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(54) Title: PROCESS FOR PRODUCING HIGH SOLIDS POLYSILICIC ACID WITH HIGH SODA EFFICIENCY AND SILICA YIELD

(57) Abstract: Provided is a method for the preparation of high solids, low sodium content polysilicic acid (PSA). The method includes the steps of acidifying a waterglass solution such that the pH of the solution falls to 4 or less in a time period of less than about 20 seconds; and contacting the reduced pH waterglass solution with an acid exchange resin. In a preferred embodiment, the PSA is prepared in a recirculating loop.

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PROCESS FOR PRODUCING HIGH SOLIDS POLYSILICIC ACID WITH HIGH SODA EFFICIENCY AND SILICA YIELD

TECHNICAL FIELD

[0001] This invention relates to new polysilicic acid compositions and their preparation.

BACKGROUND

[0002] Polysilicic acid (PSA) is used in a variety of specialty chemical, construction, and other applications, such as, for example, the preparation of catalyst substrates and zeolites, as well as the stabilizing of sandy soils prior to pouring building foundations. One of the most important applications of PSA is the preparation of colloidal silica.

[0003] One common method for the preparation of PSA is the contacting of an alkali silicate solution, such as a sodium silicate solution with a hydrogen exchange resin which is in the hydrogen form. Such resins exchange the alkali cations of the alkali silicate for protons. Ultimately, a PSA product, generally containing a residual presence of alkali ion is produced. In a common practice, the alkali silicate is waterglass, which is generally an aqueous solution of sodium or other alkali silicate comprising monomeric silicates, and short lengths of polymeric silicate. Methods for preparing waterglass solutions are known in the art. It is generally prepared from silica (sand) and either caustic (an alkali hydroxide such as sodium hydroxide) or soda ash (sodium carbonate). Use of soda ash in a high temperature furnace with sand is the most common method.

[0004] The preparation of PSA with exchange resins has been fraught with problems which limit the efficiency of many PSA preparation processes. At many pH values, silicates tend to polymerize and/or aggregate, leading to the onset of gelling and even rapid solidification. Above a pH of about 11, silicates are generally indefinitely stable and the tendency to polymerize and gel is extremely weak at best. Below pH 4, the solutions are metastable, and stability time (*i.e.*, the time until gel forms and ability to flow is destroyed) is roughly in the range of from about 2 to 48 hours. Stability times exhibit a dependence on the pH, concentration of silicates, solution temperature, as well as other variables, such as, for example, the salt content of the PSA solution. At pH values in the range of from about 4 to about 8, instability is much greater than at other pH values, with extremely short stability times which can be on the order of minutes, seconds, or even less.

[0005] The pH-dependent polymerization and aggregation is a detriment from the standpoint of PSA preparation. When an exchange resin and column are used, the

waterglass solution is often introduced into the column at a pH above 10. (Such high pH values generally occur because, among other reasons, the silicate source is usually stored at pH values at which it exhibits at least moderate storage stability, which is generally a pH of about 10.5 or greater.) As the cation exchange reaction takes place in the column, the pH of the exchange product solution falls, with the drop corresponding to the degree of ion-replacement in the waterglass solution. As the ion-replacement proceeds, the pH of the PSA solution can quickly fall into the pH range which favors gel formation, *i.e.*, in the range of from about 4 to about 8, and small molecular weight silica species rapidly aggregate into larger molecular weight silica species. The effect of pH is described in detail in figure 4.13 by Iler, R. K. *The Chemistry of Silica* 367 (Wiley, New York, 1979). Ordinarily, the PSA eluant is withdrawn or collected in a product tank after eluting from the column. However, gel formation, even in small amounts, can impede the ability of the PSA product to flow, and gel formation in large amounts can effectively stop the passage of 1) waterglass into the column, and 2) product PSA through and out of the column. Gel formation also has a strongly negative impact on product yield.

[0006] In order to minimize gel formation, it has heretofore been thought necessary to conduct the ion exchange reaction at relatively low waterglass (low SiO_2) concentration. At such low concentrations, the stability time of the solution is long enough that gel formation is absent or at least hindered such that the flow of waterglass solution through the column is not impeded during passage through the column.

[0007] U.S. Patent 3,468,813 discloses a method of producing an acid silica sol (otherwise known as PSA) at concentrations up to 12% SiO_2. However, in order to minimize gel formation in the column, which remains at a pH conducive to gel formation, the waterglass feed requires refrigeration to a temperature between 24°F and 60°F, as well as an elevated flow rate through the column.

[0008] A detriment of other methods for producing polysilicic acid is the relatively low quality PSA product produced. For example, high total surface area is critical for many PSA applications. It is thus desirable to produce a PSA having relatively small particles to increase total surface area. However, known methods which produce relatively high solids content PSA also tend to produce relatively large particles, giving a relatively low surface area product. For example, U.S. Patent 2,727,008 discloses a method of producing metastable silica sol by mixing an alkali metal silicate and a sol having particles of less than 4 nm size. A mixture of a metal silicate and water is subjected to deionization with a cation exchange resin. The product is mixed with alkali metal silicate and deionized again.

This stepwise process is continued, incrementally increasing the silica concentration. With this stepwise method, a 10% SiO_2 sol was obtained with surface area greater than 1000 m^2/g. In another method, alkali metal silicate is continuously added to a heel of aqueous silica sol recirculating through an ion exchange column and tanks in series. By this method, pH after addition of the alkali metal silicate is allowed to rise to 10.5 to 10.9. As a result, the silica sol phase passes repeatedly through the unstable pH range of 4-8 during the recirculation. In accord with the inventor's observation (section 5, line 8), aggregation or particle growth occur with this method. The result is low surface area and large particle size. With this recirculation method, a 11.8% SiO_2 sol was prepared but with relatively low surface area, 640 m^2/g.

[0009] The propensity to form a gel limits the amount and concentration of PSA product which can be formed from a waterglass solution. Because the silicate concentration has to be reduced by dilution with water in order to prevent gelling, particularly upon contact with an ion exchange resin, available processes are limited to producing PSA products having low equivalent SiO_2 content or "low solids." For example, methods presently available are generally limited to 12 wt % PSA, with limits of about 8 wt% and the like being more common. In general gel formation acts as a real limit on process efficiency. The time and cost required for drying or concentrating the PSA product scales with the amount of water in the PSA eluant; thus, reducing the amount of water in the product is desirable.

