p-aminocyclohexyl)methane, bis(aminomethyl)norbornane, C2-C16 aliphatic diamine optionally substituted with one or more CI to C4 alkyl groups, aliphatic polyether diamines and furanic diamines, such as 2,5-bis(aminomethyl)furan, and mixtures thereof. In preferred embodiments, the diacid is adipic acid and the diamine is hexamethylene diamine which are polymerized to form nylon 6,6.

[0031] As described above, the polymer synthesis is operated in multiple stages or cycles, where the temperature and pressure conditions are carefully adjusted for progressive removal of the byproduct water from the polymer melt. The conditions are maintained to reduce the water content in a stepwise manner while keeping foaming from building up. In most cases antifoaming agents are introduced in the process to maintain the level of foaming. The foaming problem becomes severe when the hydrophilic functionality is introduced into the polymer. Other than the use of antifoaming agents and/or standard gas-liquid disengagement equipment designs to facilitate better steam evolution from the melt, there are no simple methods to avoid
foaming. At commercial scale, the problem of foaming is to be dealt with by adjusting process parameters and routine maintenance cycles, adding cost to the process.

[0032] In particular, one aspect of the disclosed process is a polyamide wherein the polyamide comprises a nylon and a polyetherdiamine, the polyetherdiamine having a molecular weight of at least 1500 and an AHEW of less than 10 percent higher than the idealized AHEW for the polyetherdiamine, and preferably wherein the polyamide has a moisture regain ranging from about 10% to about 30%, e.g., from about 10% to about 25% or from about 15% to about 25%.

[0033] In another aspect the disclosed process relates to a process for producing a polyamide which comprises contacting a diacid, a polyetherdiamine, and a nylon salt; forming a mixture; heating the mixture in a closed vessel to a temperature and autogenous pressure sufficient to cause polymerization of the mixture; and forming a polyamide; preferably where the polyamide is characterized by a moisture regain of about 10% to about 30%, e.g., from about 10% to about 25% or from about 15% to about 25%.

[0034] In another aspect the disclosed process relates to a yarn comprising a polyamide, said polyamide comprising a nylon and a polyetherdiamine, the polyetherdiamine having a molecular weight of at least 1500 and an Amine Hydrogen Equivalent Weight (AHEW) of less than 10 percent higher than the idealized AHEW for the polyetherdiamine, and preferably wherein the polyamide has a moisture regain value ranging from about 10% to about 30%, e.g., fi-om about 10% to about 25% or from about 15% to about 25%. The disclosed invention also includes fabrics made from the disclosed yarn as well as textile products such as apparel made from the disclosed yarn.

[0035] The polyamides of the disclosed process are well-suited for making hydrophilic polyamide compositions. As such, the disclosure herein generally also relates to improved synthetic polyamide polymer compositions, e.g., nylon. Generally, the polyamides of the disclosed process comprise a nylon and a polyetheramine. As used herein, the term "composition" refers to a composition which is not a yarn or fibre or is not a textile or fabric or garment containing such a yarn or fibre. Such a composition is, however, suitable for making a yarn or fibre and a textile or fabric or garment containing such yarns or fibres.

[0036] Generally, such polyamides comprise a nylon and a polyetheramine, e.g., polyetherdiamine, and may have a moisture regain ranging (measured as described herein) ranging from about 10% to about 30%, preferably from about 10% to about 25%, preferably from
about 15 to about 25%. Such regain may allow for improved processability during subsequent processing of the present polyamide compositions. For example, the polyamide may have an elongation to break of from 20% to 90% when spun into a yarn. The polyamide composition may be either an acid (anionic) or base (cationic) dyeable polymer, as discussed herein. In one embodiment, at least 85% of the polymer backbone (between amide units) may comprise aliphatic groups. The nylon discussed herein may be polyhexamethylene adipamide (nylon 6,6), polycaproamide (nylon 6), or copolymers of either of these. In one embodiment, the nylon may be nylon 6,6. Generally, the nylon may be present in the polyamide in an amount ranging from about 50% to 95% by weight.

[0037] The polyetherdiamine may be made by reacting polyethylene glycol of molecular weight of about 2000 with typically three to ten molecules of propylene oxide to ensure a high statistical conversion of the primary terminal hydroxyl groups to secondary hydroxyl ends. The secondary hydroxyl ends are subsequently converted into amine groups. Incomplete conversion of the hydroxyl to amine groups results in a polyetherdiamine product containing residual hydroxyl end groups, such hydroxyl groups are incapable of forming amide groups during a polyamide polymerization process, limiting the rate and degree of polymerization, and are hence undesirable. Such incomplete conversion is reflected in the AHEW value of the polyetherdiamine being higher than the idealised value. The Technical Data Sheet for Elastamine® RE-2000 describes the polyetherdiamine as being a polyetherdiamine of approximate number average molecular weight 2000, hence it has an idealised AHEW of 500 g per equivalent, the datasheet further reports the actual AHEW as being 505 g per equivalent. For comparison, the Technical Data Sheet for Jeffamine® ED-2003 describes the polyetherdiamine as being a polyetherdiamine of approximate molecular weight 2000; hence it also has an idealised AHEW of 500 g per equivalent, the datasheet further reports the actual AHEW as being 575 g per equivalent.

[0038] The polyamides generally comprise a polyetheramine with an AHEW less than 10% higher than the idealized AHEW for the polyetheramine. The polyetheramine is preferably a polyetherdiamine. In one embodiment, the polyetheramine may be an alkylpolyetheramine. In one aspect, the polyetheramine may include aliphatic groups. In still another aspect, the polyetheramine may be Elastamine® RE-2000 (Huntsman International LLC). In one embodiment, the polyetheramine is a polyetherdiamine and may have the following structure:
In a further embodiment, the polyetheramine may be α,ω-diamino poly(oxyaikylene-co-oxyalkylene ether) copolymer. In one aspect, the α,ω-diamino poly(oxyalkylene-co-oxyalkylene ether) copolymer may be α,ω-diamino poly(oxyethylene-co-oxytetramethylene ether) copolymer, as disclosed in United States Patent Application No. 20120065362A1. Such a polyetheramine may be made by reacting polyethyleneglycol of molecular weight of 2000 with typically three to ten molecules of propyleneoxide to ensure high statistical conversion of the primary terminal hydroxyl groups to secondary hydroxyl ends.

