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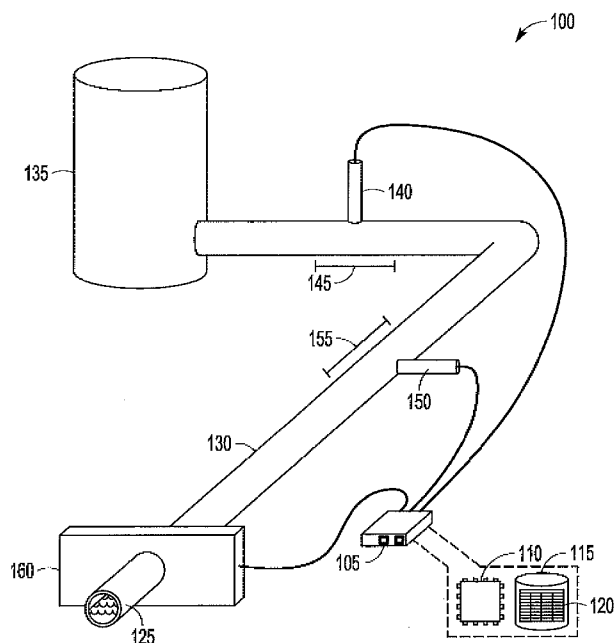


FIG. 1

(57) Abstract: A method for the measurement and character-  
ization of aqueous solutions of polyamide precursors by  
means of electrical conductivity assessed under multiple con-  
ditions and the use of these measurements for the control of  
processes for producing these solutions.

## **ELECTRICAL CONDUCTIVITY OR RESISTIVITY MEASUREMENT AND POLYAMIDE SYNTHESIS**

### **CROSS-REFERENCE TO RELATED APPLICATION**

**[0001]** This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 62/315,882, filed March 31, 2016, the disclosure of which is incorporated herein in its entirety by reference.

### **FIELD**

**[0001]** This disclosure relates to the use of electrical conductivity measurement taken at multiple conditions and its use as an analytical method to measure a variety of characteristics of aqueous solutions of polyamide precursors and the application of these measurements for the control of processes preparing these solutions.

### **BACKGROUND**

**[0002]** The preparation of aqueous solutions containing diamines and dicarboxylic acids is an important and common intermediate step in their conversion into useful polyamides. Industrial processes for production of these solutions require control schemes that are affordable and capable of maintaining the process streams at their desired composition and concentration. Avoiding costly problems requires control of both composition and concentration to avoid problems related to precipitation and polymer quality.

**[0003]** Conventional methods of analyzing the preparation of aqueous solutions which combine dicarboxylic acids and diamines suffer from various shortcomings. Methods relying on charge weights or feed-rates often have insufficient accuracy for robust manufacturing. Testing of pH more accurately measures mole balance, providing an opportunity for closer control to yield more nearly constant process conditions. These pH methods are at their most accurate near the inflection point, and have limitations when operating streams stray far from a molar ratio between the dicarboxylic acids and diamines that will polymerize to high molecular weight. Cyclic off-line pH testing, batch adjustment, and then repeating is problematic for industrial production. Direct on-line pH testing can be limited by insufficient accuracy at process conditions. Dilution and cooling of slip streams to provide a stable basis for on-line pH

measurement can introduce additional sources of error, creates another material stream to be managed, and increases installation costs. The most suitable on-line pH instruments are expensive and they must be suitably maintained in the field.

[0004] With respect to determining concentration of dissolved solids, conventional methods have various shortcomings. Reliance on charge weights and feed-rates fails to provide the improved process stability of a feedback signal. Measuring solution density or refractive index requires installation of instrumentation dedicated for that purpose alone which increases costs. Also, the sensitivity of these measurements to varying composition is a concern for stream compositions far from a molar ratio between the dicarboxylic acids and diamines that will polymerize to high molecular weight.

### SUMMARY

[0005] Disclosed is a method for determining the total concentration of dicarboxylic acids and diamines, the molar ratio of dicarboxylic acids to diamines in an aqueous solution, or a combination thereof. The method can include a) correlating (i) change in conductivity or resistivity of a reference aqueous solution comprising dicarboxylic acids and diamines as a function of temperature with (ii) at least one of total concentration of dicarboxylic acids and diamines and molar ratio of dicarboxylic acids to diamines in the reference aqueous solution. The method can include b) measuring electrical conductivity or resistivity of an aqueous solution comprising the dicarboxylic acids and the diamines at two or more different temperatures. The method can include c) applying the correlation of step a) to the measurements of step b) to determine at least one of (i) total concentration of dicarboxylic acids and diamines in the aqueous solution and (ii) the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution. The method may optionally be used to determine both total concentration and molar ratio. The correlation can be a mathematical model.

[0006] In one aspect, the disclosed method is operated continuously. In another aspect, the disclosed method is operated on-line.

[0007] In a further aspect, step (c) of the disclosed method determines the molar ratio of i) the sum of the concentrations of dicarboxylic acids to ii) the sum of the concentrations of diamines.

[0008] In another aspect, the disclosed method determines the total concentration of dicarboxylic acids and diamines in aqueous solution and the molar ratio of dicarboxylic acids to diamines.

[0009] In one aspect, step (c) of the disclosed method includes determining the degree of amidation.

[0010] In various aspects, the present disclosure provides a relatively simple, lower-cost on-line method for analyzing polyamidation feedstreams that functions reliably, consistently, and accurately within the normal ranges of process conditions. Such a simple and reliable method is much desired in polyamide manufacturing. The method can be affordable to implement at commercial scale.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a block diagram of a system for determining the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution

[0012] FIG. 2 is a block diagram illustrating an example of a machine upon which one or more embodiments may be implemented.

[0013] FIG. 3 is a representation of the measured electrical conductivity in mS/cm versus total dissolved solids in wt% for an aqueous solution containing adipic acid and hexamethylenediamine.

[0014] FIG. 4 is a representation of model estimates of conductivity versus the data presented in TABLE 1, showing a fit within 0.7% ( $R^2 = 0.9936$ ).

[0015] FIG. 5 is a representation of the data of Example 1, illustrating the observed conductivity temperature dependence versus the dicarboxylic acid to diamine molar ratio, showing that the change in electrical conductivity is proportional to the molar ratio.

[0016] FIG. 6 is a representation the model estimate of conductivity temperature dependence of Equation 12 versus the observed conductivity temperature dependence from Example 1, with  $R^2$  of 0.9917.

[0017] FIG. 7 is a representation the model estimate of dissolved solids concentration versus the controlled dissolved solids concentration of TABLE 3.

[0018] FIG. 8 is a representation of the model estimate of adipic acid to hexamethylenediamine molar ratio to the controlled ratio of TABLE 3.

[0019] FIG. 9 is a simplified schematic diagram of a first embodiment of the disclosed process.

[0020] FIG. 10 is a simplified schematic diagram of a second embodiment of the disclosed process.

### DETAILED DESCRIPTION

[0021] Polyamide resins and their manufacture are well known in the polymer industry. These resins may be manufactured by polymerization of dicarboxylic acids or derivatives thereof and diamines. In some cases, polyamides may be produced via polymerization of aminocarboxylic acids, aminonitriles, or lactams.

[0022] This disclosure provides techniques for the measurement of characteristics of aqueous solutions of precursors of polyamides and polyamide copolymers, such as the concentration of dissolved components (e.g., electrolytic components, having electrolytic moieties such as carboxylic acids and amines) and the molar ratio of dicarboxylic acids to diamines. It will be understood that for copolymers the relevant molar ratio is that of total carboxylic acid moieties to amine moieties. The aqueous solution can be substantially free of electrolytic materials other than the dicarboxylic acids and the amines, such as having a trivial amount of other electrolytic materials, such that the aqueous solution is about 0 wt% to about 5 wt% other electrolytic materials, or about 0 wt% to about 1 wt%, or about 5 wt% or less, or less than, equal to, or greater than about 4.5 wt%, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.01, or about 0.001 wt% or less, or about 0 wt%.

[0023] Disclosed is the use of measurements of electrical conductivity for the characterisation of aqueous solutions of dicarboxylic acids and diamines. The disclosed process offers process control flexibility, effectively characterizing solutions far from or near to stoichiometric balance between the dicarboxylic acids and the diamines. The disclosed process can be used with solutions over a wide range of concentrations of dissolved solids. Advantages of the disclosed process may include robust performance across commercially useful ranges of temperatures enabling use off-line under controlled laboratory conditions or on-line under the process conditions.

[0024] One aspect of the disclosed process includes on-line process measurement and control (e.g., direct measurement and control of an active polyamide synthesis process). Another aspect of the disclosed process includes off-line process measurement and control via collected samples (e.g., indirect measurement and control of an active or model polyamide synthesis process, such as via testing at a physical location separate from that used for the polyamide synthesis process).

[0025] In an industrial process of making adipamide salt solution starting from diamine (such as hexamethylene diamine or HMD) and diacid (such as adipic acid) components, the classical method for establishing adipamide salt concentration based on temperature-pressure-concentration relationships at the boil - salt concentration stage can be inadequate, especially when a batch forced circulation evaporator is used.

[0026] During this salt concentration process, the combination of short cycle time for the batch evaporation process and long turnover time (i.e., volume of adipamide salt divided by forced circulation rate) result in the temperature and pressures monitored during the boiling process as not being predictive of the salt concentration as it is transferred to the next processing vessel. Additionally, the lag in measured temperature while boiling may not provide an adequate indication of when the proper concentration end-point has been reached during the boiling/concentration cycle.

[0027] In one aspect of this disclosure, an on-line measurement of stream density and temperature may provide the capability to dynamically calculate the solids content during the evaporation stage. This on-line measurement may be performed by using an on-stream detection device such as Coriolis measurement device or equivalent. The forced circulation evaporator setup may provide an easy, practical way to integrate such measurement device for the salt concentration control via accurate stream density and temperature measurements. The motor-driven circulation pump allows for either the entire flow stream or a side stream to be sampled through the Coriolis measurement device to measure density and corresponding temperature measurement for accurate concentration determination. This may allow determination of the concentration at the pump discharge and may negate the issue of the non-homogeneity within the catch-all stage of the evaporator.

[0028] Use of a Coriolis measurement device allows for more accurate determination of salt concentration for control purposes versus the classic temperature/pressure/concentration for

a vessel which is not well-mixed. Further, as the concentration measurement occurs at the pump discharge, the control system can be configured to dynamically calculate the dry weight of material being transferred to the downstream equipment. Conventionally, the transfer of material to the downstream equipment is made near the discharge of the forced circulation pump. Alternatively, the Coriolis measurement device may be installed at any suitable location in the process that can provide a representative stream sample for density and temperature measurements.

**[0029]** A method for determination of solid content (concentration) and amount of material discharged from a non-ideal batch evaporator may be devised by using Coriolis density/temperature measurements. While such a scheme may be applicable in a wide field of copolymerization by salt strike methods, this application may be preferably used in the manufacture of polyhexamethylene adipamide copolymer (industrially known as nylon-6,6 or N66 or PA66) from HMD and adipic acid. Using a Coriolis meter, one may develop an accurate method to determine the amount of concentrated adipamide salt to be transferred from the pre-evaporator to the evaporator step during N66 manufacture. A control scheme for online solids concentration determination in non-ideal batch operation may also be designed and implemented for consistent and reliable process steps. The operational benefits may be realized in terms of waste reduction, streamlined processing and controls, consistent product quality and accurate and predictable salt concentration performance during the evaporation stage.

**[0030]** Changes in electrical conductivity at different temperatures can enable the determination of dicarboxylic acid/diamine molar ratio and concentration of dissolved solids. For temperatures below the boiling point (e.g., at the operating pressure), conductivity varies proportionally with temperature for any specific solution composition. In the disclosed process, this temperature dependence is assessed as a characteristic feature of that solution enabling the estimation of various aspects of the solution composition.

**[0031]** The disclosed method of analysis uses a multivariate model to estimate the dicarboxylic acid/diamine molar ratio and the concentration of dissolved solids of an aqueous fluid from a conductivity measurement based on the thermal dependence of conductivity. More general multivariate models include the temperature of the fluid at the point of the conductivity measurement as a third factor, but models can be developed without that factor if the process has a stable enough temperature to enable useful correlations to be assessed. The multivariate

models may or may not include temperature without departing from the disclosed use. For some applications, less accurate estimation of dissolved solids concentration and molar ratio are sufficient, and for those uses simpler models may be developed and used as described without departing from the disclosed use.

**[0032]** Optionally, the measuring step (b) of the disclosed method can further comprise collecting samples for conductivity or resistivity measurement at a location physically separated from a polyamide manufacturing facility. The conductivity and temperature measurements can be made on-line either continuously or periodically within the production process piping or equipment.

**[0033]** The disclosed method can be used for the control of process related equipment including flow rates, temperatures, pressures, and operational liquid level.

**[0034]** For making nylons, the dicarboxylic acid can be adipic acid and/or the diamine can be hexamethylene diamine. For example, if the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine, the resulting polyamide can be nylon-6,6.

**[0035]** When applied in an on-line process embodiment, the disclosure provides fast indications of the quality of the precursor aqueous solutions. The disclosure thus also provides means of controlling processes preparing solutions of these precursors. By monitoring concentration, for example, the solubility of process streams can be maintained within safe and effective operational limits. Molar ratio monitoring can be used in feed-back and feed-forward schemes for attaining stable control of the stoichiometric balance between the dicarboxylic acids and the diamines.