BRIEF DESCRIPTION OF THE INVENTION

[0010] Surprisingly, it has been found that high solids PSA can be produced by a procedure which includes the rapid pH reduction of a waterglass component prior to or upon introducing it into a system which includes a phase, which may be a circulating phase, having a pH of less than about 4, and preferably less than about 3.2. In some embodiments, the phase recirculates through the acid exchange medium. The phase is referred to herein as the "circulating phase." In further embodiments, the recirculation takes place after the introduction of additional waterglass solution. In still other embodiments, the waterglass is introduced into the circulating phase in a continuous manner, and the circulating phase is recirculated continuously. It is preferred to acidify the circulating phase, the water glass solution, or both, as described herein. In many embodiments, the PSA produced by the present inventive method is particularly high quality in that in addition to being high in solids, it has a relatively small equivalent

particle diameter and relatively high surface area. By the methods disclosed herein, PSA having, simultaneously, solids as high as or higher than about 20 wt %, surface areas as high as or higher than about 2500 m^2 per gram, and equivalent particle diameters as small as about 1.0 nm or even smaller can be produced.

[0011] The production of high-solids PSA product from such a system is surprising because it could be expected that acid exchange resins generally would not function well at low pH, particularly at pH values as low as 4 or lower, values easily reached in the preparation of the inventive PSA product. As indicated above, one could expect that the loss in resin efficiency would generally happen quickly with drop in pH as a drop in one pH unit corresponds to a ten fold increase in the concentration of free protons. Note that the presence of protons would be expected to drive the desired proton exchange reaction in reverse, such as when they are used to regenerate the resin to its protonated form.

[0012] It has been found that with the inventive method, acid exchange resins have a good efficacy of cation exchange when used with solutions of sodium or other silicates/PSA solutions at pH values as low as 1.3, and a high-solids PSA product having a high surface area and a low equivalent particle diameter can be formed. The process of the present invention is a process for preparing PSA, the process including the steps of:

1) circulating a circulating phase through a system, said system including:

a recirculation loop having:

a contact chamber which includes an inlet and an outlet, said contact chamber also comprising a volume, at least a portion of which contains one or more acid exchange resins;

2) introducing a waterglass solution into the recirculation loop, such that it joins with the circulating phase; wherein the pH of the introduced waterglass solution is less than about 4 within a time of 5 minutes or less, preferably a time of 50 seconds or less, and more preferably a time of 20 seconds or less of introduction; wherein steps 1 and 2 are conducted such that a PSA solution is formed in the contact chamber; and, if desired,

3) withdrawing at least a portion of the formed PSA solution from said recirculation loop;

wherein the solution contained in the volume of the system is the circulating phase, and wherein, during PSA solution formation, the circulating phase has a pH average of about 4 or less throughout its volume, and the contact chamber has a pH of less than about 4 throughout its volume. In a preferred embodiment, the PSA product is high-solids, having

a solids content of more than about 8 wt% PSA, and in some embodiments more than about 12 wt% PSA.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **Fig. 1**-Depicted is an apparatus in which the waterglass is introduced near a mixing element located in a product tank contained within a recirculation loop.

[0014] **Fig. 2**-Depicted is an apparatus in which the waterglass is introduced into a mixing element located immediately before the contact chamber contained within a recirculation loop.

[0015] **Fig. 3**-Depicted is an apparatus in which the contact chamber is part of a Higgins Loop contactor.

[0016] **Fig. 4**-Depicted is an apparatus in which the contact chamber is a stirred tank reactor containing an ion exchange resin.

[0017] **Fig. 5**-Depicted is a staged product tank.

DETAILED DESCRIPTION OF THE INVENTION

[0018] By "high-solids," it is meant herein a PSA product greater than about 6 wt % solids, where "solids" refers to the weight percent of PSA in the PSA product.

[0019] By "PSA product," it is meant herein a metastable acid silicate solution having a pH of less than about 4.

[0020] By "metastable point," it is meant the pH at which the circulating phase has a gel time of greater than about 1 minute.

[0021] By "gel time" is meant the length of time before the circulating phase exhibits signs of gel formation, *i.e.*, changes to its fluid nature which inhibit its ability to circulate through the contact chamber.

[0022] "Waterglass" as used herein can mean an alkali silicate solution such as sodium silicates, potassium silicates, lithium silicates, and ammonium silicates. However, preferred are sodium silicates.

[0023] By "recirculation loop" is meant a system including one or more components, each component including an input where a fluid input enters the component and an output, where fluid output exits the component, wherein the components are at least serially connected in fluid communication and wherein fluid output from each component can travel through each of the other components before reentering the component as fluid

input. As used herein, the recirculation loop includes at least a contact chamber. The total circulating volume of fluid in the recirculation loop is the "circulating phase."

[0024] By "circulating phase" is meant a volume of fluid which circulates in the recirculation loop. The volume can be added to or withdrawn from. For example, in the present invention, a waterglass solution is added to, and becomes part of, the circulating phase. The addition can be continuous or discrete. Furthermore, portions of the circulating system can be withdrawn, separated from the circulating phase bulk. For example, PSA product can be removed from the circulating phase by, for example, being drained from the circulation loop or otherwise sequestered in a vessel, such as a product tank. In one embodiment, the sequestering can be out of circulation, or, in another embodiment, if the PSA product is such that it can be sequestered without appreciably hindering the flow of the circulating phase, it is permissible for the sequestering to be within the recirculation loop. In another embodiment, the PSA product is withdrawn from the circulating phase, continuously or discretely as desired. The PSA product as referred to herein includes water associated with the PSA, such as water withdrawn with the PSA. Such water would be present in the circulation loop by, for example, being introduced with the waterglass solution into the circulation loop. The waterglass input into the system is added to the circulating phase and becomes part of the circulating phase upon introduction.

[0025] In one embodiment, the present invention is a process for the preparation of polysilicic acid (PSA), said process comprising: i) circulating a circulating phase, said circulating phase having a volume, through a system, said system comprising a recirculation loop comprising a contact chamber comprising an inlet and an outlet, said contact chamber also comprising a volume, at least a portion of which contains one or more acid exchange resins; and ii) introducing a waterglass solution into the recirculation loop such that it joins with the circulating phase; wherein the pH of the introduced waterglass solution is less than about 4 within 5 minutes of introduction into the recirculation loop; said circulating and introducing occurring such that PSA is formed in the contact chamber; wherein, during PSA formation, the pH of the circulating phase has a volume average pH value of less than about 4, and the pH throughout the volume in the contact chamber is less than about 4. In another embodiment, the present invention comprises a polysilicic acid (PSA) product formed by the foregoing process.

[0026] The present inventive method can be used to fabricate (PSA) compositions characterized by higher solids content and higher surface area than PSA compositions

produced by other methods. Thus, in one embodiment the present invention comprises a (PSA) composition produced by a process comprising converting a sodium or other alkali silicate solution via sodium or other alkali cation/hydrogen exchange, to PSA, wherein upon said exchange, said PSA composition is characterized by a PSA solids content of greater than about 8 wt %, and an equivalent particle diameter of less than about 3.0 nm.