As discussed herein, a polyetherdiamine may be employed in the polymerization of nylon monomers to form a polyamide which may be spun into nylon yarns which exhibit good hydrophilicity properties. Such properties may impart tactile aesthetics and wear comfort highly desired in apparel goods manufactured from these yarns.

Furthermore, the polyetheramines may be present in the polyamide and may have various molecular weights depending upon the desired properties of the resulting polymer, including processability as discussed herein. In one embodiment, the polyetheramine may have a molecular weight of at least 1500. In other aspects, the polyetheramine may have a molecular weight of at least 2500, or even at least 5000. Additionally, the polyetheramine may be present in an amount ranging from about 1 to about 20 wt.% of the polyamide. In one aspect, the polyetheramine may be present in an amount ranging from about 5 to about 15 wt.%, preferably from about 10 to about 15 wt.%. In another preferred embodiment, the polyetheramine is present in an amount from about 8 to about 18 wt.%.

The polyamides described herein may further comprise a diacid in addition to the diacid used to form the nylon salt. In one example, the diacid may be a diacid as disclosed herein. In further embodiments, the diacid may be an aliphatic diacid containing from 6 to 12 carbon atoms, terephthalic acid, isophthalic acid, and mixtures thereof. In one aspect, the diacid may be adipic acid. The diacid may be present in the polymer in an amount to give substantially equimolar proportions of acid groups to amine groups of the polyetheramine. The polyamides described herein may have various physical properties. In one embodiment, the polyamide may
have 42 to 49 amine end group gram-equivalents per 1000 kilograms of polymer. Additionally, the polyamide may have a relative viscosity ranging from about 35 to about 45. In another embodiment, the relative viscosity may be calculated based on a formic acid test method according to ASTM D789-86 known at the time of filing the present disclosure in the United States Patent and Trademark Office. The polyamide may have a yellowness index from about 30 to about 45. In a more detailed aspect, the polyamide may have an L* color coordinate from about 75 to about 85. In another aspect, the polyamide may have an a* color coordinate from about -5 to about 5. In still another aspect, the polyamide may have a b* color coordinate from about 5 to about 25.

[0043] Whiteness may be determined using a test method conforming to the CIE whiteness rating for each sample. Samples may be measured individually for whiteness (W) and yellowness (Y), using a GRETAG MACBETH "COLOR EYE" reflectance spectrophotometer. First, by determining the CIELAB color coordinates L, a* and b*; and then, calculating W and Y by means known in the art (see: ASTM Method E313-1996 Standard Practice for Calculating Whiteness and Yellowness Indices from Instrumentally Measured Color Coordinates). Details of this measurement are found in Color Technology in the Textile Industry 2nd Edition, published by Committee RA 36, AATCC (1997); see in this volume: Special Scales for White Colors by Harold and Hunter, pp 140-146, and the references therein, all are incorporated herein by reference in their entirety.

[0044] Additionally, the present polyamides may further comprise a catalyst. In one embodiment, the catalyst may be present in the polyamide in an amount ranging from 10 ppm to 1,000 ppm by weight. In another aspect, the catalyst may be present in an amount ranging from 10 ppm to 100 ppm by weight. The catalyst may include, without limitation, phosphoric acid, phosphorous acid, hypophosphoric acid arylphosphonic acids, arylphosphinic acids, salts thereof, and mixtures thereof. In one embodiment, the catalyst may be sodium hypophosphite, manganese hypophosphite sodium phenylphosphinate, sodium phenylphosphonate, potassium phenylphosphinate, potassium phenylphosphonate, hexamethylenediammonium bis-phenylphosphinate, potassium tolylphosphinate, or mixtures thereof. In one aspect, the catalyst may be sodium hypophosphite.

[0045] The polyamides and polyamide compositions in accordance with the disclosed process may include an "optical brightener." Such an optical brightener may be provided according to
the disclosures of United States Patent Application No. 20080090945 Al; POLYAMIDE COMPOSITION WITH IMPROVED HEAT STABILITY AND WHITENESS; to INVISTA NORTH AMERICA S.a r.l.

[0046] The polyamides and polyamide compositions in accordance with embodiments disclosed herein may be improved in whiteness appearance through the addition of an optical brightener. Such polyamides may exhibit a permanent whiteness improvement and may retain this whiteness improvement through operations such as heat setting. In one embodiment, the optical brightener may be present in the polyamide in an amount ranging from 0.01 wt.% to 1 wt.%.

[0047] In another embodiment an improvement in whiteness appearance may be achieved by addition of a delustering agent, the delustering agent may be titanium dioxide.

[0048] In addition, these polyamide compositions may contain an antioxidant stabilizer or an antimicrobial additive. Additionally, the polyamide compositions may contain an anti-foaming additive. In one embodiment, the anti-foaming additive may be present in the polyamide in an amount ranging from 1 ppm to 500 ppm by weight.

[0049] The polyamides of the disclosed process are inherently acid (anionic) dyeable, but may also be rendered into a basic (cationic) dyeing form by modifying these polymers or copolymers with a cationic dye receptive monomer copolymerized in the polymer. This modification makes compositions particularly receptive to coloration with base (cationic) dyes. 5-sodium sulfoisophthalic acid is an example of such a cationic dye receptive monomer.

[0050] In a further aspect, the disclosed process provides a process for producing a polyamide, comprising nylon polymer precursors (typically a nylon salt, lactam, or aminoacid and mixtures thereof); optionally forming a mixture of the precursors in water; heating the mixture in a closed vessel to a temperature and autogenous pressure sufficient to cause polymerization of the mixture; and partially forming the polyamide thereby; then further addition comprising at least a polyetherdiamine to form a desired composition.

[0051] The processes for producing the polyamides may further comprise providing to the mixture a catalyst, including those discussed herein. The processes may further comprise providing an anti-foaming additive to the mixture. The processes may further comprise providing an optical brightener to the mixture.
Generally, the nylon monomers of the polyamide may be added as a salt, aminoacid, or lactam. The nylon monomer may be a nylon 6,6 salt formed from adipic acid and hexamethylene diamine and may be present in the polyamide in an amount ranging from about 50 wt.% to 95 wt.%.

Various processing parameters may be used in the polymerization of the present polyamides including temperature and pressure. The temperature may range from 190°C to 290°C and the autogenous pressure may range from 250 pounds per square inch absolute (psia) to 300 pounds per square inch absolute (psia). Additionally, the heating may be performed under partial vacuum. The partial vacuum attained is subject to autoclave design and economic considerations with the process.