**[0036]** Dimonomeric polyamides are those which are derived from the condensation polymerization of a dicarboxylic acid and a diamine. Adipic acid and hexamethylenediamine, for example, are commonly polymerized to form nylon 6,6. The most industrially important processes for the preparation of these polymers is from the starting point of a stable aqueous solutions of reactants. As shown in the prior art, much effort is applied to the optimisation of processes for the preparation of solutions of these precursors. Polyamides copolymers are often prepared from aqueous solutions or blends of aqueous solutions that contain more than two monomers.

**[0037]** The dicarboxylic acid component is suitably at least one dicarboxylic acid of the molecular formula (I):  $\text{HO}_2\text{C}-\text{R}^1-\text{CO}_2\text{H}$ ; wherein  $\text{R}^1$  represents a divalent aliphatic,

cycloaliphatic or aromatic radical or a covalent bond.  $R^1$  suitably comprises from 2 to 20 carbon atoms, preferably 2 to 12 carbon atoms, more preferably 2 to 10 carbon atoms.  $R^1$  may be a linear or branched, preferably linear, alkylene radical comprising 2 to 12 carbon atoms, or 2 to 10 carbon atoms, for example 2, 4, 6 or 8 carbon atoms, an unsubstituted phenylene radical, or an unsubstituted cyclohexylene radical. Optionally,  $R^1$  may contain one or more ether groups. Preferably,  $R^1$  is an alkylene radical, more preferably a linear alkylene radical, comprising 2 to 12 carbon atoms, or 2 to 10 carbon atoms, for example 2, 4, 6 or 8 carbon atoms.

**[0038]** Examples of suitable dicarboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid, pimelic acid, hexane-1,6-dioic acid (adipic acid), octane-1,8-dioic acid (suberic acid), azelaic acid, decane-1,10-dioic acid (sebacic acid), undecanedioic acid, dodecane-1,12-dioic acid, maleic acid, glutaconic acid, traumatic acid, muconic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,2- or 1,3-phenylenediacetic acids, 1,2- or 1,3-cyclohexane diacetic acids, benzene-1,2-dicarboxylic acid (phthalic acid), benzene-1,3-dicarboxylic acid (isophthalic acid), benzene-1,4-dicarboxylic acid (terephthalic acid), 4,4'-oxybis(benzoic acid), 4,4-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, p-t-butyl isophthalic acid and 2,5-furandicarboxylic acid and mixtures thereof. The preferred dicarboxylic acid is adipic acid. These dicarboxylic acids may be supplied in powder form, molten form, as a cake, as a slurry or as aqueous solutions. These dicarboxylic acids may be supplied in a pure form with low levels of impurities or they may be supplied as blended ratios with other dicarboxylic acids or monomers.

**[0039]** The diamine component is suitably at least one diamine of the formula (II):  $H_2N-R^2-NH_2$ ; wherein  $R^2$  represents a divalent aliphatic, cycloaliphatic or aromatic radical.  $R^2$  suitably comprises from 2 to 20 carbon atoms, preferably 4 to 12 carbon atoms, more preferably 4 to 10 carbon atoms.  $R^2$  may be a linear or branched, preferably linear, alkylene radical comprising 4 to 12 carbon atoms, more preferably 4 to 10 carbon atoms, for example 4, 6 or 8 carbon atoms, an unsubstituted phenylene radical, or an unsubstituted cyclohexylene radical. Optionally,  $R^2$  may contain one or more ether groups. Preferably,  $R^2$  is an alkylene radical, more preferably a linear alkylene radical, comprising 4 to 12 carbon atoms, or 4 to 10 carbon atoms, for example 2, 4, 6 or 8 carbon atoms.

**[0040]** Examples of suitable diamines include ethanol diamine, trimethylene diamine, tetramethylene diamine (putrescine), pentamethylene diamine (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, C<sub>2</sub>-C<sub>16</sub> aliphatic diamine optionally substituted with one or more C<sub>1</sub>-C<sub>4</sub> alkyl groups, aliphatic polyether diamines and furanic diamines such as 2,5-bis(aminomethyl)furan, xylylenediamine and mixtures thereof. Hexamethylenediamine is the preferred diamine. It commonly contains a fraction of water to improve handling aspects but it may be supplied in anhydrous form. It may also be supplied to a process in a more dilute form to enhance metering accuracy.

**[0041]** Besides these di-functional monomers, it is sometimes useful to include other monomers. These monomers may include mono-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 monomers may also include lactams such as  $\alpha$ -acetolactam,  $\alpha$ -propiolactam,  $\beta$ -propiolactam,  $\gamma$ -butyrolactam,  $\delta$ -valerolactam,  $\gamma$ -valerolactam, caprolactam and the like. These monomers may also include lactones such as  $\alpha$ -acetolactone,  $\alpha$ -propiolactone,  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\delta$ -valerolactone,  $\gamma$ -valerolactone, caprolactone and the like. These monomers may include di-functional 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, ethohexadiol, p-menthane-3,8-diol, 2-methyl-2,4-pentandiol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol and the like. Monomers may include those with one carboxylic acid functional group and one amine functional group such as 6-aminohexanoic acid, 5-aminopentanoic acid, 7-aminoheptanoic acid and the like. Molecules with higher degrees of functionality may be used such as glycerine, trimethylolpropane, triethanolamine and the like. These monomers may also be suitable hydroxylamines such as ethanolamine, 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,

pentanolmaine, hexanolamine and the like. It will be understood that precursor solutions may include any one or more of these monomers without departing from this disclosure.

**[0042]** Suitable examples of the polyamide may include, but are not limited to, AABB type polyamide (nylon) resins such as PA22, PA46, PA66, PA77, PA610, PA612, PA1010, PA1212, and the like. In the polymer industry, the term “polyamide” is interchangeably used with “nylon”, both having the same meaning to a person skilled in polymer science. For example, Polyamide 6 (PA6) is also referred to as Nylon 6 (N6). Likewise, Polyamide 66 (PA66) is also referred to as Nylon 66 or nylon-6,6 (N66).

**[0043]** Examples of suitable polyamides include, but are not limited to, polytetramethylenedipamide (PA46), polyhexamethylenedipamide (PA66), polyhexamethylenedodecamide (PA612), and any combination thereof. Other examples may include, but are not limited to, amorphous and semi-aromatic copolyamides such as poly-hexamethyleneterephthalamide (known as “6T”), poly-hexamethyleneisophthalamide (known as “6I”), 2-methyl-1,5-pentamethyleneterephthalamide (known as “MPMD-T” or “DT”), 2-methyl-1,5-pentamethyleneisophthalamide (known as “MPMD-I” or “DI”), and their combinations such as “66/6T”, “66/6I”, “6I/6T”, “DT/DI”, “66/DT/DI”, and the like.

**[0044]** It should be understood that the concept of producing a polyamide from diamines and dicarboxylic acids also encompasses the concept of other suitable comonomers, such as amino acids or lactams. Without limiting the scope, examples of aminoacids can include: 6-aminohexanoic acid, 7-aminoheptanoic acid, 11-aminoundecanoic acid, and 12-aminododecanoic acid. Without limiting the scope of the disclosure, examples of lactams can include caprolactam, enantholactam, and lauryllactam. Suitable feeds for the disclosed process can include mixtures of diamines, dicarboxylic acids, aminoacids, and lactams, and can include monofunctional monomers as well as multifunctional monomers.

**[0045]** Unexpectedly, it is found that electrical conductivity of suitable precursor solutions can be modeled as a function of four independent factors: dicarboxylic acid/diamine molar ratio, concentration of dissolved solids, temperature, and the degree of amidation. When applied at temperatures where degree of amidation can be neglected, the concentration of dissolved solids is the dominant term.

**[0046]** Throughout this disclosure and unless otherwise indicated, the term “C” represents conductivity, the term “S” represents the concentration of dissolved solids (e.g., the

wt% of dissolved solids having electrolytic moieties such as carboxylic acids or diamines), the term “T” represents temperature, the term “M” represents the dicarboxylic acid/diamine molar ratio and the term “A” represents the degree of amidation; then the function “F” may be represented generally as:

$$C = f(S, T, M, A) \quad \text{[Equation 1]}$$

**[0047]** It is also unexpectedly found that the dependence of electrical conductivity on temperature for these precursor solutions can be modeled as a function of three factors: dicarboxylic acid/diamine molar ratio “M”, concentration of dissolved solids “S” and the degree of amidation “A”. When applied at temperatures where degree of amidation can be neglected, the dicarboxylic acid/diamine molar ratio is the dominant term. Throughout this disclosure and unless otherwise indicated, the term “dC/dT” represents the thermal sensitivity of electrical conductivity on temperature and the other symbols are kept the same; then this function “g” may be represented generally as:

$$dC/dT = g(S, M, A) \quad \text{[Equation 2]}$$

**[0048]** The precise form of the two functions, i.e., “f” and “g” functions, is a matter of convenience adapted to describe the system being modelled. This is accomplished using techniques familiar to those skilled in the art as will be made clear in the Examples. These two functions may be developed by performing a calibration study for the system of interest in which the range of variables is chosen to provide descriptive models with predictive capability, for example, using a reference aqueous solution that is substantially similar to the aqueous solution wherein total concentration of dicarboxylic acids and diamines or the molar ratio thereof is desired to be determined.

**[0049]** In one embodiment, algebraic substitution of one function into the other is applied to derive a single robust model that enables estimation of at least one of dicarboxylic acid/diamine molar ratio “M” and the concentration of dissolved solids “S” from measurements of conductivity at least at two different temperatures. Once developed, the models represented by Equations 1 or 2 may be reformed.

**[0050]** In some embodiments, Equation 1 may be reformed as required into functions f’, f”, or f''' per Equations 3, 4 or 5:

$$S = f'(C, T, M, A) \quad [\text{Equation 3}]$$

$$M = f''(C, S, T, A) \quad [\text{Equation 4}]$$

$$A = f'''(C, S, T, M) \quad [\text{Equation 5}]$$

[0051] In other embodiments, Equation 2 may be reformed as required into functions  $g'$ ,  $g''$ , or  $g'''$  of Equations 6, 7 or 8:

$$S = g'(dC/dT, M, A) \quad [\text{Equation 6}]$$

$$M = g''(dC/dT, S, A) \quad [\text{Equation 7}]$$

$$A = g'''(dC/dT, S, M) \quad [\text{Equation 8}]$$

[0052] In the embodiment of algebraic substitution, the skilled person can select appropriate equations for substitution and manipulation.

[0053] In many of the subject aqueous solutions the degree of amidation "A" is effectively zero and may be neglected. In such cases the amidation term "A" in the equations can be dropped, thereby leaving two independent equations with two factors to be determined.

[0054] Equation 3 for the "S" term may be used by substituting function  $f'$  in Equation 7, which is then solved for the dicarboxylic acid/diamine molar ratio "M". The exact algebraic or sometimes numeric method of solving this is directly determined by the form of the models developed in the calibration stage that lead to the specifics of Equations 1 and 2 for that system; however, the generalized process is always the same. Following substitution of Equation 3 for "S" into Equation 7, a new function  $g'''$  is developed which is generally represented as below Equation 9 in which the amidation term "A" has been dropped.

$$M = g'''(C, dC/dT, T) \quad [\text{Equation 9}]$$

[0055] The model now allows the dicarboxylic acid/diamine molar ratio "M" to be estimated at any point in time from the experimental measurements of conductivity "C", the thermal dependence of electrical conductivity " $dC/dT$ ", and the temperature "T". The estimated value of the dicarboxylic acid/diamine molar ratio "M" is then used in Equation 3 along with the known "C" and "T" for the estimation of the concentration of dissolved solids "S".

[0056] It is equally possible and sometimes preferable to substitute function  $f''$  for "M" from Equation 4 in Equation 6. Following that substitution, a new function  $g''''$  is developed for "S" which is generally represented as below Equation 10 in which the amidation term "A" has been dropped.

$$S = g''''(C, dC/dT, T) \quad [\text{Equation 10}]$$

**[0057]** The model now allows the concentration of dissolved solids “S” to be estimated at any point in time from the experimental measurements of conductivity “C”, the thermal dependence of electrical conductivity “ $dC/dT$ ”, and the temperature “T”. The estimated value of concentration of dissolved solids “S” is then used in Equation 4 along with the known “C” and “T” for the estimation of the dicarboxylic acid/diamine molar ratio “M”.

**[0058]** In some processes the degree of amidation “A” may not be neglected. When the temperature of the process is high enough and the residence time is long enough, then the degree of amidation exerts a statistically significant effect. A third independent characterisation is required to solve the system of equations. It is found that estimates of concentration of dissolved solids, either by process modelling or by direct instrumentation such as by refractive index or specific gravity, enable the system of equations to be used for determination of dicarboxylic acid/diamine molar ratio and degree of amidation. Alternatively, it is found that by estimates of degree of amidation, either by process models of residence time or by direct instrumentation such as spectral techniques, enable the system of equations to be used for determination of dicarboxylic acid/diamine molar ratio or total dissolved solids concentration (e.g., total concentration of dicarboxylic acids and diamines). The general process outline previously is followed, wherein a calibration study is used to develop descriptive models which are then transformed into useful forms as needed.

**[0059]** In other embodiments, alternative modelling techniques are used to achieve similar models with identical functionality. The exact technique of model development is not critically important so long as a useful model is developed that estimates dicarboxylic acid/diamine molar ratio “M” and concentration of dissolved solids “S” from the measurement of conductivity at least at two different temperatures.

