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(54) **AN ON-LINE CONTROL AND REACTION PROCESS FOR PH ADJUSTMENT**

ONLINE-STEUERUNG UND REAKTIONSVERFAHREN ZUR PH-ANPASSUNG

PROCÉDÉ DE CONTRÔLE ET DE RÉACTION EN LIGNE POUR AJUSTEMENT DE PH

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Description**Technical field**

5 [0001] The present disclosure relates to an on-line control and reaction process for pH adjustment and to an on-line automatic control device for pH adjustment.

Background art

10 [0002] Strength (including dry strength, wet strength and temporary wet strength, etc.) is a structural property of paper, which mainly depends on the interfiber bond and the nature of fibers in the paper sheet. During the paper making process, the strength properties of paper can be improved by adding enhancers to the paper stock by adjusting the ratio of fibers and pulping to fibrillate as well as by virtue of film-forming properties of a surface sizing agent. An enhancer is usually divided into a dry strength and a wet enhancer.

15 [0003] Di-aldehyde modified cationic, anionic and amphoteric acrylamide polymers, particularly the glyoxalated modified diallyldimethylammonium chloride (DADMAC)/acrylamide copolymers (GPAMs), are widely used as a dry strength and temporary wet strength aid in the paper and paperboard area. Such polymer strength aid is of great interest for paper and paperboard manufacturer since (1) it provides good temporary wet strength together with good dry strength, and (2) it also helps improve the drainage ability and the paper machine runnability. Amphoteric polyacrylamides can impart a good dry strength to paper. In the meantime, such enhancers comprise components of high activity, without any problem in this regard throughout the shelf life. At present, glyoxal modified acrylamide copolymers and amphoteric polyacrylamides are widely-used enhancers.

20 [0004] By comparison with using separately dialdehyde-modified acrylamide polymers such as dialdehyde-modified cationic polyacrylamides (GPAM) (e.g. DADMAC-acrylamide copolymers), and unmodified polyacrylamides (PAM) (e.g., amphoteric polyacrylamides), using the combination of these two types of polymers, e.g., the combination of dialdehyde-modified cationic polyacrylamides with amphoteric polyacrylamides, as the binary enhancers can result in better performances, which combines a plurality of advantages of each component, such as dry strength, wet strength and dehydration capability.

25 [0005] The pH value is important to the property of final enhancing products. If pH of the binary enhancer system can be accurately adjusted to the desired value prior to use, the binary enhancer system can particularly result in the significantly increased ash retention of paper in addition to the improvements in dry strength and wet strength and dehydration capability.

30 [0006] Therefore, there is a need for an on-line control and reaction process for pH adjustment, particularly for a binary enhancer solution, which can flexibly realize the accurate adjustment to pH value and control it within an expected numerical range.

Summary of the invention

35 [0007] The present invention relates to an on-line control and reaction process for pH adjustment. The process is particularly suitable for the binary enhancer composition comprising a first enhancer and a second enhancer, wherein the first enhancer and the second enhancer comprise dialdehyde-modified polyacrylamides (GPAM) respectively polyacrylamides (PAM) as the active component.

[0008] In the present invention, assuming the polyacrylamides act as the first enhancer, the second enhancer is dialdehyde-modified polyacrylamide, and vice versa.

40 [0009] As known by a person skilled in the art, the pH of final output product can be controlled within the desired range by adding a pH adjuster to the binary enhancer mixture. However, due to the complexity and variability of the in-situ operation conditions, e.g., changes of the output, variable amounts of the enhancer needed and different sources of the enhancer, it is very different to obtain the desired pH value by accurately controlling the flux of the pH adjuster.

45 [0010] However, the inventors of the present application have found out that despite various impact factors during the process, the ideal dosage of the pH adjuster is in particular influenced by the solid content and pH value, concentration (e.g., the ratio of polyacrylamides in the final output product) of the two components in the binary enhancer, target pH value as well as flux of the final output product. It is possible to obtain a suitable flow rate of the pH adjuster by acquiring and rectifying these parameters, and thus further obtain an ideal dosage of the pH adjuster in virtue of simple and direct adjustments.

50 [0011] In practice, the pH values and solid contents of enhancers and pH adjuster products as received in different batches are usually inconstant. Even the nominal pH values and solid contents will usually vary within a certain scope. Due to the inaccuracy of pH value and solid content, it is very difficult to accurately control the desired dosage of the pH adjuster, i.e., the pH value of the final product. Hence, there is a need for providing a process for rectifying the parameters

to eliminate the impact of such inaccuracy.

[0012] Therefore, the on-line control and reaction process according to the invention comprises the following steps:

- 1) providing a first enhancer and a second enhancer as well as pH adjuster to the reaction system,
- 2) mixing the first enhancer and the second enhancer, optionally after diluting each of both with water,
- 3) setting a base pH value (δ_1) and a target pH value, i.e. target reaction index (δ_2),
- 4) adding pH adjuster into the mixture via pH control unit and mixing them, to obtain the final output product with the target pH value;

wherein said pH control unit adjusts the amount of pH adjuster by measuring or inputting the following parameters:

- a. the solid content ratio of the first enhancer in relation to the mixed product (r), said mixed product consisting of the first enhancer and the second enhancer,
- b. the solid content of the first enhancer (α) and the solid content of the second enhancer (β),
- c. the pH value of the first enhancer (a) and the pH value of the second enhancer (b),
- d. the base pH value (δ_1) and the target pH value (δ_2) as set in step 3),
- e. the flux of the final output product (X) which is consisting of pH adjuster, a first enhancer and a second enhancer.

[0013] In one embodiment according to the invention, said pH control unit adjusts the flux of pH adjuster by acquiring at least the related parameter, K_1 , K_2 , K_3 and K_4 and utilizing the following formula (1), so as to realize the accurate control of the flux of the pH adjuster:

$$\text{Flux of pH adjuster} = X \times (K_1 - K_2 + K_3 + K_4) \quad (1)$$

in which

X represents the flux of final output product which is consisting of the pH adjuster, the first enhancer and the second enhancer;

K_1 represents the amount of pH adjuster consumed with pH value increasing from the initial pH value to the base pH value (δ_1) under varying solid content ratios of the first enhancer or second enhancer in relation to the mixed product (r), and satisfies $K_1 = k_1 \times r + t$, wherein k_1 is the slope obtained by linear fitting and t is the intercept;

K_2 represents the amount of pH adjuster consumed in relation to different pH values of the first enhancer (a) and different pH values of the second enhancer (b) under varying solid content ratios of the first enhancer or second enhancer in relation to the mixed product (r), and satisfies $K_2 = 2 \times r \times k_2 \times \Delta_{pH1} + 2 \times (1-r) \times k_2' \times \Delta_{pH2}$,

wherein k_2 and k_2' represents slope or average slope obtained by linear fitting in plotting the amounts of pH adjuster consumed with pH value increasing from the respective low limit pH value, high limit pH value and average pH value of two enhancers, in which said low limit pH value and high limit pH value are respectively the nominal lowest and highest pH value of the enhancer sample, and