[0027] In one embodiment, the circulating phase at the start of the PSA preparation process comprises an amount of waterglass or PSA. In other embodiments, the circulating phase at the start of the PSA preparation process comprises PSA or waterglass, or both, as well as water, if desired.

[0028] The present invention comprises a contact chamber in which the circulating phase of the inventive method comes into contact with an acid exchange resin. The contact chamber holds the resin immobile such that the circulating phase flows through it. During recirculation, the circulating phase is exposed to the resin. It is permissible for the resin to move to a degree. As shown in **Fig. 4**, the resin may be stirred. As shown in **Fig. 3**, the resin may move with a pulse of the Higgins Loop. For example, after packing the resin in the chamber, the resin may be subject to further settling, particularly upon circulation or other motion of the circulating phase. The resin may expand in volume once exposed to the circulating phase. Preferably, the resin is placed such that it is distributed perpendicularly to the flow of the circulating phase, and such that it preferably occupies the cross section of flow at one or more locations in the path of circulation.

[0029] The inventive method preferably utilizes one or more exchange resins. The one or more exchange resins are ion exchange resins capable of exchanging protons for waterglass cations, such as, for example sodium, potassium, lithium, ammonium or other alkali cations. Preferred are acid exchange resins, particularly strong acid exchange resins, although weak acid exchange resins can be utilized in addition to or instead of strong acid exchange resins. The resin is preferably in the form of beads or granules. While it may be preferable in some embodiments to use a resin having average particle diameters in the range of from about 600 microns to about 700 microns, it is permissible to use resins having a wide range of other particle sizes and particle size distributions.

[0030] Examples of preferred strong acid exchange resins include Amberjet 1500H, Amberlite IR120H, and Dowex G-26H. Examples of suitable strong acid resins include Amberjet 1500H, Amberlite IRA120H, Amberlite IR-122, Amberlite IR-200, available from Rohm and Haas; Dowex G-26, Marathon C, Marathon C-10, Marathon MSC, available from Dow Chemical; Diaion SK1B, SK-110, other SK resins, PK-228, available

from Mitsubishi; Ionac C-249, C-250, CFP-110, available from Sybron; Lewatit S-100, KP-10, SP-120, available from Bayer; C-100, C100X10, C-150, available from Purolite. In some embodiments, one or more weak acid resins can be used, such as, for example, Amberlite IRC84SPIH, IRC-76, IRC-86; available from Rohm and Haas; Lewatit CNP-80, available from Bayer; Ionac CCP, CC, available from Sybron; Diaion WK20N, available from Mitsubishi; Dowex MAC-3, available from Dow Chemical; C-106, C-105, available from Purolite.

[0031] In other embodiments, the contact chamber includes one or more cation exchange membranes which are used in the contact chamber in addition to or instead of exchange resins. In still other embodiments, acid regenerable zeolite, such as, for example that described in United States Patent No. 2,244,325 could be used in the contact chamber instead of or in addition to one or more acid exchange resins.

[0032] The contact chamber is a void which can be wholly or partially filled with resin. It preferably has both an inlet and an outlet. The disposition of the resin in the void is preferably such that circulating phase entering through the inlet is constrained to pass through the resin before exiting through the outlet. The contact chamber is most conveniently an exchange column, as indicated in Figures 1and 2. Preferably, the resin is disposed across the bore of the column such that the resin intercepts the entire cross section of flow. In one embodiment, the resin is disposed in the vertically positioned column across the cross section of flow, and the circulating phase is pumped up through the resin. In other embodiments, the circulating phase is pumped down though the resin, or allowed to gravitationally seep down through the resin.

[0033] The dimensions of the column and the thickness of the resin layer are not critical. However, it is preferred that the dimensions and resin layer thickness are such that for a given flow rate, the desired degree of ion exchange can take place. If the resin is exhausted and further production of PSA is desired, the resin can be replaced or regenerated. However, in some embodiments, the desired degree of exchange takes place without replacement or regeneration of the exchange resin.

[0034] In one embodiment, the regeneration of the resin is simplified by including it in a loop configuration which allows spent resin to be "swapped" for new or recharged, functional resin, as illustrated in Figure 3. In such as embodiment, functional resin resides in a continuous loop, such as, for example, a Higgins loop, such that the circulating phase can be passed through it. Upon becoming spent, the resin can be moved out of the path of the circulating phase, and functional resin can be moved in place. In some embodiments,

the circulation of the circulating phase is slowed or stopped during the exchange of the spent resin for the functional resin. Once the exchange is accomplished, the circulation of the circulating phase can be reestablished. In this manner, the resin can be refreshed without dismantling the circulation loop. In another embodiment, the spent resin, once moved from the path of the circulating phase, is relocated to a place on the loop where it can be recharged, or in other embodiments, replaced.

[0035] The recirculation loop preferably contains a "product tank" which can be used to collect the PSA product as it forms. In some embodiments, the product tank serves as a reservoir which accommodates the increased volume of the circulating phase as the waterglass solution is added to the circulating phase. In additional or alternative embodiments, the product tank serves as a reservoir from which PSA solution can be withdrawn from the circulating phase. In other embodiments, collection of the PSA product is accomplished by draining all or a portion of the circulating phase into the product tank, and withdrawing PSA product from the product tank.

[0036] The PSA product can be withdrawn, either from the circulating phase or from a collection vessel such as the product tank. The withdrawal can be continuous. Alternatively, it can be withdrawn in discrete amounts, such as at intervals throughout the formation process, or all at once at the end of the formation process. In an exemplary embodiment, the tank has a volume, an inlet and an outlet. The circulating phase flows through the product tank, and a portion of the PSA-containing circulating phase can be removed from the volume of the product tank. Note that in most cases, the circulating phase is a colloidal solution of the PSA, and removal of the PSA product generally entails the direct removal of a portion of the circulating phase. However, it is contemplated by the present invention that the PSA could be removed from the circulating phase in a greater concentration than present in the circulating phase itself, such as by use of an osmotic membrane or ultrafiltration membrane or other means for partially or substantially separating PSA from the bulk of the circulating phase. If desired, the PSA product can be used as-is or processed into another product such as colloidal silica with larger particle diameter by controlled polymerization. If desired, the product can be concentrated through known means such as drying, or other methods, such as evaporation, ultrafiltration, or reverse osmosis.

[0037] The method of the present invention also comprises a means for combining a waterglass input, such as an incoming waterglass supply or stream, with the circulating phase, such that it becomes part of the circulating phase. In a preferred embodiment, the

method of the present invention comprises the use of a prechamber mixer component which mechanically combines an incoming waterglass stream with the circulating phase. After or upon the action by the mixer or other combining means, the pH of the combination of the introduced waterglass and the circulating phase is less than about 4. Preferably, the mixing and pH drop occur in a time of less than about 5 minutes or 1 minute, more preferably less than about 50 seconds, less than about 40 seconds, less than about 20 seconds, and in some embodiments, less than about 12, 8, 6 or 4 seconds. However, depending upon variables such as temperature, the reduced or absent gelling obtainable from the present invention may be present to some degree even at longer times of mixing. Thus, the present invention generally includes within its ambit situations in which reduced or absent gelling is observed with the production of high solids or low particle size PSA in association with rapid pH reduction of input waterglass.