Generally, the present polymerization may involve various serial heating cycles. Such cycles have been described in Nylon Plastic Handbook; Ed Melvin I Kohan; Hanser; 1995; ISBN 1-56990-189-9, Figure 2.5 of which shows a typical PA-66 batch polymerization process and details of pressure, melt temperature, % water off (and by inference % water remaining). Such cycles may individually comprise a heating temperature profile and a pressure profile. Generally the intent is to keep the system fluid through a combination of temperature for sufficient melt, and water content for sufficient solubility. The serial heating cycles may comprise: a first heating cycle (C1) having a temperature starting between 170 to 215°C and finishing between 190 to 230°C over a period of 20 to 40 minutes under a pressure of between 130 to 300 psia; a second heating cycle (C2) having a temperature stalling between 190 to 230°C and finishing at between 240 to 260°C over a period of 20 to 45 minutes under a pressure of between 130 to 300 psia; a third heating cycle (C3) having a temperature starting between 240 and 260°C and finishing between 250 to 320°C over a period of between 15 to 45 minutes under a pressure of between 300 psia to atmospheric pressure; and a fourth heating cycle (C4) having a temperature starting between 250 to 320°C and finishing between 250 to 320°C over a period of 15 to 80 minutes under a pressure of between atmospheric pressure and about 200 mBar absolute vacuum. Finally the polymer is extruded using methods well known in the art. Generally, the polyamide composition is inherently acid dyeable and may, as an option, comprise a cationic dyeable polymer. The polyamide composition may contain polyhexamethylene adipamide (nylon 6,6), or polycaproamide (nylon 6), or copolymers of either of these.
The disclosed process adds a polyetheramine during the second or later heating cycle. In an embodiment, the process adds the polyetheramine to at least one of the second, third, fourth, or subsequent heating cycles. The polyetheramine additive may also be charged to the polymerization reaction mixture when the reaction mixture has lost sufficient water to no longer maintain a stable foam at reaction conditions. For example, the polyetheramine additive may be charged to the polymerization reaction mixture when the reaction mixture contains less than 70 wt.% water, for example less than 60 wt.% water, preferably less than 20% water (typical water level at start of C3 described above) and most preferably less than 7% water (typical water level at start of C4 described above). Generally, the process for producing the polyamide composition may be made by an autoclave process. The process may start with a concentrated slurry (the term slurry also incorporating the concept of a solution) prepared from an aqueous solution of a nylon salt, aminoacid or lactam or mixtures of e.g., a nylon 6,6 salt, that is provided to an autoclave vessel. Optionally, the slurry may be dilute and become more concentrated by means of an evaporation step. The slurry may be prepared from an aqueous solution of the monomers, such as, hexamethylene diamine and adipic acid, in the manner known in the art. In another specific embodiment, the slurry may contain a minor amount of nylon 6 monomer with the aqueous solution of the nylon 6,6 monomers in the form of an aqueous caprolactam solution. The optionally added aqueous caprolactam solution may be mixed with the nylon salt in an amount to provide a nylon 6 content of about 0.5 wt.% to about 10 wt.%.

The autoclave vessel may then be heated to 230°C (or some other functional temperature) allowing the internal (autogenous) pressure to rise. A delusterant, titanium dioxide (Ti02) may optionally be injected into the autoclave and monomer mixture as an aqueous dispersion.

In one embodiment, an aqueous slurry or a melt of a polyetheramine may be injected to the mixture in the autoclave vessel along with a quantity of a diacid, e.g., adipic acid, to give substantially equimolar proportions of acid groups to amine groups of the polyetheramine The mixture may then be heated in the autoclave to about 245°C (or some other functional temperature). While at this temperature, the autoclave pressure may be reduced to atmospheric pressure and further reduced in pressure by application of a vacuum in the known manner, to form the polyamide composition. The autoclave, containing the polyamide composition, may be maintained at this temperature for about 30 minutes. This step may be followed by further heating of the polyamide polymer composition in the autoclave to about 285°C, for example, and
introducing dry nitrogen to the autoclave vessel and pressurizing the autoclave by introducing dry nitrogen to about 4 to about 5 bar absolute pressure. The polymer composition may be released from the autoclave by opening a port in the autoclave vessel and allowing the molten poiyamide composition to flow from the vessel in the form of laces. These laces may be cooled and quenched the in a current of water. Next, the laces of poiyamide polymer may be granulated by known means and further cooled with water.

[0057] The autoclave process described above may provide a poiyamide composition with a formic acid method RV of about 25 to about 60. In another embodiment, the autoclave process described above may provide a poiyamide composition with a formic acid method RV of about 38 to about 45.

[0058] Optionally, the process may be modified to make a poiyamide composition having about 25 to about 130 gram equivalents of amine ends per 1000 kilograms of polymer, provided by the addition of an excess of an aqueous hexamethylene diamine solution to the aqueous solution of nylon salt.

[0059] The nylon polymers and copolyamides described herein may be inherently acid-dyeable. In one embodiment, the number of free amine end groups (AEG) in these polymers is at least 25 gram equivalents per 1000 kilograms of nylon polymer. In order to make the polymers more deeply acid dyeable, an enhanced level of free amine end groups may be utilized. More deeply acid dyeing nylon polymers have an enhanced AEG level, e.g., at least 35 gram equivalents per 1000 kilograms of nylon polymer or AEG levels of 60 to 130 gram equivalents per 1000 kilograms of nylon polymer may be used.