Δ_{pH1} and Δ_{pH2} represent the difference between the inherent pH value of first enhancer, respectively second enhancer (a or b), and the average pH value of first enhancer, respectively second enhancer ($a_{ave.}$ or $b_{ave.}$), i.e. represent $(a - a_{ave.})$ and $(b - b_{ave.})$ respectively, in which each of said average pH value ($a_{ave.}$ or $b_{ave.}$) is an average determined from the pH values of n samples of the first or second enhancer and $n \geq 50$, preferably ≥ 70 ;

K_3 represents the effect of the difference between the target reaction index (δ_2) and base pH value (δ_1) on the amount of pH adjuster on the basis of K_2 , and satisfies $K_3 = (2 \times r \times k_2 + 2 \times (1-r) \times k_2') \times (\delta_2 - \delta_1)$;

K_4 represents the effect of varying solid content (α) and solid content (β) on the amount of pH adjuster under base pH value (δ_1), and satisfies $K_4 = k_4 \times (r \times \alpha / (1-r) \times \beta) - C_1$, wherein k_4 represents slope obtained by linear fitting in plotting the amounts of pH adjuster consumed when the pH value is adjusted up to base pH value (δ_1) against different solid content ratios of first enhancer to second enhancer,

C_1 is a value calculated from the formula $r_0 \times \alpha_{theo.} / ((1-r_0) \times \beta_{theo.})$ in case of the theoretical solid content of first enhancer ($\alpha_{theo.}$) and the theoretical solid content of second enhancer ($\beta_{theo.}$), in which r_0 is a standard ratio of first enhancer to the mixed product and is set to 1/2.

[0014] In the process of the present disclosure and the relation formula as shown above, α , β and r are represented by the mass percentage (%), and X represents the flux of the mixed product, i.e. the amount of the binary enhancer needed as determined according to the amount of paper pulp to be treated on-site per unit time, which can be represented by the unit of l/min.

[0015] In addition, what needs to be explained is that when conducting the final calculation according to the above formula (1), the dimensions of the parameters K_1 to K_4 are not taken into account, i.e. dimensionless.

[0016] Said first enhancer is selected from one of polyacrylamide enhancer and dialdehyde modified polyacrylamide enhancer, while said second enhancer is the other one.

[0017] In the process of the present disclosure and the above formulae, the solid content (α , β) of the polyacrylamide enhancer is from 5 to 100%, preferably from 10 to 30%, and the solid content (α , β) of the dialdehyde-modified polyacrylamide enhancer is from 5 to 100%, preferably from 6 to 20%; the pH value (a, b) of the polyacrylamide enhancer is from 2 to 8, preferably from 3 to 5, and the pH value (a, b) of the dialdehyde-modified polyacrylamide enhancer is from 2 to 7, preferably from 2 to 4; in addition, $\delta 2$ is from 7.5 to 11 and preferably from 8.5 to 9.5. The base pH value ($\delta 1$) is set between the initial pH value and target pH value ($\delta 2$) of the mixture obtained in step 3), and it is preferably >7 , e.g., 8. Generally, the initial pH values of polyacrylamide and dialdehyde-modified polyacrylamide enhancers will not exceed 7.

[0018] In step 1) of the process in accordance with the present invention, the two enhancers selected from dialdehyde-modified polyacrylamide enhancer (GPAM) and polyacrylamide enhancer (PAM) and a pH adjuster are provided. Here, the three reagents can be provided separately. The dialdehyde-modified polyacrylamide enhancer (GPAM) and the polyacrylamide enhancer (PAM) can be directly introduced into the reaction system, while the pH adjuster can be introduced into the reaction system via the pH control unit. The flux of the dialdehyde-modified polyacrylamide enhancer (GPAM) is generally from 0.5 to 15 ml/min, while the flux of the polyacrylamide enhancer (PAM) is generally from 0.5 to 15 ml/min. Thus, the flux of the pH adjuster may vary between 10 and 250 ml/min.

[0019] In step 2) of the process in accordance with the present invention, each of two enhancers selected from dialdehyde-modified polyacrylamide enhancer (GPAM) and polyacrylamide enhancer (PAM) can be diluted with water if required. When diluted with water, for example, due to the overhigh viscosity of the products that may be adverse for the operations, the polyacrylamide enhancer may be diluted to at least 9 times, preferably from 15 to 20 times. In addition, if necessary, the pH adjuster can be also diluted and the dilution multiple may range from 50 to 500, preferably from 50 to 300. Here, the dilution process may be conducted in any suitable mixing device, such as a static mixer.

[0020] Furthermore, in steps 2) and 4), it is necessary to mix the dialdehyde-modified polyacrylamide enhancer with the polyacrylamide enhancer, and mix these two enhancers with the controlled amount of pH adjuster. Here, the mixing can be conducted in any suitable mixing device, such as a static mixer. In the meantime, some auxiliary devices such as a centrifugal pump may be employed to ensure the thorough mixing.

Interpretation to parameters

[0021] In the process in accordance with the present invention, K1 reflects the effects of varying solid content ratios (r) of polyacrylamide or dialdehyde-modified polyacrylamide enhancers in the mixed product on the amount of pH adjuster consumed with pH value increasing from the initial pH value to the base pH value ($\delta 1$).

[0022] There is a linear relationship between K1 and r, that is, $K1 = k_1 \times r + t$. Although different binary enhancers result in different k_1 and t values, a person skilled in the art can rapidly determine the values of the fixed slope k_1 and intercept t according to a plurality of measured discrete points and by means of the linear fitting, once the binary enhancer is determined.

[0023] With respect to the linear fitting, a person skilled in the art surely knows how to conduct the linear fitting to K1 (and also K2-K4 as will be discussed in the following). For example, at least three measured points with suitable intervals may be acquired for the linear fitting. Herein, more measured points, such as 5 or 8 points, are also possible.

[0024] K2 reflects the effects of different pH values of the first enhancer (a) and different pH values of the second enhancer (b) on the amount of the consumed pH adjuster under varying different ratios (r) of polyacrylamide enhancer or dialdehyde-modified polyacrylamide enhancer in the mixed product. This parameter takes into consideration the impact of the difference between actual pH values (a, b) of polyacrylamide enhancer and dialdehyde-modified polyacrylamide enhancer and measured average pH values thereof in the same batch on the amount of the consumed pH adjuster.

[0025] In one embodiment according to the invention, the parameter r, for example, represents the ratio of the polyacrylamide enhancer (the first enhancer) in the mixed product, and thus $K2 = 2 \times r \times k_2 \times (a - a_{ave.}) + 2 \times (1-r) \times k_2 \times (b - b_{ave.})$, wherein k_2 and k_2 represents slope or average slope obtained by linear fitting in plotting the amounts of pH adjuster consumed with pH value increasing from the respective low limit pH value, high limit pH value and average pH value of polyacrylamide enhancer and dialdehyde-modified polyacrylamide enhancer.

