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(54) Title: NYLON SALT SOLUTION PREPARATION PROCESSES WITH TRIM DIAMINE

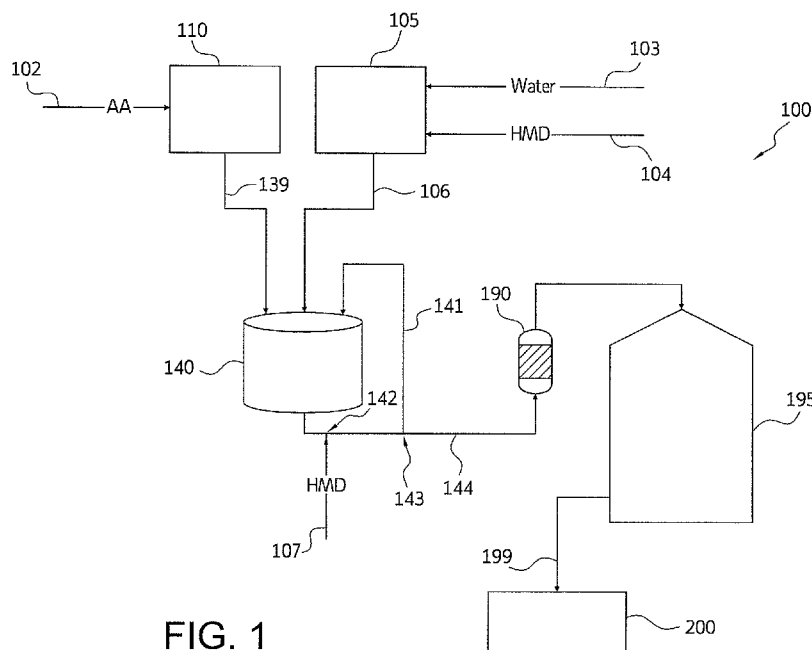


FIG. 1

(57) Abstract: Disclosed are nylon salt solution preparation processes including a trim diamine feed. The nylon salt solution is prepared by feeding a dicarboxylic acid monomer and a diamine monomer to a single continuous stirred tank reactor. The dicarboxylic acid is metered, based on weight, from a loss-in-weight feeder to the reactor. The nylon salt solution is formed continuously and has low variability from a target pH and/or a target salt solution concentration. The nylon salt solution is transferred directly to a storage tank, without further monomer addition, pH adjustment, or salt solution adjustment after exiting the continuous stirred tank reactor.



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NYLON SALT SOLUTION PREPARATION PROCESSES WITH TRIM DIAMINE**CROSS REFERENCE TO RELATED APPLICATION**

[0001] This application claims priority to U.S. App. No. 61/818,065, filed May 1, 2013, the entire contents and disclosures of which are incorporated herein.

FIELD OF THE INVENTION

[0002] The present invention relates to the preparation of nylon salt solutions, and in particular to the preparation of nylon salt solutions using a trim diamine feed.

BACKGROUND OF THE INVENTION

[0003] Polyamides are commonly used in textiles, apparel, packaging, tire reinforcement, carpets, engineering thermoplastics for molding parts for automobiles, electrical equipment, sports gear, and a wide variety of industrial applications. Nylon is a high performance material used in plastic and fiber applications that demand exceptional durability, heat-resistance and toughness. Aliphatic polyamides, referred to as nylon, may be produced from a salt solution of a dicarboxylic acid and a diamine. The salt solution is evaporated and then heated to cause polymerization. One challenge in this production process is ensuring that there is a consistent molar balance of dicarboxylic acid and diamine in the end polyamide. For example, when producing nylon 6,6 from adipic acid (AA) and hexamethylene diamine (HMD), an inconsistent molar balance adversely decreases the molecular weight and may affect the dyeability of the nylon. The molar balance has been achieved using a batch salt process, but batch processes are not suitable for large industrial production. In addition, the molar balance has been achieved in a continuous mode by multiple reactors, each with a separate charge of diamine during the salt production.

[0004] U.S. Patent No. 2,130,947 describes a salt solution of a diamine of the formula $H_2NCH_2RCH_2NH_2$, and a dicarboxylic acid of the formula $HOOCCH_2R'CH_2COOH$, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms. The pH of the salt solution is measured and the inflection point is located. The salt solution is charged to a reactor to form polyamides.

[0005] U.S. Pub. No. 2012/0046439 describes a method for manufacturing a solution of a diacid and diamine salt for manufacturing polyamide. The method comprises mixing at least two diacids and at least one diamine, with a weight concentration of salt between 40% and 70%,

including, in a first step, preparing an aqueous solution of diacid(s) and diamine(s) with a diacid/diamine mole ratio of less than 1 using one diacid and one diamine, and in a second step, adjusting the mole ratio of diacid(s)/diamine(s) to a value of between 0.9 and 1.1, and fixing the weight concentration of salt by adding another diacid and, optionally, additional water and/or diamine.

[0006] U.S. Pub. No. 2010/0168375 describes solutions of a salt of a diamine and of a diacid, more particularly concentrated solutions of hexamethylene diammonium adipate salt, which are useful starting materials for the production of polyamides, more specifically of PA66. The solutions may be prepared by mixing a diacid and a diamine, at a salt concentration by weight of from 50% to 80%, in a first stage, to provide aqueous solutions of diacid and diamine having a diacid/diamine molar ratio of greater than 1.1 and, in a second stage, adjusting the diacid/diamine molar ratio, by adding diamine, to a value of from 0.9 to 1.1, preferably from 0.99 to 1.01, and in fixing the salt concentration by weight by, optionally, adding water thereto.

[0007] U.S. Pat. No. 4,233,234 describes a process for the continuous preparation of an aqueous solution of a salt of an alkanedicarboxylic acid of 6 to 12 carbon atoms and an alkanediamine of 6 to 12 carbon atoms by reacting the particular alkanedicarboxylic acid with the particular alkanediamine in an aqueous solution of the salt to be prepared. The aqueous salt solution is recycled from a first mixing zone via a transport zone and a second mixing zone into the first mixing zone, liquid alkanediamine and an aqueous solution of alkanedicarboxylic acid are introduced between the first and second mixing zones. Less than the equivalent amount of alkanediamine is introduced, the remaining amount of liquid alkanediamine is added after the second mixing zone, and aqueous salt solution is taken off the first mixing zone at the rate at which it is formed.

[0008] Polymerization reactors are described in U.S. Pat. Nos. 6,995,233, 6,169,162, 5,674,794, and 3,893,811.

[0009] Despite efforts to improve the process to achieve target specifications, e.g., proper pH, molar balance, and/or salt concentration in the nylon salt solution, challenges still remain. In particular, dicarboxylic acid, and more specifically adipic acid, is a powder having a variable particle size that leads to wide variations in bulk density. Using a dicarboxylic acid powder introduces another variable that makes it difficult to achieve uniformity of the target

specifications in a continuous process. Volumetric feeders for dicarboxylic acid powder amplify this difficulty. To account for the difficulty in achieving uniformity of the target specifications in a continuous process, prior art processes add the stoichiometric amount of diamine through a series of reactors. In addition, using a series of reactors increases the amount of equipment, capital costs and energy costs.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The present invention will be better understood in view of the appended non-limiting figures, in which:

[0011] FIG. 1 is a schematic diagram of a nylon salt solution production process in accordance with an embodiment of the present invention.

[0012] FIG. 2 is a schematic diagram of a loss-in-weight feeder used in producing a nylon salt solution in accordance with an embodiment of the present invention.

[0013] FIG. 3 is a schematic diagram of a single continuous stirred tank reactor used in producing a nylon salt solution in accordance with an embodiment of the present invention.

[0014] FIG. 4 is a cut-away perspective view of a single continuous stirred tank reactor used in producing a nylon salt solution in accordance with an embodiment of the present invention.

[0015] FIG. 5 is a schematic diagram of a nylon salt solution production process in accordance with an embodiment of the present invention.

[0016] FIG. 6 is a schematic diagram of process controls for a nylon salt solution production process in accordance with an embodiment of the present invention.

[0017] FIG. 7 is a schematic diagram of process controls having secondary controls for a nylon salt solution production process in accordance with an embodiment of the present invention.

[0018] FIG. 8 is a schematic diagram of process controls having tertiary controls for a nylon salt solution process in accordance with an embodiment of the present invention.

[0019] FIG. 9 is a schematic diagram of process controls having on-line pH measurements taken under laboratory conditions for a nylon salt solution process in accordance with an embodiment of the present invention.

[0020] FIG. 10 is a schematic diagram for a nylon 6,6 production process in accordance with an embodiment of the present invention.

[0021] FIGS. 11-13 are graphs showing the feed rate variability of adipic acid from a loss-in-weight feeder in accordance with an embodiment of the present invention.

SUMMARY OF THE INVENTION

[0022] In a first embodiment, the present invention is directed to a continuous process for producing a nylon salt solution comprising: a) controlling feed rate variability of dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH; b) continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor, wherein the combination of the diamine introduced by the first feed rate and the trim diamine introduced by the third feed rate is the stoichiometric amount of diamine to achieve the target pH; and c) continuously withdrawing the nylon salt solution from the recirculation loop of the single continuous stirred tank reactor directly into a storage tank, wherein the nylon salt solution has a salt concentration between 50 wt.% and 65 wt.% and wherein the pH varies by less than ± 0.04 from the target pH or by less than ± 0.03 from the target pH. The target pH may be selected from within the range between 7.200 and 7.900. The trim diamine feed may be introduced into the recirculation loop upstream of the nylon salt solution withdrawal. The recirculation loop may comprise a pump that is selected from the group consisting of vane pumps, piston pumps, flexible member pumps, lobe pumps, gear pumps, centrifugal pumps, circumferential piston pumps, and screw pumps, and the trim diamine feed is introduced upstream of the pump. The recirculation loop may comprise one or more on-line analyzers and the trim diamine feed is introduced upstream of the one or more on-line analyzers. The third feed rate may be controlled by a valve that is maintained to provide a midrange flow through the valve from 20 to 60%. The diamine introduced by the first feed rate may comprise between 80% and 99% of the total diamine fed to the single continuous stirred tank reactor. The trim diamine introduced by the third feed rate may comprise between 1% and 20% of the total diamine fed to the single continuous stirred tank reactor. The nylon salt solution may comprise between 60 wt.% and 65 wt.% salt concentration. The salt concentration of the nylon salt solution may vary by less than $\pm 0.5\%$ from a target salt concentration. The continuous stirred

tank reactor may be maintained at a temperature between 60°C and 110°C and may be maintained at atmospheric pressure in an inert atmosphere. The dicarboxylic acid may be adipic acid and the diamine may be hexamethylene diamine, and the nylon salt solution may comprise hexamethylene diammonium adipate salt.

[0023] In a second embodiment, the present invention is directed to a continuous process for producing a nylon salt solution comprising: a) controlling feed rate variability of dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH and a target salt concentration; b) continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor, wherein the combination of the diamine introduced by the first feed rate and the trim diamine introduced by the third feed rate is the stoichiometric amount of diamine to achieve the target pH; and c) continuously withdrawing the nylon salt solution from the recirculation loop of the single continuous stirred tank reactor directly into a storage tank, wherein the nylon salt solution has a salt concentration that varies by less than $\pm 0.5\%$ from the target salt concentration and wherein the pH varies by less than ± 0.04 from the target pH.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms “a,” “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, group of elements, components, and/or groups thereof.

[0025] Language such as “including,” “comprising,” “having,” “containing,” or “involving,” and variations thereof, is intended to be broad and encompass the subject matter listed thereafter, as well as equivalents, and additional subject matter not recited. Further, whenever a

composition, a group of elements, process or method steps, or any other expression is preceded by the transitional phrase “comprising,” “including” or “containing,” it is understood that it is also contemplated herein the same composition, group of elements, process or method steps or any other expression with transitional phrases “consisting essentially of,” “consisting of,” or “selected from the group of consisting of,” preceding the recitation of the composition, the group of elements, process or method steps or any other expression.

[0026] The corresponding structures, materials, acts, and equivalents of all means or step plus function elements in the claims, if applicable, are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope and spirit of the invention. The embodiment(s) was/were chosen and described in order to best explain the principles of the invention and the practical application, and to enable others of ordinary skill in the art to understand the invention for various embodiments with various modifications as are suited to the particular use contemplated. Accordingly, while the invention has been described in terms of embodiments, those of skill in the art will recognize that the invention may be practiced with modifications and in the spirit and scope of the appended claims.

[0027] Reference will now be made in detail to certain disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which may be included within the scope of the presently disclosed subject matter as defined by the claims.

Introduction

[0028] The present invention is directed to a continuous process for producing a nylon salt solution comprising a loss-in-weight feeder and a continuous stirred tank reactor, e.g., a single continuous stirred tank reactor. Dicarboxylic acid powder is metered through the loss-in-weight feeder at a low variability feed rate to a single continuous stirred tank reactor along with diamine

and water. The diamine is added to the single continuous stirred tank reactor in two portions: as an aqueous solution and as a trim diamine feed. The process advantageously uses the trim diamine feed to adjust pH of the nylon salt solution within a single continuous stirred tank reactor to form a uniform nylon salt solution. This process is an improvement over the prior art because the low variability of the dicarboxylic acid powder allows for addition of the trim diamine upstream of pH measurement of the nylon salt solution. Addition of the trim diamine upstream of pH measurement allows for nearly instantaneous measurement of the effect of the trim diamine feed due to the mixing effect of the pump on the diamine and nylon salt solution. The process therefore achieves nylon salt solution uniformity and advantageously reduces equipment, energy costs and capital costs as compared to existing processes.

[0029] Dicarboxylic acids suitable for the present invention are 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, dodecandioic acid, maleic acid, glutaconic acid, traumatic acid, and muconic acid, 1,2- or 1,3-cyclohexane dicarboxylic acids, 1,2- or 1,3-phenylenediacetic 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. In one embodiment, the dicarboxylic acid monomer comprises at least 80% adipic acid, e.g., at least 95% adipic acid.

[0030] For making nylon 6,6, adipic acid (AA) is the most suitable dicarboxylic acid and is used in the powder form. AA generally is available in a pure form containing very low amounts of impurities. Typical impurities include other acids (monobasic acids and lower dibasic acids), less than 60 ppm, nitrogenous materials, trace metals such as iron (less than 2 ppm) and other heavy metals (less than 10 ppm or less than 5 ppm), arsenic (less than 3 ppm) and hydrocarbon oil (less than 10 ppm or less than 5 ppm).

[0031] Diamines suitable for the present invention are 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 diamine selected may have a boiling point higher than the dicarboxylic acid, and the diamine is preferably not xylylenediamine. In one embodiment, the diamine monomer comprises at least 80% hexamethylene diamine, e.g., at least 95% hexamethylene diamine. Hexamethylene diamine (HMD) is most commonly used to prepare nylon 6,6. HMD solidifies at about 40°C to about 42°C and water is commonly added to depress this melt temperature and ease handling. Thus, HMD is commercially available as a concentrated solution, e.g., between 80 wt.% and 100 wt.% or between 92 wt.% and 98 wt.% diamine.

[0032] In addition to polyamides based solely on dicarboxylic acids and diamines, it is sometimes advantageous to incorporate other monomers. When added at proportions of less than 20 wt.%, e.g., less than 15 wt.%, these monomers may be added into the nylon salt solution without departing from this invention. Such monomers may include monofunctional carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, benzoic acid, caproic acid, enanthic acid, octanoic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, myristoleic acid, palmitic acid, palmitoleic acid, sapienic acid, stearic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, erucic acid and the like. These may also include lactams such as α -acetolactam, α -propiolactam, β -propiolactam, γ -butyrolactam, δ -valerolactam, γ -valerolactam, caprolactam and the like. These may also include lactones such as α -acetolactone, α -propiolactone, β -propiolactone, γ -butyrolactone, δ -valerolactone, γ -valerolactone, caprolactone, and such like. These may include difunctional alcohols such as monoethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol, 1,5-pentanediol, etohexadiol, p-menthane-3,8-diol, 2-methyle-2,4-pentanediol, 1,6-hexanediol, 1,7-heptanediol, and 1,8-octanediol. Higher functionality molecules such as glycerin, trimethylolpropane, triethanolamine and the like may also be useful. Suitable hydroxylamines may also be selected such as ethanalamine, diethanolamine, 3-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-

butanol, 3-amino-1-butanol, 2-amino-1-butanol, 4-amino-2-butanol, pentanolamine, hexanaolamine, and the like. It will be understood that blends of any of these monomers may also be utilized without departing from this invention.

[0033] It is also sometimes advantageous to incorporate other additives into the polymerization process. These additives may include heat stabilizers such as copper salts, potassium iodide, or any of the other antioxidants known in the art. Such additives may also include polymerization catalysts such as metal oxides, acidic compounds, metal salts of oxygenated phosphorous compounds or others known in the art. Such additives may also be delustrants and colorants such as titanium dioxide, carbon black, or other pigments, dyes and colorants known in the art. Additives used may also include antifoam agents such as silica dispersions, silicone copolymers, or other antifoams known in the art. Lubricant aids such as zinc stearate, stearylceramide, stearyl alcohol, aluminum distearate, ethylenebisstearamide or other polymer lubricants known in the art may be used. Nucleating agents may be included in the mixtures such as fumed silica or alumina, molybdenum disulfide, talc, graphite, calcium fluoride, salts of phenylphosphinate or other aids known in the art. Other common additives known in the art such as flame retardants, plasticizers, impact modifiers, and some types of fillers may also be added into the polymerization process.

[0034] In the description below, the terms adipic acid (AA) and hexamethylene diamine (HMD) will be used to denote the dicarboxylic acid and the diamine. However, this process also applies to other dicarboxylic acids and other diamines indicated above.

[0035] The present invention advantageously achieves a nylon salt solution comprising an AA/HMD salt having a target pH. In particular, the present invention achieves the target pH using a fewer number of vessels than conventional processes, and in particular, achieves the target pH in a single reactor, e.g., a single continuous stirred tank reactor (CSTR) where formation of the nylon salt solution occurs. The single reactor is advantageously used in a continuous process that can achieve higher production rates than batch processes. In a batch process, the amount of time and capital costs for equipment to achieve production rates similar to those achievable with a continuous process make a batch process impractical. The target pH may be any pH value chosen by one skilled in the art and may be selected based on the desired end polymer product. Without being bound by theory, the target may be selected from the

highest inflection slope of the pH curve, at a level that is optimum for the range of intended polymer products.