[0060] Furthermore, it is noted that a masterbatch of polyetheramine comprising the amine end equivalent of a suitable diacid, e.g. adipic acid, may be made. This masterbatch may then be provided to the autoclave process. In an alternative embodiment, the poiyamide composition herein may be made by a masterbatch process in which a flake or melt form is used comprising a polyetheramine dispersed in nylon, either nylon 6,6 or nylon 6. The flake or melt form is then subsequently added as a masterbatch comprising the nylon. In an embodiment, the masterbatch nylon flake containing the polyetheramine and the nylon, in flake form, are both melted. In an embodiment, the nylon flake containing polyetheramine is melted and added to the nylon melt. In either case, in a further embodiment the melt is forced from an extruder to a pump, which pumps the poiyamide compositions to a pack and a spinneret for making yarns, for example.
The nylon polymers and copolyamides described herein may also be rendered into a basic dyeing form, i.e., receptive to coloration with base dyes also called cationic dyes. Such base-dyeing compositions are made from polyamide polymer with a cationic dye modifier copolymerized in the polymer. United States Patent No. 5,164,261 to Windley describes the preparation of such cationic dye modified polyamides. In one embodiment, the polymer may be modified during polymerization with from 0.5 wt.% to 4 wt.% of a cationic dye modifier, e.g., 5-sulfoisophthalic acid. Typically, a weighed quantity of the sodium salt of 5-sulfoisophthalic acid may be combined with a known amount of the polyamide precursor salt in an autoclave using standard polymerization procedures known in the art. In one embodiment, the amount of cationic dye modifier present in the polymer may be from 0.75 wt.% to 3 wt.%, as determined by total sulfur analysis of the polymer. This amount of cationic dye modifier is reported as equivalent sulfonate groups. The sulfonate group concentration may be at least 25 gram equivalents per 1000 kilograms polymer up to 150 gram equivalents per 1000 kilograms polymer.

Polyamide Yarns

The polyamide composition of the present disclosure is particularly useful when spun into yarns. In one embodiment, the polyetheramine may be provided to the polyamide composition, and hence inherent to the yarn itself when formed into a fabric, as opposed to being applied on a fabric. In one embodiment, said yarn exhibits improved hydrophilic properties as measured by various water wicking and moisture regain tests.

A yarn made from the polyamides described herein may be a multifilament textile yarn in the form of either a low orientation yarn (LOY), a partially oriented yarn (POY) or a fully drawn yarn (FDY). The yarn may be a textured yarn made from partially oriented yarn. Moreover, the yarn may be substantially continuous, i.e. formed by one or more continuous filaments. In other embodiments, a continuous filament may be cut into staple fibers and the latter may be converted into a continuous thread by a spinning process, resulting in a continuous article of manufacture or comprised of shorter fibers. Such yarns may be used to make fabrics, which in turn may be used to make garments.

In one embodiment, apparatuses and methods for spinning yarns are disclosed in United States Patent No. 6,855,425, and similar techniques may be likewise in the context of the polyamides prepared and described herein. Yarns made from the polyamides described herein
may be textile yarns that are especially useful for apparel fabric applications. That is to say, yarns having a yarn weight of from 5 to 300 dtex, and a filament weight of from 0.5 to 7 dtex may be desirable. In certain embodiments, the yarn comprises from 1 to 300 filaments. According to some embodiments the yarn comprises 3 to 150 filaments. According to further embodiments the yarn has a DPF (dtex per filament) from 0.5 to 2.5, for example from 1 to 1.5.

[0065] Yams made from the polyamides described herein may have a filament uniformity in Uster percent (U%) of 1.5% or less, more typically 1% or less. Such uniformity may be desirable in order for the yarn to have the high appearance uniformity needed for apparel applications, and also to reduce yam breaks in texturing, weaving and knitting operations.

[0066] Yams made from the polyamides described herein may have an elongation to break of from 20% to 120%. According to some embodiments the yams have an elongation to break of from 20% to 90%. Typically, the yams have a tenacity of from 25 to 65 cN/tex, for example from 30 to 45 cN/tex. These tensile properties are all desirable for apparel textile applications.

[0067] In certain embodiments, the yarn of the polyamide may have a titanium dioxide content less than 0.1 wt.%, and more typically, less than 0.01 wt.%, giving the yarn a clear or bright luster. In other embodiments, the yarn of the polyamide may have a titanium dioxide content greater than 0.3 wt.% and or even greater than 2 wt.%, giving the yarn a matt or dull luster. Titanium dioxide content between these ranges may also be used, e.g., from 0.1 wt.% to 0.3 wt.%, as well.

[0068] In one specific embodiment, yams of the polyamide may be prepared by using known melt spinning process technology. With such technology, the granulated polyamide composition made by using the autoclave process, or the melt made by the masterbatch process, may both have an optical brightener therein as described above, and may be provided to the spinning machine. The molten polymer is forwarded by a metering pump to a filter pack, and extruded through a spinneret plate containing capillary orifices of a shape chosen to yield the desired filament cross-section at the spinning temperature. These cross-sectional shapes known in the art may include circular, non-circular, trilobal, hollow and diabolo shapes. Typical hollow filaments may be produced as disclosed in US Pat. N. 6,855,425. Spinning temperatures may range from 270°C to 300°C, for example. The bundle of filaments emerging from the spinneret plate is cooled by conditioned quench air, treated with spin finish (an oil/water emulsion), optionally interlaced, e.g. using an interlacing ah jet.
In some embodiments the continuous yarn thus obtained is cut and transformed into staple fibers, which are subsequently used to produce threads or yarns by spinning, or for manufacturing nonwovens, by hydro-entanglement, needlepunching, ultrasonic bonding, chemical bonding, heat bonding or the like.

In the case of FDY, the in-line processing on the spinning machine typically includes making several turns around a set of Godet rolls (feed rolls), the number of turns being sufficient to prevent slippage over these rolls, then passing the yarn over another set of rolls (draw rolls) rotating at sufficient speed to stretch the yarn by a predetermined amount (the draw ratio). Finally, the process is continued by heat setting and relaxing the yarn with a steam-box before winding up at a speed of at least 3000m/min, preferably at least 4000m/min, for example 4800 m/min or more. Optionally, an alternative heat setting (or relaxing) method may be used, such as heated rolls, and an additional set of Godet rolls may be incorporated between draw rolls and winder to control the tension while the yarn is set or relaxed. Also, optionally, a second application of spin finish and/or additional interlacing may be applied before the final winding step.

In the case of POY, the additional in-line processing typically includes only making an S-wrap over two Godet rolls rotating at the same speed, and then passing the yarn to a high speed winder, winding at a speed of at least 3000m/min, preferably at least 4000m/min, for example 4800 m/min or more. Use of the S-wrap is beneficial to control tension, but not essential. Such a POY may be used directly as a flat yarn for weaving or knitting, or as a feedstock for texturing.

The LOY spinning process is similar to POY except that a windup speed of 1000 m/min or below is used. These low orientation yarns, in general, are further processed via a second stage, e.g., on a conventional draw-twister or draw-wind machine.