[0026] Said low limit pH value and high limit pH value are respectively the nominal lowest and highest pH value of the enhancer sample. For example, these two pH values may be the upper limit value and lower limit value of the pH range signed by the manufacturer of the enhancer reagents in the same batch. For the same manufacturer and the same batch, these two values are substantially fixed. For example, the lower limit and upper limit pH values of polyacrylamide enhancer are respectively 2.5 and 3.49, and the lower limit and upper limit pH values of dialdehyde-modified polyacrylamide enhancer are respectively 2.91 and 3.46.

[0027] The average pH value can be acquired by measuring actual pH values of n enhancer samples in the same batch. For the same manufacturer and the same batch, this value can be fixed by simple measurement and calculation.

Here, n is ≥ 50 , preferably ≥ 70 and such as 80.

[0028] K3 reflects the effects of the difference between the target reaction index (δ_2) (i.e., the final target pH value) and base pH value (δ_1) on the amount of pH adjuster under the set target reaction index (δ_2), and satisfies $K3 = (2 \times r \times k_2 + 2 \times (1-r) \times k_2) \times (\delta_2 - \delta_1)$, wherein δ_2 is from 7.5 to 11 and preferably 8.5 to 9.5. In addition, in the calculation of K1 and K3, the base pH value δ_1 may be set to be >7 , preferably 8.

[0029] K4 reflects the effects of varying ratios of polyacrylamide enhancer or dialdehyde-modified polyacrylamide enhancer in the final product on the amount of pH adjuster under base pH value (δ_1), in case that there exists difference between the solid content (α) of first enhancer or the solid content (β) of second enhancer and the standard values.

[0030] Specifically, K4 satisfies $K4 = k_4 \times (r \times \alpha / (1-r) \times \beta) - C_1$, wherein k_4 represents the slope obtained by linear fitting in plotting the amounts of pH adjuster consumed when the pH value is adjusted up to base pH value (δ_1) against different ratios of polyacrylamide enhancer to dialdehyde-modified polyacrylamide enhancer, C_1 is a value calculated from the formula $r_0 \cdot \alpha_{\text{theo.}} / ((1-r_0) \cdot \beta_{\text{theo.}})$ in case of the theoretical solid content of first enhancer ($\alpha_{\text{theo.}}$) and the theoretical solid content of second enhancer ($\beta_{\text{theo.}}$), in which r_0 is a standard ratio of first enhancer to the mixed product and may be set to 1/2.

[0031] In practice, with respect to the enhancer, the theoretical solid content of the polyacrylamide and dialdehyde-modified polyacrylamide depends on the formulation or the nominal formulation of the enhancer. Generally speaking, an enhancer product with constant quality of a certain manufacturer will have the relatively steady formulation, rendering $\alpha_{\text{theo.}}$ and $\beta_{\text{theo.}}$ easily calculated and the parameter C_1 constant.

[0032] Moreover, in one preferred embodiment, in addition to the above factors K1 to K4, the factor K5 may be taken into account for more accurately adjusting the flux of the pH adjuster, i.e. the concentration deviation of the pH adjuster per se that is used to correct the actual flux of the pH adjuster.

[0033] The pH adjuster, e.g., NaOH, may be on-site prepared or may be commercially-available products, either used in the form of solid or liquid or in the form of dispersion or solution. In case of commercially-available products used, there exists usually a deviation between the nominal concentration and the actual concentration. Under this situation, the parameter K5 is set to correct the actual concentration of the pH adjuster, for example, $K5 = C_{\text{nominal}}/C_2$, wherein C_{nominal} represents the nominal concentration of the product and C_2 represents the measured actual concentration. Accordingly, the calculation formula as above described is as follows:

$$\text{flux of the pH adjuster} = X \times (K1 - K2 + K3 + K4) \times K5.$$

[0034] Obviously, a person skilled in the art will understand that the value of K5 may theoretically range from greater than 0 to 100%.

[0035] In one embodiment, for example, the ratio of the polyacrylamide enhancer in the mixed product may be set to r (the first enhancer). Accordingly, a person skilled in the art will understand that the parameter α represents the solid content of the polyacrylamide enhancer; the parameter β represents the solid content of the dialdehyde-modified polyacrylamide enhancer; the parameter a represents the pH value of the polyacrylamide enhancer; and the parameter b represents the pH value of the dialdehyde-modified polyacrylamide enhancer. Thus, the above parameters can be used for the above formula (1) to conduct the corresponding calculations.

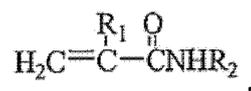
Binary enhancer composition

[0036] In the specification, the binary enhancer comprises dialdehyde-modified polyacrylamide enhancer and polyacrylamide enhancer as the active ingredients. The dialdehyde-modified polyacrylamide enhancer per se is a commonly-used additive for papermaking, and it can be obtained by modifying polyacrylamide enhancer with dialdehyde.

[0037] In the context of the present disclosure, the abbreviation "GPAM" used herein refers to a dialdehyde modified polyacrylamide, especially glyoxal-modified polyacrylamide. The abbreviation "PAM" used herein refers to the polyacrylamide.

[0038] Said polyacrylamide may be cationic, anionic or amphoteric. Accordingly, the dialdehyde-modified polyacrylamide may be also cationic, anionic or amphoteric. The cationic polyacrylamide is a copolymer of one or more acrylamide monomers with one or more cationic monomers (see, e.g., US7641766B2, US7901543B2). The anionic polyacrylamide is a copolymer of one or more acrylamide monomers with one or more anionic monomers (see, e.g., WO0011046A1). The amphoteric polyacrylamide is a copolymer of one or more acrylamide monomers, one or more cationic monomers and one or more anionic monomers (see, e.g., WO0011046A1). Herein, The contents disclosed in these three references US7641766B2, US7901543B2, and WO0011046A1.

[0039] "Acrylamide monomer" means the monomer of formula



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wherein R₁ is H or C₁-C₄ alkyl and R₂ is H, C₁-C₄ alkyl, aryl or arylalkyl. Acrylamide monomers may include acrylamide or methylacrylamide, for example, acrylamide.

[0040] "Alkyl" means a monovalent group derived from a straight or branched chain saturated hydrocarbon by the removal of a single hydrogen atom. Representative alkyl groups include methyl, ethyl, n- and iso-propyl, cetyl, and the like.

10 **[0041]** "Alkylene" means a divalent group derived from a straight or branched chain saturated hydrocarbon by the removal of two hydrogen atoms. Representative alkylene groups include methylene, ethylene, propylene, and the like.