[0036] In some exemplary embodiments, the target pH of the nylon salt solution may be a value within the range between 7.200 and 7.900, e.g., preferably between 7.400 and 7.700. The variation of the actual pH of the nylon salt solution from the target pH of the nylon salt solution may be less than ± 0.04 , more preferably less than ± 0.03 , and most preferably less than ± 0.015 . Thus, for example, if the target pH is 7.500, then the pH of the nylon salt solution is between 7.460 and 7.540, and more preferably between 7.470 and 7.530. Thus, for example, if the target salt concentration is 60%, then a uniform nylon salt solution has a salt concentration variability between 59.5% and 60.5%, and more preferably between 59.9% and 60.1%. For purposes of the present invention, variability of pH refers to the average variation over a continuous operation. This variation is very low, less than $\pm 0.53\%$, and more preferably less than $\pm 0.4\%$, and produces a nylon salt solution with a uniform pH. A uniform nylon salt solution that has a low variability from the target pH is beneficial to improve the reliability of the polymerization process to produce a uniform, high quality polymer product. The nylon salt solution having a uniform pH also allows for a consistent quality feed to the polymerization process. The target pH may vary depending on the manufacturing site. Generally, a pH of 7.620, as measured at 9.5% salt concentration at 25°C, produces a nylon salt solution having a molar ratio of AA to HMD of 1, based on the free and chemically combined AA and HMD. For purposes of the present invention, the molar ratio may vary within the range of 0.8:1.2 depending on the target pH. Having a uniform pH also means that the molar ratio of the nylon salt solution has a corresponding low variability.

[0037] In addition to the target pH, the present invention may also achieve a target salt concentration. The target salt concentration may be any salt concentration chosen by one skilled in the art and may be selected based on the desired end polymer product and storage considerations. The water concentration of the nylon salt solution may be between 35 wt.% and 50 wt.%. The nylon salt solution may have a salt concentration between 50 and 65 wt.% e.g., between 60 and 65 wt.%. The nylon salt solution may be stored as a liquid at a temperature of less than 110°C at atmospheric pressure, e.g., between 60°C and 110°C, or between 100°C and 105°C. Concentrations above 65 wt.% require higher temperature and may require

pressurization to maintain the nylon salt solution as a liquid, e.g., a homogeneous liquid. The salt concentration may affect the storage temperature and generally it is efficient to store the nylon salt solution at a lower temperature and at atmospheric pressure. However, lower salt concentrations undesirably increase the energy consumption to concentrate the nylon salt solution prior to polymerization.

[0038] When producing nylon salt solution continuously according to the present invention, the variability of the salt concentration of the nylon salt solution is preferably very low, e.g., less than $\pm 0.5\%$ from a target salt concentration, less than $\pm 0.3\%$, less than $\pm 0.2\%$, or less than $\pm 0.1\%$. For purposes of the present invention, variability of salt concentration refers to the average variation over a continuous operation. The target salt concentration may vary depending on the manufacturing site.

[0039] The temperature of the nylon salt solution is controlled independently from the molar ratio of the AA to HMD. Although the molar ratio and concentration of solids in the nylon salt solution affect temperature of the nylon salt solution, the process relies on heat exchangers, coils and/or a jacketed CSTR to remove heat from the process and thus control the temperature of the nylon salt solution. The temperature of the nylon salt solution may be controlled to vary by less than $\pm 1^\circ\text{C}$ from a desired temperature. The temperature of the nylon salt solution is selected to be below the boiling point of the nylon salt solution but above the crystallization temperature. For example, a nylon salt solution with a solids concentration of 63% has a boiling point from 108°C to 110°C at atmospheric pressure. Therefore, the temperature is controlled to be less than 110°C , e.g., less than 108°C , but above the crystallization temperature.

[0040] Prior art solutions to achieving low variability in the nylon salt focus on adjusting the AA: HMD molar ratio and HMD concentration in the salt solution using multiple reactors. This focus is due, at least in part, to variability in the AA powder bulk density and poor flowability characteristics, leading to an inherent unpredictability of an AA powder feed. The variability in the AA powder bulk density is amplified when using a volumetric feeder for feeding the AA powder to the reactor(s). Due to AA's high melt temperature, AA is typically supplied as a powder, which increases the difficulty of handling AA. AA powder typically has an average size that varies between 75 and 500 microns, e.g., between 100 and 300 microns. The finer powder has substantially more surface area and particle contact which leads to clumping. Preferably, AA

powder contains less than 20% of particulates that are less than 75 microns, e.g., less than 10%. Because the AA powder is generally metered on a volumetric basis directly to the reactor in powder form, variations in powder size affect bulk packing and density of the AA powder fed to the nylon salt reactor. These variations in bulk packing and density then lead to variations in pH and in the molar ratio of AA to HMD in the nylon salt solution. To account for this variation, the prior art solution was to arrange nylon salt reactors in series. See, for example, U.S. Publication Nos. 2012/0046439 and 2010/0168375. This conventional approach uses measurements of the target specifications and feeds monomers within the series of reactors. However, this process requires numerous reactors, measurement, and adjustments that increase cost and limit production rates. Additionally, this conventional approach may be more suited to a batch process than to a continuous process. Finally, these conventional approaches cannot use a model to predict pH and/or salt concentration, and thus adjustments are constantly made to bring the nylon salt solution into target specifications.

[0041] The role of particle size and particle size distribution associated with feeding AA powder to a nylon salt process was addressed in the prior art by using multiple reactors to add AA and HMD. It has been found that by metering the AA powder on a weight basis instead of a volumetric basis, the variability of the AA powder feed rate may be greatly reduced. In some aspects, the AA powder feed rate may vary by less than $\pm 5\%$ from the target AA powder feed rate, e.g., less than $\pm 3\%$ or less than $\pm 1\%$. With this stable feed, the disclosed process allows for the use of one single reactor, instead of numerous reactors in series, to form a nylon salt solution to target specifications. It is difficult to control the variation of the nylon salt solution from target pH and target salt concentration using a single reactor operating under high continuous production rates without a stable feed of AA because there is a limit on the ability to adjust the monomers. Having a stable feed of AA allows the process controls to take advantage of feed forward rates for HMD and allows for adjusting trim HMD to adjust the pH to achieve the target pH. Advantageously, the contemplated embodiments provide simpler designs than previous disclosures by reducing the number of unit operations in the process. Thus, the disclosed process omits steps previously believed necessary. This reduces plant footprint and capital costs. The resulting nylon salt solution may then be polymerized to form the desired polyamide.

[0042] To achieve acceptable production in the industrial manufacture of nylon salts, a continuous process may be used to produce the nylon salt solution. A batch process would require significantly larger vessels and reactors. Further, the batch process would not be able to achieve the production rates achievable by smaller continuous production equipment. It is beneficial in the polymerization to start with a nylon salt solution having uniformity in both the pH and salt concentration. Slight variations can cause production quality problems with the polymerization that requires additional monitoring, control and adjustment of the polymer process.

[0043] FIG. 1 provides a general outline of the process to produce the nylon salt solution according to embodiments of the present invention. As shown in FIG. 1, a nylon salt solution process 100 comprises feeding adipic acid via line 102 to a loss-in-weight feeder 110, which produces a metered adipic acid feed 139 that is directed to continuous stirred tank reactor 140. Additionally, water via line 103 and HMD via line 104 are combined in static mixer 105 to form an aqueous HMD solution that is fed to continuous stirred tank reactor 140 via line 106. A liquid comprising the nylon salt solution is withdrawn from reactor 140 via recirculation loop 141 and returned to reactor 140. Additional HMD, referred to herein as trim HMD, may be added to the liquid from line 107 at junction 142 to adjust the pH of the nylon salt prior to analyzing the pH or salt concentration. The nylon salt solution is withdrawn at junction 143 from the recirculation loop 141 into conduit 144. The nylon salt solution in conduit 144 passes through filters 190 to remove impurities and is collected in storage tank 195. Generally, these impurities may include corrosion metals and may include impurities from monomer feeds such as AA powder 102. The nylon salt solution is removed via line 199 to polymerization process 200. The nylon salt solution may be kept in storage tank 195 until needed for polymerization. In some embodiments, storage tank 195 may be transportable.

Nylon Salt Solution Equipment

Weight-Based AA Powder Feeder

[0044] In one embodiment, as shown in FIG. 2, AA powder 102 is fed to a continuous stirred tank reactor 140 using a loss-in-weight feeder 110. Loss-in-weight feeder 110 meters AA powder 102 to produce an AA powder feed stream 139 having a low variability feed rate and is able to account for changes in density of AA powder 102 during the feeding process. As

indicated above, AA powder **102** may vary greatly in bulk density and flow characteristics, leading to the introduction of imbalances in the molar ratio and producing a non-uniform pH for the nylon salt solution. The present invention is advantageous over a volumetric feeder or other types of feeders that cannot achieve a low variability feed rate of AA powder. For purposes of the present invention, a low variability feed rate of AA powder is within $\pm 5\%$ of the target feed rate of AA powder, e.g., within $\pm 3\%$, within $\pm 2\%$, or within $\pm 1\%$. For purposes of the present invention, variability of feed rate refers to the average variation over a continuous operation. Because of the low variability of the AA powder feed rate, the feed rate of the AA is stable and predictable and the diamine and water feed rates may be tailored to achieve a target pH and/or a target salt concentration using a single reactor. Additional reactors are not needed for blending or adjustment because of the low variability of the AA powder feed rate from a target feed rate.

[0045] In general, a loss-in-weight feeder **110** operates to load a hopper **111** during a replenishment phase and dispense the contents of hopper **111** during a feed phase. Preferably, this replenishment-feed phase cycle is sufficient to receive a feedback signal from loss-in-weight feeder **110** at least 50% of the time, e.g., preferably at least 67% of the time. In one embodiment, the replenishment phase may be less than 20% of the total cycle time (e.g., total time for the feed and replenishment phases), e.g., less than 10% of the total cycle time or less than 5% of the total cycle time. The replenishment phase and total cycle phase times may be dependent on production rates. During the feed phase, the contents of hopper **111** are dispensed into a feeding conduit **112** that transfers the AA powder into continuous stirred tank reactor **140** via line **139**. In addition, during the replenishment phase, the AA remaining in hopper **111** may also be dispensed into feeding conduit **112** so that feeding conduit **112** receives a constant supply of AA powder. A controller **113** may be used to regulate loss-in-weight feeder **110**. Controller **113** may be a distributed control system (DCS) or a programmable logic controller (PLC) that is capable of outputting a function in response to a received input. In one embodiment, there may be multiple controllers for various components of the system. For example, a PLC may be used to regulate the replenishment phase and a DCS may be used to control the feed rate through the feeding conduit **112** from a target speed set in the DCS.

[0046] As shown in **FIG. 2**, conveyance system **114** loads AA powder **102** into a supply vessel **115**. Conveyance system **114** may be a mechanical or pneumatic conveyance system to transfer

adipic acid from bulk bags, lined bulk bags, lined box containers or hopper railcar unloading stations. Mechanical conveyance systems may include screws or drag chains. Pneumatic conveyance systems may include enclosed tubes to deliver AA powder **102** using pressurized air, vacuum air, or closed loop nitrogen to supply vessel **115**. In some embodiments, conveyance system **114** may provide mechanical functions to break clumps of AA powder while loading supply vessel **115**. Supply vessel **115** may have a cylinder, trapezoid, square or other suitable shape having an entry **116** at the top. Shapes having angled sides are useful to assist the flow of AA powder **102** out of supply vessel **115**. The upper edge of supply vessel **115** may be less than 20 meters (m), e.g., preferably less than 15 m above a system floor elevation **130**. System floor elevation **130** refers to the planar surface upon which the various equipment to produce the nylon salt solution rests and generally defines a planar surface through which no monomers pass. The system floor elevation may be above the inlets of the CSTR. Due to the lower height of supply vessel **115** relative to system floor elevation **130**, less energy is needed to drive conveyance system **114** and load supply vessel **115**.

[0047] Supply vessel **115** also has lower valve **117** that when closed, defines an internal cavity for holding AA powder **102**. Lower valve **117** may be a rotary feeder, a screw feeder, a rotating flow device or a combination device comprising a feeder and a valve. Lower valve **117** may be kept closed when filling the internal cavity with AA powder **102**. Lower valve **117** may be opened during the replenishment phase to convey AA powder **102** on a volumetric basis to hopper **111**. AA powder **102** may be loaded into supply vessel **115** when lower valve is conveying AA powder to hopper **111**. Lower valve **117** may comprise one or more flaps that form a seal when closed. In one embodiment, there may be a conveying belt (not shown) to transfer AA powder **102** from supply vessel **115** to hopper **111**. In other embodiments, supply vessel **115** may transfer AA powder **102** by gravity. The loading of supply vessel **115** may be independent of the loading of hopper **111**.

[0048] Supply vessel **115** may have capacity that is larger than hopper **111**, preferably a capacity that is at least twice as large or at least three times as large. The capacity of supply vessel **115** should be sufficient to replenish the entire volume of hopper **111**. AA powder **102** may be held in supply vessel **115** for longer period of time than hopper **111**, and depending on

the moisture concentration, AA powder **102** may form clumps. The clumps may be broken by a mechanical rotator or vibration (not shown) at the base of supply vessel **115**.

[0049] The upper edge of hopper **111** may be less than 15 m, e.g., preferably less than 12 m above system floor elevation **130**. Hopper **111** may have cylinder, trapezoid, square or other suitable shape having an entry **118** at the top. Preferably, the internal surfaces of hopper are steep to prevent bridging of AA powder. In one embodiment, the internal surfaces have an angle from 30° to 80°, e.g., from 40° to 65°. The internal surfaces may be U-shaped or V-shaped. Hopper **111** may also have a removable lid (not shown) with an aperture for the entry **118** and vent opening. Hopper **111** may be mounted to duct **119** that connects hopper **111** to feeding conduit **112**. In one embodiment, hopper **111** has an equivalent volume to maintain desired production rates. For example, hopper **111** may have a capacity of at least 4 tonnes. Duct **119** has a maximum diameter that is smaller than the maximum diameter of hopper **111**. As shown, duct **119** has a rotary feeder **120**, or similar transfer device, for dispensing the contents of hopper **111** through an exit **129** into feeding conduit **112**. Rotary feeder **120** may be operated in on/off mode or the rotation rate can be controlled as a function of the desired feed rate. In other embodiments, duct **119** may have no internal feeder mechanisms. Depending on the type of loss-in-weight feeder, rotary feeder **120** may be replaced by external massage paddles or vibrators that dispense the discharge from hopper **111** to feeding conduit **112**. Exit **129** may have a mechanical means to break clumps of AA. In another embodiment, loss-in-weight feeder **110** may have a drier or dry gas purge (not shown) to remove moisture from the AA powder to prevent the AA powder from setting up in hopper **111** and forming clogs.

[0050] A weight measuring subsystem **121** is connected to hopper **111**. Weight measuring subsystem **121** may comprise a plurality of sensors **122** that weigh hopper **111** and provide a signal indicative of the weight to controller **113**. In some embodiments there may be three sensors or four sensors. Sensors **122** may be connected to an external side of hopper **111** and may be tared to account for the initial weight of hopper **111** and any other equipment connected to hopper **111**. In another embodiment, sensors **122** may be positioned underneath hopper **111**. Based on the signals from weight measuring subsystem **121**, controller **113** controls the replenishment phase and feed phase. Controller **113** compares the weight measured at regular

intervals to determine the weight of AA powder 102 dispensed to feeding conduit 112 over a period of time. Controller 113 may also control the speed of rotating auger 123, described below.

[0051] In other embodiments, weight measuring subsystem 121 may be positioned under hopper 111, duct 119, and feeding conduit 112 to measure the weight of material in these locations of loss-in-weight feeder 110.

[0052] Feeding conduit 112 is located underneath duct 119 and receives AA powder 102. In one embodiment, feeding conduit 112 may be mounted to duct 119. Feeding conduit 112 may extend substantially perpendicular to the plane of exit 129 of duct 119 or may extend at an angle between 0° and 45°, e.g., between 5° and 40°, from that plane and toward the reactor 140.

Feeding conduit 112 has at least one rotating auger 123 that conveys AA powder 102 through an open outlet 124 and into reactor 140. Rotating auger 123 is driven by motor 125 and may comprise an endless screw. A double screw configuration may also be used. Motor 125 drives rotating auger 123, at fixed or variable speed. In one embodiment, feeding conduit 112 transfers AA powder 102 at a low variability feed rate into reactor 140. The feed rate of AA may be adjusted depending on the desired production rates. This allows the establishment of a fixed AA feed rate and using the model described herein, the feed rates of the other solution components are then varied to achieve desired salt concentrations and/or pH targets. Controller 113 receives feedback signals from loss-in-weight feeder 110 and adjusts the speed of rotating auger 123. Controller 113 also adjusts the feed rate of feeding conduit 112 based on the signals from weight measuring subsystem 121. The command signals to rotating auger 123 affect the motor speed, either increasing, maintaining, or decreasing it, to achieve the set weight loss.

[0053] In other embodiments, feeding conduit 112 described herein may be any equivalent, controllable feeder type such as a belt feeder, compartment feeder, plate feeder, vibrating feeder, etc. Feeding conduit 112 may also comprise a vibration dampener (not shown). In addition, feeding conduit 112 may have one or more gas ports (not shown) for injecting nitrogen to remove oxygen.

[0054] Hopper 111 may also comprise a high level probe 127 and a low level probe 128. It should be understood that for purposes of convenience, one high and low level probe are shown, but there may be multiple probes. The probes may be used in conjunction with weight measuring subsystem 121. For purposes of the present invention, the probes may be point level

indicators or capacitive proximity sensors. The locations of high level probe **127** and low level probe **128** may be adjusted within hopper **111**. High level probe **127** is positioned near the top of hopper **111**. When material in hopper **111** is detected by high level probe **127**, the replenishment phase is completed and the feed phase begins. Conversely, low level probe **128** is positioned below high level probe **127** and closer to the bottom of hopper **111**. The position of low level probe **128** may allow a sufficient remaining amount of AA powder **102** to be dispensed during the replenishment phase. When low level probe **128** detects no material in hopper **111** at its position, the replenishment phase begins. As stated above, the feeding may continue during the replenishment phase.