**[0060]** Multiple temperatures are required in order to estimate the dependence of conductivity on temperature for use in the model. It is sufficient to measure conductivity at least at two different temperatures so long as the temperatures are different enough to provide an adequate resolution for that specific process. This will be illustrated in the Examples.

**[0061]** It is common in polyamide salt production facilities to observe temperature changes across the flowlines, especially around the heat exchange equipment such as heaters, coolers, evaporation devices, concentrators, and the like. Most commonly this occurs in recirculation lines around a mixing vessel as the recirculation line passes through a heat

exchanger for temperature regulation. The skilled person will therefore recognize the simplicity of finding process locations for conductivity measurements of a single composition at different temperature points in the system. Many different variations of such measurement can be used.

[0062] Another benefit of this analysis approach is that there is no requirement that measurements be made at the same temperature all the time or even within a set tolerance of temperature variation. In processes where the temperatures fluctuate, it is imperative that the temperature at the location and time of the conductivity measurement be determined for the analysis. Improving the precision on the temperature measurement has a beneficial effect to improve resolution of the model estimates. For the highest resolution, it is also required that the temperatures be warm enough to avoid a slurry condition or the formation of precipitates. Above that critical solution temperature, there is no need for the temperature to be controlled or maintained so long as it is known. This reduction in process requirements eases process design and is highly desired from the industrial production viewpoint.

[0063] In one embodiment, instruments are installed for monitoring the quality of solutions in the process without requiring frequent sampling for off-line analysis. These instruments may be configured for continuous signaling or for periodic use. A general procedure is that two or more conductivity probes are installed in suitable locations in the process to ensure adequate differences in temperature between them. It is necessary to follow the installation guidance of the conductivity meters to ensure quality measurements. Temperature sensors are installed in locations suitable to provide indication of the system. It is preferred that true indicative temperature readings are taken as near as possible to the point of conductivity measurement. From the standpoint of modelling, however, those skilled in the art will recognize that it is also possible to use temperature estimates from process models or nearby instruments as may be appropriate. After the instruments are installed, a calibration data set is then developed by correlating readings from the instruments with the off-line testing of process samples for dicarboxylic acid/diamine molar ratio. One or more models are then developed which describe the measured changes in conductivity and the thermal dependence of conductivity as a function of temperature, concentration, and dicarboxylic acid/diamine molar ratio. These models are then useful for indicating changes in concentration and dicarboxylic acid/diamine molar ratio from the readings of the process instruments. This will be illustrated in the Examples.

[0064] In processes where the temperature will be held practically constant at the respective points of conductivity measurement, then models of the dissolved solids concentration and dicarboxylic acid/diamine molar ratio are derived which do not explicitly incorporate temperature terms. The thermal dependence of conductivity is still estimated from the difference in temperatures at the respective points of conductivity measurement, and this enables estimation of both the dissolved solids concentration and the dicarboxylic acid/diamine molar ratio. Such models are another embodiment of the inventive use of conductivity.

[0065] In another embodiment, the concentration of dissolved solids is maintained such that it is practically constant at the respective points of conductivity measurement. Models are then developed which only incorporate terms for changes in dicarboxylic acid/diamine molar ratio. Such models are aspects of the inventive use of conductivity.

[0066] In another embodiment, the molar ratio of dicarboxylic acid to diamine is maintained such that it is practically constant at the respective points of conductivity measurement. Models are then developed which incorporate terms for changes in concentration and temperature. Alternatively, if the temperature variation is practically negligible at the points of measurement, then a model is developed with only terms related to the concentration. Such variations are all aspects of the disclosed use.

[0067] Many operations that involve aqueous solutions of polyamide precursors occur at conditions wherein the formation of oligomers (e.g., amidisation) is negligible. As described above this allows for the development of useful models based on the terms described. In some embodiments, however, higher temperatures, lower moisture contents or both factors together lead to non-negligible development of oligomers. These oligomers can represent the conversion of electrolytic moieties (e.g., carboxylic acids and amines) into covalent linkages (e.g., amides) and so have an effect on the conductivity of the solution. For applications where the oligomeric formation is constant then no related terms for this are found to be necessary in the models. Solution quality may be modelled in the manner previous described using an appropriate calibration for the system behaviour. Some applications include varying factors that change the level of oligomeric formation – most commonly the vessel residence time – and it is found that these systems can be modelled by including the appropriate descriptive terms in the multivariate analysis. Such considerations are well known to practitioners and all such variations are aspects of the disclosed use.

[0068] The disclosed technique requires measurements of the electrical conductivity of the process fluid. It will be understood by those skilled in the art that, as the reciprocal of the electrical conductivity, the electrical resistivity may also be used without departing from the inventive use. Any of the various methods for measuring electrical conductivity or electrical resistivity may be used effectively for the specific application. The unit of measure of the selected conductivity instrument is also of no importance to the technique. The important factors are instrument sensitivity and calibration and that the stability and required maintenance are suitable for the use. It is also very convenient to use probes with integrated temperature measurements, but this is not required.

[0069] Instruments that use contacting probes can be effectively applied in this technique. Suitable amperometric and potentiometric type probes are available and where suitable for the solution of interest can be used. It is found that the conductivity range for many commercially interesting aqueous solutions of dicarboxylic acids and diamine is above the functional working range of some amperometric devices. In addition, problems of salt deposition on the probes limit the utility of amperometric probes for reliable on-line continuous instrumentation. They appear to be most suitable to off-line testing situations in which the probes will be routinely inspected and calibrated without disruption to the process.

[0070] Potentiometric probes generally exhibit a working sensitivity range more suitable for the solutions of commercial interest. They can enable a wider range of conductivity measurements and exhibit less tendency to foul than the amperometric probes. Suitable instruments are available for both off-line and on-line testing. The wide range of sensitivity and the ease of use make the potentiometric probe the preferred instrument for off-line testing in the laboratory. For off-line testing the HORIBA CONDUCTIVITY METER ES-14E with probe 3582 is found to be useful as an example.

[0071] The non-contacting instrument types referred to as inductive or toroidal probes are available in sensitivity ranges suitable for solutions of commercial interest. These sensors do not expose any electrode surface to the process fluid and so are robust for long term usage in continuous process environments. There can be effects from close proximity of pipes or vessel walls, so it is critical that proper installation guidelines be followed. Various vendors offer sensors useful for continuous process applications such as the Mettler-Toledo InPro 7250 series sensors, the Endress-Hauser Indumax CLS50 or H CLS52 sensor, the Krohne OPTISYS IND

8100 sensor, and the Emerson Rosemount Analytical type 226 or 228 General Purpose Toroidal conductivity sensor.

[0072] Regardless of the type of instrument selected, many offer temperature-correction functions. It is simpler in this technique if those functions are switched off so that the direct reading of conductivity is used. This allows for the models to be developed to account for temperature effects directly. It is possible to model systems based upon temperature-corrected readings and doing so does not depart from the disclosed use.

[0073] Many of the in-line process style probes are offered in various mounting options. One common option is that of a retractive assembly that allows the probe to be removed without shutting down the process. These types of variations are well known to the practitioner and any may be used without departing from the inventive use.

[0074] FIG. 1 is a block diagram of a system for controlling the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution. The system 100 may include a machine 105 with interfaces to connect to a first probe 140, a second probe 150, and a process controller 160.

[0075] These components may be used in a process in which an aqueous solution 125 is processed from the tank (or other material provider) and through the pipe 160. The tank 135 and pipe 160 are provided for illustrative purposes as other physical component arrangements may also be used. The aqueous solution 125 comprises dicarboxylic acids and diamines. In an example, the dicarboxylic acid is adipic acid. In an example, the diamine is hexamethylene diamine. In an example, the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine.

[0076] In an example, the aqueous solution 125 is in an aqueous feed for a polyamidation process. In an example, the first probe 140 or the second probe 150 are at a location physically separated from a polyamide manufacturing facility (e.g., tank 135). In an example, the first probe 140 or the second probe 150 are located within production process piping 130 or equipment and provide on-line measurements of conductivity or temperature either continuously or periodically within the production process piping 160 or equipment.

[0077] The first probe 140 is disposed in the aqueous solution 125 at a first temperature 145, here illustrated as a portion of the pipe 130 in which the aqueous solution 125 has a constant

temperature. The first probe 140 is arranged to produce a first measure of electrical conductivity or resistivity of the aqueous solution 125, at, for example, the first temperature 145.

[0078] The second probe 150 is disposed in the aqueous solution 125 at a second temperature 155 different than the first temperature 145. The second probe 150 is arranged to produce a second measure of electrical conductivity or resistivity of the aqueous solution 125 at, for example, the second temperature 155.

[0079] The processing circuitry 110 is arranged to obtain (e.g., retrieve or receive) an electrical model 120 for a reference aqueous solution comprising dicarboxylic acids and diamines. The electrical model 120 correlates a combination of electrical conductivity (or resistivity) and temperature with at least one of a total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines in the reference aqueous solution. In an example, the electrical model 120 may be stored on a storage device 115 in the device 105. In an example, the electrical model 120 may be stored externally to the device 105. In an example, the electrical model 120 is a table, matrix, or other data structure relating temperature, electrical conductivity or resistivity, and at least one of a total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines. In an example, the electrical model 120 may be implemented in a machine learning model, such as an artificial neural network (ANN), vector space, or the like.

[0080] The processing circuitry 110 is also be arranged to obtain the first measure and the second measure respectively from the first probe 140 and the second probe 150. In an example, the processing circuitry 110 is arranged to also obtain the first temperature 145 or the second temperature 155 when, for example, these temperatures are not controlled, or otherwise, unvarying.

[0081] The processing circuitry 110 is also arranged to apply the first measure and the second measure to the electrical model 120 to determine at least one of total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution. In applying the measures to the electrical model 120, the processing circuitry 110 may provide the first measure and the second measure as parameters to a function. In this example, the parameters correspond to temperatures, such that, for example, a first parameter is associated with the first temperature 145, the processing circuitry 110 applying the first measure to the first parameter. In an example, the processing

circuitry 110 provides the measures and the corresponding temperatures to the electrical model 120. In these examples, the electrical model 120 includes processing components (e.g., machine implemented functions, interfaces, etc.) such that the measurements may be given and the electrical model 120 returns the determination. However, the electrical model 120 may be a simple table or data structure. In these examples, the processing circuitry 110 applies the measurements by looking up the result as keyed, for example, by the measurements and temperatures.

**[0082]** In an example, the processing circuitry 110, via application of the first measurement and the second measurement to the electrical model 120, is arranged to determine a molar ratio of: the sum of the molar concentrations of dicarboxylic acids; to the sum of the molar concentrations of diamines. In an example, the processing circuitry 110, via application of the first measurement and the second measurement to the electrical model 120, is arranged to determine a degree of amidation.

**[0083]** The processing circuitry 110 is also arranged to actuate the process controller 160 to adjust the aqueous solution 125 based on the determination of the total concentration of dicarboxylic acids and diamines in the aqueous solution 125, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution 125. The process controller 160 may add a component of the aqueous solution 125, may heat or cool the aqueous solution 125, may adjust the flow of the aqueous solution 125, or otherwise changed the operational parameters of the system 100. Thus, in an example, the process controller 160 controls at least one of flow rates, temperatures, pressures, or operational liquid level. This control allows the system 100 to maintain tolerances in production that would otherwise be difficult to achieve given off-line solution testing and process adjustments.

**[0084]** In an example, when in operation, the processing circuitry 110 continuously obtains the first measure, obtains the second measure, and applies the first measure and the second measure to the electrical model to determine whether to actuate the process controller 160. Thus, a real-time monitoring and feedback control of the aqueous solution 125 in a production environment is achieved.

**[0085]** FIG. 2 illustrates a block diagram of an example machine 200 upon which any one or more of the techniques (e.g., methodologies) discussed herein may perform. Examples, as described herein, may include, or may operate by, logic or a number of components, or

mechanisms in the machine 200. Circuitry (e.g., processing circuitry) is a collection of circuits implemented in tangible entities of the machine 200 that include hardware (e.g., simple circuits, gates, logic, etc.). Circuitry membership may be flexible over time. Circuitries include members that may, alone or in combination, perform specified operations when operating. In an example, hardware of the circuitry may be immutably designed to carry out a specific operation (e.g., hardwired). In an example, the hardware of the circuitry may include variably connected physical components (e.g., execution units, transistors, simple circuits, etc.) including a machine readable medium physically modified (e.g., magnetically, electrically, moveable placement of invariant massed particles, etc.) to encode instructions of the specific operation. In connecting the physical components, the underlying electrical properties of a hardware constituent are changed, for example, from an insulator to a conductor or vice versa. The instructions enable embedded hardware (e.g., the execution units or a loading mechanism) to create members of the circuitry in hardware via the variable connections to carry out portions of the specific operation when in operation. Accordingly, in an example, the machine readable medium elements are part of the circuitry or are communicatively coupled to the other components of the circuitry when the device is operating. In an example, any of the physical components may be used in more than one member of more than one circuitry. For example, under operation, execution units may be used in a first circuit of a first circuitry at one point in time and reused by a second circuit in the first circuitry, or by a third circuit in a second circuitry at a different time. Additional examples of these components with respect to the machine 200 follow.