[0038] The water glass solution generally has a pH above the stability range of waterglass prior to its introduction into the circulating phase, but in general, regardless of it's pH, it should have a stability time which is long enough such that it does not begin to gel significantly such that its passage through the column is impeded. In some embodiments, the waterglass solution has a pH above 8, 9, 10, 11, or 12 prior to its introduction into the circulating phase.

[0039] The pH of the waterglass solution at various times after introduction, particularly short times, such as times less than about 20 seconds, can be measured with a pH meter inserted into the flow of the circulating phase at a point which is approximately 20 seconds downstream from the introduction of the waterglass solution. Preferably, the pH is measured at times shorter than 10, 8, 6, 4, 2, 1 or 0.5 seconds downstream from the introduction of the waterglass solution.

[0040] In additional embodiments, which can be a consequence of the quick pH decrease preferred by the method of the present invention, during PSA formation, the pH of the circulating phase has a volume average pH value of less than about 4. In an additional or alternative embodiment, additionally or alternatively, the pH throughout the volume in the contact chamber is less than about 4.

[0041] The pH average throughout the circulating phase can be ascertained or estimated by taking measurements of the circulating phase with pH measuring or monitoring devices at intervals throughout the circulating phase. In order to establish an accurate estimate of the volume average, at least two measurements should be taken: one at the location of the contact chamber inlet, and another at the location of the contact chamber outlet.

Importantly, the two measurements give an indication of the drop caused by the medium in the contact chamber. It is possible that the volume average can only be estimated. However, even if the volume average at any or every time is not easily measured, measuring the place in the circulating phase after waterglass addition at which the circulating phase pH is 4 or below, and assuming a linear drop in pH from the point of waterglass addition will, in most cases, allow the estimation of whether the volume average pH is less than 4, particularly if a linear drop over the length of the column is assumed, and no further pH changes occur in the recirculating loop. With respect to the pH in the contact chamber, whether it is 4 or less throughout can be established by a pH measurement at the inlet and a pH measurement at the outlet, both of which should be less than about 4.

[0042] In one embodiment of the invention, waterglass is introduced into the system in a continuous manner, such as shown in Figures 1, 2, 3, and 4. In the systems depicted in Figures 1-4, the waterglass is stored in a storage tank. In one embodiment, depicted in Figure 1, the water glass is introduced into the product tank where it is mixed into the circulating phase by a mixer which is suitable for achieving the fast drop in waterglass pH as indicated below. In another embodiment, such as that of Figures 2, 3 and 4, the waterglass is introduced into an inline mixer. In Figures 2, 3 and 4, the line which carries the waterglass is joined to the circulating phase at a point after the product tank and before the contact chamber.

[0043] In an exemplary embodiment, a waterglass solution with a pH above 4, and preferably above 8, is combined with a circulating phase having a pH of less than about 4, such that the pH of the combined streams is less than about 4. The combination is performed using a mixing element, such that the pH of the waterglass solution drops to less than about 4 in a time which is less than about 20 seconds, and preferably less than about 6 seconds. The foregoing times can be subject to deviation. In general, it is preferred that the pH undergo a drop from its premixing value to its post-mixing value in a time which is on the order of, or preferably less than, the shortest stability time of the waterglass solution in the range of pH values through which the solution drops upon mixing. As a non-limiting example, the waterglass solution may have a starting pH of 11 and a final pH of 3. For example, the solution may have a stability time of only 10 seconds at a pH of 6.0, but longer stability times at pH values on either side of pH 6.0. The pH drop time during mixing is preferably less than about the shortest stability time, or less than about 10 seconds. To be "stable" for a period of time as used herein means that

gelling (detectible by visual gelled phase and/or agglomeration of the resin beads/granules) is not apparent for the aforementioned period of time. For the sake of formality, it is noted that it may be formally correct to refer to the solution at pH values of less than 7 as PSA, rather than waterglass.

[0044] In another embodiment, the pH of the waterglass solution is greater than about 4, and preferably greater than about pH 8. The waterglass solution has its pH reduced to less than 4 in a time which is less than the minimum stability time for the actual pH range through which the waterglass solution is dropped. In an additional embodiment, the drop is accomplished by mixing the waterglass stream, via the mixer, with a pH lowering component, such as a low pH solution. The pH-lowered waterglass solution is then combined with a recirculating phase which has a pH of less than about 4.

[0045] The mixing can be accomplished by mechanical or other means capable of performing the mixing operation such that the downward shift of the pH of the waterglass solution occurs quickly enough such that gel-formation is minimized. A mixing element, such as a mechanical mixer, can be a static mixer, a stirred tank reactor, a venturi-action based mixer, a pipe T, centrifugal pump, or other appropriate means for combining, either in bulk or continuously, the waterglass solution with the circulating phase, or other acidic medium for eventual introduction into the circulating phase. Other means can be used. In most embodiments, the mixer rapidly effectuates the reduction of the pH of the waterglass solution as it is combined with the circulating phase. In one embodiment, the waterglass is introduced into the product tank, where the pH reduction occurs via an appropriate mixing means, such as, for example, a stirred-tank reactor.

[0046] Most waterglass solutions are prepared from alkali silicate, such as, for example, sodium silicate, and thus, prior to ion exchange, waterglass solutions contain significant amounts of sodium or other alkali cations. Ion exchange via the use of resins is generally an incomplete process, particularly when the resin is not fully regenerated or changed out once its efficiency drops. Many applications involving PSA are sensitive to the levels of sodium or other alkali cation contaminant present in the PSA product, and it can thus be desirable to minimize the content of such cations. For a given amount of waterglass and, thus, exchangeable sodium (or alkali cation), it has been found that the efficiency of alkali cation/resin binding can be increased by dropping the initial level of the circulating phase in the contact chamber. In particular, surprisingly, the degree of sodium or alkali cation replacement can often be increased by dropping the level of circulating phase below the uppermost portion of the resin in the contact chamber. Such a result is surprising because

it could be expected to lower the degree of contact between the resin and the circulating phase, reducing the effectiveness of the resin and hindering ion exchange.

[0047] Preferred are ion exchange columns meeting common industrial and laboratory standards. The dimensions and standards of such columns are well described by Dardel and Arden in "Ion Exchangers", section 10.2, *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed; Wiley-VCH, 2003. Preferred are flow rates sufficient to generate turbulent mixing at the point of waterglass addition and greater than the minimum contact time in the contact chamber. Criteria for minimum contact time and flowrate are routinely established by resin manufacturers in manufacturer's product data sheets.