[0055] AA solids can be corrosive. Loss-in-weight feeder **110** may be constructed of corrosion-resistant material such as an austenitic stainless steel or a, for example, 304, 304L, 316 and 316L, or other suitable corrosion-resistant material to provide an economically viable balance between equipment longevity and capital cost. Additionally, the corrosion-resistant material may prevent corrosion contamination of the product. Other corrosion-resistant materials preferably are more resistant to attack by AA than carbon steel. HMD in high concentrations, e.g., greater than 65%, is not corrosive to carbon steel, and therefore carbon steel may be used for storing concentrated HMD, whereas stainless steel may be used to store more dilute HMD concentrations.

[0056] Although one exemplary loss-in-weight feeder **110** is shown, other acceptable loss-in-weight feeders, may include Acrison Models 402/404, 403, 405, 406, and 407; Merrick Model 570; K-Tron Models KT20, T35, T60, T80, S60, S100, and S500; and Brabender FlexWall™Plus and FlexWall™Classic. Acceptable loss-in-weight feeders **110** should be capable of achieving a feed rate sufficient for continuous commercial operation. For example, the feed rate may be at least 500 Kg/hr, e.g., at least 1000 Kg/hr, at least 5,000 Kg/hr or at least 10,000 Kg/hr. Higher feed rates may also be used with embodiments of the present invention.

Reactor

[0057] In one embodiment the present invention comprises a reactor for producing a nylon salt solution comprising: a continuous stirred tank reactor to produce the nylon salt solution comprising: a first inlet for introducing a dicarboxylic acid powder into the continuous stirred tank reactor; a second inlet for introducing a first diamine feed into the continuous stirred tank

reactor, wherein the second inlet is adjacent to the first inlet; one or more baffles affixed to an internal wall of the continuous stirred tank reactor; an agitator shaft extending through the center of the continuous stirred tank reactor, wherein the agitator shaft comprises at least one upper impeller and at least one lower impeller; and a recirculation loop comprising a junction for introducing a second diamine feed upstream of a pump and a sample loop; and a conduit for transferring the nylon salt solution from the recirculation loop of the continuous stirred tank reactor directly into a storage vessel, wherein the conduit does not have any inlets for introducing additional monomers selected from the group consisting of dicarboxylic acids, diamines, and combinations thereof, to prevent transferring the additional monomers into the conduit or into the storage vessel, wherein the reactor comprises a single reactor.

[0058] The nylon salt solution is prepared in a single continuous stirred tank reactor **140** as shown in **FIG. 3**. Reactor **140** creates sufficient turbulent flow for producing a homogeneous nylon salt solution. For purposes of the present invention, “a continuous stirred tank reactor” refers to one reactor and does not include multiple reactors. The present invention is able to achieve the uniform nylon salt solution in a single vessel and does not require multiple cascading vessels as used in conventional processes. Suitable continuous stirred tank reactors are a single vessel reactor such as a non-cascading reactor. Advantageously, this reduces the capital investment in producing a nylon salt solution on a commercial scale. When used in combination with the loss-in-weight feeder described herein, the continuous stirred tank reactor is able to achieve a uniform nylon salt solution that achieves the target pH and target salt concentrations.

[0059] The nylon salt solution is withdrawn from reactor **140** and is directly transferred to storage tank **195**. No subsequent introduction of monomers, either AA or HMD, are introduced into the nylon salt solution between withdrawal from continuous stirred tank reactor **140** and entry into storage tank **195**. More specifically, the nylon salt solution is withdrawn in conduit **144** from recirculation loop **141** and no monomers are added into conduit **144**. In one aspect, conduit **144** does not have inlets for introduction of additional monomers that may include dicarboxylic acids and/or diamines. Thus, the pH of the nylon salt solution is not further adjusted by introducing additional monomers to the conduit, and in particular is not adjusted by adding additional HMD. There may be additional mixing and filtration of the nylon salt solution as needed, but the monomers are only fed to the single continuous stirred tank reactor as

described herein. Thus the disclosed process avoids the need for the sequence of multiple vessels and successive steps of pH measurement and adjustment previously believed to be needed to maintain a stable stoichiometric balance between AA and HMD for making nylon 6,6.

[0060] Reactor **140** may have a height to diameter ratio between 1.5 and 6, e.g., between 2 and 5. Reactor **140** may be constructed of a material selected from the group consisting of Hastelloy C, aluminum, and an austenitic stainless steel such as 304, 304L, 316 and 316L, or other suitable corrosion-resistant material to provide an economically viable balance between equipment longevity and capital cost. The selection of the material may be made by considering temperature in continuous stirred tank reactor **140**. The residence time in continuous stirred tank reactor **140** may vary depending on the size and feed rates, and is generally less than 45 minutes, e.g., less than 25 minutes. The liquid is withdrawn in a lower outlet **148** into recirculation loop **141** and a nylon salt solution is withdrawn in conduit **144**.

[0061] In general, a suitable continuous stirred tank reactor comprises at least one monomer inlet for introducing AA, HMD, and/or water. The inlets are directed to an upper portion of the reactor. In some embodiments, the monomers drop into the liquid. In other embodiments, dip tubes may be used to feed the monomers at the liquid level. There may be multiple inlets for introducing each component in the reaction medium. An exemplary continuous stirred tank reactor is shown in **FIG. 3**. As shown in **FIG. 3**, there is an AA inlet **145** and HMD inlet **146**. The diamine may be introduced as pure HMD or as an aqueous solution **106** comprising between 20 wt.% and 55 wt.% HMD, e.g., between 30 wt.% and 45 wt.%, and between 45 wt.% and 80 wt.% water, e.g., between 55 wt.% and 70 wt.%. Aqueous solution **106** may be introduced through inlet **146** that is adjacent to inlet **145** of dicarboxylic acid powder **139**. In one embodiment inlet **146** may be between 0.3 m and 1 m from inlet **145**. Aqueous solution **106** may aid in the dissolution and may at least partially dissolve dicarboxylic acid powder **139** being fed to reactor **140**. Water may be introduced along with the diamine. Optionally, there may be an inlet **147** for separately introducing the water. Water may also be introduced through a reactor recovery column **131**. In some aspects, recovery column **131** is a vent condenser.

[0062] The liquid in reactor **140** is continuously withdrawn and passes through recirculation loop **141**. Recirculation loop **141** may comprise one or more pumps **149**. Recirculation loop **141** may also comprise a temperature control device, e.g., coils, a jacket, or a device comprising a

heat exchanger, temperature measurement device and controller. The temperature control device controls the temperature of the nylon salt solution in recirculation loop **141** to prevent boiling or slurring of the nylon salt solution. When additional HMD, e.g., trim HMD, is introduced via line **107**, it is preferred to introduce HMD upstream of one or more pumps **149** at junction **142** and upstream of any pH or salt concentration analyzers. As discussed further herein, trim HMD **107** may contain between 1% and 20% of the HMD needed to form the nylon salt solution, e.g., between 1% and 10% of the HMD needed. Junction **142** may be a feed port into recirculation loop **141**. In addition to recirculating the liquid, the pumps **149** also function as secondary mixers. The pumps may function to both introduce the trim HMD into recirculation loop **141** and to mix the trim HMD with the liquid withdrawn from the reactor. The pumps may be selected from the group consisting of vane pumps, piston pumps, flexible member pumps, lobe pumps, gear pumps, circumferential piston pumps, and screw pumps. In some embodiments, pumps **149** are located at junction **142**. In other embodiments, as shown, pumps **149** are located downstream of junction **142** but before junction **143**. It is preferred that the secondary mixing occur after the addition of all the HMD, including the trim HMD through line **107**, and prior to any analyzing or withdrawing into storage tank **195**. In alternative embodiments, the one or more static mixers (not shown) may be placed downstream of pumps **149** in recirculation loop **141**. Exemplary static mixers are further described in Perry, Robert H., and Don W. Green. *Perry's Chemical Engineers' Handbook*. 7th ed. New York: McGraw-Hill, 1997: 18-25 to 18-34, hereby incorporated by reference.

[0063] At junction **143**, the nylon salt solution may be withdrawn in conduit **144**. The residence time in conduit **144** may vary depending on the location of storage tank **195** and filters **190**, and is generally less than 600 seconds, e.g., less than 400 seconds. In one embodiment, valve **150** may be operated to control the pressure of the nylon salt solution. Although one valve is shown, it should be understood that additional valves may be used in recirculation loop **141**. No monomers, e.g., AA or HMD, are introduced downstream of junction **143** or into conduit **144**. In addition, no monomers are introduced into storage tank **195** under normal operating conditions.

[0064] Recirculation loop **141** may also comprise a heat exchanger **151** for regulating the temperature of the liquid in reactor **140**. The temperature may be regulated by using a

temperature controller (not shown), either in reactor **140** or at a continuous stirred tank reactor **140** outlet (not shown). The temperature of the liquid may be regulated using an internal heat exchanger, such as a coil or a jacketed reactor (not shown). Heat exchanger **151** may be supplied with cooling water that is maintained above the freezing point of the salt for a given concentration. In one embodiment, the heat exchanger may be an indirect shell and tube exchanger, a spiral or plate and frame heat exchanger, or a reboiler for heat recovery from reactor **140**. The temperature in reactor **140** is maintained within a range between 60°C and 110°C to prevent slurry formation and crystal formation. As the water concentration increases, the temperature to maintain a solution decreases. In addition, the temperature in reactor **140** is maintained at low temperature to deter oxidation of HMD. A nitrogen blanket may also be provided to deter oxidation of HMD.

[0065] As shown in **FIG. 3**, in one embodiment, reactor **140** has an internal coil **152** into which a coolant may be fed to regulate the temperature of the reactor within a temperature that is between 60°C and 110°C. In another embodiment, reactor **140** may also be jacketed with a coolant (not shown). The internal coil may also regulate the temperature by recovering heat produced by the reaction.

[0066] In addition to a temperature controller, reactor **140** may also have an atmospheric vent with a vent condenser to maintain atmospheric pressure within reactor **140**. The pressure controller may have internal and/or external pressure sensors.

[0067] In one embodiment, there may also be a sample line **153** for measuring the pH and/or salt concentration of the nylon salt. Sample line **153** may be in fluid communication with recirculation loop **141** and preferably receives a fixed flow therethrough to minimize the influence of flow on the analyzers. In one aspect, sample line **153** may withdraw less than 1% of the nylon salt solution in recirculation loop **141**, and more preferably less than 0.5%. There may be one or more analyzers **154** in sample line **153**. In some embodiments, sample line **153** may comprise a filter (not shown). In another embodiment, sample line **153** may contain suitable heating or cooling devices such as heat exchangers to adjust and control the temperature of the sample stream. Similarly, sample line **153** may include a water charge line (not shown) for adding water to the sample stream to adjust concentration. If water is added to the sample stream, the water can be deionized water. The water fed through sample line **153** is calculated to

maintain the target salt concentration and the other feeds of water may be adjusted. Analyzers **154** may include on-line analyzers for real-time measurement. Depending on the type of sampling, the tested portion may be returned to reactor **140** via line **155** or discharged. Sample line **153** may be returned through recirculation loop **141**. Alternatively, sample line **153** is returned at a separate location into reactor **140**.

[0068] Continuous stirred tank reactor **140** maintains liquid level **156** that is at least 50% full, e.g., at least 60% full. The liquid level is selected so that it is sufficient to submerge the blades of the CSTR and thus prevent foaming of the nylon salt solution. Nitrogen or another inert gas may be introduced into head space above liquid level **156** through a gas port **157**.

[0069] The internals of continuous stirred tank reactor **140** may provide sufficient mixing to produce the desired nylon salt solution having a uniform pH. As shown in **FIG. 4**, there is an agitator shaft **158** that extends vertically into and through the center of reactor **140**. Preferably, agitator shaft **158** extends along the center line of reactor **140**, but in some embodiments agitator shaft **158** may pass through the center. In optional embodiments, the agitator shaft may be inclined. Eccentric agitator shafts may also be used provided that the desired mixing is achieved.

[0070] Agitator shaft **158** may have one or more impellers **159** such as mixing paddles, helical ribbons, anchors, screw-types, propellers, and/or turbines. Axial flow impellers are preferred for mixing AA and HMD because these impellers tend to prevent the solid particles from settling at the bottom of reactor **140**. In other embodiments, the impeller may be a flat-blade radial turbine having multiple blades equally spaced around a disk. In total agitator shaft **158** may have between 2 and 10 impellers, e.g., between 2 and 4 impellers. Blades **160** on impeller **159** may be straight, curved, concave, convex, angled, or pitched. The number of blades **160** may vary between 2 and 20, e.g., between 2 and 10. If needed, blades **160** may also have stabilizers (not shown) or scrapers (not shown).

[0071] As shown in **FIG. 4**, there is shown a triple-pitch turbine assembly **161**. Agitator shaft **158** comprises at least one upper pitch blade turbine **162** and at least one lower pitch blade turbine **163**. In triple-pitch turbine assembly **161**, the angled faces **164** of the upper pitch blade turbine **162** are preferably offset from the angled faces **164'** of the lower pitch blade turbine **163**.

[0072] Multiple agitator shafts with different types of impellers, such as spirals and anchors, may also be used. Also, side mounted agitator shafts may be used, in particular those with marine propellers.

[0073] Returning to FIG. 3, agitator shaft 158 is driven by an external motor 165 that may mix the liquid between 50 and 500 rpm, e.g., between 50 and 300 rpm. Agitator shaft 158 may be removably mounted to the motor drive shaft 166 at connector 167. The speed of the motion may vary, but generally the speed should be sufficient to maintain the entire surface area of solid particles in contact with the liquid phase ensuring maximum availability of the interfacial area for mass transfer in a solid-liquid.

[0074] Reactor 140 may also comprise one or more baffles 168 for mixing and to prevent formation of dead zones. The number of baffles 168 may vary between 2 and 20, e.g., between 2 and 10, and are evenly spaced around the perimeter of reactor 140. Baffles 168 may be mounted on the internal wall of reactor 140. Generally, vertical baffles 168 are used, but curved baffles may also be used. Baffles 168 may extend above the liquid level 156 in reactor 140.

[0075] In one embodiment, reactor 140 comprises a vent for removing off-gas through line 135 and a recovery column 131 for returning condensable HMD to reactor 140. Water 132 may be fed to recovery column 131 and recovered in bottoms 133 of recovery column 131. Water 132 is fed at a minimum rate to maintain efficiency of recovery column 131. The amount of water 132 is calculated to maintain the target salt concentration and the other feeds of water may be adjusted. Vent gases 134 may be condensed to recover any water and monomer off-gas and may be returned via line 133. Non-condensable gases, including nitrogen and air may be removed as an off-gas stream 135. When recovery column 131 is a vent condenser, recovery column 131 may be used to recover off-gas and remove non-condensable gases.

Nylon Salt Solution Storage

[0076] As shown in FIG. 3, as the nylon salt solution is formed, it is fed to a storage tank 195 where the nylon salt solution may be held until needed for polymerization. In some embodiments, storage tank 195 may comprise a recirculation loop 193 to circulate nylon salt solution. An internal jet mixer 194 may be used to maintain circulation within storage tank 195. In one embodiment, internal jet mixers 194 may be located between 0.3 and 1.5 meters from the bottom of storage tank 195, preferably between 0.5 and 1 meter. Additionally, in some

embodiments, at least a portion of the nylon salt solution may be returned to reactor **140** to prevent process lines from freezing and/or to correct the nylon salt solution in the case of a system upset or a desired change in the target pH and/or target salt solution. Any unused nylon salt solution from the polymerization process **200** may also be returned to storage tank **195**.

[0077] Storage tank **195** may be constructed of corrosion-resistant material such as an austenitic stainless steel, for example, 304, 304L, 316 and 316L, or other suitable corrosion-resistant material to provide an economically viable balance between equipment longevity and capital cost. Storage tank **195** may comprise one or more storage tanks, depending on the storage tank size and volume of nylon salt solution to be stored. In some embodiments, the nylon salt solution is stored in at least two storage tanks, e.g., at least three storage tanks, at least four storage tanks, or at least five storage tanks. Storage tank **195** may be maintained at a temperature above the solution freezing point, such as at a temperature between 60°C and 110°C. For nylon salt solutions having a salt concentration between 60 wt.% and 65 wt.%, the temperature may be maintained between 100°C and 110°C. There may be an internal heater **196** in the storage tank. In addition, the recirculation loop may have one or more heaters **197** for supplying heat to the storage tank. For example, the storage tank may have a capacity for up to a 5-day inventory of nylon salt solution, and more preferably up to a 3-day inventory. The storage tank may be maintained under a nitrogen atmosphere at atmospheric pressure or slightly above atmospheric pressure.

[0078] In some embodiments, before entering storage tank **195**, the nylon salt solution may be filtered to remove impurities. The nylon salt solution may be filtered through at least one filter **190**, e.g., at least two filters or at least three filters. The filters **190** may be arranged in series or in parallel. Suitable filters may include membrane filters comprising polypropylene, cellulose, cotton and/or fiberglass. In some embodiments, the filters may have pore sizes between 1 and 20 microns, e.g., between 2 and 10 microns. The filter may also be an ultrafiltration filter, a microfiltration unit, a nanofiltration filter, or an activated carbon filter.

Trim HMD

[0079] As indicated in the above description, HMD used to form the nylon salt solution is introduced in different portions in two locations in the process, a main HMD and a trim HMD. To allow for the use of a single continuous stirred tank reactor and to form a uniform nylon salt

solution, HMD is not added once the nylon salt solution is withdrawn from the reactor **140** into conduit **144**, and subsequently to storage tank **195**. Control of variance from the target specifications, e.g., target pH, may further be refined by including the trim HMD via line **107** as shown in **FIG. 5** at junction **142**. The trim HMD is generally the smallest portion of HMD added and is used as a fine tuning control for the pH of the nylon salt solution, due to the use of a smaller valve that has higher control of small changes in flow as compared to the main HMD feed. Adjusting the feed rate or flow rate of the main HMD is a less preferred method for controlling pH of the nylon salt solution because of the lag between the adjustment of the main HMD and the pH measurement. In addition, because the trim HMD is the smallest portion of HMD added to the CSTR, the trim HMD allows for more accurate adjustments of the pH of the nylon salt solution and the pH analyzer provides near instantaneous feedback. Trim HMD is added upstream of the pH measurement to reduce the delay in measuring the pH effect of adding the trim HMD. As the trim HMD is adjusted, the water feed rate may also be adjusted to control the concentration of solids in the nylon salt solution. Such adjustments may be set by controllers and may be monitored by refractometers in sample line **153**, described herein.

[0080] Trim HMD **107** may be combined with the nylon salt solution before it enters conduit **144**. Without being bound by theory, it is believed that trim HMD **107** may react with any remaining free AA in the nylon salt solution. Additionally, adding trim HMD **107** may be used to adjust the pH of the nylon salt solution as described above.