[0086] In alternative embodiments, the machine 200 may operate as a standalone device or may be connected (e.g., networked) to other machines. In a networked deployment, the machine 200 may operate in the capacity of a server machine, a client machine, or both in server-client network environments. In an example, the machine 200 may act as a peer machine in peer-to-peer (P2P) (or other distributed) network environment. The machine 200 may be a personal computer (PC), a tablet PC, a set-top box (STB), or any machine capable of executing instructions (sequential or otherwise) that specify actions to be taken by that machine. Further, while only a single machine is illustrated, the term “machine” shall also be taken to include any collection of machines that individually or jointly execute a set (or multiple sets) of instructions to perform any one or more of the methodologies discussed herein, such as cloud computing, software as a service (SaaS), other computer cluster configurations.

[0087] The machine (e.g., computer system) 200 may include a hardware processor 202 (e.g., a central processing unit (CPU), a graphics processing unit (GPU), a hardware processor core, or any combination thereof), a main memory 204, a static memory (e.g., memory or storage for firmware, microcode, a basic-input-output (BIOS), unified extensible firmware interface (UEFI), etc.) 206, and mass storage 221 (e.g., hard drive, tape drive, flash storage, or other block devices) some or all of which may communicate with each other via an interlink (e.g., bus) 208. The machine 200 may further include a display unit 210, an alphanumeric input device 212 (e.g., a keyboard), and a user interface (UI) navigation device 214 (e.g., a mouse). In an example, the display unit 210, input device 212 and UI navigation device 214 may be a touch screen display. The machine 200 may additionally include a storage device (e.g., drive unit) 216, a signal generation device 218 (e.g., a speaker), a network interface device 220, and one or more sensors 221, such as a global positioning system (GPS) sensor, compass, accelerometer, or other sensor. The machine 200 may include an output controller 228, such as a serial (e.g., universal serial bus (USB), parallel, or other wired or wireless (e.g., infrared (IR), near field communication (NFC), etc.) connection to communicate or control one or more peripheral devices (e.g., a printer, card reader, etc.).

[0088] Registers of the processor 202, the main memory 204, the static memory 206, or the mass storage 216 may be, or include, a machine readable medium 222 on which is stored one or more sets of data structures or instructions 224 (e.g., software) embodying or utilized by any one or more of the techniques or functions described herein. The instructions 224 may also reside, completely or at least partially, within any of registers of the processor 202, the main memory 204, the static memory 206, or the mass storage 216 during execution thereof by the machine 200. In an example, one or any combination of the hardware processor 202, the main memory 204, the static memory 206, or the mass storage 216 may constitute the machine readable media 202. While the machine readable medium 222 is illustrated as a single medium, the term "machine readable medium" may include a single medium or multiple media (e.g., a centralized or distributed database, and/or associated caches and servers) configured to store the one or more instructions 224.

[0089] The term "machine readable medium" may include any medium that is capable of storing, encoding, or carrying instructions for execution by the machine 200 and that cause the machine 200 to perform any one or more of the techniques of the present disclosure, or that is

capable of storing, encoding or carrying data structures used by or associated with such instructions. Non-limiting machine readable medium examples may include solid-state memories, optical media, magnetic media, and signals (e.g., radio frequency signals, other photon based signals, sound signals, etc.). In an example, a non-transitory machine readable medium comprises a machine readable medium with a plurality of particles having invariant (e.g., rest) mass, and thus are compositions of matter. Accordingly, non-transitory machine-readable media are machine readable media that do not include transitory propagating signals. Specific examples of non-transitory machine readable media may include: non-volatile memory, such as semiconductor memory devices (e.g., Electrically Programmable Read-Only Memory (EPROM), Electrically Erasable Programmable Read-Only Memory (EEPROM)) and flash memory devices; magnetic disks, such as internal hard disks and removable disks; magneto-optical disks; and CD-ROM and DVD-ROM disks.

**[0090]** The instructions 224 may be further transmitted or received over a communications network 226 using a transmission medium via the network interface device 220 utilizing any one of a number of transfer protocols (e.g., frame relay, internet protocol (IP), transmission control protocol (TCP), user datagram protocol (UDP), hypertext transfer protocol (HTTP), etc.). Example communication networks may include a local area network (LAN), a wide area network (WAN), a packet data network (e.g., the Internet), mobile telephone networks (e.g., cellular networks), Plain Old Telephone (POTS) networks, and wireless data networks (e.g., Institute of Electrical and Electronics Engineers (IEEE) 802.11 family of standards known as Wi-Fi®, IEEE 802.16 family of standards known as WiMax®, IEEE 802.15.4 family of standards, peer-to-peer (P2P) networks, among others. In an example, the network interface device 220 may include one or more physical jacks (e.g., Ethernet, coaxial, or phone jacks) or one or more antennas to connect to the communications network 226. In an example, the network interface device 220 may include a plurality of antennas to wirelessly communicate using at least one of single-input multiple-output (SIMO), multiple-input multiple-output (MIMO), or multiple-input single-output (MISO) techniques. The term “transmission medium” shall be taken to include any intangible medium that is capable of storing, encoding or carrying instructions for execution by the machine 200, and includes digital or analog communications signals or other intangible medium to facilitate communication of such software. A transmission medium is a machine readable medium.

## EXAMPLES

[0091] To provide a clearer indication of the use of the disclosure, some non-limiting and illustrative examples are provided.

### EXAMPLE 1

[0092] This demonstrates the off-line characterization of solutions of dicarboxylic acids and diamines in different concentrations and different molar ratios.

[0093] A 700 mL reaction flask is fitted with a multi-necked lid that is secured with a spring clamp. The assembly is supported by a ring and submerged in a TECHNE TE-10A temperature-controlled water bath such that the water level is 2 cm below the flange joint of the glassware. The temperature of the bath is controlled by varying the dial of the TECHNE TE-10A and monitoring the water temperature using a HANNA INSTRUMENTS HI 93530 temperature sensor with a calibrated Type K thermocouple. An inert atmosphere is maintained in the flask by a nitrogen feed the flow of which is confirmed by use of a water bubbler on the supply side. On the vent of the vessel a double-walled water condenser is mounted of sufficient length that at no test temperature is the interior condensation observed to reach above half the vertical length of the inner tube. A PTFE half-moon blade agitator which is a third of the flask inner diameter is mounted near the base of the flask and fitted such that the shaft passes through a sealed gland in the centre port of the lid. The agitator is driven at 300 rpm by a HEIDOLPH RZR-2000 motor mounted on a ring stand above the assembly.

[0094] For each test, the charge weights are adjusted so that each test contains 700 g of total solution in the flask. All materials are charged to the flask via the largest port in the lid according to the weights shown in the tables for each test. After the materials are charged, the solution is warmed with agitation until it forms a clear solution. The electrical conductivity of the solution is then measured using a HORIBA CONDUCTIVITY METER ES-14E with probe 3582. The probe is inserted through the same large port previously used for charging materials to the flask. It is fitted in a manner to seal the opening around the probe to exclude oxygen ingress. Care is taken to insert the probe to the same depth for each run and such that the probe is submerged per the instructions of the meter.

**[0095]** A set of tests are executed according to TABLE 1 to develop the data set for modelling this mixture. Adipic acid is used as the dicarboxylic acid and hexamethylene diamine is used as the diamine. The concentration of each non-aqueous component is calculated based on weight and the total is described as % dissolved solids. Another set of tests are executed according to TABLE 2 to provide data independent of the model development and used to test model predictive ability.

**[0096]** The measured electrical conductivity is found to be proportional to total dissolved solids. As shown in FIG. 3, a linear fit describes the observed variation within 15% error. This simple direct conductivity measurement is useful as a coarse estimate of dissolved solids for some applications.

**[0097]** A higher resolution model is preferred for some analyses. A multivariate model is developed using a commercial data analysis software (Minitab® 17.1.0 is available from Minitab, Inc., Quality Plaza, 1829 Pine Hall Road, State College, PA 16801-3210). The software choice is not critical. For example, other data analysis tools such as OriginLab, commercially available from OriginLab Corporation, One Roundhouse Plaza, Suite 303, Northampton, MA 01060, can also be used. In this case, it is found that descriptive ability is improved by including not just effect of the dissolved solids content, but also the effect of molar ratio, the effect of temperature, and the two-factor interaction of dissolved solids content with molar ratio. The model is presented as Equation 11. As illustrated in FIG. 4, this model describes the TABLE 1 data predictability within 0.7%.

$$\text{Conductivity} \left[ \frac{\text{mS}}{\text{cm}} \right] = 52.82 - 3.59 * M - 0.784 * S + 0.1865 * T + 0.0507 * M * S$$

[Equation 11]

Where: M = Dicarboxylic acid / Diamine Molar Ratio  
 S = Total weight percent of non-aqueous components in solution  
 T = Temperature [°C]

TABLE 1

| <b>Solution Composition</b> | <b>Diacid/Diamine Molar Ratio</b> | <b>% Dissolved Solids</b> | <b>Temperature [°C]</b> | <b>Conductivity [mS/cm]</b> |
|-----------------------------|-----------------------------------|---------------------------|-------------------------|-----------------------------|
| 1                           | 2.19                              | 52.1                      | 50.0                    | 19.48                       |
| 1                           | 2.19                              | 52.1                      | 70.0                    | 23.40                       |
| 2                           | 2.68                              | 63.7                      | 50.0                    | 11.74                       |
| 2                           | 2.68                              | 63.7                      | 70.0                    | 14.79                       |
| 3                           | 2.68                              | 52.1                      | 48.2                    | 18.20                       |
| 3                           | 2.68                              | 52.1                      | 70.0                    | 22.10                       |
| 4                           | 2.19                              | 63.7                      | 50.0                    | 11.50                       |
| 4                           | 2.19                              | 63.7                      | 70.0                    | 14.98                       |
| 5                           | 3.10                              | 70.0                      | 55.0                    | 8.33                        |
| 5                           | 3.10                              | 70.0                      | 70.0                    | 10.49                       |
| 6                           | 1.00                              | 53.0                      | 50.0                    | 18.90                       |
| 6                           | 1.00                              | 53.0                      | 70.0                    | 24.00                       |

[0098] The data of TABLE 1 is then used to estimate the thermal dependence of electrical conductivity for each solution. For each specific solution composition, this is calculated by dividing the difference in conductivity measurements by the difference in temperatures for those measurements. The result is presented in TABLE 2. This estimation method is used to make the illustration of this process clear. It is well known in the art that other techniques may be used to develop estimates of the change in electrical conductivity with respect to temperature and these may be applied without departing from the disclosed use.

TABLE 2

| <b>Solution Composition</b> | <b>Diacid/Diamine Molar Ratio</b> | <b>% Dissolved Solids</b> | <b>Thermal Dependence [mS/cm/°C]</b> |
|-----------------------------|-----------------------------------|---------------------------|--------------------------------------|
| 1                           | 2.19                              | 52.1                      | 0.20                                 |
| 2                           | 2.68                              | 63.7                      | 0.15                                 |
| 3                           | 2.68                              | 52.1                      | 0.18                                 |
| 4                           | 2.19                              | 63.7                      | 0.17                                 |
| 5                           | 3.10                              | 70.0                      | 0.14                                 |
| 6                           | 1.00                              | 53.0                      | 0.26                                 |

[0099] The change in electrical conductivity of these aqueous solutions is found to be proportional to the molar ratio of dicarboxylic acid to diamine. As shown in FIG. 5, a linear fit

describes the observed variation with 9% error. This simple direct relationship to the thermal dependence of conductivity is useful as an indicator of the molar ratio of the components.

[00100] A higher resolution model is preferred for some analyses. A multivariate model is developed using Minitab® 17.1.0 statistical analysis software. In this case it is found that descriptive ability is improved by including not just the effect of the molar ratio, but also the effect of the total dissolved solids content and the two-factor interaction of dissolved solids content with molar ratio. This model is presented as Equation 12. As illustrated in FIG. 6, this model describes the TABLE 2 data predictability within 0.9%.

$$\frac{dC}{dT} \left[ \frac{mS}{cm \cdot ^\circ C} \right] = 0.641 - 0.1452 * M - 0.00639 * S + 0.0507 * M * S \quad [\text{Equation 12}]$$

[00101] It is desired that the two direct measurements of conductivity and temperature will be made for any solution. It is also desired that the conductivity is assessed at a sufficient quantity of different temperatures to estimate the thermal dependence of that property for that solution. As shown in this example, the minimum quantity of temperatures can be two so long as they are sufficiently far apart to resolve changes in conductivity from measurement error and system fluctuation. In the end, the experimentalist will have an estimate of three properties of the system: conductivity “C”, temperature “T” and the thermal dependence of conductivity “dC/dT”. As may be observed from Equation 1 and Equation 2, this leaves two unknowns and two equations. It is a simple matter of algebra to reform them such that the molar ratio “M” and total dissolved solids “S” of an unknown sample may be characterized.

[00102] TABLE 3 presents a set of test conditions and solutions not included in the construction of the model of Equations 11 and 12. FIG. 7 represents the predictive ability of the derived model for total dissolved solids “S” against the TABLE 3 data. This shows the model estimates the total dissolved solids concentration within 1.5% ( $R^2 = 0.9859$ ).