[0042] "Aryl" means an aromatic monocyclic or multicyclic ring system of 6 to 10 carbon atoms.

[0043] The aryl is optionally substituted with one or more C₁-C₂₀ alkyl, alkoxy or haloalkyl groups. Representative aryl groups include phenyl or naphthyl, or substituted phenyl or substituted naphthyl.

15 **[0044]** "Arylalkyl" means an aryl-alkylene-group where aryl and alkylene are as defined above. Representative arylalkyl groups include benzyl, phenylethyl, phenylpropyl, 1-naphthylmethyl, and the like, e.g., benzyl.

[0045] There is no special limitation to the di-aldehyde. The di-aldehyde may be selected from glyoxal, malonaldehyde, succinic aldehyde and glutaraldehyde, preferably glyoxal.

20 **[0046]** There is no special limitation to the cationic monomer. The cationic monomer can be one or more selected from a group consisting of diallyldimethylammonium chloride, N-(3-dimethylaminopropyl)methyl acrylamide, N-(3-dimethylaminopropyl)acrylamide, methylacryloyloxyethyltrimethyl ammonium chloride, acryloyloxyethyltrimethyl ammonium chloride, methylacryloyloxyethyltrimethylbenzyl ammonium chloride, acryloyloxyethyltrimethylbenzyl ammonium chloride, (3-acrylamidopropyl)trimethyl ammonium chloride, methylacrylamidopropyltrimethyl ammonium chloride, 3-acrylamido-3-methylbutyltrimethyl ammonium chloride, 2-vinylpyridine, 2-(dimethylamino)ethyl methacrylate, and 2-(dimethylamino)ethyl acrylate. For example, the cationic monomers may be diallyldimethylammonium chloride (DADMAC).

25 **[0047]** There is no special limitation to the anionic monomer. The anionic monomer can be one or more selected from a group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, and maleic anhydride and the salts thereof. For example, the anionic monomer can be acrylic acid.

30 **[0048]** In the context, there is no special limitation to the sum of the anionic monomers and/or cationic monomers, as long as a stable polymer is prepared. For example, the sum of the anionic monomers and/or cationic monomers can be 0.1-50 mol%, such as 1-20 mol%, of the copolymer, depending on the practical application, but without being limited to those.

[0049] In the context, there is no special limitation to the ratio of dialdehyde to acrylamide (G/A ratio) in the dialdehyde modified polyacrylamide. The G/A ratio can be 0.01:1-1:1 (molar ratio), e.g., 0.1:1-0.8:1 (molar ratio).

35 **[0050]** In the context, there is no special limitation to the ratio of cationic monomers to anionic monomers in the amphoteric dialdehyde modified polyacrylamide. For example, the ratio of cationic monomers to anionic monomers may be 1:100 - 100:1 by molar, such as 1 : 10 - 10:1 by molar, depending on the practical application, but without being limited to those.

40 **[0051]** In order to achieve the effects of the present invention, the weight average molecular weight of the dialdehyde-modified polyacrylamide is critical which may range from 100,000 to 2,000,000 daltons, such as from 120,000 to 1,500,000 daltons, such as from 200,000 to 1,200,000 daltons, such as from 150,000 to 1,100,000 daltons, and such as from 200,000 to 1,000,000 daltons. The weight average molecular weight of the dialdehyde-modified polyacrylamide may also range from 100,000 to 300,000 daltons, such as from 150,000 to 300,000 daltons and such as from 200,000 to 300,000 daltons.

45 **[0052]** Preferably, the weight average molecular weight of the polyacrylamide ranges from 500,000 to 5,000,000 g/mol. Preferably, the weight average molecular weight of the dialdehyde-modified polyacrylamide ranges from 200,000 to 2,000,000 g/mol.

50 **[0053]** There is no special limitation to the solid content of the dialdehyde-modified polyacrylamide in the enhancer solution. Taking into consideration the facilities of the preparation and operation, the solid content may range from 0.1 to 50 wt%, for example from 1 to 20 wt%, and further for example from 5 to 15 wt%.

55 **[0054]** The dialdehyde-modified polyacrylamide can be prepared according to the known technology, for example, the process disclosed in US Patent No. 7641766 B2. It should be noted that, in the process of producing the dialdehyde-modified polyacrylamide, a cross-linking agent and / or a chain transfer agent can be used to provide a branched / cross-linked structure of the copolymer. As commercially available dialdehyde-modified polyacrylamide enhancers, Nalco 64280, Nalco 64170, and Nalco 64180 can be exemplarily listed.

pH adjuster

[0055] In the present invention, the pH adjuster is well known for a person skilled in the art, and it is an inorganic or organic alkaline substance with pH value ranging from 9 to 14, for example, sodium hydroxide, potassium hydroxide or ammonia, and carbonate salts of alkali metals.

Illustrations to the drawings

[0056] Fig. 1 schematically shows an on-line automatic control device for pH adjustment in accordance with the process of the present disclosure. According to Fig. 1, a binary enhancer is provided at first which comprises dialdehyde-modified polyacrylamide GPAM1 and polyacrylamide PAM2. Meanwhile, the solid contents α and β of both compounds are measured and also the respective inherent pH values, e.g., 3 to 4, as the parameters a and b, respectively. Herein, optionally, GPAM 1 and PAM 2 are introduced separately via pipelines into a diluting unit 3 comprising a mixer such as a static mixer, so as to be mixed with water. The dilution step may be carried out as required and depend on the source and viscosity of these two enhancers GPAM 1 and PAM 2. Subsequently, after mixing these two enhancers, the base pH value δ_1 4 is set to e.g. pH=8 and compared with the target pH value δ_2 , i.e., the target reaction index 6 (e.g., the pH = 9). Then the ideal indication for the amount (or flux) of the pH adjuster can be obtained from the pH control unit 5, according to which a suitable dosage of the pH adjuster 7 (e.g., the aqueous NaOH solution) is added to the mixture of GPAM 1 and PAM 2. The mixture is mixed in the mixer 8 for a sufficient period, thereby obtaining the final output product PM which satisfies the target pH value. In the pH control unit, the parameter X, i.e., the flux of the final product PM can be determined according to the on-site output.

[0057] Said pH control unit 5 may be operated manually or automatically, preferably automatically. In one embodiment of the present disclosure as shown in Fig. 7, which is just illustrative and depicts the structure essential for understanding the present invention, the pH control unit 5 is an automatic control device comprising at least input port A, output port B and calculation center C, in which input port A receives the signals corresponding to the following parameters and input them into the calculation center C: the solid content ratio of the first enhancer in relation to the mixed product (r), the solid content of the first enhancer (α) and the solid content of the second enhancer (β), the pH value of the first enhancer (a) and the pH value of the second enhancer (b), the base pH value (δ_1) as set, the target pH value, i.e. target reaction index (δ_2), the flux of the final output product (X) and optionally actual concentration of pH adjuster as measured (C_2); and then calculation center C transmits into output port B the flux of pH adjuster as calculated according to the process as described above, especially according to formula (1), said output port B adapting the pH adjuster flux to the calculated flux of pH adjuster via pipeline and flux control apparatus.