[0081] In one embodiment, the present invention is directed to metering AA powder **102**, based on weight, from a loss-in-weight feeder **110** to a feeding conduit that transfers the metered AA powder feed **139** at a low variability feed rate into a continuous stirred tank reactor **140**; separately introducing an aqueous solution **106** comprising a first portion of HMD **104** and water **103** to continuous stirred tank reactor **140** to form a nylon salt solution; and introducing a second portion of HMD, e.g., trim HMD via line **107** to the nylon salt solution. Trim HMD **107** may be added to nylon salt solution in the recirculation loop **141** at junction **142**. Trim HMD **107** is continuously fed to recirculation loop **141** at a feed rate that allows the flow of trim HMD **107** to be within the midrange flow through the valve, e.g., from 20 to 60%, from 40 to 50%, or about 50%. Midrange flow refers to maintaining a continuous flow through the valve to prevent a loss of control.

[0082] To achieve a target pH with low variability, the process involves providing a constant feed rate of AA powder **102** using loss-in-weight feeder **110**, and adjusting the feed rates of HMD and water in response to process controls. Advantageously, high production rates may be achieved from a continuous process. When changing salt production rates, the HMD feed rate is adjusted proportionately as the AA feed rate is changed in discrete intervals. The feed rate of HMD may be adjusted by either changing the feed rate of the main HMD fed or the feed rate of the trim HMD. In one preferred embodiment, the feed rate of trim HMD **107** may be adjusted and the feed rate of HMD **104** or the feed rate of the aqueous HMD solution feed **106** may be constant for a given salt production rate. In alternative embodiments, the feed rate of trim HMD **107** may be set at a constant rate and the feed rate of HMD **104** or the feed rate of the aqueous HMD solution feed **106** may be adjusted, if necessary, to achieve the target pH and/or salt concentration. In still other embodiments, the feed rate of both HMD **104** and trim HMD **107** or the feed rate of the aqueous HMD solution feed **106** may be adjusted to achieve the target pH and/or salt concentration.

[0083] Trim HMD **107** may have the same HMD source as HMD **104**. HMD **104** may comprise between 80% and 99% of the total HMD in the nylon salt solution, e.g., between 90% and 99%. Trim HMD **107** may comprise between 1 and 20% of the total HMD in the nylon salt solution, e.g., between 1% and 10%. The ratio of HMD **104** and trim HMD **107** may be adjusted depending on the target pH and target salt concentration. As discussed herein, the ratio of HMD **104** and trim HMD **107** may be set by the model for the total HMD feed rate.

[0084] The HMD may be supplied as neat HMD, e.g., comprising at least 99.5 wt.% HMD, e.g., 100% HMD and no water, or may be supplied in an aqueous solution comprising between 80 wt.% and 99.5 wt.% HMD. Trim HMD **107** is fed to the nylon salt solution as neat HMD or as an aqueous solution of HMD. When trim HMD **107** is an aqueous solution of HMD, the aqueous solution of trim HMD **107** may comprise between 50 wt.% and 99 wt.% HMD, e.g., between 60 wt.% and 95 wt.% HMD or between 70 wt.% and 90 wt.% HMD. As with the aqueous solution for HMD **104**, the amount of water may be adjusted based on the source of HMD and the target salt concentration of the nylon salt solution. Advantageously, the HMD concentration of trim HMD **107** is from 90 wt.% to 100 wt.% to enhance effect on pH control while minimizing the effect of trim HMD **107** in salt concentration control.

[0085] Trim HMD **107** is added to the nylon salt solution in the recirculation loop upstream of pumps 149 and sample line 153. The pH of the nylon salt solution in recirculation loop **141** may be measured in sample line **153**, using analyzer **154**, after trim HMD **107** has been added. This allows a small delay between adjusting pH through the feed rate of trim HMD **107** and pH measurement. No additional AA is added to recirculation loop **141**. No HMD, other than trim HMD **107** is added to recirculation loop **141**. Trim HMD **107** is added upstream of pH measurement to allow for a pH measurement that includes trim HMD **107**.

[0086] Unlike prior process shown in U.S. Pub. No. 2010/0168375 and U.S. Pat. No. 4,233,234, trim HMD is not added after the pH measurement. Adding HMD after the pH measurement creates a large delay in measuring the effect of the added HMD on the pH because the added HMD must pass through the reactor before being measured. Thus, adding HMD in such a manner may undershoot or overshoot the target pH which causes these processes to operate inefficiently by constantly chasing the target pH. Advantageously, the present invention adds trim HMD upstream of the pH measurement so that the effect of the trim HMD is accounted for with little delay and avoids the problems of undershooting or overshooting the target pH. In addition, the present invention constantly feeds trim HMD **107** because the valve is maintained at a midrange flow.

Process Controls

[0087] As described herein, in a continuous process for producing a polyamide salt solution, e.g., a nylon salt solution, in prior art processes, there may be variability in target specifications in the nylon salt solution, including pH and salt concentration. This variability in the target specifications may be caused, at least in part, by unpredictable and fluctuating AA powder feed rate. Such unpredictability and fluctuations make controlling the process difficult, because the process must be constantly monitored and adjusted downstream of the initial reactor prior to storage. Thus, a single reactor operating continuously could not efficiently account for the unpredictable and fluctuating AA powder feed rate. Conventionally, in order to account for this unpredictability and fluctuation, numerous reactors, mixers, and multiple monomer feed locations, in particular for adding HMD, are used to produce the nylon salt solution with target specifications. Using a single continuous stirred tank reactor according to the present invention removes the ability to adjust the nylon salt solution in numerous reactors. However, by reducing

the unpredictability and fluctuation in the AA powder feed rate by using a loss-in-weight feeder to achieve an AA powder feed rate that varies by less than $\pm 5\%$, the present invention can take advantage of feed forward controls based on a model, with or without feedback, to achieve a nylon salt solution with a target pH and salt concentration.

Feed Forward Controls

[0088] Prior to beginning the continuous process for producing the nylon salt solution, a reaction model may be prepared based on a desired nylon salt solution production rate. Based on this production rate, an AA powder feed rate is set, and then target pH and target salt concentration are set. The HMD feed rate and water feed rate are then stoichiometrically calculated to achieve a target pH and target salt concentration. The HMD feed rate includes the main HMD and trim HMD. The water feed rate includes all sources of water fed to the reactor **140**. It is understood that a target pH reflects a target molar ratio of AA to HMD. In further embodiments, additional features may be added to the model, including but not limited to reaction temperature and reaction pressure. This model is used to set feed forward controls of feed rates for the HMD and/or water to the continuous stirred tank reactor.

[0089] In some aspects, the model is prepared by inputting the feed rate of AA powder provided by the loss-in-weight feeder described herein. For a given production rate, the feed rate of AA should be constant. The loss-in-weight feeder may contain discrete controls, as described herein, to produce an AA powder feed rate with low variability. The AA powder feed rate from the loss-in-weight feeder may be provided continuously, semi-continuously, or at discrete intervals, e.g., every 5 minutes, every 30 minutes, or hourly, to the model. In other aspects, because of the low variability of the AA powder feed rate, once the feed rate of the AA powder is set, the model may set an HMD feed rate and a water feed rate. These feed rates are set by the model to achieve a target pH and a target salt concentration.

[0090] The model may be dynamic and may be adjusted by feedback signals from on-line and off-line analyzers. For example, if a change in production rate, pH or salt concentration is desired, the model may be adjusted. The model may be stored in memory of a controller, such as a programmable logic controller (PLC) controller, distributed control system (DCS) controller or a proportional-integral-derivative (PID) controller. In one embodiment, a PID controller, with

feedback signals, may be used to account for errors in the model calculations and flow measurements.

[0091] Feed forward controls, by themselves, have previously been impractical to form a nylon salt solution with low variability from target specifications due to the inability to accurately predict AA powder feed rate with the use of volumetric feeders. This is due, at least in part, to variation in AA powder feed rates caused by the use of volumetric feeders. Because of the variability of the AA powder feed, a model could not be generated to control the AA and HMD ratio. Consequently, these conventional processes could use feedback controls, thus requiring frequent adjustments, or would be a batch process. However, when the AA powder is metered on a weight basis to a continuous stirred tank reactor, feed forward controls are sufficient to continuously produce a nylon salt solution with low variability from target specifications.

[0092] Thus, in one embodiment, the present invention is directed to a process for controlling the continuous preparation of a nylon salt solution comprising: generating a model for setting a target feed rate of dicarboxylic acid powder to produce the nylon salt solution having a target pH; controlling feed rate variability of the dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder at the target feed rate into a single continuous stirred tank reactor; separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor, wherein the first and/or the second feed rates are based on the model; and continuously withdrawing the nylon salt solution from the single continuous stirred tank reactor directly into a storage tank, wherein the withdrawn nylon salt solution has a pH less than ± 0.04 of the target pH.

[0093] To further exemplify the process control schemes according to the present invention, a schematic diagram is shown in **FIG. 6**. For simplicity **FIG. 6** excludes various pumps, recirculation loops, and heaters. Several flow meters, such as coriolis mass flow meters, positive displacement flow meters, electromagnetic flow meters, and turbine flow meters, are shown in **FIG. 6** for measuring flow through the system. In some embodiments, the flow meters may also be capable of measuring temperature and/or density. The outputs of the flow meters may be inputted to controller **113** on a continuous or regular basis. Preferably, there is at least one flow meter upstream of each of the flow meter valves. In some embodiments, the flow meters and

flow meter valves may be integral and provided together in a compact package. Although one controller is shown, in some embodiments there may be a plurality of controllers. As shown in **FIG. 6**, the AA powder is fed to loss-in-weight feeder **110** via line **102** to produce a metered AA powder feed **139**. Controller **113** sends a signal **211** to rotating auger **123**. The signals may be wireless signals. Using the model, the model for the feed forward feed rates for the HMD and water may be stored in controller **113**. Loss-in-weight feeder **110** adjusts for the variability in AA powder, as described above, to provide a metered AA powder feed **139** having low variability from a target feed rate. For example, loss-in-weight feeder **110** may use a feedback loop from weight measuring subsystem **121** to adjust the speed of rotary auger **123**.

[0094] Controller **113** sends a feed forward signal **213** to flow meter valve **214** to regulate the flow of water **103** into reactor **140** via line **106**. Similarly, controller **113** sends a feed forward signal **215** to flow meter valve **216** to regulate the flow of HMD **104** into reactor **140** via line **106**. This feed forward signal is set by the model to achieve the target pH and target salt concentration. In another embodiment, controller **113** sends a feed forward signal (not shown) to a flow meter valve (not shown) to regulate the feed rate of HMD aqueous solution **106** into reactor **140**. Because the feed forward signals **213** and **215** are used for the HMD and water to reactor **140**, it is not necessary to take any on-line or off-line measurements of aqueous HMD solution **106**. In addition, there is a feed forward signal **217** to flow meter valve **218** to regulate the flow of trim HMD **107** into recirculation loop **141**. The model may determine the relative amounts of HMD fed through the main HMD **104** and trim HMD **107**. Feed forward signal **217** is adjusted to ensure that there is a midrange output flow to flow meter valve **217** of trim HMD **107**. In one embodiment, the model may establish a feed rate that is transmitted by feed forward signal **217** to flow meter valve **218** to ensure that a constant flow, i.e. midrange flow, is maintained from trim HMD **107**.

Secondary Process Controls

[0095] In addition to using feed forward controls based on modeling, as shown in **FIG. 6**, the process controls may include feedback signals as secondary process controls to achieve the target pH and target salt concentration. These feedback signals may be measurements taken from flow meters and on-line analyzer **154** that are used to adjust the HMD and water feeds, preferably trim

HMD and water feeds. On-line analyzers **154** may include pH probes, refractometers, and combinations thereof. The pH probes and refractometers may be in series or in parallel

[0096] As described herein, when metering the AA powder based on weight, the feed rate of the AA powder may have low variability. This low variability provides a reliable feed rate of AA powder, improving the ability to achieve the target pH and target salt concentration, and to adjust the feed rates of HMD and water based on the feedback signals. Thus, in one embodiment, the present invention is directed to a process for controlling the continuous production of a nylon salt solution comprising: generating a model for setting a target feed rate of dicarboxylic acid powder to produce a nylon salt solution having a target pH; controlling feed rate variability of dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH; continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor; detecting a change in pH of the nylon salt solution using an on-line pH measurement of the nylon salt solution downstream of the trim diamine introduction; and adjusting the third feed rate in response to the change in pH to produce the nylon salt solution having a pH that varies by less than ± 0.04 from the target pH.

[0097] As shown in **FIG. 7**, the process generates feedback signals using an on-line analyzer **154**, e.g., on-line pH meter **154** to measure the pH of the nylon salt solution in recirculation loop **141**. To facilitate the on-line measurement of the pH of the nylon solution, the nylon salt solution is continuously withdrawn from the reactor and at least a portion of the nylon salt solution is directed to recirculation loop **141** and to sample line **153**. Recirculation loop **141** may comprise a flow meter (not shown) and flow meter valve. In another embodiment, recirculation loop **141** may comprise a pressure controller (not shown) to control flow of the nylon salt solution. Preferably, the flow of nylon salt solution through recirculation loop **141** is constant. Sample line **153** comprises a means for pH measurement, e.g., a pH meter and/or a means for salt concentration measurement, e.g., a refractometer. In one embodiment, the pH of the at least a portion of the nylon salt solution is measured at reactor conditions, without any dilution or cooling. The at least a portion of the nylon salt solution is then returned to reactor **140**, either

directly or through vent condenser **131**. When the at least a portion of the nylon salt solution is returned to the reactor through vent condenser **131**, the nylon salt solution may replace water fed to the vent condenser. Sample line **153** may also comprise a cooler (not shown) to cool the nylon salt solution and a temperature sensor (not shown) to measure the temperature prior to pH measurement. In some embodiments, the nylon salt solution is cooled to a target temperature prior to pH measurement. This target temperature may be a target within the range between 5°C and 10°C cooler than the nylon salt solution as it exits reactor **140**. The temperature may vary by less than $\pm 1^\circ\text{C}$ from the target temperature, e.g., by less than $\pm 0.5^\circ\text{C}$. There may be a temperature sensor (not shown) to monitor the temperature of the nylon salt solution upstream of the pH measurement.

[0098] On-line pH meter **154** then provides output **226** to controller **113**. This output **226** transmits the pH value measured in on-line pH meter **154** to controller **113**. On-line pH meter **154** is used to determine the variability of the pH of the nylon salt solution during a continuous process. In other words, due to varying conditions, on-line pH meter **154** may measure a pH that may be different than the target pH, but controller **113** adjusts monomer feeds when the measured pH has variations. In preferred embodiments, the pH of the nylon salt solution varies by less than ± 0.04 , e.g., less than ± 0.03 or less than ± 0.015 . Because of drift in on-line pH meter measurement values, the on-line pH meter is used to measure variability of pH instead of an absolute pH value. This is due at least in part to the feed forward controls which allow for a target pH to be set. By using the on-line pH meter to determine if the pH varies, changes in the production process may be detected. Using the secondary controls, a change in pH may cause a corresponding adjustment of at least one of the feed rates sent via signal lines **215** and **217** to flow meter valves **216** and **218** respectively. To provide a responsive pH adjustment, a signal is sent via line **217** to valve **218** to adjust the trim HMD **107**. The amount of adjustment made to trim HMD **107** may be accounted for by a corresponding change to the main HMD **104** by flow meter valve **216**. This adjustment is responsive and should be able to revert to the feed rates set by the feed forward controls once pH variation is not shown. These adjustments to trim HMD **107** may also affect the salt concentration of the nylon salt solution. Such salt concentration changes may be controlled by adjusting the water via signal **213** through flow meter valve **214**.

[0099] Because the process described to form the nylon salt solution is continuous, the pH measurements in on-line pH meter **154** may be obtained in real time (e.g., continuously) or in near real time. In some embodiments, the pH measurement is taken every 60 minutes, e.g., every 45 minutes, every 30 minutes, every 15 minutes, or every 5 minutes. The pH meter may have accuracy to within ± 0.05 , e.g., ± 0.02 .

[0100] The process may also further comprise measuring the salt concentration in the nylon salt solution using a refractometer in addition to on-line pH meter **154**, and adjusting the water feed rates. In one embodiment, the water feed rates may be adjusted by the water feed to recovery column **131**. The salt concentration may also be adjusted by adding or removing water from the nylon salt solution downstream of the reactor.

[0101] Depending on the adjustment needed based on the feedback, the secondary controls may also be used by the model to adjust the main HMD and water. This is particularly advantageous when there is a pH trend that causes a long-term adjustment of the trim HMD **107**.

[0102] In addition to the feedback from on-line pH meter **154**, each flow meter may provide information, or mass flow rates, to controller **113**. As shown in **FIG. 7**, each flow meter valve is associated with a flow meter that preferably is capable of measuring mass flow. Flow meter **214'** provides information to controller **113** via line **213'**. Flow meter **216'** provides feedback to controller **113** via line **215'**. Flow meter **218'** provides feedback to controller **113** via line **217'**. This information from the flow meters may be used to maintain overall production rates.

[0103] Prior art processes using pH probes to measure the pH of a nylon salt solution have been disclosed. *See* U.S. Pat. No. 4,233,234 and U.S. Pub. No. 2010/0168375. However, each of these prior art processes measure the pH of the nylon salt solution and then add additional diamine and/or acid to adjust the pH. The effect of the additional diamine and/or acid is not determined until the additional diamine and/or acid is blended into the reactor and withdrawn again for measurement. This method results in “chasing” the pH and creates an unresponsive process control that may overshoot or undershoot the target pH.

[0104] In the present invention, as shown in **FIGS. 3 and 5, 6, 7, 8 and 9**, trim HMD **107** is preferably fed upstream of the on-line pH meter. Thus, the HMD in trim HMD **107** is combined with the nylon salt solution in the reactor recirculation loop and the pH of the nylon salt solution is measured prior to being recirculated through reactor **140**.