TABLE 3

| Solution Composition | Diacid/Diamine Molar Ratio | % Dissolved Solids | Temperature [°C] | Conductivity [mS/cm] |
|----------------------|----------------------------|--------------------|------------------|----------------------|
| 1                    | 2.19                       | 52.1               | 53.9             | 20.10                |
| 1                    | 2.19                       | 52.1               | 55.0             | 20.50                |
| 1                    | 2.19                       | 52.1               | 60.0             | 21.47                |
| 1                    | 2.19                       | 52.1               | 65.0             | 22.50                |
| 2                    | 2.68                       | 63.7               | 50.0             | 11.74                |
| 2                    | 2.68                       | 63.7               | 51.8             | 11.97                |
| 2                    | 2.68                       | 63.7               | 55.0             | 12.51                |
| 2                    | 2.68                       | 63.7               | 60.0             | 13.26                |
| 2                    | 2.68                       | 63.7               | 65.0             | 14.12                |
| 3                    | 2.68                       | 52.1               | 48.2             | 18.20                |
| 3                    | 2.68                       | 52.1               | 50.0             | 18.60                |
| 3                    | 2.68                       | 52.1               | 55.0             | 19.41                |
| 3                    | 2.68                       | 52.1               | 60.0             | 20.10                |
| 3                    | 2.68                       | 52.1               | 65.0             | 21.30                |
| 4                    | 2.19                       | 63.7               | 55.0             | 12.38                |
| 4                    | 2.19                       | 63.7               | 60.0             | 13.26                |
| 4                    | 2.19                       | 63.7               | 65.0             | 14.19                |
| 5                    | 3.10                       | 70.0               | 59.1             | 8.89                 |
| 5                    | 3.10                       | 70.0               | 60.0             | 9.05                 |
| 5                    | 3.10                       | 70.0               | 65.0             | 9.89                 |
| 6                    | 1.00                       | 53.0               | 55.0             | 20.30                |
| 6                    | 1.00                       | 53.0               | 60.0             | 21.60                |
| 6                    | 1.00                       | 53.0               | 65.0             | 22.80                |
| 7                    | 2.44                       | 57.9               | 50.0             | 15.52                |
| 7                    | 2.44                       | 57.9               | 52.9             | 15.95                |
| 7                    | 2.44                       | 57.9               | 55.0             | 16.41                |
| 7                    | 2.44                       | 57.9               | 60.0             | 17.34                |
| 7                    | 2.44                       | 57.9               | 65.0             | 18.26                |
| 7                    | 2.44                       | 57.9               | 70.0             | 19.10                |
| 8                    | 2.01                       | 54.9               | 50.0             | 17.72                |
| 8                    | 2.01                       | 54.9               | 55.0             | 18.71                |
| 8                    | 2.01                       | 54.9               | 60.0             | 19.76                |
| 8                    | 2.01                       | 54.9               | 65.0             | 20.70                |
| 8                    | 2.01                       | 54.9               | 70.0             | 21.60                |
| 9                    | 1.20                       | 55.0               | 50.0             | 17.76                |
| 9                    | 1.20                       | 55.0               | 55.0             | 18.60                |
| 9                    | 1.20                       | 55.0               | 60.0             | 19.80                |
| 9                    | 1.20                       | 55.0               | 65.0             | 21.00                |
| 9                    | 1.20                       | 55.0               | 70.0             | 22.10                |

[00103] FIG. 8 represents the predictive ability of the derived model for dicarboxylic acid/diamine molar ratio “M” against the TABLE 3 data. This shows the model estimates the molar ratio of the solutions within 3.6% ( $R^2 = 0.964$ ).

[00104] This example demonstrates the principle of utilizing these three measurable process variables, i.e., “C”, “T” and “dC/dT” for assessing solution composition in terms of the molar ratio “M” and dissolved solids concentration “S”. It will be appreciated by those skilled in the art that common techniques for multivariate model development can greatly improve the accuracy and precision of the models for estimating solution composition without departing from this disclosure. It is also noted that it is sometimes found that omitting or including different factors in the model is observed to have a statistically significant effect and improves the predictive ability of the model for that solution type in that application. It will be understood by practitioners that such descriptive system factors are either included or discarded as required to improve predictive ability for the subject process and specific application. Such common modelling approaches may be used without deviating from the disclosed use of electrical conductivity and its thermal dependence.

## EXAMPLE 2

[00105] This example demonstrates the direct monitoring in a bulk process flow of the quality of solutions of dicarboxylic acids and diamines with respect to their dissolved solids concentration and the dicarboxylic acid/diamine molar ratio at process points around a heat exchanger.

[00106] FIG. 9 represents a dissolution tank 900 in which a solution is prepared from feeds of molten diamines “HMD” 901, demineralized water “DEMIN” 902 and powdered dicarboxylic acid “AA” 903 by mixing them together under appropriate mechanical agitation and regulating the temperature of the vessel. The dissolution tank 900 is illustrated as a baffled vessel with baffles 904 and uses a multi-level agitator 905 of conventional design for the dissolution. A centrifugal pump 906 recirculates the tank contents through a recycle loop 907 with a heat exchanger 908 which maintains the dissolution tank 900 at about 60°C bulk temperature. The recycle loop 907 also has a branch pipe 909 with a valve 910 that is used to control the flow from the dissolution tank to downstream vessels (not shown).

[00107] The diamine in this example is anhydrous hexamethylenediamine (or HMD), and it is fed as a liquid at between 55-60°C and at a rate of about 395.4 kg/hr. The dicarboxylic acid is adipic acid (or AA), and it is fed at ambient temperature using a volumetric screw feeder at a rate averaging about 1209.9 kg/hr. The demineralized water is fed at about 1167.4 kg/hr. A nitrogen flow 911 is provided to inert the headspace of the vessel.

[00108] The temperature of the flow into the heat exchanger varies between 55-60°C. The temperature out of the heat exchanger varies between 65-70°C. A typical temperature difference across the heat exchanger 908 is about 6°C.

[00109] Two Endress-Hauser Indumax CLS50D conductivity sensors (912 and 913) are installed as shown in FIG. 9 to indicate the change in conductivity across the heat exchanger 908. These probes are supplied with an integrated PT1000 temperature sensor (shown as 914 and 915) which is used for temperature indication. The conductivity sensors are used with Liquiline CM44x transmitters (not shown) and these are configured with the plant DCS system (not shown) to enable precise tracking of data.

[00110] As shown in FIG. 9, the plant is designed with a sampling point with a valve downstream of the pump 906 for collecting process samples for off-line characterization. A calibration set of 41 samples is collected with careful tracking of sampling time against the DCS timestamp. The dicarboxylic acid/diamine molar balance is assessed using pH measurements of the collected samples. The concentration of dissolved solids is estimated using refractive index correlations against lab standards.

[00111] Multivariate models for conductivity and the thermal dependence of conductivity are developed using the method of Example 1. Testing of the system is checked against the model by collecting samples periodically over a period of two weeks of continuous operation.

[00112] It is observed that the models developed describe concentration data within the experimental error of the lab measurements. It is also observed that the models developed describe the molar balance data within 3% of the off-line pH tests.

### EXAMPLE 3

[00113] This example demonstrates the fine control of molar balance of dicarboxylic acids and diamines in a bulk process flow at a point around a heat exchanger. The sensitivity of conductivity to changes in temperature reaches a maximum at or near a composition

corresponding to the inflection point for solutions of dicarboxylic acids and diamines (e.g., a stoichiometric ratio of diamine and dicarboxylic acid that will polymerize to high molecular weight polyamide). This example shows the use of that maximum of thermal dependence of conductivity for control using it for adjustment of a trim diamine flow.

**[00114]** FIG. 10 represents a mixing tank 1000 in which an imbalanced solution of dicarboxylic acids and diamines is brought closer to molar balance by adding molten diamine “HMD” 1001. A demineralized water feed “DEMIN” 1002 is used to tune the final solution concentration of the balanced salt. The balanced salt solution is prepared by mixing the feed streams (1001, 1002 and 1003) together under appropriate mechanical agitation. The mixing tank 1000 in FIG. 10 is a baffled vessel (baffles shown as 1004) and uses a multi-level agitator 1005 of conventional design for the dissolution. A centrifugal pump 1006 recirculates the mixing tank 1000 contents through a recycle loop 1007 with a heat exchanger 1008 which maintains the vessel contents at about 100-105°C bulk temperature. The recycle loop 1007 also has a branch pipe 1009 with a valve 1010 that is used to control the flow from the mixing tank 1000 to downstream vessels (not shown).

**[00115]** The diamine in this example is anhydrous hexamethylenediamine (or HMD), and it is fed as a liquid at between 55-60°C and at a rate of about 526.4 kg/hr. The imbalanced solution (1003) fed in this example is a 58% aqueous solution of adipic acid and hexamethylenediamine in which the AA/HMD molar ratio is 2.43. That solution (1003) is fed to the mixing tank at a rate of about 1209.9 kg/hr. Demineralized water is fed to the vessel at a rate of about 38.1 kg/hr. A nitrogen flow 1011 is provided to inert the headspace of the vessel. These bulk flows are kept in control using conventional means to maintain the vessel at operationally desired liquid level and at about 63.9% concentration in an AA/HMD molar ratio of between 1.03-1.05.

**[00116]** A separate trim feed of hexamethylenediamine, labeled “40% aq HMD”, is fed upstream of the pump 1006 for the fine adjustment of molar balance. Molten hexamethylenediamine may be used directly. In this example a 40 wt% aqueous solution of hexamethylenediamine is used. It is adjusted between the rates of 55 – 161 kg/hr for controlling the final molar balance in the AA/HMD molar ratio range of 0.98 – 1.02.

[00117] The temperature of the flow into the heat exchanger 1008 varies between 100-105°C. The temperature out of the heat exchanger 1008 varies between 88-92°C. A typical temperature difference across the heat exchanger 1008 is about 10-12°C.

[00118] Two Endress-Hauser Indumax CLS50D conductivity sensors (1012, 1013) are installed as shown in FIG. 10 to indicate the change in conductivity across the heat exchanger. These probes are supplied with an integrated PT1000 temperature sensor (1014, 1015) which is used for temperature indication. The conductivity sensors are used with Liquiline CM44x transmitters (not shown) and these are configured with the plant DCS system (not shown) to enable precise tracking of data.

[00119] As shown in FIG. 10, the plant is designed with a sampling point with a valve 1016 downstream of the pump 1006 for collecting process samples for off-line characterization. A calibration set of 16 samples is collected with careful tracking of sampling time against the DCS timestamp. The dicarboxylic acid/diamine molar balance is assessed using pH measurements of the collected samples. The concentration of dissolved solids is estimated using refractive index correlations against lab standards.

[00120] The concentration of dissolved solids in this example is controlled within a range that its variation does not contribute significantly to the thermal dependence of conductivity. The sample analysis is used to find that the thermal dependence of conductivity exhibits a maximum of 0.2589 mS/cm/°C at molar balance. This maximum is then applied as the first tuning constant in Equation 13.

$$\text{Offset} = \text{Constant} - (C2 - C1)/(T2 - T1) \quad [\text{Equation 13}]$$

[00121] In Equation 13, C1 and C2 are the thermal conductivity values measured by Sensors 1012 and 1013 (FIG. 10), respectively. T1 and T2 are the corresponding temperature values measured by Sensors 1014 and 1015 (FIG. 10), respectively.

[00122] Equation 13 is used in a feedback control loop in the DCS to vary the flow of the HMD trim to minimize the Offset. It is found that this maintains the outlet flow to the downstream processes in an AA/HMD molar ratio of between 0.99 and 1.01 or within 1% of set-point.

[00123] It will be understood that variations in the form of the offset equation may be conveniently used without departing from the disclosure. In one embodiment, for example, an

equation for the Constant is used to adjust the Constant for the current temperature of the mixing vessel. Such approaches are well known to practitioners.

[00124] The preceding details and examples have provided a clear description of the disclosure and its use. Many modifications and variations within the scope of the disclosure will be readily apparent to those skilled in the art. All publications and references discussed above are incorporated by reference. Aspects of the disclosure, portions of the various embodiments, other embodiment referred to and any of the various features discussed may be combined or interchanged either in whole or in part. It will be understood that the preceding discussion is by way of example only and is not intended to limit the disclosure or its use.

#### EXEMPLARY EMBODIMENTS.

[0002] The following exemplary embodiments are provided, the numbering of which is not to be construed as designating levels of importance:

[0003] Embodiment 1 provides a method for determining the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution comprising:

- a. correlating (i) change in conductivity or resistivity of a reference aqueous solution comprising dicarboxylic acids and diamines as a function of temperature with (ii) at least one of total concentration of dicarboxylic acids and diamines and molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;
- b. measuring electrical conductivity or resistivity of an aqueous solution comprising the dicarboxylic acids and the diamines at two or more different temperatures; and
- c. applying the correlation of step (a) to the measurements of step (b) to determine at least one of (i) total concentration of dicarboxylic acids and diamines in the aqueous solution and (ii) the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

[0004] Embodiment 2 provides the method of Embodiment 1 wherein steps (b) and (c) are carried out continuously.

[0005] Embodiment 3 provides the method of any one of Embodiments 1-2 wherein the measurements of step (b) and the determination of step (c) are carried out on an aqueous feed for a polyamidation process.

[0006] Embodiment 4 provides the method of any one of Embodiments 1-3 wherein step (c) further comprises determining the concentration of dicarboxylic acids and diamines in the aqueous solution.

[0007] Embodiment 5 provides the method of any one of Embodiments 1-4 wherein step (c) further comprises determining the molar ratio of:

- i. the sum of the molar concentrations of dicarboxylic acids; to
- ii. the sum of the molar concentrations of diamines.