[0048] As indicated herein, it can be particularly convenient to utilize a product tank in the process of the present invention, and such a tank can be positioned inline such that the circulating phase passes into it, and the tank can accommodate any increases in system volume due to the addition of waterglass precursor. It also provides a collection point for embodiments where the product PSA is drained into a common tank after the resin exchange capacity is exhausted and no further waterglass can be fed. It has been found that the use of a bypass line which allows a portion of the undeposited circulating phase to remain circulating without entering the product tank can also increase the efficiency of binding of sodium or other alkali cation to the resin. The bypass line allows the operator to minimize the amount of water required in the system for startup, which generally gives a higher resin/liquid ratio, and thus a higher concentration of silica in the final PSA product.

[0049] In the method of the present invention, the circulating phase is kept at a pH of less than about 4. A suitable mode for maintaining the pH of the circulating phase is the addition of one or more acids. The acids can be conveniently added as a solution, continuously introduced. It is preferred to add the acid such that the pH of the circulating phase is less than about 4. Suitable inorganic acids include, but are not limited to nitric, hydrochloric, sulfuric and phosphoric acids, and suitable organic acids include, but are not limited to oxalic, formic, and acetic. In general, the reduction in pH is more important than the identity of the acid, and thus many acids not specifically mentioned herein are suitable.

[0050] The acid is preferably added to the circulating phase continuously, such that the pH of the circulating phase does not exceed about 4. The acid may alternatively be added discretely as long as the pH does not exceed about 4. In general, as the basic waterglass is introduced, the acid resin and acidified recirculating phase have the dominant effect and

the pH of the newly introduced silicate drops rapidly. The circulating phase is preferably circulated at a rate which allows the cation exchange reaction to proceed at an acceptable rate.

[0051] By the methods disclosed herein, high quality PSA having high surface areas can be prepared. It is possible to prepare PSA having, simultaneously, a solids content as high as or higher than about 20 wt %, and equivalent particle diameters as small as about 1.2 nm or even smaller. With such small particle sizes, surface areas as high as or higher than about 2500 m^2 per gram can be prepared. In some embodiments, the solids content is above about 8 wt %, above about 10 wt %, above about 12 wt%, above about 14 wt %, above about 16 wt %, above about 18 wt % or above about 20 wt %. In such embodiments, the equivalent particle diameter is less than about 4 nm, less than about 3 nm, less than about 2.5 nm or less than about 2.0 nm. In another embodiment, the solids content is above about 10 wt % and the equivalent particle diameter is less than about 3 nm. In another embodiment, the solids content is above about 10 wt % and the equivalent particle diameter is less than about 2.5 nm. In another embodiment, the solids content is above about 12 wt % and the equivalent particle diameter is less than about 2.5 nm. In yet another embodiment, the solids content is above about 14 wt % and the equivalent particle diameter is less than about 2.5 nm. In yet another embodiment, the solids content is above about 14 wt % and the equivalent particle diameter is less than about 2.0 nm.

[0052] By the methods disclosed herein, PSA product with a soda content of less than about 1000 ppm, less than about 500 ppm, less than about 300 ppm, less than about 200 ppm, less than about 100 ppm, less than about 75 ppm, less than about 40 ppm, less than about 20 ppm, less than about 10 ppm or less than about 5 ppm can be prepared.

[0053] Particle size, silica content, and soda content of the polysilicic acid sols was determined by common laboratory methods. Solids content as weight percent SiO_2 was determined by igniting the sample in a furnace to 815°C and measuring the mass of solid residue. Soda content was determined with a sodium ion selective electrode (Na ISE). Those skilled in the art recognize titration with sodium hydroxide as an effective method to quickly determine surface area and equivalent particle diameter. A sample below pH 4 is titrated with 0.1 N NaOH in the presence of NaCl. The amount of titrant required to adjust pH from 4 to 9 is correlated with the actual surface area determined by other methods such as Transmission Electron Microscopy (TEM) or nitrogen adsorption (BET method). The method is empirical and relies on correlation; therefore, different details of the method have been reported in the literature. In the present case, this author uses the

original pioneering method proposed by G.W. Sears (*Anal. Chem.*, 1956, 28 (12), pp 1981–1983). In this case, the silica surface area, A (m^2/g), is equal to 32 times the titrant volume in milliliters minus 25.

$$A = 32V_t - 25$$

If the silica particles are assumed to be monodisperse and spherical, one can convert the surface area to particle size. This additional calculation requires knowledge of the silica density. In the present case, the authors take the density to be 2.2 g/cc. Thus, the equivalent particle diameter, d_p (nm), relates to surface area (m^2/g) by the following equation:

$$d_p = \frac{2727.27}{SA}$$

DETAILED DESCRIPTION OF THE DRAWINGS

[0054] **Fig. 1** depicts the introduction of a waterglass solution into a recirculation loop which includes a mixing element **10**, depicted as a stirred tank reactor, and a contacting chamber **3**, depicted as a resin column. Fluid connections, for example, sections of an appropriate tubing, **2**, **5** and **8**, join the components of the loop in fluid communication. An aqueous recirculating phase, for example, water, is acidified to a pH of 1.3 with an appropriate acid, such as nitric acid, and recirculated over the resin bed **4** which is in the hydrogen form. A waterglass solution from tank **9** having a pH in the range of from about 8-11 is introduced into the stirred tank reactor **6** such that the pH in the product tank rises slowly, but remains in the pH range such that no appreciable gelling occurs. A pH of, for example, about 1.8 can be chosen as a target value. Tank reactor **6** is both a stirred tank reactor (as it contains a mixing element) and a product tank since the tank allows product to accumulate as the volume of the system increases due to waterglass introduction into the circulating phase. During the waterglass addition, the concentration of sodium or other alkali cations remains low because the recirculation rate is high, and the resin exchange reaction proceeds. Once the pH of the system has risen to 1.8 or other target value as indicated above, the recirculation loop is drained, and the product collected. Prior to generation of the next PSA batch, the resin bed can be cleaned and regenerated using a base and acid, respectively, as well as intermediate water washes. Additional hardware can be present for cleaning and regeneration cycles of the resin bed.