Secondary Process Controls With On-Line Laboratory Measurement

[0105] As stated above, the pH measurement from the secondary process control is not necessarily reflective of the target pH, but rather is used to account for pH variations. To improve the sensitivity of the pH measurement, the secondary process controls may also involve measuring the pH of the nylon salt solution under laboratory controls. Without being bound by theory, measuring the pH of the nylon salt solution under laboratory conditions improves the accuracy of the measurement due to increased sensitivity of pH measurements near the inflection point under conditions of reduced concentration and temperature. This may allow detection of small pH changes that might not be noticed under reaction conditions. For purposes of the present invention, laboratory conditions refer to measuring the nylon salt solution sample at a temperature between 15°C and 40°C, e.g., between 20°C and 35°C or at 25°C, $\pm 0.2^\circ\text{C}$. The nylon salt solution sample measured under laboratory conditions may have a salt concentration between 8 and 12%, e.g., 9.5%. This pH measurement under laboratory conditions is made on-line by diluting and cooling the nylon salt solution in sample line **153**.

[0106] Thus, in one example, the present invention is directed to a process for controlling the continuous production of a nylon salt solution comprising: generating a model for setting a target feed rate of dicarboxylic acid powder to produce a nylon salt solution have a target pH; controlling feed rate variability of the dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH; continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor; obtaining a sample portion of the nylon salt solution downstream of the trim diamine introduction; diluting and cooling the sample portion to form a diluted nylon salt solution having a concentration between 5% and 15% and a temperature between 15°C and 40°C; detecting a change in pH of the diluted nylon salt solution using an on-line pH measurement of the nylon salt solution downstream of the trim diamine introduction; and adjusting the third feed rate in response to the change in pH to produce the nylon salt solution having a pH that varies by less than ± 0.04 from the target pH.

[0107] As shown in **FIG. 9**, to facilitate the on-line measurement of the pH of the nylon solution at laboratory conditions, the nylon salt solution is continuously withdrawn from the reactor and at least a portion of the nylon salt solution, e.g., less than 1%, is directed to recirculation loop **141** and to sample line **153**. Sample line **153** comprises a means for pH measurement under laboratory conditions. Sample line **153** may also comprise a cooler (not shown) to cool the nylon salt solution. In other embodiments, this cooler may be omitted. The temperature and concentration of the nylon salt solution in sample line **153** may be adjusted by adding water via line **220**. This water is a small part of the total water feed rate that is accounted by the model. The water is added in an amount and at a temperature sufficient to reach the desired temperature and strength of diluted nylon salt solution sample for pH measurement. Further cooling of the diluted sample may be included. The pH of the at least a portion of the nylon salt solution is taken at laboratory conditions and the at least a portion of the nylon salt solution is then returned to reactor **140** as described herein. On-line pH meter **154** then provides output **226** to controller **113**.

[0108] As described above, on-line pH meter **154** is used to measure variability in pH of the nylon salt solution. In preferred embodiments, the pH of the nylon salt solution varies by less than ± 0.04 , e.g., less than ± 0.03 or less than ± 0.015 . Similar to the pH measurements at reaction conditions, because of drift in on-line pH meter measurement values, the on-line pH meter under laboratory conditions is used to measure variability of pH instead of the target pH. This is due at least in part to the feed forward controls which allow for a target pH to be set. By using the on-line pH meter to determine if the pH varies, changes in the production process may be detected. Similar to the secondary process controls, the feed rates may be adjusted by sending a signal to lines **215** and **217** to flow meter valves **216** and **218**. These adjustments may also affect the salt concentration of the nylon salt solution. Such salt concentration changes may be controlled by adjusting the water via signal **213** to flow meter valve **214**.

[0109] Because the process described to form the nylon salt solution is continuous, the pH measurements in on-line pH meter **154** may be obtained in real time (e.g., continuously) or in near real time. In some embodiments, the pH measurement is taken every 60 minutes, e.g., every 45 minutes, every 30 minutes, every 15 minutes, or every 5 minutes. The pH measurement means should have accuracy to ± 0.05 , e.g., ± 0.03 or ± 0.01 .

Tertiary Process Controls

[0110] Although the use of feed forward controls and feedback signals as shown in **FIGS. 6, 7** and **9** may assist in reducing the variability of the nylon salt solution specifications, further analysis, particularly off-line pH analysis conducted at laboratory conditions, may be used to detect nylon salt solution uniformity. These off-line process controls at laboratory conditions, referred to as tertiary process controls, may include pH and/or salt concentration measurements. In one embodiment, the pH of the nylon salt solution may be measured off-line at laboratory conditions to determine whether the target pH is being achieved. The off-line pH measurements may also detect any instrument problems or biasing that may be adjusted. In another embodiment, the pH of the nylon salt solution measured off-line at laboratory conditions may also be used to adjust signal lines **215** and **217** to flow meter valves **216** and **218**. The off-line pH measurements under laboratory conditions may have a capacity to measure pH within ± 0.01 .

[0111] Thus, in one example, the present invention is directed to a process for controlling the continuous production of a nylon salt solution comprising: generating a model for setting a target feed rate of dicarboxylic acid powder to produce a nylon salt solution having a target pH; controlling feed rate variability of dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH; continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor; removing a sample from the nylon salt solution downstream of the trim diamine introduction for an off-line pH measurement of the nylon salt solution in an aqueous solution at a temperature between 15°C and 40°C; determining a bias of an on-line pH measurement with the off-line pH measurement; detecting a change in pH of the nylon salt solution using the biased on-line pH measurement of the nylon salt solution downstream of the trim diamine introduction; and adjusting the third feed rate in response to the change in pH to produce the nylon salt solution having a pH that varies by less than ± 0.04 from the target pH.

[0112] As shown in **FIG. 8**, the at least a portion of the nylon salt solution in sample line **153** is directed through on-line pH meter **154**, where a pH measurement is obtained and output **226** is

directed to controller **113**. Sample line **153** may also comprise a cooler (not shown) to cool the nylon salt solution prior to passing through pH meter **154**. At least a portion of nylon salt solution in sample line **153** may be removed via line **221** and measured with laboratory pH meter **222**. Water is added to line **221** via line **220** to dilute to a specific concentration and the sample is then cooled to a target temperature, e.g., between 15°C and 40°C or approximately 25°C. In one embodiment, cooling water may be used to dilute and cool the sample. The pH of the nylon salt solution in line **221** is measured and output **226** is sent to controller **113**. The portion of nylon salt solution tested at laboratory conditions may then be combined with tested sample return line **155** and returned to reactor **140** via line **224**. In some embodiments, a portion of the nylon salt solution tested at laboratory conditions may be disposed of outside of process **100** via line **223**.

[0113] To reach the laboratory conditions temperature and concentration, the nylon salt solution sample removed from the recirculation loop may be diluted and cooled with water added via line **220**. A temperature bath may be used to cool the diluted nylon salt solution sample. The sample may be withdrawn on an as-needed basis, such as every 4 to 6 hours, daily or weekly. In the case of a system upset, the sample may be withdrawn more frequently, e.g., hourly. In general, the off-line pH analyzer may be used to account for instrument bias of the on-line analyzer. For example, if the target pH is 7.500, the on-line pH analyzer may report a pH of 7.400 while the off-line analyzer reports a pH of 7.500, indicating an on-line pH analyzer instrument bias. In one aspect, an exponential weighted moving average may be used to automatically bias the on-line analyzers each time an off-line measurement is made. In some aspects, the output of the off-line analyzer is used to correct any bias or drift in the on-line analyzer. In other aspects, the on-line analyzer is not corrected but the drift or bias is monitored by the off-line analyzer. In this aspect, the on-line analyzer is relied upon to determine variation in pH, e.g., outside of a preset acceptable variability.

[0114] In another embodiment, an off-line analyzer may be used to measure the target salt concentration of the nylon salt solution. The off-line salt concentration measurements may also detect any instrument problems or biasing that may be adjusted. Each refractometer may be independently biased when multiple refractometers are used.

Nylon Polymerization

[0115] The nylon salt solution described herein may be directed to polymerization process **200** to form a polyamide, in particular nylon 6,6. The nylon salt solution may be sent directly from the continuous stirred tank reactor **140** to a polymerization process **200** or may first be stored in a storage tank **195** and then sent to polymerization process **200**, as is shown in **FIG. 10**.

[0116] The nylon salt solution of the present invention has a uniform pH that improves the performance of the polyamide polymerization process. The uniform pH of the nylon salt solution provides a reliable starting material to produce various polyamide products. This greatly improves the reliability of the polymer product. In general, the polymerization process comprises evaporating water from the nylon salt solution to concentrate the nylon salt solution and polymerizing the concentrated nylon salt via condensation to form the polyamide product. One or more evaporators **202** may be used. The evaporating of water may be done in a vacuum or under pressure to remove at least 75% of the water in the nylon salt solution, and more preferably at least 95% of the water in the nylon salt solution. The concentrated nylon salt **203** may comprise between 0 and 20 wt.% water. The condensation may be carried out in a batch or continuous process. Depending on the desired end polymer product, additional AA and/or HMD may be added to the polymerization reactor **204**. In some embodiments, additives may be combined with the polyamide product.

[0117] For purposes of the present invention, suitable polyamide products may have at least 85% of the carbon chains are aliphatic between the amide groups.

[0118] The nylon salt solution may be maintained at a temperature above its melt pointing when being transferred from the storage tank **195** to evaporators **202**. This prevents fouling of the lines. In some embodiments, steam captured from evaporators **202** may be used to maintain the temperature. In other embodiments, cooling water that is heated may also be used.

[0119] The polymerization may be in a single stage reactor or multi-stage condensation reactor **204**. Additional monomers, either AA or HMD, but preferably HMD, may be added via line **205** to produce different nylon products **208**. Reactor **204** may comprise an agitator for mixing the nylon salt. Reactor **204** may also be jacketed using a heat transfer medium to regulate the temperature. The condensation reaction in reactor **204** may be carried out in an inert atmosphere and nitrogen may be added to reactor **204**. The temperature of the polymerization may vary

depending on the starting dicarboxylic acid and diamine, but is generally greater than the melt temperature of the nylon salt, and more preferably at least 10°C above the melt temperature. For example, a nylon salt comprising hexamethylene diammonium adipate salt has a melt temperature within the range between 165°C and 190°C. Thus, the condensation reaction may be conducted at a reactor temperature between 165°C and 350°C, e.g., between 190°C and 300°C. The condensation reaction may be carried out at atmospheric pressure or under a pressurized atmosphere. The nylon product **208** is removed from the reactor as a free-flowing solid product.

[0120] Water generated during the condensation reaction may be removed as a vapor stream through reactor vent line **209**. The vapor stream may be condensed and vapor monomers, such as diamine, escaping with the water may be returned to the reactor.

[0121] Subsequent processing may be performed, e.g., extruding, spinning, drawing, or draw-texturing, to produce the polyamide product. The polyamide product may be selected from the group consisting of nylon 4,6; nylon 6,6; nylon 6,9; nylon 6,10; nylon 6,12; nylon 11; and nylon 12. In addition, the polyamide product may a copolymers, such as nylon 6/6,6.

[0122] The following non-limiting examples describe the process of this invention.

EXAMPLES

Example 1

[0123] AA powder is transferred from an unloading system by either bulk bag unloading, lined bulk bag unloading, lined box container unloading, or hopper railcar unloading stations by means of either mechanical (i.e. screw, drag chain) or pneumatic (i.e. pressure air, vacuum air, or closed loop nitrogen) conveyance system(s) to supply vessel.

[0124] The supply vessel transfers AA powder on demand to a loss-in-weight (L-I-W) feeder, and is regulated by a PLC based on selected L-I-W hopper low and high levels. The supply vessel meters AA powder by screw conveyor or rotary feeder at a sufficient loading rate to allow filling of the L-I-W feeder hopper at a maximum interval equal to one-half, and preferably less than one half, the minimum L-I-W discharge time from high to low level of the L-I-W bin, in order to receive feedback of L-I-W feeder feed rate at least 67% of the time.

[0125] The L-I-W feeder system PLC regulates the L-I-W feeder screw speed to maintain feed rate, as measured from the L-I-W feeder hopper load cells, at a feed rate target received from the Distributed Control System (DCS).

[0126] As shown in **FIG. 11** the feed rate variability of adipic acid through a loss-in-weight feeder has a feed rate variability of less than $\pm 5\%$ over a 48 hour period of continuous feeding. As shown in **FIG. 12**, the feed rate variability may be less than $\pm 3\%$ over a 40 hour period. As shown in **FIG. 13**, the feed rate variability may be less than $\pm 1\%$ over an 18 hour period. Using a loss-in-weight feeder for adipic acid results in an improved feed rate variability performance by eliminating the disturbances to the adipic acid feed rate causes by using a volumetric feeder.

Example 2

[0127] A model is prepared for producing a nylon salt solution according to a continuous process. The nylon salt solution comprises water and hexamethylene diammonium adipate salt. The model is set to achieve a 63% salt concentration in the nylon salt solution and to achieve a target pH of 7.500. The feed rate of AA is determined based on the desired production of nylon salt solution. Based on the salt concentration and pH to be achieved, the feed rate for HMD and water are determined. Adipic acid is transferred from a powder unloading system to a loss-in-weight feeder at a low variability as described in Example 1.

[0128] The AA powder from the loss-in-weight feeder is supplied directly to the continuous stirred tank reactor by means of a drop chute that is nitrogen sparged at a rate between 20 and 30 m^3/hour to continuously purge the feeder discharge and chute of vapor generated in the reactor.

[0129] The DCS set point for the loss-in-weight adipic acid feed rate is determined by a DCS model based on salt feed rate from the salt reactor continuous stirred tank reactor and target inventory level for salt storage. The salt feed rate is measured by means of a coriolis mass flow meter and may be adjusted to a target at configurable intervals based on the inventory model in lieu of direct use of adipic acid feed rate. Typically, the adipic feed rate is used directly with loss-in-weight feeder feed rate feedback to DCS.

[0130] HMD solution, having a concentration of 98%, is supplied to an in-line static mixer from a pressure controlled HMD storage recirculating header. Using coriolis mass flow meter measurement with input to the DCS, the DCS, using a feed forward ratio control loop, regulates the HMD feed stream flow rate to the static mixer to accurately control the HMD added to the

continuous stirred tank reactor based on the AA powder feed rates. This primary HMD charge is about 95% of the required HMD charge to the process.

[0131] The set point of the DCS HMD ratio flow controller is adjusted, by means of a feedback loop for trim HMD valve output control, to maintain the output of the trim HMD valve to midrange to ensure the valve is in control range continuously.

[0132] De-ionized water is supplied to the in-line static mixer from a pressure controlled de-ionized water supply header. Using coriolis mass flow meter measurement with input to the DCS, the DCS, using a feed forward ratio control loop, regulates the de-ionized water feed stream flow rate to the static mixer to accurately control the aqueous concentration of AA and HMD in the continuous stirred tank reactor. The de-ionized water feed rate is set within DCS to allow for the required injection rate of de-ionized water to the reactor's vent condenser.

[0133] The in-line static mixer product stream is charged directly to the top of the CSTR within between 0.3 and 1.0 meters of the adipic acid feed chute, the specified location in order to assist in dissolution of the incoming adipic acid feed.

[0134] The pH is continuously measured by redundant pH meters in a filtered, temperature and flow controlled sample recirculation loop supplied by the reactor's recirculation pump. Using the DCS selected pH input of the continuously compared pair of on-line pH measurements, the DCS regulates the feed rate of trim HMD in order to maintain pH to a target set point in DCS. The trim HMD charge is about 5% of the total HMD charged to the process.

[0135] The setpoint of the pH controller is adjusted based on a statistically based algorithm using pH analysis of samples that are taken at discrete intervals downstream of the reactor and which are conditioned to 9.5% concentration and 25°C to achieve maximum sensitivity of acid/amine balance as a function of pH, or by continuous input of pH from an on-line analyzer that continuously dilutes/conditions the reactor's product, or product from a subsequent storage vessel if preferred, to 9.5% concentration and 25°C.

[0136] The trim HMD is injected into the main reactor recirculation loop pump suction in order to achieve fastest response time to the pH meters and to ensure the reactor product is adjusted to target in the shortest time. The pump is used to blend the HMD and reactor salt product in order to ensure that the pH and concentration meters have a homogeneous solution for their respective measurements.

[0137] The CSTR comprises a reactor tank and a recirculation loop. The recirculation loop comprises a first loop that recycles a portion of the nylon salt solution to the reactor and a sample line that directs a portion of the nylon salt solution through a pH meter and then back to the reactor. The sample line may comprise a cooler to cool the nylon salt solution by approximately 5°C to 10°C from the temperature of the nylon salt solution as it exits the reactor. The pH of the cooled nylon salt solution is measured continuously. The cooled nylon salt solution is returned to the reactor. The pH measurements are fed back to the process control computer and the model is adjusted. The model makes adjustments to the HMD feed rate.

[0138] A portion of the nylon salt solution is taken off-line and the pH of this portion of the nylon salt solution is then measured at laboratory conditions. To measure the nylon salt solution at laboratory conditions, the nylon salt solution is diluted with water to a concentration of approximately 9.5%. The diluted nylon salt solution may be cooled by a temperature bath to approximately 25°C. The pH of the nylon salt solution at laboratory conditions is measured and compared to the target pH and to the on-line pH measurement. The model is then adjusted to provide a feed rate of the HMD that ensures low variation from the target pH.

[0139] The reactor's concentration is continuously measured by redundant refractometers in the same filtered, temperature and flow controlled sample recirculation loop supplied by the reactor's recirculation pump. Using the DCS selected concentration input of the continuously compared pair of in-line concentration measurements, the DCS, by means of a feedback loop, adjusts the set point of the DCS de-ionized water ratio flow controller in order to maintain concentration to a target set point.

[0140] The reactor product is continuously fed, by means of level control of the reactor, to salt storage. This transfer includes at least one bank of parallel arranged, cartridge type filter housings, designed for a maximum of 34.5 kPa (5 psig) initial clean pressure drop at maximum instantaneous salt solution transfer rate to storage. Cartridge removal efficiency has a minimum of 10µm absolute rating with use of synthetic fiber depth or pleated membrane cartridges, or a minimum of 1µm nominal rating when wound cotton fiber cartridges are used. Filter selection is based on cartridges with a rating for a minimum of a 110°C operating temperature.

[0141] The nylon salt solution is continuously recirculated through the salt storage tank(s), with preference for use of tank mixing eductors, located between 0.5 and 1 meter from the tank bottom, for more rapid turnover of tank concentrations to maximize blending efficiency.

[0142] For 63% salt concentration, the salt storage tank temperature is regulated between 100°C and 105°C by adjustment of the steam flow rate to the recirculation line heat exchanger. The nylon salt solution in the storage tank has a uniform pH of 7.500 ± 0.0135 .

Example 3

[0143] A nylon salt solution is prepared as in Example 2, except that the on-line pH measurement is conducted at laboratory conditions: a concentration of approximately 9.5% at a temperature of approximately 25°C.