In one embodiment, the polyamide polymer disclosed herein may be highly suited for spinning into continuous filaments which may be converged to form multifilament yarns. The process of spinning synthetic polymers as continuous filaments and forming multifilament yarns is known to the skilled person. In general, successful spinning of filaments uses a spinneret plate having at least a single capillary orifice. The capillary orifices correspond to each individual filament comprising the yarn. Circular and non-circular cross-section spinneret capillary orifices (or extrusion orifice) are employed depending upon the cross sectional shape sought for the
filament. In general, for a certain polymer throughput $G$ (e.g., in grams per minute) per capillary, the following equation applies:

$$G = p (\text{melt}) D^2 (\text{capillary}) \frac{7n}{4} v(\text{extrusion})$$  
Equation 1.

[0074] In this equation, $p$ is the polymer melt density (e.g., for melted nylon 6,6 at 290°C equal to 1.0 gram per cm$^3$), $D$ is the diameter (equal to twice the radius) of the capillary assuming a circular orifice, and $v$ is the velocity of the filament.

[0075] The extrusion velocity is given by the following equation:

$$v(\text{extrusion}) = \frac{G(4/\pi) D^2 (\text{capillary})}{p(\text{melt})}$$  
Equation 2.

[0076] In one embodiment, the polymer is extruded at an extrusion velocity in the range of 20 centimeters per second to 80 centimeters per second. In another embodiment, the freshly extruded filaments may be quenched with conditioned air in the known manner. In this step, the individual filaments are cooled in a quench cabinet with a side draft of conditioned air and converged and oiled with a primary finish, as known in the art, into a yarn. The yarn is forwarded by feed roll onto a draw roll pair where the yarn is stretched and oriented to form a drawn yarn which is directed by roll into a yarn stabilization apparatus. Such a stabilization apparatus is common to the art and here optionally employed as a yarn post-treatment step. Finally, the yarn is wound up as a yarn package at a yarn speed in the range of 1000 to 6500 meters per minute. The yarn RV (or relative viscosity by the formic acid method) is 51 to 54.

[0077] In an embodiment, the yarn is a drawn yarn with elongation of 22% to 60%, the boiling water shrinkage is in the range of 3% to 10%, the yarn tenacity is the range of 3 to 7 grams per denier, and the RV of the yam may be varied and controlled well within a range of 40 to 60. The yarn is a dull luster multifilament polyamide yarn.

[0078] A derived parameter characterizing the superior properties of this yarn is called the Yarn Quality and found by the product of the yarn tenacity (grams per denier) and the square root of the % elongation, as in Equation 3.

$$\text{YARN QUALITY} = \text{tenacity} \times (\text{elongation})^{1/2}$$  
Equation 3.

[0079] The Yarn Quality is an approximation to the measure of yarn "toughness." As is known to those skilled in the art, the area under the yarn load elongation curve is proportional to the work done to elongate the yarn. Where tenacity is expressed in terms of force per unit denier, for example, and the elongation expressed as a per cent change per unit of length, the load elongation curve is the stress-strain curve. In this case the area under the stress-strain curve is the
work to extend the yarn or the yarn toughness. The yarn quality improvement provides an apparel polyamide yarn which is more acceptable in varied applications. These applications may include, without limitation, warp knit fabrics, circular knit fabrics, seamless knit garments, hosiery products, nonwoven fabrics and light denier technical fabrics.

[0080] In certain embodiments, the polyamide yarns have different dyeing characteristics with anionic dyes or cationic dyes. These dyeing characteristics may arise from different numbers of amine end groups. The concentration of amine end groups (AEG) influences how deeply the polyamide is dyed by anionic dyes. Alternatively or additionally, the polyamides may contain anionic end groups, such as sulfonate or carboxylate end groups, that render the polyamide cationic-dyeable.

[0081] In certain embodiments, the polyamide yarns are dyed with fiber reactive dyes which incorporate vinylsulfonyl and/or β-sulfatoethylsulfonyl groups. Such fiber reactive dyes are known from United States Patent No. 5,810,890.

[0082] In certain embodiments, the polyamide yarns are dyed with fiber reactive dyes which incorporate halogen derivatives of nitrogen heterocyclic groups, such as, triazine, pyrimidine and quinoxaline. Such fiber reactive dyes are described, for example, in United States Patent No. 6,869,453. In other embodiments, the filaments comprise an amine component of hexamethylene diamine. In still other embodiments, the filaments comprise an amine component which is a mixture of hexamethylene diamine with at least 20 wt.% of methyl pentamethylene diamine based on the total weight of diamine. In further embodiments, the polyamides may comprise nylon 6.

[0083] The following testing discussion may be used to characterize the various parameters as discussed herein. Yarn tenacity and the yarn elongation may be determined according to ASTM method D 2256-80 (known at the time of filing the present disclosure with the United States Patent and Trademark Office) using an INSTRON tensile test apparatus (Instron Corp., Canton, Massachusetts, USA 02021) and a constant cross head speed. Tenacity is expressed as centiNewtons per tex grams of force per denier, and the elongation percent is the increase in length of the specimen as a percentage of the original length at breaking load.

[0084] Yarn linear density evenness, also known as the yarn Uster percent (U%), may be determined using a Uster evenness tester 3, type C, which is known in the art to the skilled person.
Polymer amine ends may be measured by directed titration with standardized perchloric acid solution of weighed polymer samples taken up in solution after filtration to remove insoluble delustering pigments.

The moisture regain of a polymer is measured by the following method. A sample (100g) of the polymer is dried for 18 hours at 80°C under vacuum. The initial moisture level of this dried polymer sample is preferably measured using an Aquatrac (PET version (4 Digit); Brabender Messtechnik) at 160°C setting on about 1.9 g polymer. A moisture level measured using this method of less than 0.5 wt.% is taken to indicate that the polymer had been dried sufficiently.