[0058] In the calculation center C (e.g., a calculator), the above formula (1) and parameters in relation to K1-K4 and optional K5 like k_1 , t , k_2 , k_2' , $a_{ave.}$, $b_{ave.}$, k_4 , C_1 and optional $C_{nominal}$ are set and fixed in advance. Said calculation center C may transmit the calculated flux value of the pH adjuster via electrical signal to the output port B and control the port B to adjust the flux of the pH adjuster.

The process and the on-line automatic control device according to the present invention are in particular suitable for use in papermaking, water treatment, mining and petroleum industries.

[0059] Figure 2 is a schematic diagram for K1 calculation in the examples.

[0060] Figures 3 to 5 are schematic diagrams for K2 calculation in the examples.

[0061] Figure 6 is a schematic diagram for K4 calculation in the examples.

[0062] Figure 7 is the schematic diagram for the automatic control device for the pH adjusting unit.

Reference signs list**[0063]**

- 1 dialdehyde-modified polyacrylamide GPAM
- 2 polyacrylamide PAM
- 3 diluting unit
- 4 setting base pH value
- 5 pH control unit
- 6 setting target pH value, target reaction index
- 7 pH adjuster, aqueous NaOH solution
- 8 mixer

PM final output product

The arrow represents the flowing direction of the stream (Figure 1) or the transmitting direction of data (Figure 7).

5 **Examples**

[0064] The invention is described in more detail by referring to the following Examples, but is not limited to these Examples.

10 1. Calculation examples for the flux of pH adjuster

[0065]

(1) Reagents as used

15 TX 15241: dialdehyde-modified DADMAC/polyacrylamide (GPAM) having the solid content of 9-12% in general, the pH of 2.36 to 3.46 and the viscosity at 25 °C of 16-28 cps, available from Ecolab Company

TX 15951: polyacrylamide (PAM) having the solid content of 19.5-22% in general, the pH of 2.5-3.49 and the viscosity at 25 °C of 4000 to 10000 cps, available from Ecolab Company

20 TX 16389: 48% NaOH having the solid content of 46-50% in general, available from Ecolab Company

(2) Calculations of the parameters K1 to K5

[0066] It is well understood for a person skilled in the art that the following calculation examples are just illustrative and can be conducted by programming of the computers or other auxiliary devices.

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Calculation of K1

[0067] The base pH value δ_1 was set at 8. The amount of pH adjuster consumed with pH value increasing from the initial pH value of the product to the base pH value 8 under varying solid content ratios (r) of the polyacrylamide TX 15951 in the mixed product was measured.

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[0068] During this procedure, r value was varied with other parameters to be fixed. TX 15951 and TX 15241 were formulated into 1 kg of the respective mixed products with different ratios, and each of the compositions of TX 15921 and TX 15241 with different ratios were titrated with pH adjuster TX 16389 solution one by one. The respective amounts of TX 16389 consumed for adjusting the pH value from the initial pH value to the base pH value of 8 were recorded in Table 1. Plotting the corresponding curve according to the values as shown in Table 1, and linear fitting to obtain Figure 2 and the formula of K1:

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$$K1 = (4.9754 \times r + 3.5422).$$

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Table 1 Effects of varying r values on the amount of TX 16389

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r	Amount of TX 16389,ml
0.33	5.2317
0.497	5.8678
0.53	6.2444
0.5515	6.3424

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Calculation of K2

[0069] In this batch, the nominal low limit pH value of TX 15951 was 2.5 and the nominal high limit pH value was 3.49. The average pH value as measured from 80 samples was 3.38. The nominal low limit pH value of TX 15241 was 2.36 and the nominal high limit pH value was 3.46. The average pH value as measured from 80 samples was 2.91. Then, TX 15951 and TX15241 were formulated into a mixed product according to the ratio r of TX 15951 in the mixed product of 0.5.

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[0070] In the experiment, the amounts of TX 16389 consumed by titration with pH value gradually increasing from the respective low limit pH value, high limit pH value and average pH value of TX 15241 and TX 15951 to different pH values were studied and recorded in Tables 2 and 3. Plotting Figures 3, 4, and 5 according to the measured data in Tables 2 and 3, and calculating the average slope values k_2 and k_2' of the linear curves of TX 15241 and TX 15951.

Table 2

TX 15241					
Low limit pH value		Average pH value		High limit pH value	
pH	Amount of TX 16389	pH	Amount of TX 16389	pH	Amount of TX 16389
7.48	2.0783	8.09	1.715	7.73	1.07
8.38	2.31	8.76	1.872	8.45	1.275
9.31	2.49	9.21	2.027	9.14	1.652
9.48	2.53	9.29	2.067	9.43	1.7767
9.56	2.66	9.62	2.228	9.55	1.9967
		9.92	2.408		

Table 3

TX 15951					
Low limit pH value		Average pH value		High limit pH value	
pH	Amount of TX 16389	pH	Amount of TX 16389	pH	Amount of TX 16389
7.85	4.79	8.51	5.34	7.96	3.331
8.26	5.59	8.83	6.055	8.43	4.35
8.74	6.66	9.17	6.78	8.88	5.325
9.22	7.74	9.46	7.34	9.19	6.01
9.63	8.55	9.79	7.94	9.68	7.09

[0071] As shown in Figures 3-5, the relations of respective pH value changes as calculated by the linear fitting under the low limit pH value, the average pH value and the high limit pH value of TX 15951 with the amount of TX 16389 were respectively shown as follows, wherein Y_1, Y_1', Y_1'' and X_1, X_1', X_1'' corresponded to the Y-coordinate and the X-coordinate, respectively:

$Y_1 = 2.1391X_1 - 12.032$ (Figure 3),
 $Y_1' = 2.0506X_1' - 12.082$ (Figure 4),
 $Y_1'' = 2.1847X_1'' - 14.064$ (Figure 5), and
 the average value of slope k_2 is 2.1248.

[0072] The relations of respective pH value changes as calculated by the linear fitting under the low limit pH value, the average pH value and the high limit pH value of TX 15241 with the amount of TX 16389 were respectively shown as follows, wherein Y_2, Y_2', Y_2'' and X_2, X_2', X_2'' corresponded to the Y-coordinate and the X-coordinate, respectively:

$Y_2 = 0.2492X_2 + 0.213$ (Figure 3),
 $Y_2' = 0.4637X_2' - 2.2195$ (Figure 4),
 $Y_2'' = 0.4823X_2'' - 2.719$ (Figure 5), and
 the average value of slope k_2' was 0.3984.