Comparative Example A

[0144] The model and process are followed as in Example 2, except that instead of using a loss-in-weight feeder, a volumetric feeder is used. The model is impractical because of the large variations in AA powder feed. The pH of the nylon salt solution varies by greater than 0.120 from the target pH. The nylon salt solution therefore has varied crystallization temperatures and boiling point temperatures. Thus, the poor control in the pH results in a significantly higher freeze point that would require higher processing temperatures to prevent the risk of crystallization. The poor control also results in boiling the nylon salt solution because of the varied boiling points, thus reducing production of the nylon salt solution.

Comparative Example B

[0145] The model and process are followed as in Example 2, except that a second CSTR is used. The nylon salt solution is withdrawn from the first CSTR and fed to a second CSTR. The pH of the nylon salt solution is measured between the first CSTR and the second CSTR. Depending on the pH and the target pH, additional HMD, and/or water are added to the second CSTR. A nylon salt solution is removed from the second CSTR and the pH is measured. The pH varies by 0.120 pH units from the target pH. An additional CSTR is needed to further adjust the pH of this nylon salt solution, which leads to increased capital and operational costs.

Comparative Example C

[0146] The model and process are followed as in Example 2, except that 100% of the HMD is fed directly to the reactor. The pH of the nylon salt solution varies by greater than 0.1 pH units

from the target pH. The poor control in the pH results in significantly higher freeze point that would require higher processing temperature to prevent risk of crystallization.

[0147] While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those skilled in the art. All publications and references discussed above are incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one skilled in the art. Furthermore, those skilled in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

We claim:

1. A continuous process for producing a nylon salt solution comprising:
 - a) controlling feed rate variability of dicarboxylic acid powder by metering the dicarboxylic acid powder, based on weight, from a loss-in-weight feeder to a feeding conduit that transfers the dicarboxylic acid powder into a single continuous stirred tank reactor and separately introducing diamine at a first feed rate and water at a second feed rate to the single continuous stirred tank reactor to produce the nylon salt solution having a target pH;
 - b) continuously introducing a trim diamine at a third feed rate to a recirculation loop of the single continuous stirred tank reactor, wherein the combination of the diamine introduced by the first feed rate and the trim diamine introduced by the third feed rate is the stoichiometric amount of diamine to achieve the target pH; and
 - c) continuously withdrawing the nylon salt solution from the recirculation loop of the single continuous stirred tank reactor directly into a storage tank, wherein the nylon salt solution has a salt concentration between 50 wt.% and 65 wt.% and wherein the pH varies by less than ± 0.04 from the target pH.
2. The process of claim 1, wherein the target pH is selected from within the range between 7.200 and 7.900.
3. The process of any of the preceding claims, wherein the pH of the nylon salt solution varies by less than ± 0.03 from the target pH.
4. The process of any of the preceding claims, wherein the trim diamine feed is introduced into the recirculation loop upstream of the nylon salt solution withdrawal.
5. The process of any of the preceding claims, wherein the recirculation loop comprises a pump that is selected from the group consisting of vane pumps, piston pumps, flexible member pumps, lobe pumps, gear pumps, centrifugal pumps, circumferential piston pumps, and screw pumps, and the trim diamine feed is introduced upstream of the pump.

6. The process of any of the preceding claims, wherein the recirculation loop comprises one or more on-line analyzers and the trim diamine feed is introduced upstream of the one or more on-line analyzers.
7. The process of any of the preceding claims, wherein the third feed rate is controlled by a valve that is maintained to provide a midrange flow through the valve from 20 to 60%.
8. The process of any of the preceding claims, wherein the diamine introduced by the first feed rate comprises between 80% and 99% of the total diamine fed to the single continuous stirred tank reactor.
9. The process of any of the preceding claims, wherein the trim diamine introduced by the third feed rate comprises between 1% and 20% of the total diamine fed to the single continuous stirred tank reactor.
10. The process of any of the preceding claims, wherein the nylon salt solution comprises between 60 wt.% and 65 wt.% salt concentration.
11. The process of any of the preceding claims, wherein the salt concentration of the nylon salt solution varies by less than $\pm 0.5\%$ from a target salt concentration.
12. The process of any of the preceding claims, wherein the continuous stirred tank reactor is maintained at a temperature between 60°C and 110°C and is maintained at atmospheric pressure in an inert atmosphere.
13. The process of any of the preceding claims, wherein the dicarboxylic acid 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, dodecandioic acid, maleic acid, glutaconic acid, traumatic acid, and muconic acid, 1,2- or 1,3-cyclohexane dicarboxylic acids, 1,2- or 1,3-phenylenediacetic 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.

14. The process of any of the preceding claims, 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 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.

15. The process of any of the preceding claims, wherein the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine and wherein the nylon salt solution comprises hexamethylene diammonium adipate salt.

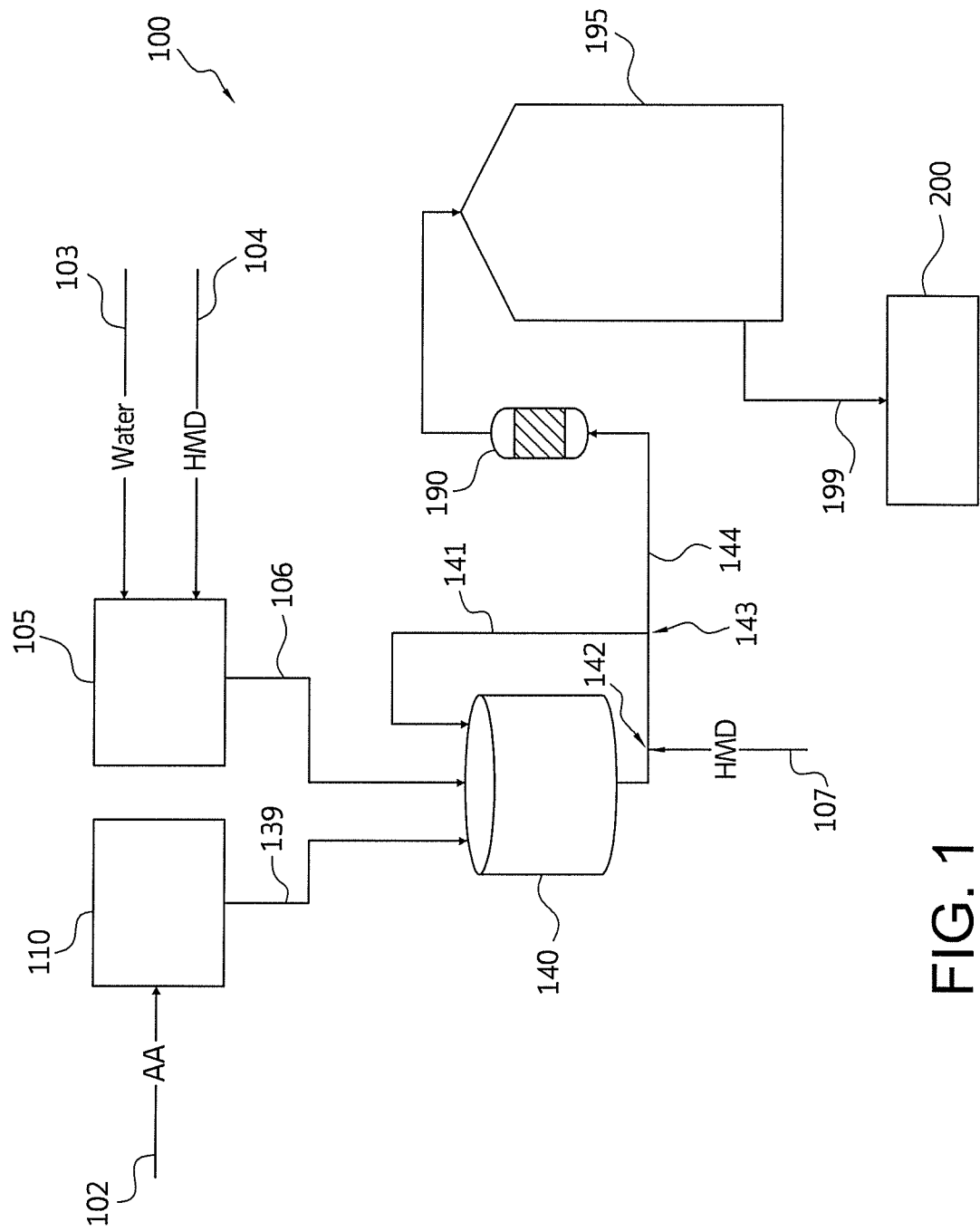


FIG. 1

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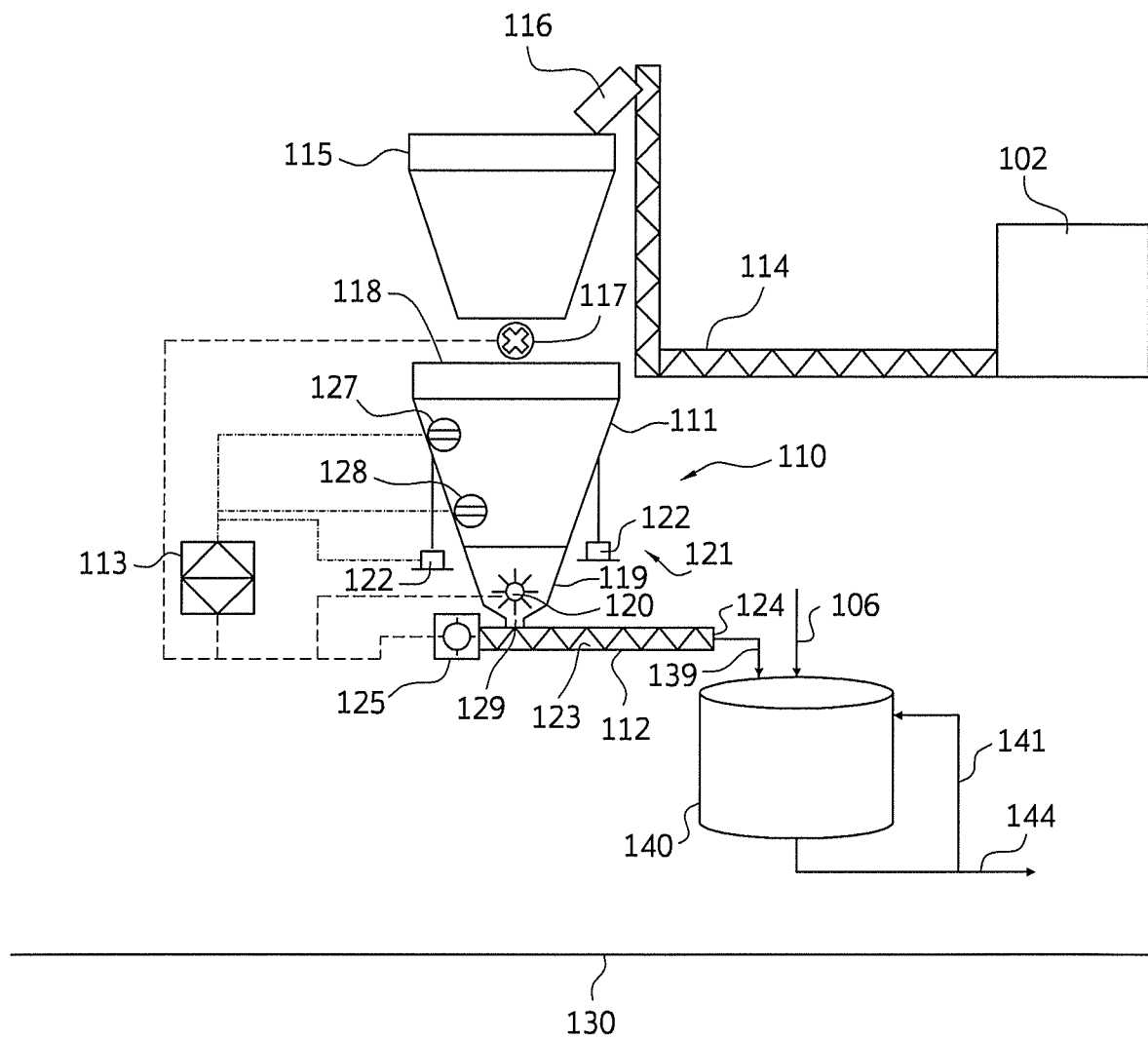
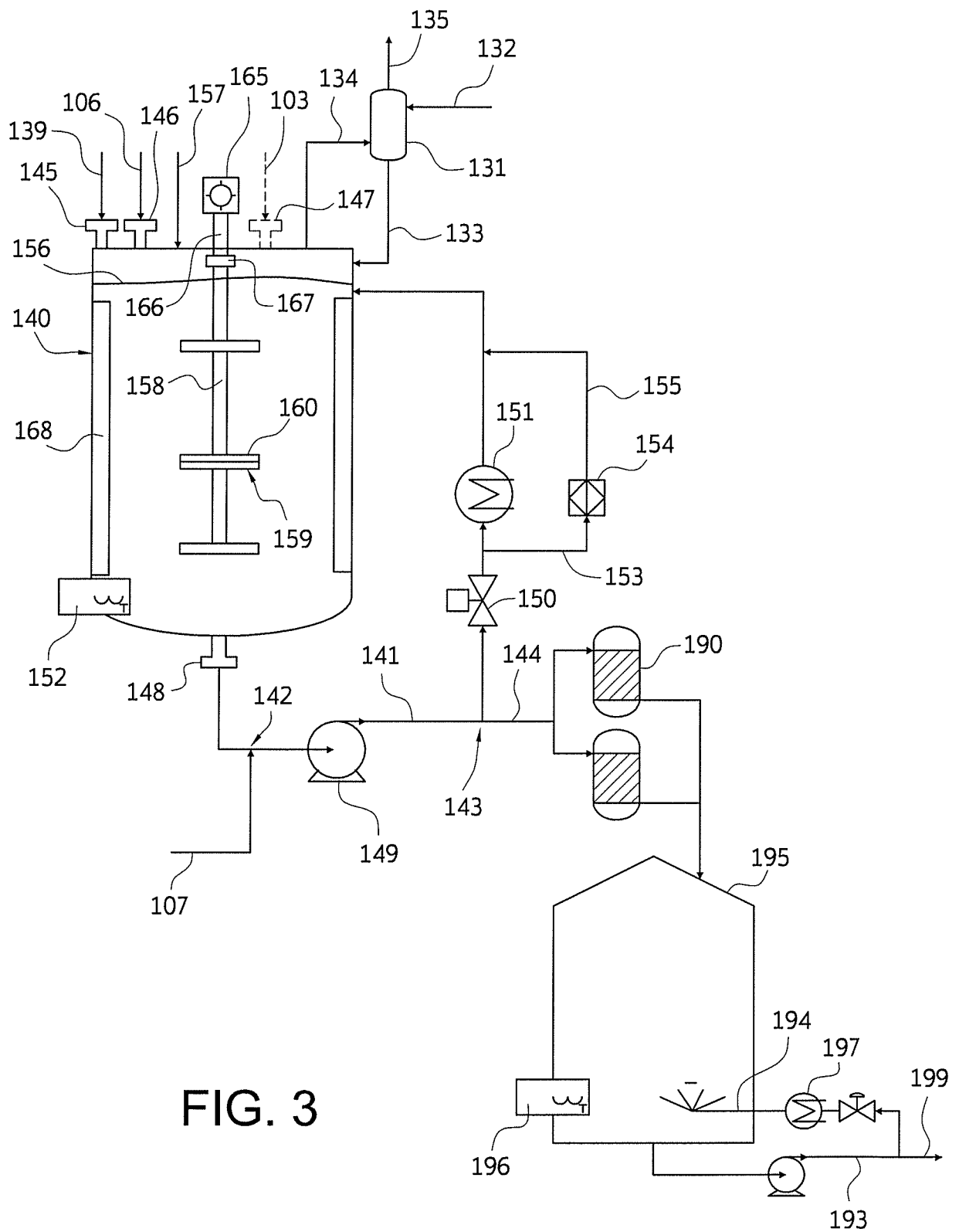


FIG. 2

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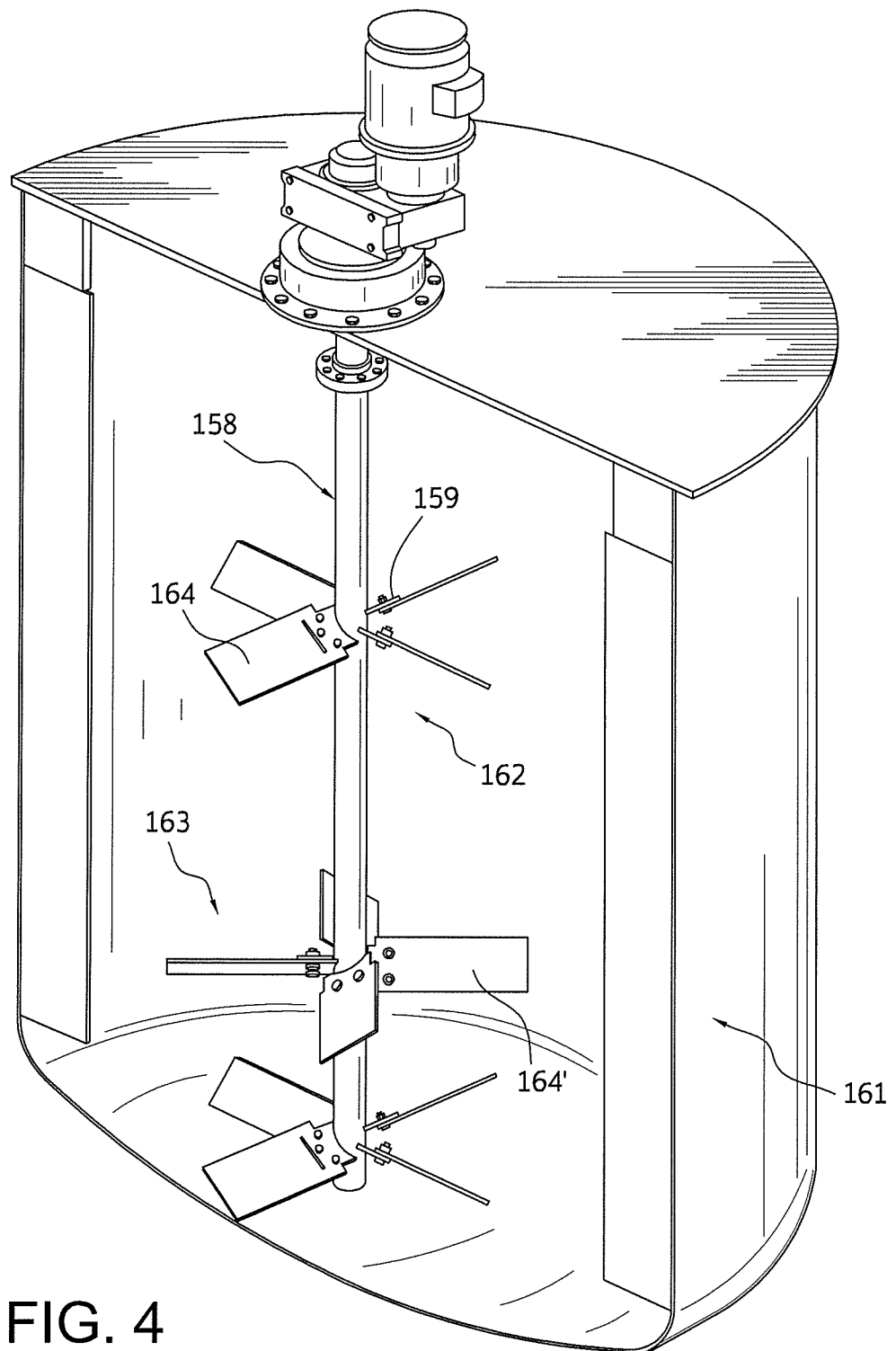