[0055] **Fig. 2** depicts a recirculation loop which includes a contacting chamber **3**, depicted as a resin column; a product tank **6**; and a mixing element **1**. The mixing element is a static mixer, centrifugal pump, pipe T, a venture action based mixer or similar device. Tubing to connect the components of the loop is identified as items **2**, **5**, and **8.** Increased silica concentration can be obtained by increasing the ratio of resin to liquid heel circulating phase at the start of the process. This increased ratio is obtained by, among other things, reducing the level of the aqueous circulating phase in the resin column. While the circulating phase level may extend above the resin level in some embodiments, the level may also be reduced such that the level is less than the level of the resin. The amount of liquid circulating phase can also be lowered by routing the circulating phase past the product tank via a bypass line **7**. The bypass allows the process to be conducted with a product tank which is empty of liquid at the outset of the waterglass introduction and has been found to be effective in the formation of a low sodium/alkali cation PSA product. The circulating phase is acidified to a pH of, for example, about 1.3, and the pH of the incoming waterglass solution is dropped to, for example, a pH in the range of from about 1.8 to about 2.7 in the mixing element **1**. Prior to exhaustion of the resin capacity, the pH measured at the outlet of the contact chamber **5** typically remains at a steady, low value, such as, for example, about 1.8. When no additional Na is being exchanged by the resin, the pH measured at **5** will begin to rise and the addition of waterglass from tank **9** is terminated. Typically, product tank **6**, as well as the recirculation loop is then drained and the PSA product is collected. Prior to generation of the next PSA batch, additional hardware can be present for cleaning and regeneration cycles of the resin bed **4** using a base and acid, respectively, as well as intermediate water washes.

[0056] **Fig. 3** depicts a recirculation loop similar to **Fig. 2**. Depicted are a mixing element **1**; connective tubing **2**, **5**, and **8**; a product tank **6**; a bypass line **7**, and a waterglass storage tank **9**. However, the contact chamber **3** and resin bed **4** are not a fixed bed column but are instead part of a Higgins Loop or other device employing a continuous or semi-continuous moving resin bed. In this embodiment, the process of producing PSA in a recirculation loop is operated similarly to the depiction in Fig **2**. A difference is the procedure to prepare the unit for further PSA production. In the method of Fig **2**, no PSA production occurs while the resin bed is cleaned and regenerated with base and acid, respectively, as well as intermediate water washes. These maintenance cycles can consume time periods greater than the production cycle and result in reduced production. Fixed bed units, then can be staggered in parallel to create continuous or semi-continuous

production. In the method of **Fig 3**, it is necessary to interrupt the flow for only short periods of time (on the order of seconds) while the Higgins Loop is pulsed to move fresh resin in the hydrogen form into the contact chamber **3**. If a continuous moving resin bed is employed, flow interruption is not necessary. As a result, a Higgins Loop or other moving bed device allows the present invention to produce high solids PSA in a continuous or semi-continuous manner without the need for staggering multiple units is parallel.

[0057] **Fig. 4** depicts a recirculation loop similar to **Fig. 2**. Depicted are a mixing element **1**; connective tubing **2**, **5**, and **8**; a product tank **6**; a bypass line **7**, and a waterglass storage tank **9**. However, the contact chamber **3** is a stirred tank reactor and the resin bed **4** is a stirred phase rather than fixed bed. This embodiment of the invention is particularly suited for resins that exhibit high swell and propensity for breakage in a fixed, constrained bed.

[0058] **Fig. 5** depicts a staged product tank having a small volume (narrowed bottom neck) which is filled at the outset, and a larger volume into which the circulating phase can expand as waterglass addition proceeds. The embodiment of a product tank **6** is particularly suited for maximizing the resin to liquid ratio in the system during startup.

[0059] The methods given above can easily give silica solids levels as high as 13-15% by weight. Solids contents of as much as 20 % by weight and higher are possible.

EXAMPLES

Example 1

[0060] A process system was constructed in the manner of **Fig. 2** containing pH meters, and conductivity meters on the inlet and outlet of an exchange column containing 7.75 liters of Amberjet 1500 resin. PSA at 8% solids by weight was prepared by a method including the exchange of a dilute waterglass in a single pass without recycle. The column was washed with water, followed by dilute sodium hydroxide to remove entrained silica. The resin was regenerated to the hydrogen form with 10% sulfuric acid, and then reclassified by an upflow cycle followed by a downflow cycle. Compressed air was used to blow down the column and remove the water. 3600 grams of the 8% PSA was reloaded into the recycle loop such that the bed and process pipes were fully wetted. The recycle pump was set to 2.2 L/min. With the recycle flow stable, 40 g of 85% phosphoric acid was slowly added to a buffer tank, and the recycle was continued until the phosphoric acid was uniformly dispersed. In a second step, a secondary pump was used to inject N-brand waterglass into a static mixer immediately before the column inlet. The N-brand

waterglass had a composition of 29.01 % silica and 8.95 % soda by weight. During operation, the column had an inlet pH of approximately 2.2 and an outlet pH of approximately 1.8. Thus, the column inlet was operated on the alkaline side of the metastable point. The conductivity of the outlet stream was higher than the inlet, indicating that sodium ions were being replaced by protons. After 4100 g of waterglass was added to the system, the temperature rise in the column began to level off, and the conductivity delta decreased in magnitude. The aforementioned trends signaled that the Na/H exchange was slowing, or in other words, the equilibrium was beginning to shift in an unfavorable direction. The waterglass flow was terminated, and the contents of the recycle loop were collected in the product tank as high-solids PSA. The PSA had a solids content of 16.9 wt % and a soda content of only 165 ppm. The PSA had a equivalent particle diameter size of only 1.9 nm by titration and a gel time of only 117 minutes. Of the total silica supplied to the system, 77% was recovered as this high solids product. With a water wash of the resin bed, additional silica was recovered as dilute PSA. In total (including the dilute PSA) the silica recovery was 99%.

Example 2

[0061] In the manner of Example 1, a heel of 8% was prepared, and the ion exchange resin was regenerated to the Hydrogen form. 6500 g of the 8% PSA was reloaded into the column, and the recycle pump was set to 2.9 lL/m. The recycle loop was operated in the reverse direction as in Example 1; the liquid flowed up through the resin bed and expanded the void fraction to 48 % by volume. 60 g of 85% Phosphoric acid was added to the buffer tank and recycle was continued until the concentration equilibrated. A steady concentration of acid in the recycle loop was indicated by consistent values of pH and conductivity on the column inlet and outlet. N-brand waterglass was dosed to the system in a static mixer such that the inlet pH was 2.2 to 2.3. The column outlet pH was 1.8 during most of the run. 17 g of additional phosphoric acid was added during the course of the run. After 4117 g waterglass was dosed to the system, the outlet conductivity began to fall, and the outlet pH began to approach a value of 2.1. The waterglass flow was terminated, and the contents of the column were collected in the product tank as high solids PSA. The PSA had a solids content of 14.9% and a soda content of 436 ppm. The PSA had an equivalent particle diameter of 1.8 nm and a gel time of 198 minutes. Of the total silica supplied to the system, 86% was recovered as this high solids product. With a

water wash of the resin bed, additional silica was recovered as dilute PSA. In total (including the dilute PSA) the silica recovery was 98%.