[0073] Meanwhile, taking into consideration the effect of the deviation of ratio r from base 0.5, the coefficient $(r/0.5)$ was multiplied, i.e., $2 \times r$.

[0074] Thereby, the formula was obtained: $K_2 = 2 \times r \times 2.1248 \times (a - 3.38) + 2 \times (1-r) \times 0.3984 \times (b-2.91)$.

Calculation of K3

[0075] After calculating the parameter K2 as above described, the following formula could be easily obtained: $K3 = (2 \times r \times 2.1248 + 2 \times (1 - r) \times 0.3984) \times (\delta 2 - 8)$.

Calculation of K4

[0076] TX 15951 and TX 15241 were formulated according to the solid content ratios as recited in the left column of Table 4 into some 1kg mixed products with different ratios, and the pH adjuster TX 16389 was used to adjust individual mixed products into the base pH of 8. The amount of the consumed TX 16389 was recorded as the data shown in the right column of Table 4. Figure 6 was plotted according to all data in Table 4.

[0077] In addition, according to the formulation, the theoretical solid content $\alpha_{theo.}$ of TX 15951 could be obtained as 20% and the theoretical solid content $\beta_{theo.}$ of TX 15241 as 10%. Considering the deviation of the actual solid content of the product from the standard value, the standard value r_0 of the ratio of TX 15951 in the mixed product was set to be 1/2, and the value of C_1 was obtained as 2 according to the formula $r_0 * \alpha_{theo.} / ((1-r_0) * \beta_{theo.})$. Furthermore, by combining the slope 1.5408 obtained from Figure 6, K4 could be obtained as follows:

$$K4 = 1.5408 \times (r \times \alpha / ((1 - r) \times \beta) - 2)$$

Table 4

TX 15951: TX 15241	TX 16389 amount, ml
1.23	5.2317
1.13	5.8678
0.99	6.2444
0.55	6.3424

Calculation of K5

[0078] Since the nominal concentration of pH adjuster TX 16389 was 48%, the parameter K5 for rectifying the amount of pH adjuster TX 16389 was $48\%/C_2$.

[0079] Substituting K1 to K5 as calculated above into the formula (1), the formula (2) about the amount of pH adjuster could be obtained as follows:

$$\text{Amount of pH adjuster} = X \times ((4.9754 \times r + 3.5422) - (2 \times r \times 2.1248 \times (a - 3.38) + 2 \times (1-r) \times 0.3984 \times (b-2.91) + (2 \times r \times 2.1248 + 2 \times (1-r) \times 0.3984) \times (\delta 2 - 8) + 1.5408 \times (r \times \alpha / ((1-r) \times \beta) - 2)) \times (48\%/C_2).$$

2. Application example

[0080] In the automatic control device as shown in Figure 7, comprising at least port A, output port B and calculation center C, the above-described formula (2) was programmed and fixed in the calculator of the calculation center C.

[0081] Then, the binary enhancer consisting of TX 15241 and TX 15951 and TX 16389 with the concentration of 48% were fed into the on-line control and reaction device for pH adjustment as shown in Figure 1. The solid contents (α , β), pH values (a, b), the solid content ratio (r) of polyacrylamide in the mixed product, flux of the final output product (X) and target pH value ($\delta 2$) were measured beforehand. Following this, these parameters were input into the output port A and then a suitable amount of pH adjuster could be achieved through the calculation in the calculator of the calculation center C and by adjusting the valve of output port B. Individual parameters and the amount of pH adjuster were shown in Table 5.

Table 5 Individual input parameters of the binary enhancer and the amount of pH adjuster

Ratio of TX 15951 in the mixed product (%) r	Solid content of TX 15951 (%) α	Solid content of TX 15241 (%) β	pH value of TX 15951 a	pH value of TX 15241 b	flux of the final output product (ml/min) X	Amount of pH adjuster (ml/min)	Target pH value $\delta 2$
0.5	20	10	2.5	3	1.6	15.78	8.80

[0082] After such an adjustment, the obtained target pH value of the resulting final output product solution was 8.80, and the actual value as measured was 8.85.

Claims

1. An on-line control and reaction process for pH adjustment for the binary enhancer composition comprising a first enhancer and a second enhancer, comprising the following steps:

- 1) providing a first enhancer and a second enhancer as well as pH adjuster to the reaction system,
- 2) mixing the first enhancer and the second enhancer, optionally after diluting each of both with water,
- 3) setting a base pH value ($\delta 1$) and a target pH value, i.e. target reaction index ($\delta 2$),
- 4) adding pH adjuster into the mixture via pH control unit and mixing them, to obtain the final output product with the target pH value;

wherein said pH control unit adjusts the amount of pH adjuster by measuring or inputting the following parameters;

- a. the solid content ratio of the first enhancer in relation to the mixed product (r), said mixed product consisting of the first enhancer and the second enhancer,
- b. the solid content of the first enhancer (α) and the solid content of the second enhancer (β),
- c. the pH value of the first enhancer (a) and the pH value of the second enhancer (b),
- d. the base pH value ($\delta 1$) and the target pH value ($\delta 2$) as set in step 3),
- e. the flux of the final output product (X) which is consisting of pH adjuster, a first enhancer and a second enhancer,

wherein said first enhancer is selected from one of polyacrylamide enhancer and dialdehyde modified polyacrylamide enhancer, while said second enhancer is the other one, and said pH adjuster is an organic or inorganic alkaline substance with the pH value ranging from 9 to 14,

characterized in that said pH control unit adjusts the flux of pH adjuster by acquiring at least the related parameter, K1, K2, K3 and K4 and utilizing the following formula (1):

$$\text{flux of pH adjuster} = X \times (K1 - K2 + K3 + K4) \quad (1)$$

in which

X represents the flux of final output product (X) which is consisting of the pH adjuster, the first enhancer and the second enhancer;

K1 represents the amount of pH adjuster consumed with pH value increasing from the initial pH value to the base pH value ($\delta 1$) under varying solid content ratios of the first enhancer or second enhancer in relation to the mixed product (r), and satisfies $K1 = k_1 \times r + t$, wherein k_1 is the slope obtained by linear fitting and t is the intercept;

K2 represents the amount of pH adjuster consumed in relation to different pH values of the first enhancer (a) and different pH values of the second enhancer (b) under varying solid content ratios of the first enhancer or second enhancer in relation to the mixed product (r), and satisfies $K2 = 2 \times r \times k_2 \times \Delta_{pH1} + 2 \times (1-r) \times k_2' \times \Delta_{pH2}$, wherein k_2 and k_2' represents slope or average slope obtained by linear fitting in plotting the amounts of pH adjuster consumed with pH value increasing from the respective low limit pH value, high limit pH value and average pH value of two enhancers, in which said low limit pH value and high limit pH value are respectively the nominal lowest and highest pH value of the enhancer sample, and