FIG. 4

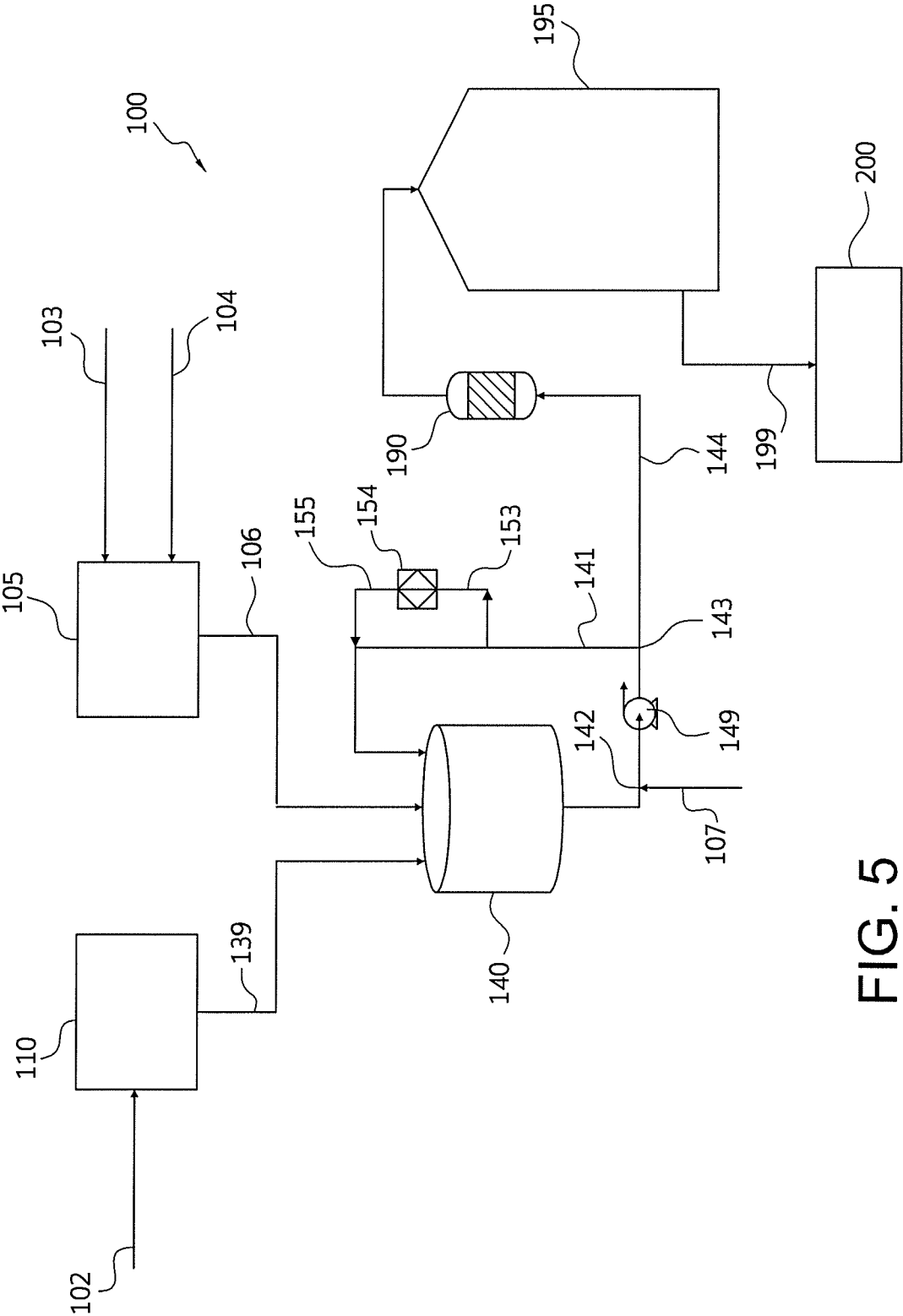


FIG. 5

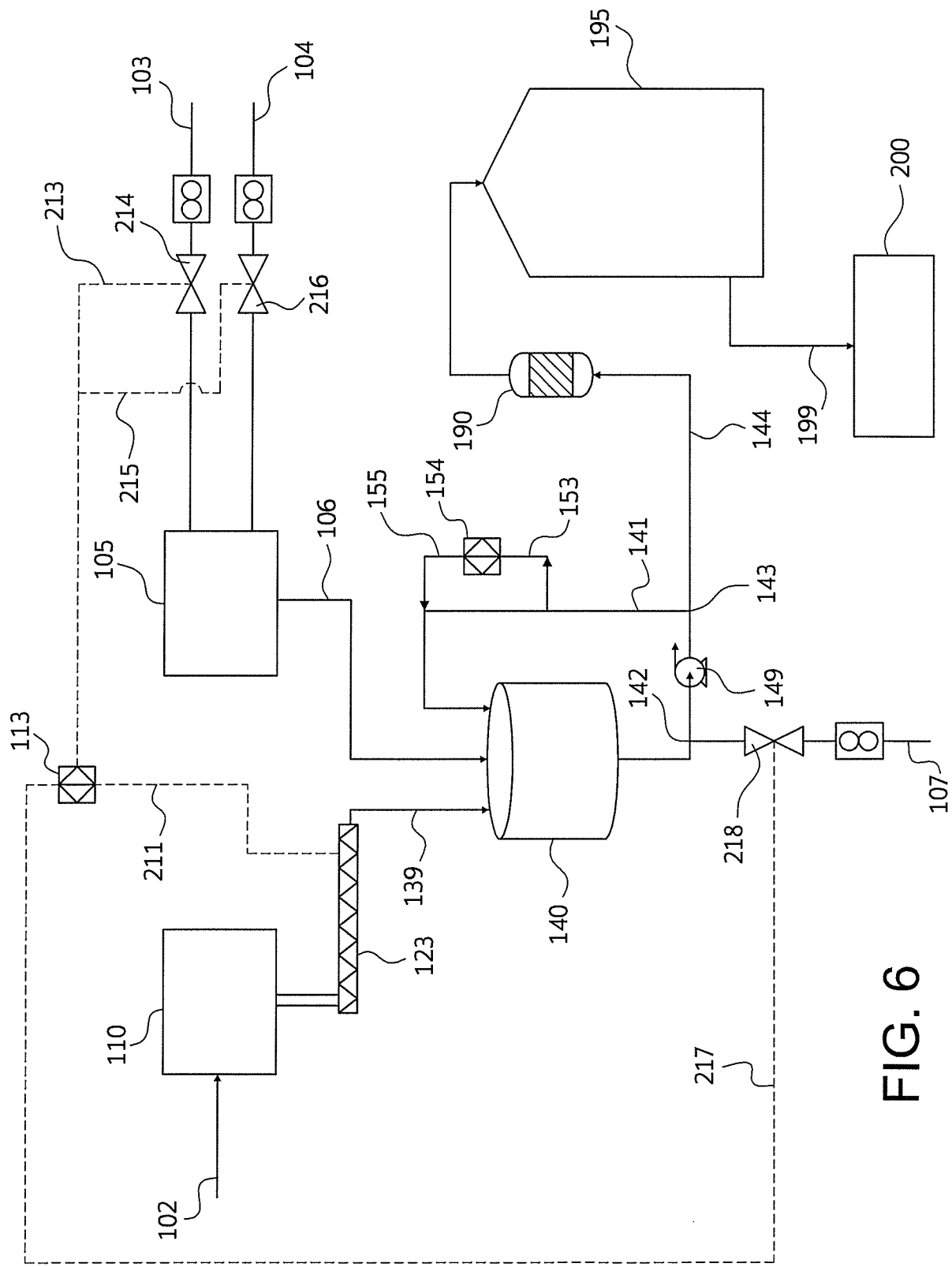


FIG. 6

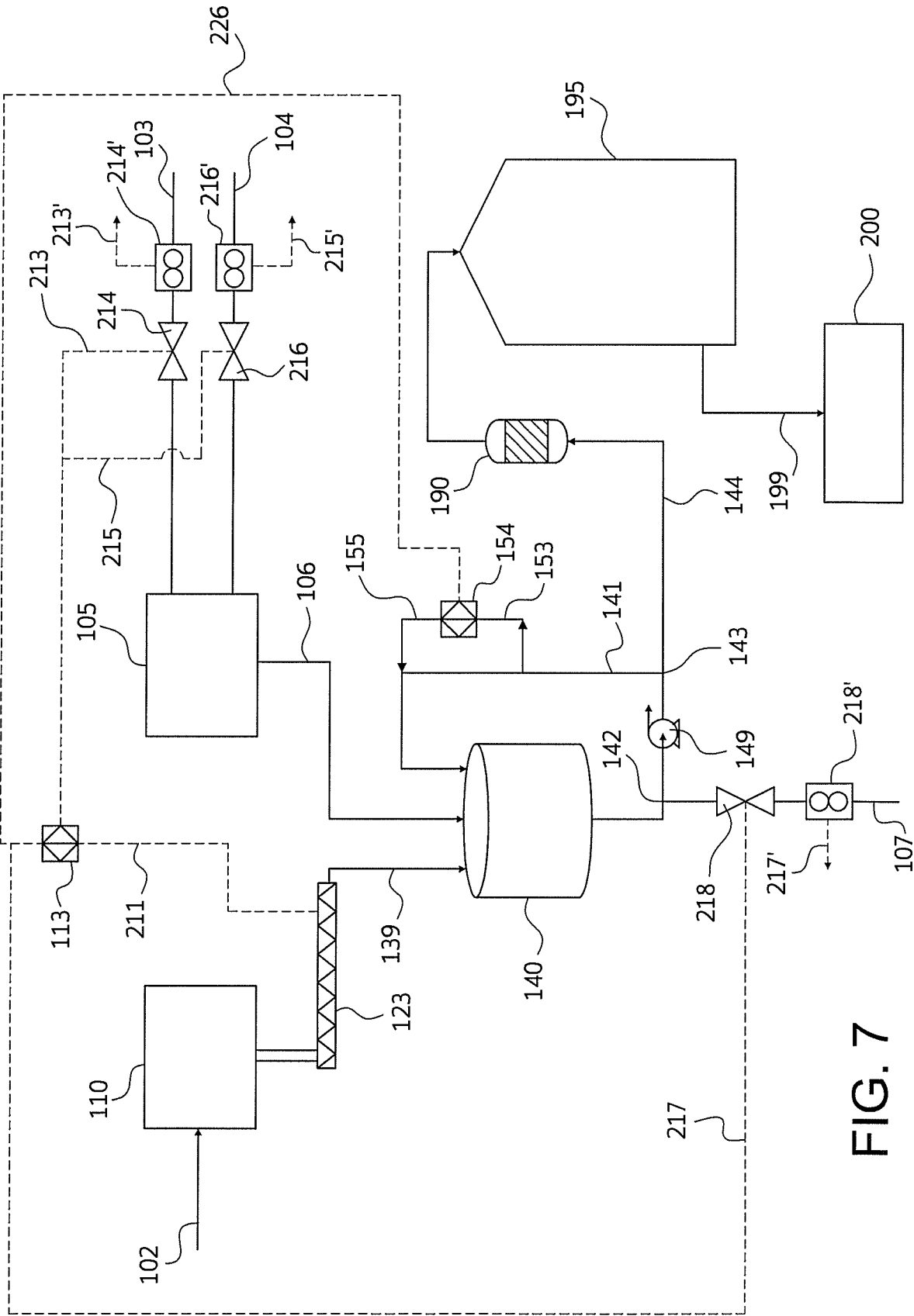


FIG. 7

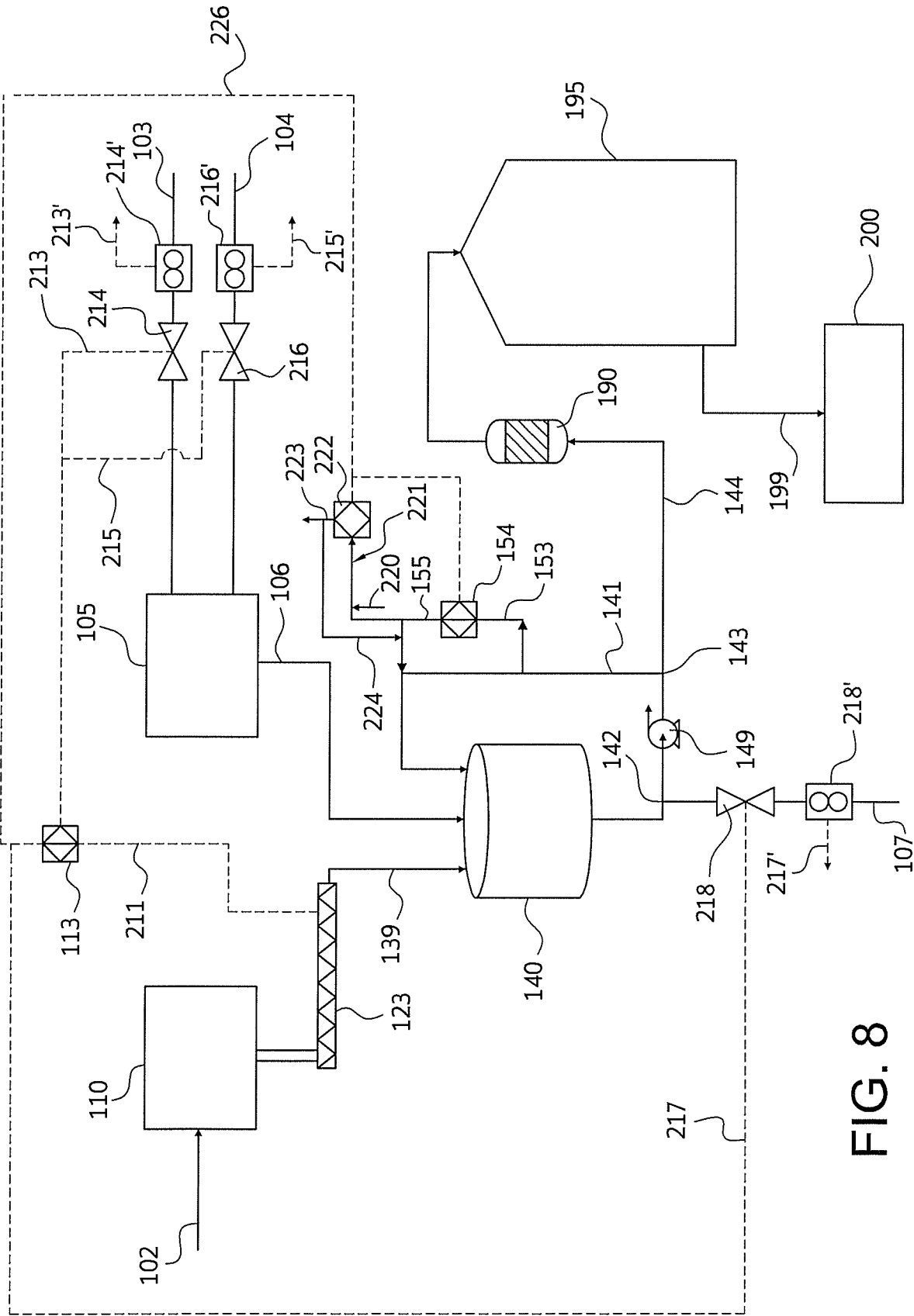


FIG. 8

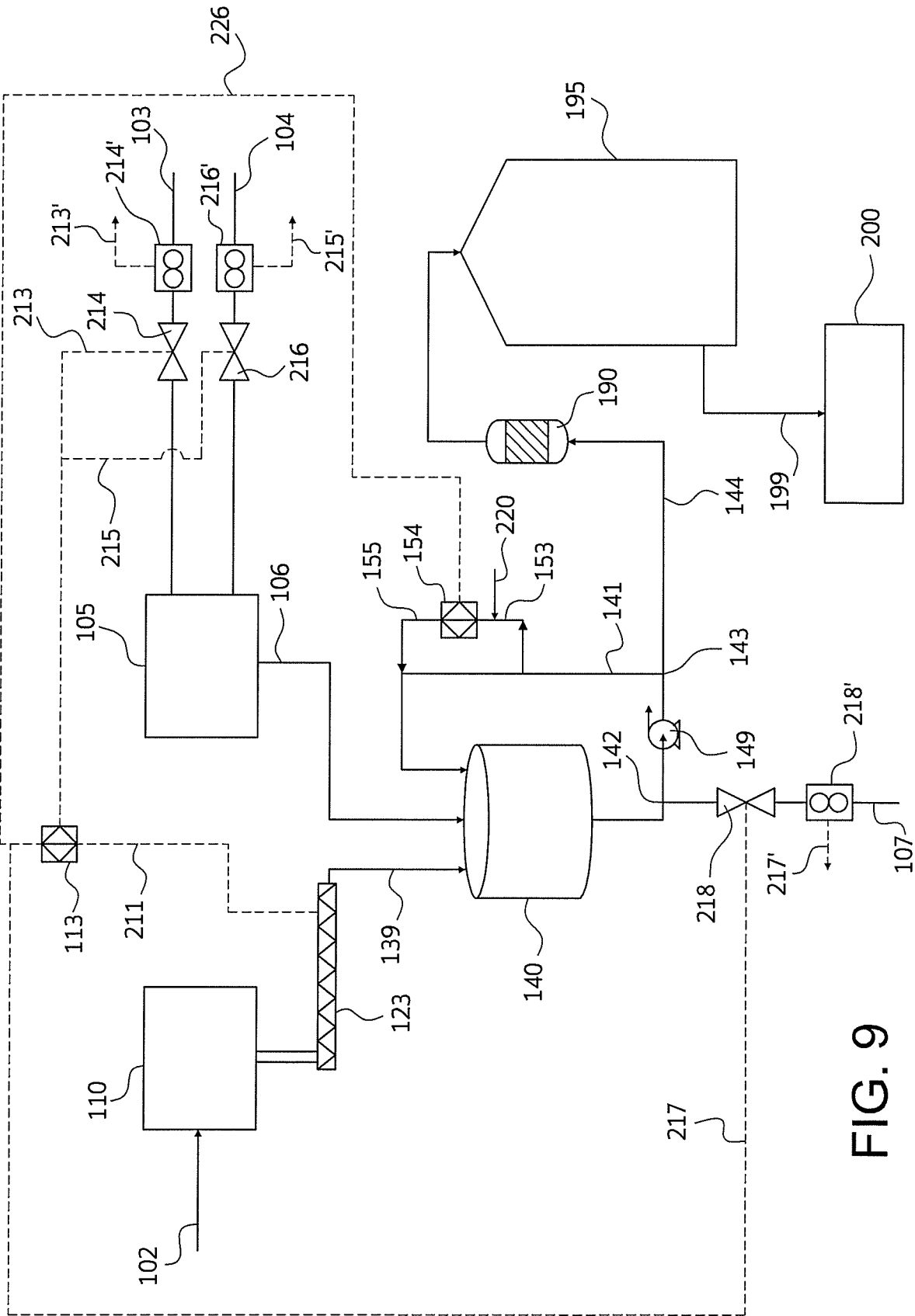


FIG. 9

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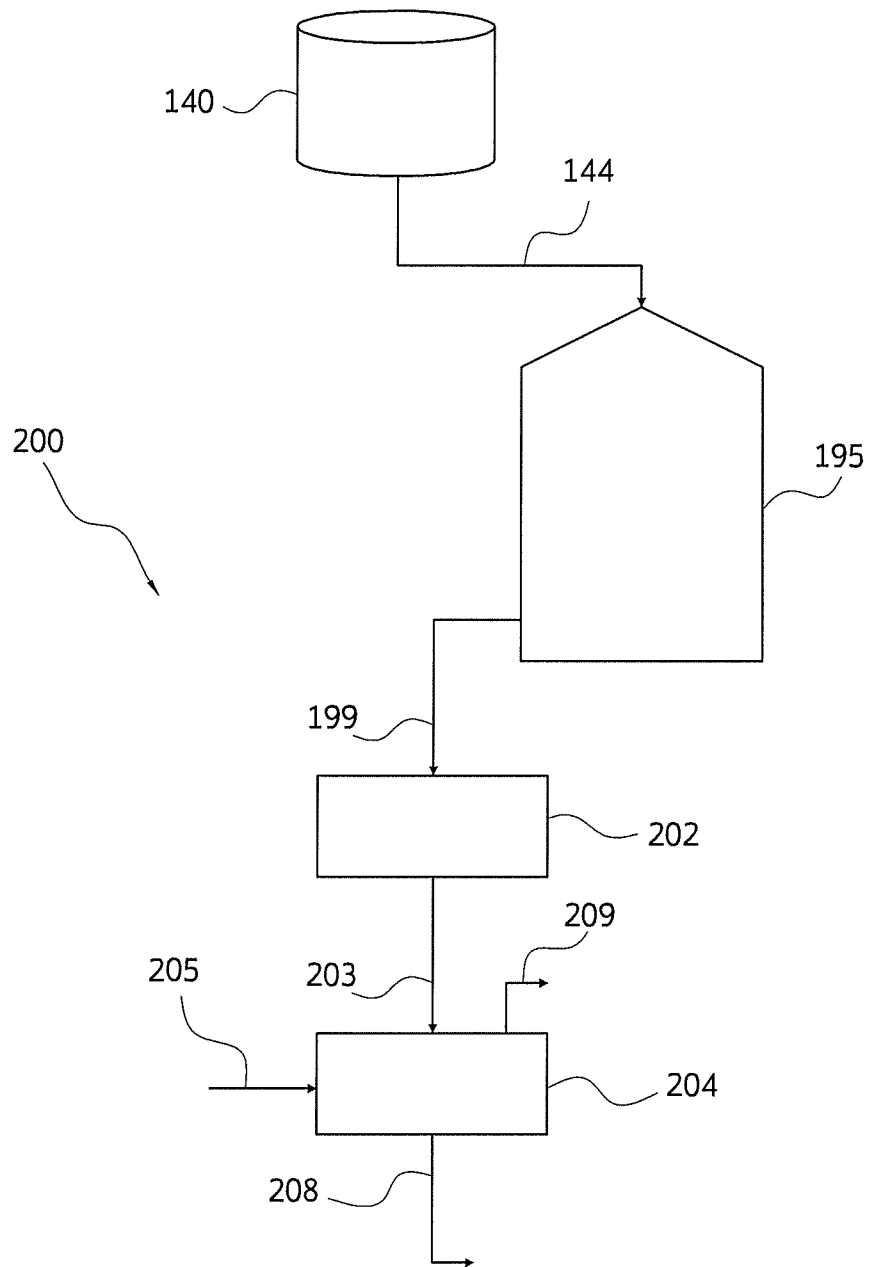


FIG. 10

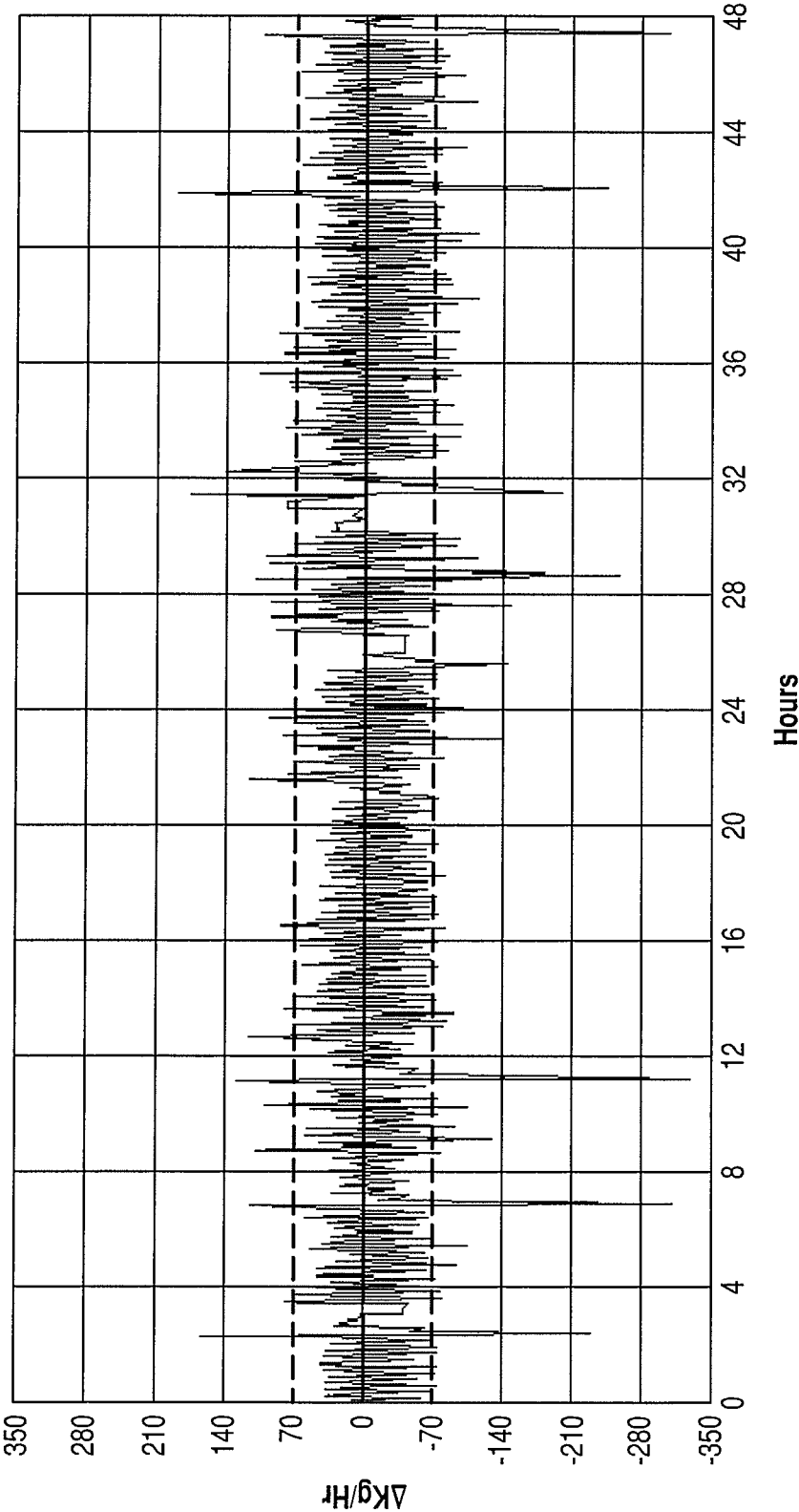


FIG. 11

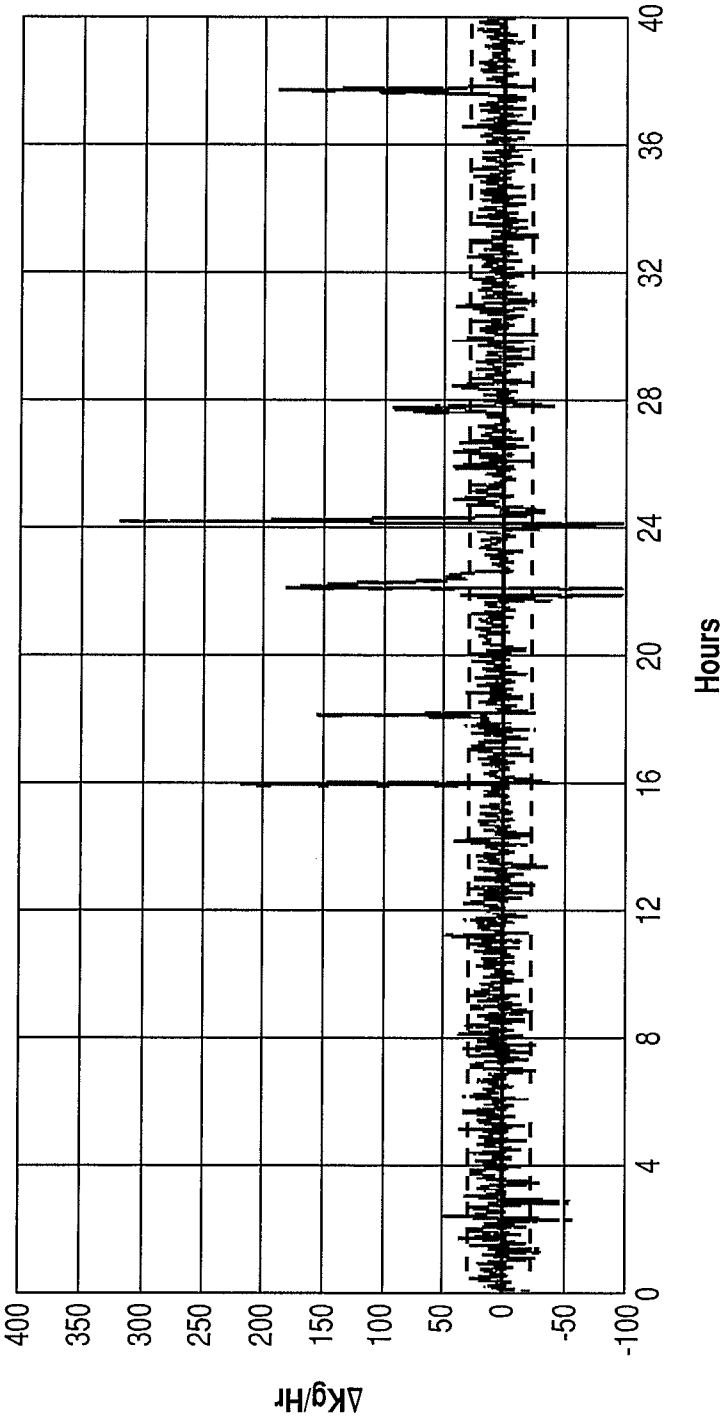


FIG. 12

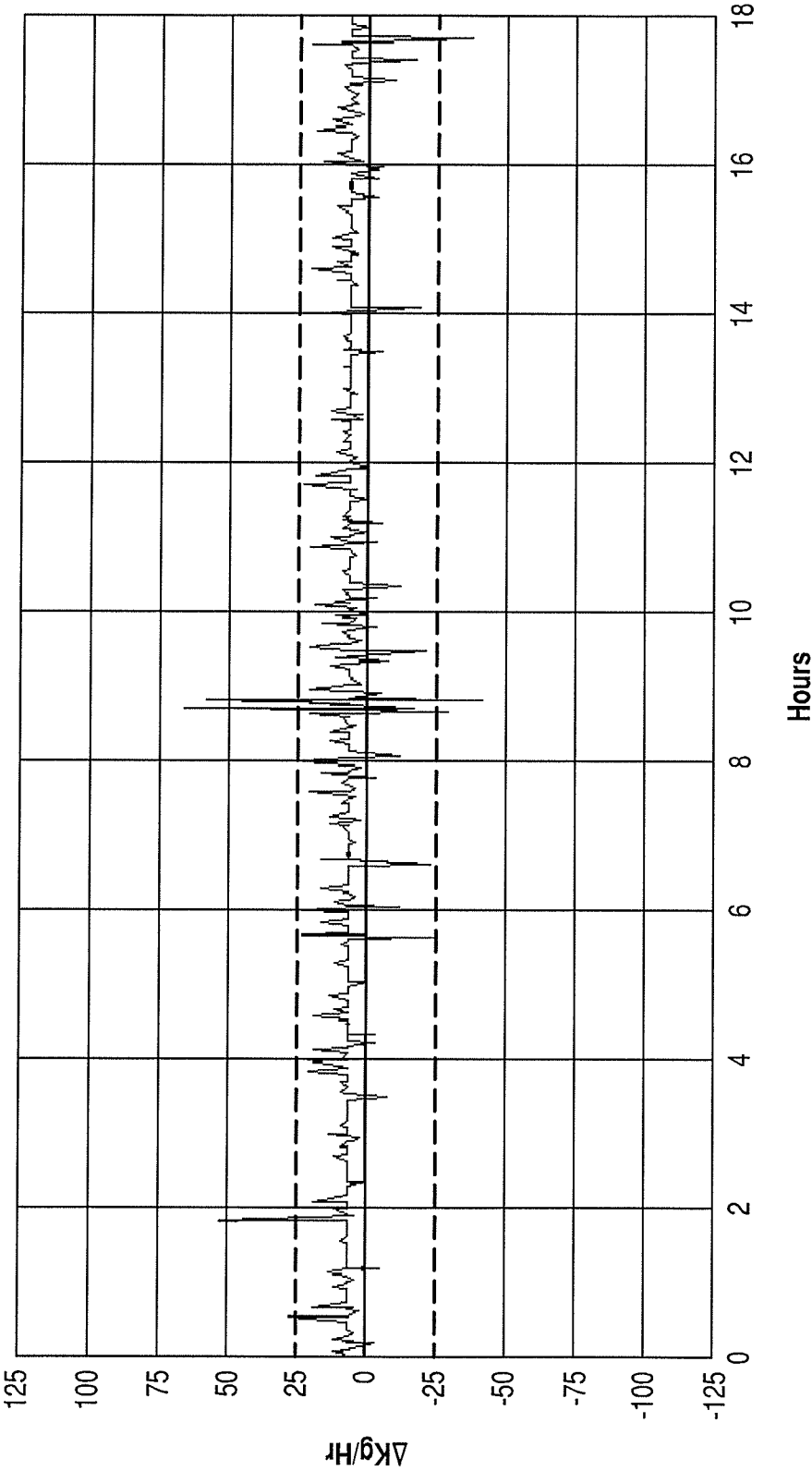


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/034216

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C51/41 C07C55/14 C07C55/02 C07C209/68 C07C211/09
C07C211/12 C08G69/28

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C08G

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

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

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/007451 A1 (UHDE INVENTA FISCHER GMBH [DE]; SIEBECKE EKKEHARD [DE]; BAER MIRKO [DE]) 17 January 2013 (2013-01-17)	1-15
Y	claim 1 figure 4 page 4, line 15 - line 17 page 4, line 19 - line 20 -----	1-15
X	US 4 233 234 A (ROTZOLL RUDI-HEINZ ET AL) 11 November 1980 (1980-11-11) cited in the application	1-15
Y	claims 1, 8 figure 1 column 3, line 1 - line 5 -----	1-15
	-/-	

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

☒ See patent family annex.

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Date of the actual completion of the international search

9 July 2014

Date of mailing of the international search report

16/07/2014

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Authorized officer

Panday, Narendra

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/034216

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	Anonymous: "PID controller", internet archive, wayback machine , 25 April 2013 (2013-04-25), XP055123639, Retrieved from the Internet: URL:https://web.archive.org/web/20130425212406/http://en.wikipedia.org/wiki/PID_controller [retrieved on 2014-06-12] the whole document & Anonymous: "PID controller", wikipedia , Retrieved from the Internet: URL:http://en.wikipedia.org/wiki/PID_controller [retrieved on 2014-06-12] -----	1-15
Y	Anonymous: "distributed control system", internet archive, wayback machine , 8 March 2013 (2013-03-08), XP055123640, Retrieved from the Internet: URL:https://web.archive.org/web/20130308034704/http://en.wikipedia.org/wiki/Distributed_control_system [retrieved on 2014-06-10] the whole document & Anonymous: "distributed control system", wikipedia , Retrieved from the Internet: URL:http://en.wikipedia.org/wiki/Distributed_control_system [retrieved on 2014-06-10] ----- -/--	1-15

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/034216

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

PCT/US2014/034216

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