[0008] Embodiment 6 provides the method of any one of Embodiments 1-5 further comprising determining the total concentration of dicarboxylic acids and diamines in the aqueous solution and the molar ratio of dicarboxylic acids to diamines in the aqueous solution.

[0009] Embodiment 7 provides the method of any one of Embodiments 1-6 wherein step (c) further comprises determining a degree of amidation.

[0010] Embodiment 8 provides the method of any one of Embodiments 1-7 wherein the measuring step (b) further comprises collecting samples for conductivity or resistivity measurement and performing the measurement at a location physically separated from a polyamide manufacturing facility.

[0011] Embodiment 9 provides the method of any one of Embodiments 1-8 wherein conductivity and temperature measurements are made on-line either continuously or periodically within the production process piping or equipment.

[0012] Embodiment 10 provides the method of any one of Embodiments 1-9 wherein the measured conductivities and temperatures are used for the control of process related equipment including flow rates, temperatures, pressures, and operational liquid level.

[0013] Embodiment 11 provides the method of any one of Embodiments 1-10 wherein the dicarboxylic acid is adipic acid.

[0014] Embodiment 12 provides the method of any one of Embodiments 1-11 wherein the diamine is hexamethylene diamine.

[0015] Embodiment 13 provides the method of any one of Embodiments 1-12 wherein the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine.

[0016] Embodiment 14 provides a method for controlling a polyamidation reaction comprising:

- a. correlating (i) change in conductivity or resistivity as a function of temperature with (ii) at least one of total concentration and molar ratio of dicarboxylic acids to diamines in a reference aqueous solution;
- b. measuring electrical conductivity or resistivity of an aqueous solution comprising the dicarboxylic acids and the diamines at two or more different temperatures; and
- c. applying the correlation of step (a) to the measurements of step (b) to adjust at least one of the total concentration of the dicarboxylic acids and the diamines in the aqueous solution and the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

**[0017]** Embodiment 15 provides at least one machine readable medium with instructions for controlling the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution, the instructions, when executed by processing circuitry, cause the processing circuitry to perform operations:

obtaining an electrical model for a reference aqueous solution comprising dicarboxylic acids and diamines, the electrical model correlating electrical conductivity or resistivity as a function of temperature with at least one of a total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;

obtaining, from a first probe, a first measure of electrical conductivity or resistivity of an aqueous solution at a first temperature;

obtaining, from a second probe, a second measure of electrical conductivity or resistivity of the aqueous solution at a second temperature, the second temperature being different than the first;

applying the first measure and the second measure to the electrical model to determine at least one of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution; and

actuating a process controller to adjust the aqueous solution based on the determination of at least one of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

**[0018]** Embodiment 16 provides the at least one machine readable medium of Embodiment 15, wherein obtaining the first measure, obtaining the second measure, and applying the first measure and the second measure to the electrical model are carried out continuously to determine whether to actuate the process controller.

**[0019]** Embodiment 17 provides the at least one machine readable medium of any one of Embodiments 15-16, wherein the aqueous solution is in an aqueous feed for a polyamidation process.

**[0020]** Embodiment 18 provides the at least one machine readable medium of any one of Embodiments 15-17, wherein the total concentration of dicarboxylic acids and diamines in the aqueous solution is determined when the first measure and the second measure are applied to the electrical model.

**[0021]** Embodiment 19 provides the at least one machine readable medium of any one of Embodiments 15-18, wherein applying the first measure and the second measure to the electrical model further includes determining a molar ratio of:

- i. the sum of the molar concentrations of dicarboxylic acids; to
- ii. the sum of the molar concentrations of diamines.

**[0022]** Embodiment 20 provides the at least one machine readable medium of any one of Embodiments 15-19, wherein both the total concentration of dicarboxylic acids and diamines in the aqueous solution, and the molar ratio of dicarboxylic acids to diamines in the aqueous solution are determined when the first measure and the second measure are applied to the electrical model.

**[0023]** Embodiment 21 provides the at least one machine readable medium of any one of Embodiments 15-20, wherein applying the first measure and the second measure to the electrical model further comprises determining a degree of amidation.

**[0024]** Embodiment 22 provides the at least one machine readable medium of any one of Embodiments 15-21, wherein the first probe or the second probe are at a location physically separated from a polyamide manufacturing facility.

**[0025]** Embodiment 23 provides the at least one machine readable medium of any one of Embodiments 15-22, wherein the first probe or the second probe are located within production process piping or equipment and provide on-line measurements of conductivity or temperature either continuously or periodically within the production process piping or equipment.

**[0026]** Embodiment 24 provides the at least one machine readable medium of any one of Embodiments 15-23, the process controller controls at least one of flow rates, temperatures, pressures, or operational liquid level.

[0027] Embodiment 25 provides the at least one machine readable medium of any one of Embodiments 15-24, wherein the dicarboxylic acid is adipic acid.

[0028] Embodiment 26 provides the at least one machine readable medium of any one of Embodiments 15-25, wherein the diamine is hexamethylene diamine.

[0029] Embodiment 27 provides the at least one machine readable medium of any one of Embodiments 15-26, wherein the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine.

[0030] Embodiment 28 provides a system for controlling the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution, the system comprising:

- a first probe disposed in an aqueous solution at a first temperature, the first probe to produce a first measure of electrical conductivity or resistivity of the aqueous solution, the aqueous solution comprising dicarboxylic acids and diamines;

- a second probe disposed in the aqueous solution at a second temperature different than the first temperature, the second probe to produce a second measure of electrical conductivity or resistivity of the aqueous solution; and

- processing circuitry to:

- obtain an electrical model for a reference aqueous solution comprising dicarboxylic acids and diamines, the electrical model correlating electrical conductivity or resistivity as a function of temperature with at least one of total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;

- obtain the first measure;

- obtain the second measure;

- apply the first measure and the second measure to the electrical model to determine at least one of total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution; and

- actuate a process controller to adjust the aqueous solution based on the determination of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

[0031] Embodiment 29 provides the system of Embodiment 28, wherein, when in operation, the processing circuitry continuously obtains the first measure, obtains the second measure, and applies the first measure and the second measure to the electrical model to determine whether to actuate the process controller.

[0032] Embodiment 30 provides the system of any one of Embodiments 28-29, wherein the aqueous solution is in an aqueous feed for a polyamidation process.

[0033] Embodiment 31 provides the system of any one of Embodiments 28-30, wherein, to apply the first measure and the second measure to the electrical model, the processing circuitry determines the concentration of dicarboxylic acids and diamines in the aqueous solution.

[0034] Embodiment 32 provides the system of any one of Embodiments 28-31, wherein, to apply the first measure and the second measure to the electrical model, the processing circuitry is to determine a molar ratio of:

- i. the sum of the molar concentrations of dicarboxylic acids; to
- ii. the sum of the molar concentrations of diamines.

[0035] Embodiment 33 provides the system of any one of Embodiments 28-32, wherein the operations further comprise determining the total concentration of dicarboxylic acids and diamines in the aqueous solution and the molar ratio of dicarboxylic acids to diamines in the aqueous solution.

[0036] Embodiment 34 provides the system of any one of Embodiments 28-33, wherein, to apply the first measure and the second measure to the electrical model, the processing circuitry is to determine a degree of amidation.

[0037] Embodiment 35 provides the system of any one of Embodiments 28-34, wherein the first probe or the second probe are at a location physically separated from a polyamide manufacturing facility.

[0038] Embodiment 36 provides the system of any one of Embodiments 28-35, wherein the first probe or the second probe are located within production process piping or equipment and provide on-line measurements of conductivity or temperature either continuously or periodically within the production process piping or equipment.

[0039] Embodiment 37 provides the system of any one of Embodiments 28-36, the process controller controls at least one of flow rates, temperatures, pressures, or operational liquid level.

[0040] Embodiment 38 provides the system of any one of Embodiments 28-37, wherein the dicarboxylic acid is adipic acid.

[0041] Embodiment 39 provides the system of any one of Embodiments 28-38, wherein the diamine is hexamethylene diamine.

[0042] Embodiment 40 provides the system of any one of Embodiments 28-39, wherein the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine.

[0043] Embodiment 41 provides the method, machine readable medium, or system of any one or any combination of Embodiments 1-40 optionally configured such that all elements or options recited are available to use or select from.

## CLAIMS

What is claimed is:

1. A method for determining the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution comprising:
  - a. correlating (i) change in conductivity or resistivity of a reference aqueous solution comprising dicarboxylic acids and diamines as a function of temperature with (ii) at least one of total concentration of dicarboxylic acids and diamines and molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;
  - b. measuring electrical conductivity or resistivity of an aqueous solution comprising the dicarboxylic acids and the diamines at two or more different temperatures; and
  - c. applying the correlation of step (a) to the measurements of step (b) to determine at least one of (i) total concentration of dicarboxylic acids and diamines in the aqueous solution and (ii) the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.
2. The method of claim 1 wherein steps (b) and (c) are carried out continuously.
3. The method of claim 1 wherein the measurements of step (b) and the determination of step (c) are carried out on an aqueous feed for a polyamidation process.
4. The method of claim 1 wherein step (c) further comprises determining the concentration of dicarboxylic acids and diamines in the aqueous solution.
5. The method of claim 1 wherein step (c) further comprises determining the molar ratio of:
  - i. the sum of the molar concentrations of dicarboxylic acids; to
  - ii. the sum of the molar concentrations of diamines.
6. The method of claim 1 further comprising determining the total concentration of dicarboxylic acids and diamines in the aqueous solution and the molar ratio of dicarboxylic acids to diamines in the aqueous solution.

7. The method of claim 1 wherein step (c) further comprises determining a degree of amidation.
8. The method of claim 1 wherein the measuring step (b) further comprises collecting samples for conductivity or resistivity measurement and performing the measurement at a location physically separated from a polyamide manufacturing facility.
9. The method of claim 1 wherein conductivity and temperature measurements are made on-line either continuously or periodically within the production process piping or equipment.
10. The method of claim 1 wherein the measured conductivities and temperatures are used for the control of process related equipment including flow rates, temperatures, pressures, and operational liquid level.
11. The method of claim 1 wherein the dicarboxylic acid is adipic acid.
12. The method of claim 1 wherein the diamine is hexamethylene diamine.
13. The method of claim 1 wherein the dicarboxylic acid is adipic acid and the diamine is hexamethylene diamine.
14. At least one machine readable medium with instructions for controlling the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution, the instructions, when executed by processing circuitry, cause the processing circuitry to perform operations:
  - obtaining an electrical model for a reference aqueous solution comprising dicarboxylic acids and diamines, the electrical model correlating electrical conductivity or resistivity as a function of temperature with at least one of a total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;
  - obtaining, from a first probe, a first measure of electrical conductivity or resistivity of an aqueous solution at a first temperature;

obtaining, from a second probe, a second measure of electrical conductivity or resistivity of the aqueous solution at a second temperature, the second temperature being different than the first;

applying the first measure and the second measure to the electrical model to determine at least one of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution; and

actuating a process controller to adjust the aqueous solution based on the determination of at least one of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

15. A system for controlling the total concentration of dicarboxylic acids and diamines or the molar ratio of dicarboxylic acids to diamines in an aqueous solution, the system comprising:

a first probe disposed in an aqueous solution at a first temperature, the first probe to produce a first measure of electrical conductivity or resistivity of the aqueous solution, the aqueous solution comprising dicarboxylic acids and diamines;

a second probe disposed in the aqueous solution at a second temperature different than the first temperature, the second probe to produce a second measure of electrical conductivity or resistivity of the aqueous solution; and

processing circuitry to:

obtain an electrical model for a reference aqueous solution comprising dicarboxylic acids and diamines, the electrical model correlating electrical conductivity or resistivity as a function of temperature with at least one of total concentration of dicarboxylic acids and diamines, or a molar ratio of dicarboxylic acids to diamines in the reference aqueous solution;

obtain the first measure;

obtain the second measure;

apply the first measure and the second measure to the electrical model to determine at least one of total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution; and

actuate a process controller to adjust the aqueous solution based on the determination of the total concentration of dicarboxylic acids and diamines in the aqueous solution, or the molar ratio of the dicarboxylic acids to the diamines in the aqueous solution.