The dried sample is then immersed in demineralised water (500g) at ambient temperature (20°C) without any agitation. After 48 hours a sample is removed (approx. 10g) and patted dry with an absorbent tissue. A portion of the sample (approx. 5g; weight of wet sample) is weighed accurately into a foil dish and placed in an oven at 80°C under vacuum for 18 hours. The dish is removed and placed in a desiccator to cool, and then reweighed (weight left after drying). This procedure is repeated at intervals thereafter (e.g. 72, 144, 190 and 220 hours) up to 220 hours. Moisture uptake was determined by the following calculation:

\[
\text{weight of wet sample} - \text{weight left after drying} \times 100 = \% \text{ uptake}
\]

Moisture regain of the polymer is defined as the moisture uptake after 220 hours or until the sample has reached moisture uptake equilibrium (which is defined as a weight change of no more than 1% in a 24 hour period), whichever is the earlier. Thus, if moisture uptake equilibrium has not been reached by 220 hours the moisture regain is the moisture uptake at 220 hours. When the moisture uptake equilibrium is reached before 220 hours, the moisture regain is the average (mean) of the moisture uptake for the first two consecutive measurements taken at equilibrium. By this test, nylon 6,6 flake without modification would have a moisture regain of 8.5 wt.%. An alternative test is to spin the nylon flake into yarn and by a similar method of immersion in water determine the equilibrium moisture uptake. A further alternative method is to spin the nylon flake into yarn and expose the yarn to a relative humidity controlled atmosphere, say 50% RH at 23°C and determine equilibrium moisture uptake. The purpose of these tests is to demonstrate improvement in moisture regain of the hydrophilic polyetheramine containing composition as against composition without the polyetheramine.
The water wicking rates of fabrics constructed from the yarn may be measured by vertically immersing the bottom 1.8 inches (4.6 cm) of a one inch (2.5 cm) wide strip of the scoured fabric in de-ionized water, visually determining the height of the water wicked up the fabric, and recording the height as a function of time. "Initial wicking rate" means the average wicking rate during the first two minutes of the wicking test.

A fabric or garment "Percent Dry Time" test may be used to characterize the hydrophilic polyamide yarns, fabric and garments. Also known as percent dry time tests or "horizontal wicking" determinations. Percent dry time tests are done using a balance and computer; e.g., Mettler balance AE163 and computer running a Mettler BalanceLink 3.0 program. The weight of a circular sample of fabric 2 inches (5.1 cm) in diameter is obtained and recorded. Using an automated pipette, 0.10 gram of tap water is placed on the balance and its weight recorded. The circular fabric sample is immediately centered over and then placed on the water. The total weight of fabric and water is recorded at that time (time = zero minutes) and every two minutes thereafter for the next 30 minutes. Percent dry results for a given time are calculated according to the following formula: %Dry = 100 - [Wtotal - Wfabric] / WH2O x 100.

Examples

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise: parts are parts by weight, temperature is in °C, and pressure is in atmospheres. Standard temperature and pressure are defined as 25°C and 1 atmosphere.

Example 1. Salt Solution Preparation.

For convenience of handling the waxy solid, Elastamine® RE 2000 was melted and diluted with water to give a room temperature pourable 80% solution/mixture. To a 20L stirred jacketed temperature controlled glass vessel filled with nitrogen and purged with nitrogen was added 4888 g water which was warmed to 35°C. Adipic acid (32.0 g 0.22 mol) was added (calculated to balance amines ends to come from Elastamine® RE 2000) and the mix stirred until dissolved. The 80 wt.% Elastamine® RE 2000 aqueous solution (547.0 g, 0.22 mol Elastamine® RE 2000 based upon a number average molecular weight of 2000) was added
followed by nylon 6,6 salt (4534 g, 17.3 mols). The mixture was left to stir until all solids had dissolved, to produce a roughly 50 wt.% solution. A sample of the mixture was taken and diluted to 9.5 wt.% and its pH determined to be 8.3. Small amounts of adipic acid were added to the 50 wt.% solution until sample pH of 8.1 was achieved. On conversion to polymer, the polymer would contain about 10 wt.% Elastamine® RE 2000 (note this excludes adipic acid used to balance).

[0093] A continuous process for polycondensation of nylon 6,6 is disclosed in the work previously cited by F. Fourne (Synthetic Fibers; Hanser Publishers, Munich, Germany 1999). On Page 60 of the Fourne monograph, the Figure 2.30 on Page 61 is described as a continuous polyamide 66 polycondensation apparatus. As an example of a continuous process of polymerization with addition of Elastamine® RÉ 2000, a molten mixture of Elastamine® and adipic acid is provided to the flasher (decompressor) which is element 10 in Figure 2.30 on Page 61 of the Fourne monograph. The precondensate polymer receiving the molten mixture of Elastamine® is depressurized to a final pressure of 1 bar in the flasher. The resulting composition is then forwarded to an evaporator section, element 12 in Figure 2.30 on Page 61 of the Fourne monograph where the final water content is achieved.

Comparative Example A: Elastamine® RE 2000 added with Nylon Salt to demonstrate unacceptable foaming that occurs during standard polymerization process.

[0094] The polymerization process was conducted in a 15L electrically heated autoclave equipped with a stirrer, pressure transducer and a pressure control valve through which volatiles could be vented, condensed and collected in a catch pot continuously being weighed for mass increase by load cells. The vessel was also equipped with thermocouples placed such that liquid phase and vapor phase temperatures could be determined. One of the vapor phase thermocouples was conveniently placed such that it was above the level of the liquid surface, where it would typically read a cooler temperature than the liquid, but should a foam develop and rise up and cover the vapor thermocouple then the temperature measured would increase to a value approaching that of the liquid.

[0095] To the autoclave 9775g of a Salt solution prepared according to Example 1 was added, together with a catalyst of sodium hypophosphite hydrate (1.21 g, 11.4 mmol, equivalent to about 85 ppm P in final polymer), and 1.41 g of antifoam agent AF 1316 (ex ACC Silicones. 10% active ingredient, about 33 ppm in final polymer).
The vessel was sealed and pressured/purged with nitrogen (at 0 psia) three times. The contents were stirred at 200 rpm while heating commenced and the temperature of the contents raised and steam pressure generated. When the autogeneous pressure had reached 170 psia, stirring was reduced to 70 rpm and the steam vented through the control valve to maintain pressure at or below 170 psia, the temperature of the contents at this stage was about 189°C. The purpose of this stage was to increase the concentration of the salt solution to around 80 to 85 wt.%.

Cycle 1 Stage: When 4.1 kg of condensate had been collected in the catch pot, which took about 30 minutes, at the end of which the liquid temperature was about 200°C, the vent valve was closed and the autogeneous pressure allowed to rise (stirrer increased to 80 rpm). The liquid temperature rose to about 219°C over about 18 minutes until the pressure reached 265 psia. The vapor temperature was at about 211°C.