Example 3

[0062] The system described in **Fig. 2** was scaled up to accommodate a column containing 53L of Amberjet 1500H ion exchange resin. The system was loaded with 23 kg of deionized water, and the recycle rate was set to 8.7 l/min. 146 g of 70% nitric acid was added to the system, and the concentration was allowed to equilibrate as in the prior examples. N-brand waterglass was dosed to the system in a static mixer such that the inlet pH was 2.3 to 2.4. The column outlet pH was 1.3 during most of the run. After 22007 grams of waterglass was dosed to the system, the flow was terminated: a solids density correlation showed that the desired solids value had been reached. The conductivity and temperature trends did not show that the resin capacity had been exhausted or that the equilibrium was shifting in an unfavorable direction. The product was drained into a collection tank. The PSA had a solids content of 12.98% and a soda content of 4 ppm. The PSA had a equivalent particle diameter of 1.8 nm and a gel time of 635 minutes. In this case the gel time was longer due to the lower desired solids content. Of the total silica supplied to the system, 84% was recovered as high solids product. With a water wash of the resin bed, additional silica was recovered as dilute PSA. Including the dilute PSA, the total silica recovery was 99.8 %.

[0063] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0064] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0065] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the

description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0066] Each and every patent or other publication or published document referred to in any portion of this specification is incorporated *in toto* into this disclosure by reference, as if fully set forth herein.

[0067] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

THAT WHICH IS CLAIMED IS:

1. A process for the preparation of polysilicic acid (PSA), said process comprising:

i) circulating a circulating phase, said circulating phase having a volume, through a system, said system comprising:

a recirculation loop comprising:

a) a contact chamber comprising an inlet and an outlet, said contact chamber also comprising a volume, at least a portion of which contains one or more acid exchange resins; and

ii) introducing a waterglass solution into the recirculation loop such that it joins with the circulating phase; wherein the pH of the introduced waterglass solution is less than about 4 within 5 minutes of introduction into the recirculation loop;

said circulating and introducing occurring such that PSA is formed in the contact chamber;

wherein, during PSA formation, the pH of the circulating phase has a volume average pH value of less than about 4, and the pH throughout the volume in the contact chamber is less than about 4.

2. A process as in claim 1, wherein said waterglass is introduced into said system continuously.

3. A process as in claim 1, wherein said waterglass is introduced into said system semi-continuously.

4. A process as in claim 2 wherein said waterglass has a pH above about 9 prior to introduction into the circulating phase, and the circulation loop comprises a mixing element which introduces the waterglass into the circulating phase.

5. A process as in claim 4 wherein said waterglass has a pH above about 11 prior to introduction.

6. A process as in claim 4, wherein the mixing element is a prechamber mixer, said waterglass has a pH above about 9 prior to introduction into the circulating phase, and said prechamber mixer causes the pH of the waterglass to fall to less than about 4 prior to introduction.

7. A process as in claim 1, wherein the pH at the contact chamber inlet is more basic than the metastable pH of the system.

8. A process as in claims 1 or 7, wherein the pH at the contact chamber outlet is more acidic than the metastable pH of the system.

9. A process as in claim 1, wherein said contact chamber is a column.

10. A process as in claim 1, wherein said contact chamber is a static column of resin or a moving column of resin.

11. A process as in claim 1 wherein said recirculation loop additionally comprises a product tank which can receive PSA.

12. A process as in claim 11 wherein said system additionally comprises a product tank bypass.

13. A polysilicic acid (PSA) product formed by a process comprising:

i) circulating a circulating phase, said circulating phase having a volume, through a system, said system comprising:

a recirculation loop comprising:

a) a contact chamber comprising an inlet and an outlet, said contact chamber also comprising a volume, at least a portion of which contains one or more acid exchange resins; and

ii) introducing a waterglass solution into the recirculation loop such that it joins with the circulating phase; wherein the pH of the introduced waterglass solution is less than about 4 within 20 seconds of introduction;

said circulating and introducing occurring such that PSA is formed in the contact chamber;

wherein the solution contained in the volume of the system is a circulating phase, and wherein, during PSA formation, the pH of the circulating phase has a volume average of less than about 4, and the contact chamber has a pH of less than about 4 throughout its volume.

14. A polysilicic acid (PSA) composition produced by a process comprising converting a sodium silicate solution via sodium/hydrogen exchange, to PSA, wherein upon said exchange, said PSA composition is characterized by a PSA solids content of greater than about 8 wt %, and an equivalent particle diameter of less than about 3.0 nm.

15. A PSA composition as in claim 14 wherein said PSA composition is characterized by a PSA solids content of greater than about 8 wt% and an equivalent particle diameter of less than about 1.5 nm.

16. A PSA composition as in claim 13-15 wherein said PSA composition is characterized by a PSA solids content of greater than about 12 wt %, and an equivalent particle diameter of less than about 3.0 nm.

17. A PSA composition as in claim 13-15 wherein said PSA composition is characterized by a PSA solids content of greater than about 12 wt% and an equivalent particle diameter of less than about 1.5 nm.