Δ_{pH1} and Δ_{pH2} represent the difference between the inherent pH value of first enhancer, respectively second enhancer ((a) or (b)), and the average pH value of first enhancer, respectively second enhancer ($a_{ave.}$) or

($b_{ave.}$), i.e. represent ($a-a_{ave.}$) and ($b-b_{ave.}$) respectively, in which each of said average pH value ($(a_{ave.})$ or ($b_{ave.}$)) is an average determined from the pH values of n samples of the first or second enhancer and n is ≥ 50 , preferably ≥ 70 ;

K3 represents the effect of the difference between the target reaction index ($\delta 2$) and base pH value ($\delta 1$) on the amount of pH adjuster on the basis of K2, and satisfies $K3 = (2 \times r \times k_2 + 2 \times (1-r) \times k_2) \times (\delta 2 - \delta 1)$;

K4 represents the effect of varying solid content (α) and solid content (β) on the amount of pH adjuster under base pH value ($\delta 1$), and satisfies $K4 = k_4 \times (r \times \alpha / (1-r) \times \beta) - C_1$,

wherein k_4 represents slope obtained by linear fitting in plotting the amounts of pH adjuster consumed when the pH value is adjusted up to base pH value ($\delta 1$) against different solid content ratios of first enhancer to second enhancer,

C_1 is a value calculated from the formula $r_0 * \alpha_{theo} / ((1-r_0) * \beta_{theo})$ in case of the theoretical solid content of first enhancer (α_{theo}) and the theoretical solid content of second enhancer (β_{theo}), in which r_0 is a standard ratio of first enhancer to the mixed product and is set to 1/2.

2. Process according to Claim 1, **characterized in that** the solid content of polyacrylamide enhancer (α or β) is ranging from 5 to 100%, preferably 10 to 30 %, while the solid content of dialdehyde modified polyacrylamide enhancer (α or β) is ranging from 5 to 100%, preferably 6 to 20%.

3. Process according to one of Claims 1 to 2, **characterized in that** pH value of polyacrylamide enhancer (a or b) is ranging from 2 to 8, preferably 3 to 5, while pH value of dialdehyde modified polyacrylamide enhancer (a or b) is ranging from 2 to 7, preferably 2 to 4.

4. Process according to one of Claims 1 to 3, **characterized in that** $\delta 2$ is 7.5 to 11 and preferably 8.5 to 9.5.

5. Process according to one of Claims 1 to 4, **characterized in that** said first enhancer is polyacrylamide enhancer.

6. Process according to one of Claims 1 to 5, **characterized in that** the weight averaged molecular weight of polyacrylamide enhancer is ranging from 500,000 to 5000,000 g/mol.

7. Process according to one of Claims 1 to 6, **characterized in that** the weight averaged molecular weight of dialdehyde modified polyacrylamide enhancer is ranging from 200,000 to 2000,000 g/mol.

8. Process according to one of Claims 1 to 7, **characterized in that** parameter K5 is introduced to calibrate the actual concentration of pH adjuster,

$$K5 = C_{nominal}/C_2,$$

in which $C_{nominal}$ is a nominal concentration of the product and C_2 is an actual concentration as measured.

9. Process according to Claim 8, **characterized in that** the flux of pH adjuster = $X \times (K1 - K2 + K3 + K4) \times K5$.

10. A control device for automatically adjusting pH value, comprising at least input port A, output port B and calculation center C, in which input port A receives the signals corresponding to the following parameters and transmits them into the calculation center C:

the solid content ratio of the first enhancer in relation to the mixed product (r), the solid content of the first enhancer (α) and the solid content of the second enhancer (β),

the pH value of the first enhancer (a) and the pH value of the second enhancer (b),

the base pH value ($\delta 1$) as set,

the target pH value, i.e. target reaction index ($\delta 2$),

the flux of the final output product (X) and

optionally actual concentration of pH adjuster as measured (C_2);

and then calculation center C transmits into output port B the flux of pH adjuster as calculated according to the process as defined in one of Claims 1 to 11, said output port B adapting the pH adjuster flux to the calculated flux of pH adjuster via pipeline and flux control apparatus,

wherein said first enhancer is selected from one of polyacrylamide enhancer and dialdehyde modified polyacrylamide enhancer, while said second enhancer is the other one, and said pH adjuster is an organic or inorganic

alkaline substance with the pH value ranging from 9 to 14.

11. Device according to Claim 10, **characterized in that** the formula (1) and parameters in relation to K1-K4 and optional K5 like k_1 , t , k_2 , k_2' , a_{ave} , b_{ave} , k_4 , C_1 and optional $C_{nominal}$ as defined in any one of claims 1 to 5 are set and fixed in advance in the calculation center C such as a calculator.
12. Use of the process or control device according to one of Claims 1 to 11 in papermaking, water treatment, mining and petroleum industries.

Patentansprüche

1. Online-Steuerungs- und Reaktionsverfahren zur pH-Wert-Einstellung für die binäre Verstärkerzusammensetzung, umfassend einen ersten Verstärker und einen zweiten Verstärker, umfassend die folgenden Schritte:

- 1) Bereitstellen eines ersten Verstärkers und eines zweiten Verstärkers sowie eines pH-Wert-Einstellers an das Reaktionssystem,
- 2) Mischen des ersten Verstärkers und des zweiten Verstärkers, optional nachdem jeder der beiden mit Wasser verdünnt wurde,
- 3) Einstellen eines pH-Grundwertes (δ_1) und eines pH-Zielwertes, d. h. eines Zielreaktionsindex (δ_2),
- 4) Hinzugeben des pH-Wert-Einstellers zu der Mischung über eine pH-Wert-Steuerungseinheit und Mischen dieser, um das Endausgabeergebnis mit dem pH-Zielwert zu erhalten;

wobei die pH-Wert-Steuerungseinheit die Menge des pH-Wert-Einstellers durch Messen oder Eingeben der folgenden Parameter anpasst;

- a. das Feststoffgehaltsverhältnis des ersten Verstärkers in Bezug auf das/die gemischte(n) Erzeugnis(e), wobei das gemischte Erzeugnis aus dem ersten Verstärker und dem zweiten Verstärker besteht,
- b. der Feststoffgehalt des ersten Verstärkers (α) und den Feststoffgehalt des zweiten Verstärkers (β),
- c. der pH-Wert des ersten Verstärkers (a) und den pH-Wert des zweiten Verstärkers (b),
- d. der pH-Grundwert (δ_1) und den pH-Zielwert (δ_2) wie in Schritt 3) eingestellt,
- e. der Fluss des Endausgabeergebnisses (X), das aus einem pH-Wert-Einsteller, einem ersten Verstärker und einem zweiten Verstärker besteht,

wobei der erste Verstärker aus einem Polyacrylamid-Verstärker oder einem Dialdehyd-modifiziertem Polyacrylamid-Verstärker ausgewählt ist, während der zweite Verstärker der andere ist und der pH-Wert-Einsteller eine organische oder anorganische alkalische Substanz mit einem pH-Wert im Bereich von 9 bis 14 ist, **dadurch gekennzeichnet, dass** die pH-Wert-Steuerungseinheit den Fluss des pH-Wert-Einstellers einstellt, indem sie wenigstens die zugehörigen Parameter K1, K2, K3 und K4 erfasst und die folgende Formel (1) verwendet:

$$\text{Fluss des pH-Wert-Einstellers} = X \times (K1 - K2 + K3 + K4) \quad (1)$$

wobei

X den Fluss des Endausgabeergebnisses (X) darstellt, das aus dem pH-Wert-Einsteller, dem ersten Verstärker und dem zweiten Verstärker besteht;