Cycle 2 Stage: The control valve then kept the pressure at 265 psia over about 39 minutes while the liquid temperature gradually rose until it had reached 243°C, and the vapor temperature was about 217°C.

Cycle 3 Stage: The pressure was then allowed to fall over about 30 minutes to atmospheric pressure (about 15 psia), while stirring at 55 rpm, during which time the liquid temperature rose to about 267°C, and the vapor temperature was about 247°C.

Cycle 4 Stage: After 13 minutes at atmospheric pressure a vacuum ramp was applied to reduce the pressure from atmospheric pressure to about 350 mbar over 15 minutes with the intention of keeping under full vacuum for a further 20 minutes. However, the pressure only dropped from 15 psia to about 11.7 psia (about 800 mbar) over 5 minutes before the pressure started to rise again. The vapor temperature rose sharply from about 250°C to about 267°C (only 10°C cooler than the liquid temperature which was 277°C) – this is taken as indicative of a foaming event. Eventually the pressure in the autoclave reached about 25 psia by the end of cycle 4.

Cycle 5 Stage: Valves to the vacuum system were closed and Nitrogen pressure (30 psia) applied to the vessel and the polymer was cast. The Polymer had an RV of 27.3 and an AEG of 71.2 mpmg.

Later inspection of the vacuum lines confirmed the lines had been blocked by polymer which would have occurred during the foaming event.
Comparative Example B: Elastamine® RE 2000 added with Nylon Salt — to demonstrate unacceptable foaming that occurs during a polymerization process on a commercial N66 autoclave even at very low levels of Elastamine® RE 2000.

[0102] 1408 kg of nylon 6,6 salt, as an about 50 wt.% aqueous solution; 3.5 kg of hexamethylenediamine, as an about 35 wt.% aqueous solution; and 1.7 kg of Dow Corning B (DCB) antifoam, as an about 5 wt.% aqueous solution, were concentrated to an about 85 wt.% solution in an Evaporator using standard conditions and methods well known in the art. The concentrated solution was transferred into an autoclave containing 13.0 kg of an aqueous solution containing about 47 wt.% Elastamine® RE 2000 and 3.4 % adipic acid, together with 2.06 kg of a titanium dioxide pigment as an about 25 wt.% aqueous slurry; 0.416 kg of manganese hypophosphite (MnHP), as an about 5.5 wt.% aqueous solution.

[0103] The intent was to produce a N66 polymer containing about; 0.5 wt.% Elastamine® RE 2000; 0.17 wt.% Titanium dioxide; 340 ppm MnHP (about 100 ppm Mn; 117 ppm P); and 70 ppm DCB.

[0104] The batch was subjected to polymerization process similar to that that would be used to produce N66 but with a slightly reduce rate of heat input, to mitigate against foaming, however it was noted that partly plugged vent lines at the top of the autoclave developed during Cycle 2/Cycle 3 as evidenced by poor pressure control in Cycle 4, indicative of unacceptable foaming behaviour.

Comparative Example C: Elastamine® RE 2000 added during polymerization process — to demonstrate unacceptable foaming that occurs during a polymerization process on a commercial N66 autoclave even at very low levels of Elastamine® RE 2000.

[0105] A polymerization similar to Comparative Example B was conducted except that the Elastamine® RE 2000/ Adipic Acid aqueous solution was added part way through Cycle 2 when the temperature of the contents had reached about 225°C. This caused immediate partial pluggage of the vent lines, indicative of unacceptable foaming behaviour. Examination of the vent lines after the batch had been cast found substantial amounts of polymer in the lines and confirmed that a foaming event had occurred.
Comparative Example D: Elastamine® RE 2000 added with Nylon Salt—to demonstrate unacceptable foaming that occurs during a polymerization process on a commercial N66 autoclave even at low levels of Elastamine® RE 2000.

[0106] A polymerization similar to Comparative Example B was conducted except that an amount of the Elastamine® RE 2000/ Adipic Acid aqueous solution was added during Cycle 1 to give about 2 wt.% Elastamine® RE 2000 in final polymer. This caused unacceptable excessive foaming to the extent that about 45% of the batch ingredients were expelled through the vent lines during the early stage of Cycle 2.

Example 2

[0107] To the autoclave described in Comparative Example A was added nylon 6,6 Salt (3595 g, 13.7 mols), water (5484 g), sodium hypophosphite (1.21 g, 11.4 mmol equivalent to about 104 ppm P in final polymer), and 1.41 g of antifoam agent AF 1316 (ex ACC Silicones. 10% active ingredient, about 40 ppm in final polymer).

[0108] The vessel was sealed and pressured/purged with nitrogen (at 100 psia) three times. The contents were stirred at 200 rpm while heating commenced and the temperature of the contents raised and steam pressure generated. When the autogeneous pressure had reached 170 psia stirring was reduced to about 70 rpm and the steam vented through the control valve to maintain pressure at or below 170 psia, the temperature of the contents at this stage was about 188°C. The purpose of this stage was to increase the concentration of the salt solution to around 80 to 85 wt.%

[0109] Cycle 1 Stage: When 4.5 kg of condensate had been collected in the catch pot, which took about 53 minutes, at the end of which the liquid temperature was about 202°C, the vent valve was closed and the autogeneous pressure allowed to rise (stirrer increased to 80 rpm). The liquid temperature rose to about 220°C over about 14 minutes until the pressure reached 265 psia. The vapor temperature was at about 215°C.

[0110] Cycle 2 Stage: The control valve then kept the pressure at 265 psia over about 28 minutes while the liquid temperature gradually rose until it had reached 243°C, and the vapor temperature was about 223°C.

[0111] Cycle 3 Stage: The pressure was then allowed to fall over about 40 minutes to atmospheric pressure (about 15 psia), while stirring at 55 rpm, during which time the liquid temperature rose to about 280°C, and the vapor temperature was about 251°C.
Cycle 4 Stage: After 32 minutes at atmospheric pressure the vapor temperature was about 247°C.

A molten mixture of Elastamine® RE 2000 (400g, 0.2 mol) and adipic acid (29.2 g, 0.2 mol) at 150°C was poured into a tundish on top of the autoclave and drawn into the autoclave by application of a slight vacuum.

A vacuum ramp was applied to reduce the pressure from atmospheric pressure to about 350 mbar over 3 minutes, the vapor temperature dropped to about 241 °C. The system was kept at 350 mbar for a further 20 minutes, at the end of which the vapor temperature was about 239°C while the contents temperature was at about 275°C.