18. A PSA composition as in any of claims 14, 15, 16 or 17 characterized by a soda content of less than about 500 ppm.

19. A PSA composition as in any of claims 14, 15, 16 or 17 characterized by a soda content of less than about 100 ppm.

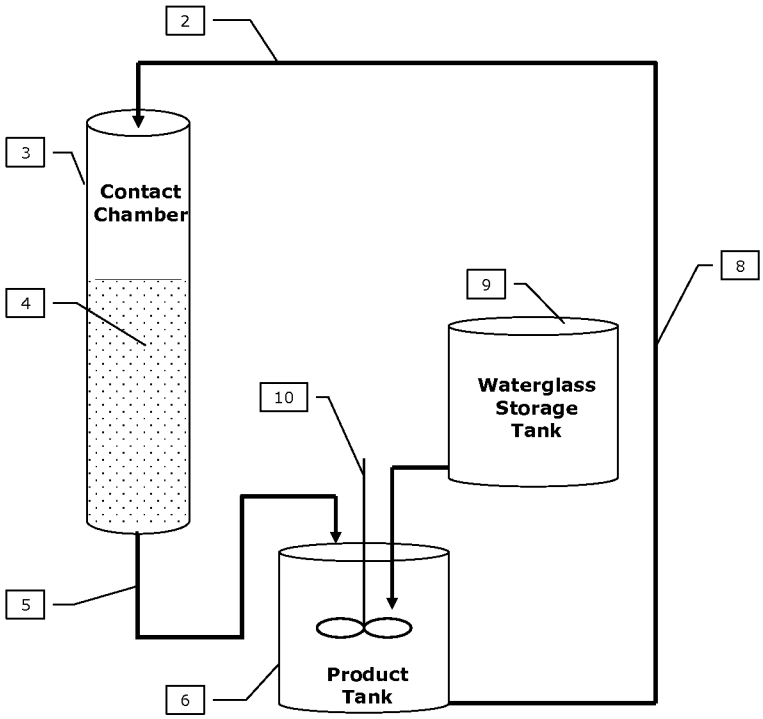

2
3
Contact Chamber
4
9
8
Waterglass Storage Tank
10
5
Product Tank
6

FIG. 1

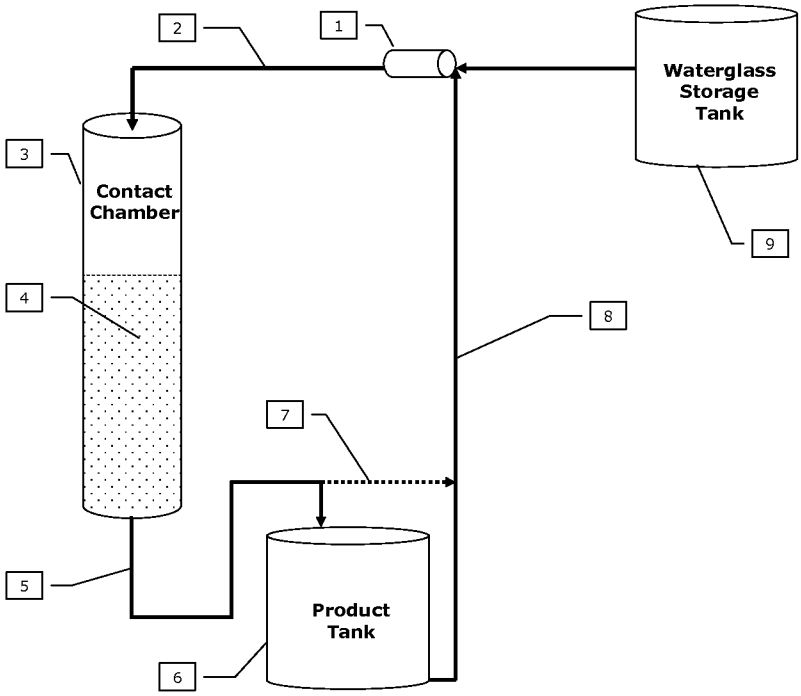
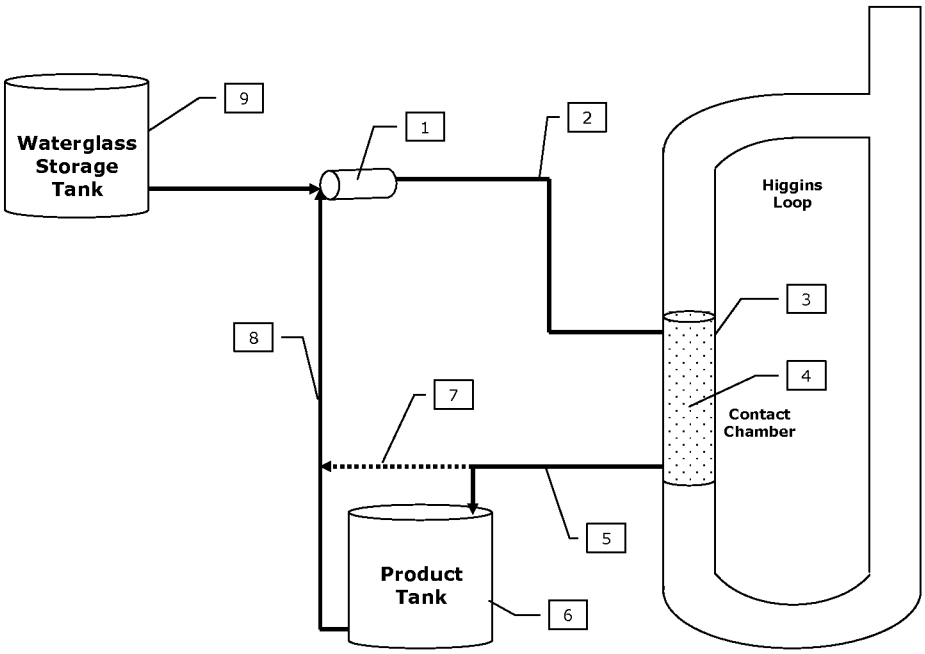

2
1
Waterglass
Storage
Tank
3
Contact
Chamber
9
4
8
7
5
Product
Tank
6

FIG. 2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9
1
2
Higgins Loop
3
4
Contact Chamber
8
7
5
Product Tank
6

FIG. 3

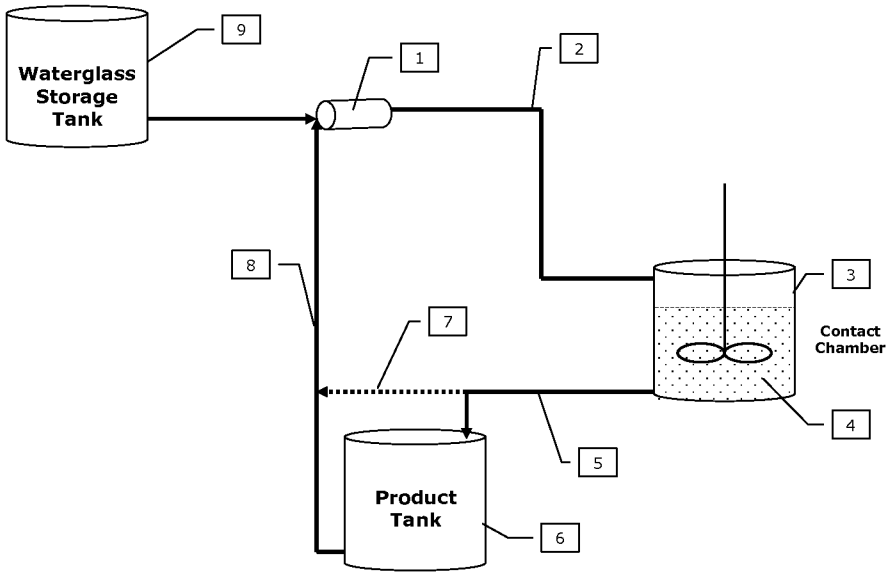
Waterglass
Storage
Tank
9
1
2
3
Contact
Chamber
4
5
Product
Tank
6
7
8

FIG. 4

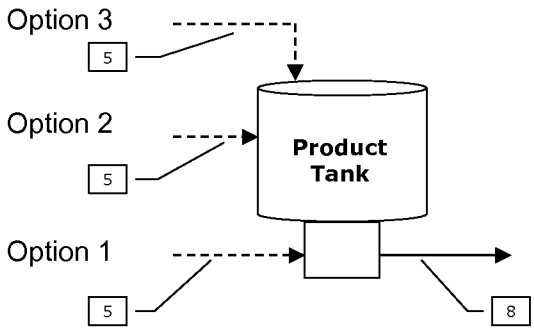

FIG. 5