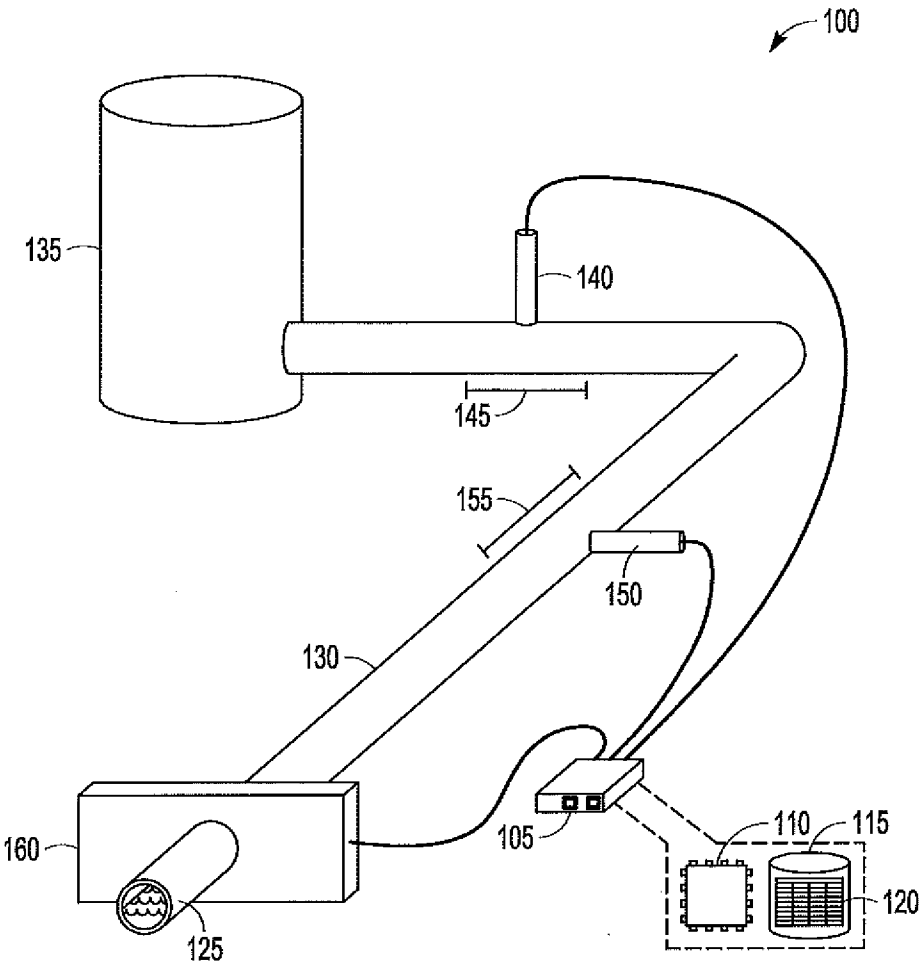


FIG. 1

2/7

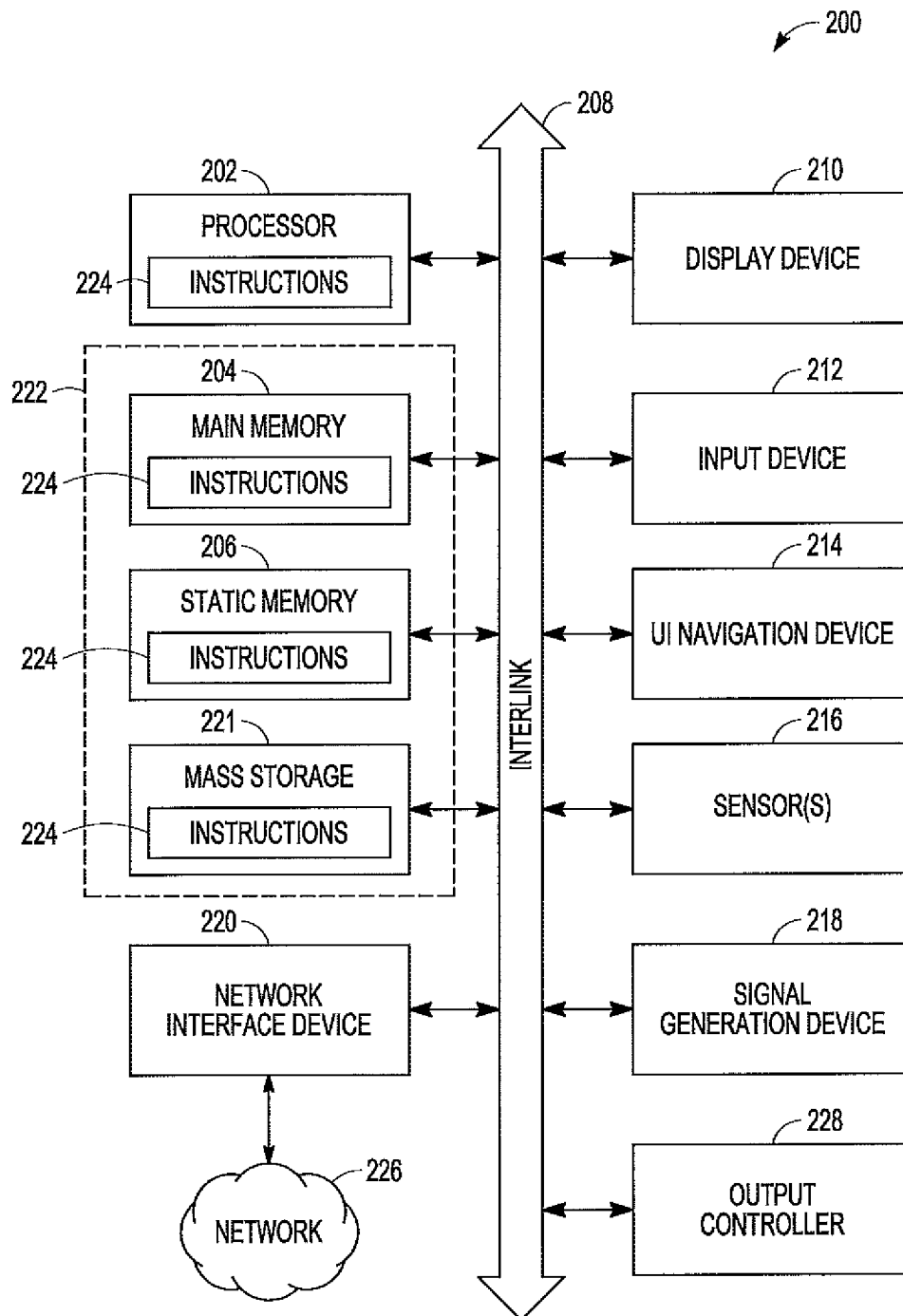


FIG. 2

3/7

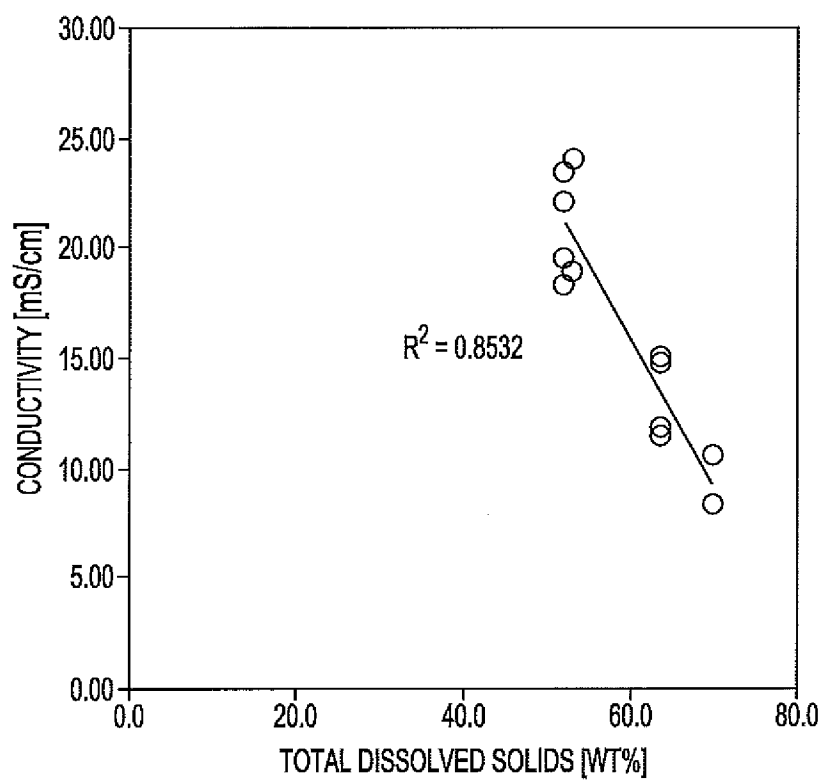


FIG. 3

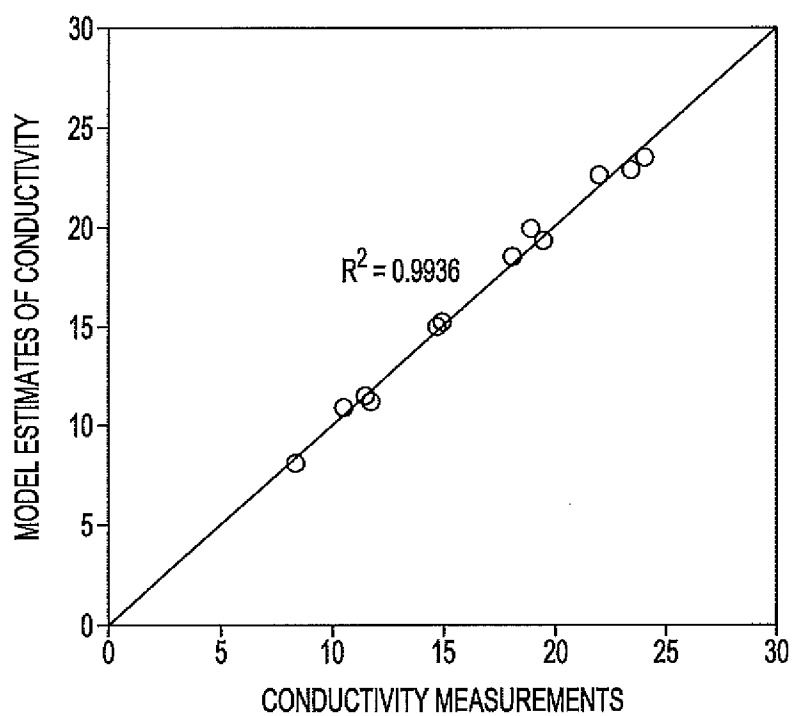


FIG. 4

4/7

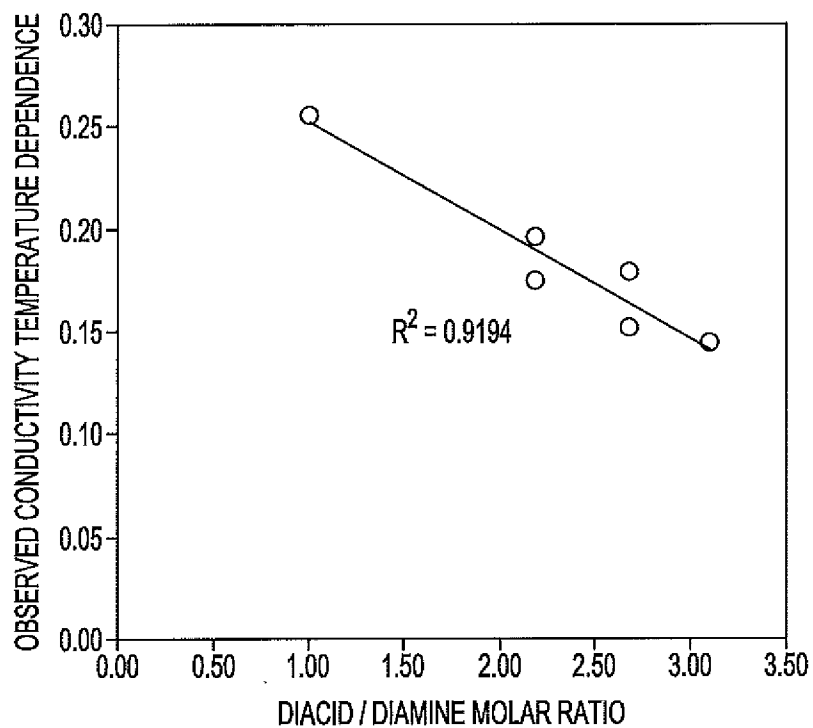


FIG. 5

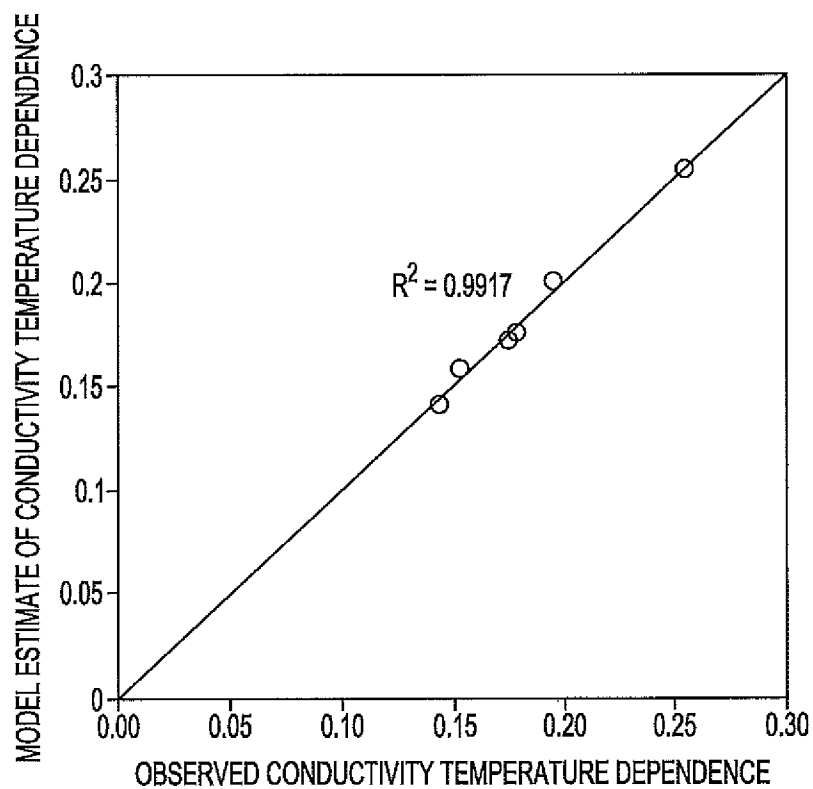


FIG. 6

5/7

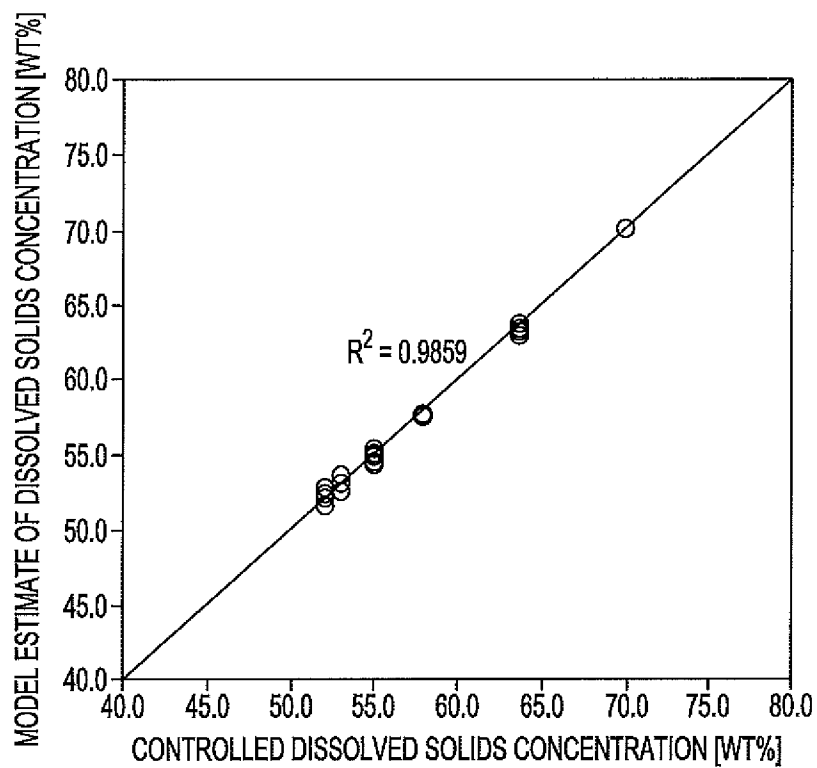


FIG. 7

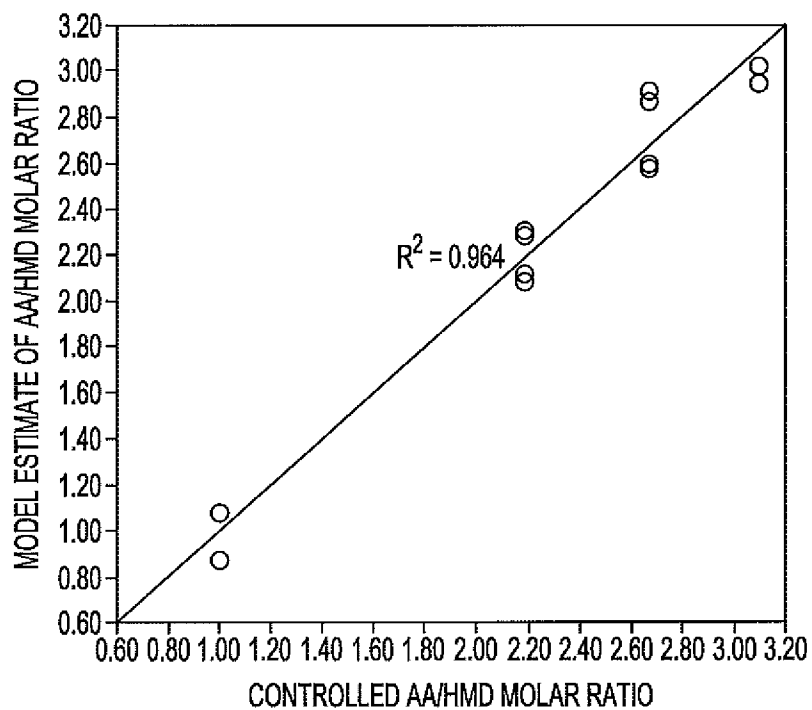


FIG. 8

6/7

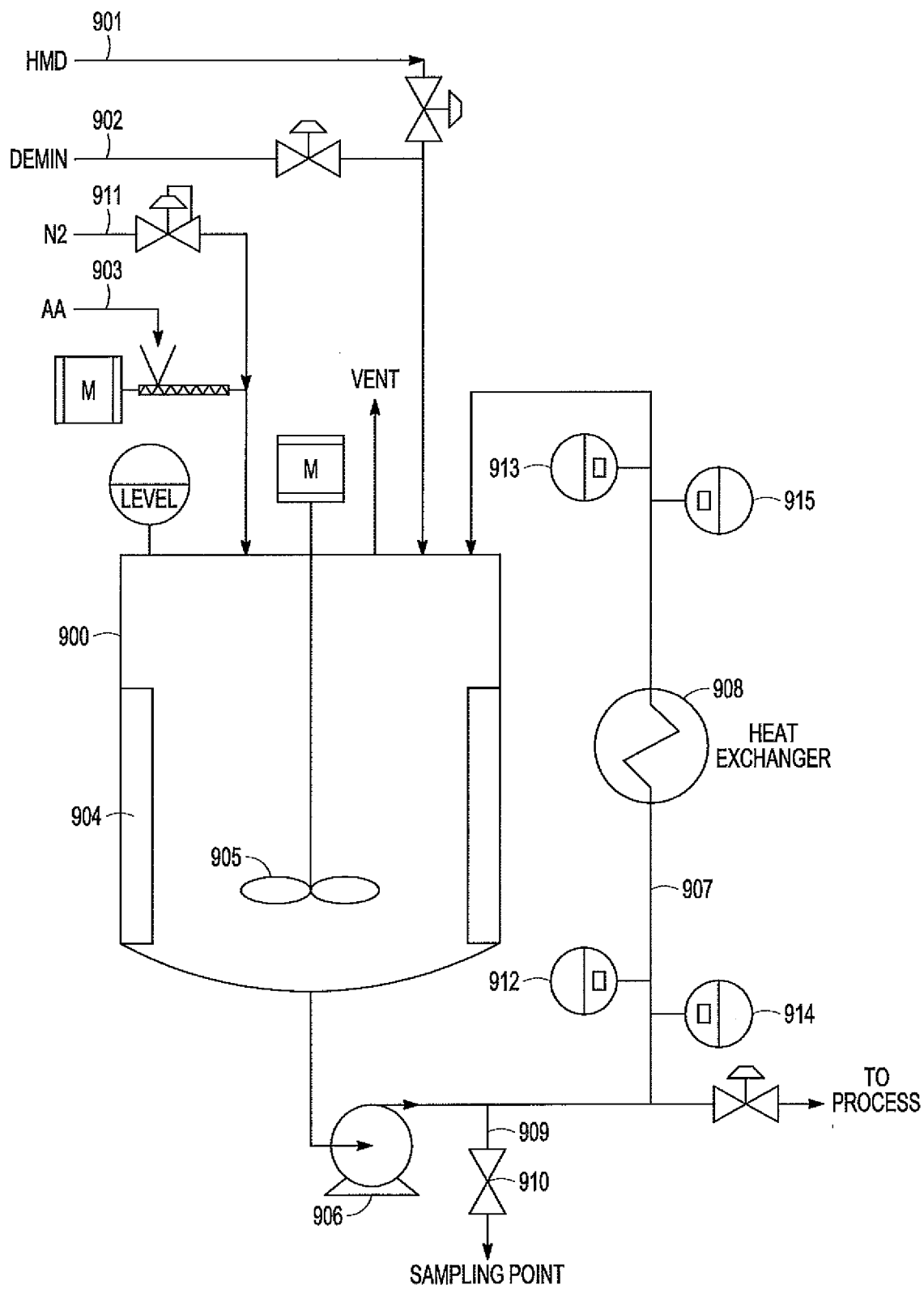


FIG. 9

7/7

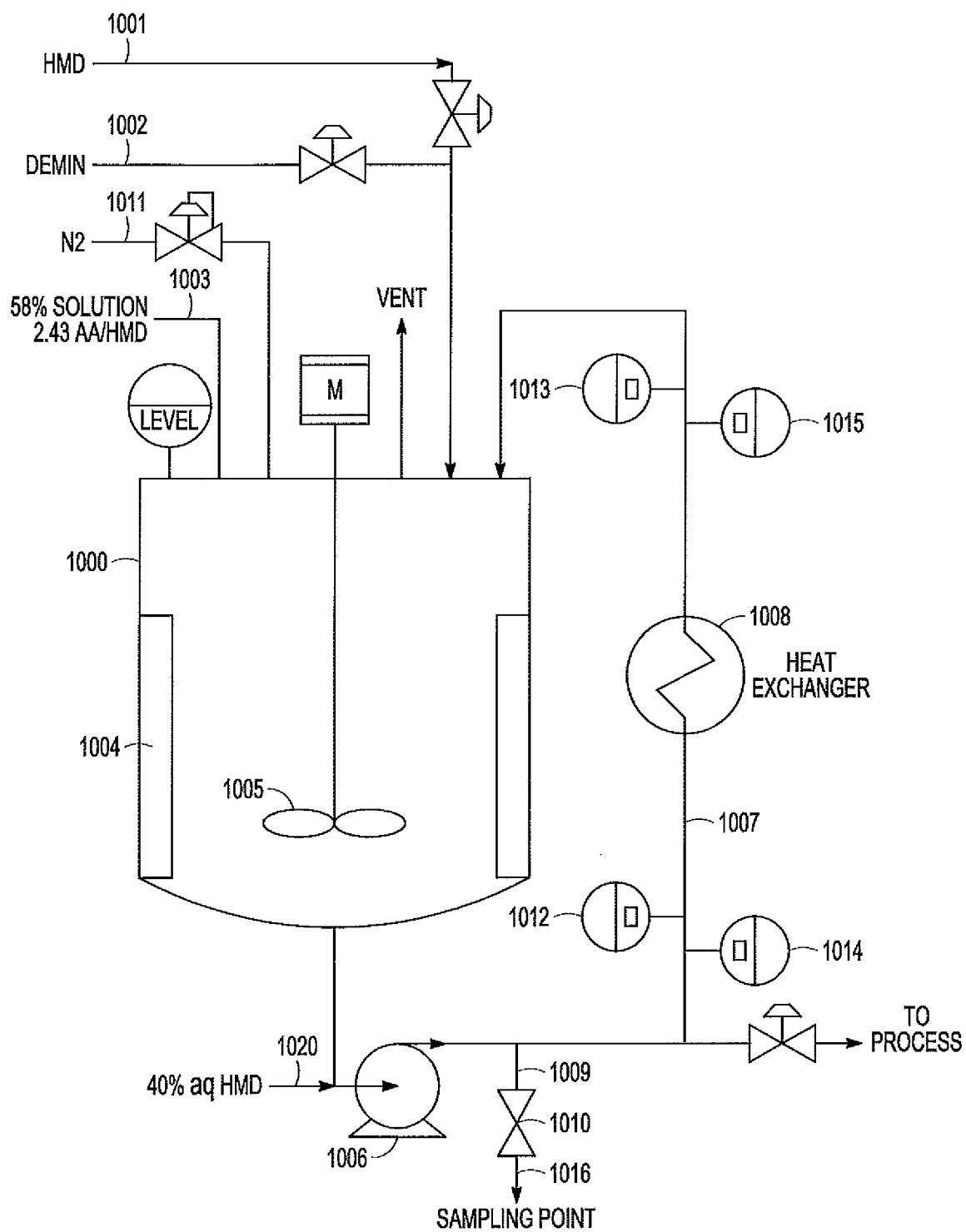


FIG. 10

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2017/024675

A. CLASSIFICATION OF SUBJECT MATTER  
INV. G01N27/10  
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)  
G01N C08G G05D C08L

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)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                      | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | DE 198 35 137 A1 (CONDUCTA ENDRESS & HAUSER [DE]) 4 May 2000 (2000-05-04)<br>column 1, lines 3-6, 22-25, 27-29, 33-35<br>-----                                          | 1-15                  |
| A         | WO 2013/154742 A1 (PHILLIPS 66 CO [US]; LORD III CHARLES JOHN [US]; NEWLAND JOHN STEPHEN) 17 October 2013 (2013-10-17)<br>paragraphs [0048] - [0051]; figure 2<br>----- | 1-15                  |
| A         | US 5 137 831 A (GRUTESER RUDOLF [DE])<br>11 August 1992 (1992-08-11)<br>column 3, lines 4-5<br>column 5, lines 46-53<br>-----                                           | 1-15                  |
| A         | US 2016/068634 A1 (WELCH ROBERT J [US] ET AL) 10 March 2016 (2016-03-10)<br>paragraphs [0002], [0010]<br>-----                                                          | 1-15                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

6 June 2017

Date of mailing of the international search report

16/06/2017

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/024675

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date                                                                                                                                                                                                                         |
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| WO 2013154742                             | A1                  | 17-10-2013                 | CA 2869558 A1 17-10-2013<br>CN 104662413 A 27-05-2015<br>EP 2836825 A1 18-02-2015<br>JP 2015514224 A 18-05-2015<br>KR 20150023255 A 05-03-2015<br>US 2013271149 A1 17-10-2013<br>US 2013273462 A1 17-10-2013<br>WO 2013154742 A1 17-10-2013 |
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