There was no indication of any foaming event occurring by these vapor temperature measurements.

Cycle 5 Stage: Valves to the vacuum system were closed and Nitrogen pressure (30 psia) applied to the vessel and the polymer was cast. The Polymer had an RV of 56.0 and an AEG of 29.5 mpmg.

There was no indication of polymer in the vent lines.

Example 3

A process very similar to Example 2 was followed except that an additional quantity of sodium hypophosphite (1.21 g, 11.4 mmol) was present in the molten Elastamine® RE 2000/Adipic acid mixture. Again no evidence of foaming was apparent. The Polymer had an RV of 78.4 and an AEG of 24.1 mpmg.

There was no indication of polymer in the vent lines.
What is claimed is:

1. A process for making polyamide comprising:
   (a) heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide;
   (b) removing water from the aqueous solution of (a) to at least partially concentrate the aqueous solution;
   (c) adding polyetheramine to the at least partially concentrated aqueous solution of (b); and
   (d) heating the solution of (c) to further polymerize the diacid, diamine and polyetheramine and to remove water from the solution.

2. The process of claim 1 wherein the partially concentrated solution of step (b) contains less than 70 wt.% water, preferably less than 60 wt.% water, more preferably less than 50 wt.% water.

3. The process of any one of the preceding claims, wherein the polyetheramine is present in an amount ranging from 1 wt.% to 20 wt.% of the polyamide, preferably from 5 to 15 wt.%, more preferably from 10 to 15 wt.%. 

4. The process of any one of the preceding claims, wherein the diacid is selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, pimelic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, maleic acid, glutaric acid, traumatic acid, and muconic acid, 1,2- or 1,3-cyclohexane dicarboxylic acids, 1,2- or 1,3-phenylenedicarboxylic acids, 1,2- or 1,3-cyclohexane diacetic acids, isophthalic acid, terephthalic acid, 4,4'-oxybisbenzoic acid, 4,4'-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, p-t-buty isophthalic acid and 2,5-furandicarboxylic acid, and mixtures thereof and wherein the diamine is selected from the group consisting of ethanol diamine, trimethylene diamine, putrescine, cadaverine, hexamethylene diamine, 2-methyl pentamethylene diamine, heptamethylene diamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,2-dimethyl pentamethylene diamine, octamethylene diamine, 2,5-dimethyl hexamethylene diamine, nonamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, decamethylene diamine, 5-methylnonane diamine, isophorone diamine, undecamethylene diamines, 1,2-oxybisbenzoic acid, 4,4'-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, p-t-buty isophthalic acid and 2,5-furandicarboxylic acid, and mixtures thereof and wherein the diamine is selected from the group consisting of ethanol diamine, trimethylene diamine, putrescine, cadaverine, hexamethylene diamine, 2-methyl pentamethylene diamine, heptamethylene diamine, 2-methyl hexamethylene diamine, 3-methyl hexamethylene diamine, 2,2-dimethyl pentamethylene diamine, octamethylene diamine, 2,5-dimethyl hexamethylene diamine, nonamethylene diamine, 2,2,4- and 2,4,4-trimethyl hexamethylene diamines, decamethylene diamine, 5-methylnonane diamine, isophorone diamine, undecamethylene diamines,
diamine, dodecamethylene diamine, 2,2,7,7-tetramethyl octamethylene diamine, bis(p-
aminocyclohexyl)methane, bis(aminomethyl)norbornane, C₂-C₁₆ aliphatic diamine optionally
substituted with one or more C₁ to C₄ alkyl groups, aliphatic polyether diamines and furanic
diamines, such as 2,5-bis(aminomethyl)furan, and mixtures thereof.

5. The process of any one of the preceding claims, wherein the aqueous solution further
comprises a catalyst.

6. The process of any one of the preceding claims, wherein the polyetheramine is a
polyetherdiamine.

7. The process of any one of the preceding claims, wherein the polyetheramine has a weight
average molecular weight of at least 1500.

8. The process of any one of the preceding claims, wherein the solution in step (a) is heated
to a temperature from 190 to 230°C.

9. The process of any one of the preceding claims, wherein the solution in step (d) is heated
to a temperature from 240 to 320°C.

10. The process of any one of the preceding claims, wherein no polyetheramine is added
during step (a) or step (b).

11. The process of any one of the preceding claims, wherein the polyamide has a moisture
regain from 10 to 30%, preferably from 10 to 25%, and more preferably from 15 to 25%.

12. A process for making polyamide comprising delaying introduction of a monomer
providing hydrophilic functionality for incorporation into the polymer to a location in the process
where water content is reduced.
13. The process of claim 12, wherein making the polyamide comprises four heating cycles, wherein an aqueous solution of diacid and diamine are added in a first heating cycle to convert at least a portion of the diacid and diamine to polyamide; and further wherein the monomer is added in a second, third or fourth heating cycle.

14. The process of claim 13, wherein water is removed from the aqueous solution prior to adding the monomer to form an at least partially concentrated aqueous solution.

15. The process of claim 14, wherein the at least partially concentrated aqueous solution contains less than 70 wt.% water, preferably less than 60 wt.%, more preferably less than 50 wt.%.

16. The process of any one of claims 13 to 15, wherein the polyamide has a moisture regain from 10 to 30%, preferably from 10 to 25%, and more preferably from 15 to 25%.

17. A process for making polyamide comprising:
   (a) heating an aqueous solution of diacid and diamine to convert at least a portion of the diacid and diamine to polyamide and to remove water from the aqueous solution; and
   (b) injecting a hydrophilic additive to the partially concentrated aqueous solution of (a) to incorporate hydrophilic functionality into a resulting polyamide copolymer at an injection rate sufficient to provide a predetermined desired water regain while suppressing foaming of the at least partially concentrated aqueous solution by delayed introduction of the hydrophilic additive.

18. The process of claim 17 wherein said heating step (a) is preceded by at least one step of heating and removing water.

19. The process of any one of claims 17 to 18, further comprising controlling the injection rate of the hydrophilic additive to provide water regain from 10 and 30 wt.%, preferably from 10 to 25 wt.%, more preferably from 15 to 25 wt.%.
20. The process of any one of claims 17 to 19, wherein the partially concentrated aqueous solution comprises less than 70 wt.% water, preferably less than 60 wt.%, more preferably less than 50 wt.%.