$K1$ die Menge des pH-Wert-Einstellers darstellt, die verbraucht wird, wenn der pH-Wert von dem anfänglichen pH-Wert auf den pH-Grundwert (δ_1) unter variierenden Feststoffgehaltsverhältnissen des ersten Verstärkers oder zweiten Verstärkers in Bezug auf das gemischte Erzeugnis (r) ansteigt, und $K1 = k_1 \times r + t$ erfüllt, wobei k_1 die Steigung ist, die durch lineares Anpassen erhalten wird, und t der Achsenabschnitt ist;

$K2$ die Menge an verbrauchtem pH-Wert-Einsteller in Bezug auf unterschiedliche pH-Werte des ersten Verstärkers (a) und unterschiedliche pH-Werte des zweiten Verstärkers (b) unter variierenden Feststoffgehaltsverhältnissen des ersten Verstärkers oder zweiten Verstärkers in Bezug auf das gemischte Erzeugnis (r) darstellt und $K2 = 2 \times r \times k_2 \times \Delta_{pH1} + 2 \times (1 - r) \times k_2' \times \Delta_{pH2}$ erfüllt,

wobei k_2 und k_2' eine Steigung oder eine durchschnittliche Steigung darstellen, die durch lineares Anpassen beim Aufzeichnen der Mengen des pH-Wert-Einstellers, der während des Ansteigens des pH-Werts von dem entsprechenden niedrigen pH-Grenzwert, hohen pH-Grenzwert und durchschnittlichen pH-Wert zweier

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Verstärker verbraucht wird, wobei der niedrige pH-Grenzwert und der hohe pH-Grenzwert jeweils der nominal niedrigste und höchste pH-Wert der Verstärkerprobe sind, und Δ_{pH1} und Δ_{pH2} die Differenz zwischen dem inhärenten pH-Wert des ersten Verstärkers beziehungsweise des zweiten Verstärkers ((a) oder (b)) und dem durchschnittlichen pH-Wert des ersten Verstärkers beziehungsweise des zweiten Verstärkers ((a_{ave}) oder (b_{ave})), d. h. ($a - a_{ave}$) beziehungsweise ($b - b_{ave}$) darstellen, wobei jeder der durchschnittlichen pH-Werte ((a_{ave}) oder (b_{ave})) ein aus den pH-Werten von n Proben des ersten oder zweiten Verstärkers bestimmter Durchschnitt ist und $n \geq 50$, vorzugsweise ≥ 70 ist;

K3 den Effekt der Differenz zwischen dem Zielreaktionsindex (δ_2) und dem pH-Grundwert (δ_1) auf die Menge des pH-Wert-Einstellers basierend auf K2 darstellt und $K3 = (2 \times r \times k_2 + 2 \times (1 - r) \times k_2) \times (\delta_2 - \delta_1)$ erfüllt;

K4 den Effekt des Variierens des Feststoffgehalts (α) und des Feststoffgehalts (β) auf die Menge des pH-Wert-Einstellers unter den pH-Grundwert (δ_1) darstellt und $K4 = k_4 \times (r \times \alpha / (1 - r) \times \beta) - C_1$ erfüllt,

wobei k_4 die Steigung darstellt, die durch lineares Anpassen beim Aufzeichnen der verbrauchten Mengen des pH-Wert-Einstellers erhalten wird, wenn der pH-Wert auf den pH-Grundwert (δ_1) gegen verschiedene Feststoffgehaltsverhältnisse von dem ersten Verstärker zu dem zweiten Verstärker angepasst wird,

C_1 ein Wert ist, der aus der Formel $r_0 \times \alpha_{theo} / ((1 - r_0) \times \beta_{theo})$ im Fall des theoretischen Feststoffgehalts des ersten Verstärkers (α_{theo}) und des theoretischen Feststoffgehalts des zweiten Verstärkers (β_{theo}) berechnet wird, wobei r_0 ein Standardverhältnis des ersten Verstärkers zu dem gemischten Produkt ist und auf 1/2 eingestellt ist.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** der Feststoffgehalt des Polyacrylamid-Verstärkers (α oder β) im Bereich von 5 bis 100 %, vorzugsweise 10 bis 30 % liegt, während der Feststoffgehalt des Dialdehyd-modifizierten Polyacrylamid-Verstärkers (α oder β) im Bereich von 5 bis 100 %, vorzugsweise 6 bis 20 % liegt.
3. Verfahren nach einem der Ansprüche 1 bis 2, **dadurch gekennzeichnet, dass** der pH-Wert des Polyacrylamid-Verstärkers (a oder b) im Bereich von 2 bis 8, vorzugsweise 3 bis 5 liegt, während der pH-Wert des Dialdehyd-modifizierten Polyacrylamid-Verstärkers (a oder b) im Bereich von 2 bis 7, vorzugsweise von 2 bis 4 liegt.
4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** δ_2 7,5 bis 11 und vorzugsweise 8,5 bis 9,5 beträgt.
5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** der erste Verstärker ein Polyacrylamid-Verstärker ist.
6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** das gewichtsgemittelte Molekulargewicht des Polyacrylamid-Verstärkers im Bereich von 500.000 bis 5000.000 g/mol liegt.
7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** das gewichtsgemittelte Molekulargewicht des Dialdehyd-modifiziertem Polyacrylamid-Verstärkers im Bereich von 200.000 bis 2000.000 g/mol liegt.
8. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** Parameter K5 eingeführt wird, um die tatsächliche Konzentration des pH-Wert-Einstellers zu kalibrieren,

$$K5 = C_{nominal} / C_2,$$

wobei $C_{nominal}$ eine nominale Konzentration des Erzeugnisses ist und C_2 eine gemessene tatsächliche Konzentration ist.

9. Verfahren nach Anspruch 8, **dadurch gekennzeichnet, dass** der Fluss des pH-Wert-Einstellers = $X \times (K1 - K2 + K3 + K4) \times K5$.
10. Steuervorrichtung zum automatischen Einstellen des pH-Werts, die wenigstens einen Eingabeanschluss A, einen Ausgabeanschluss B und eine Berechnungszentrale C umfasst, in der der Eingabeanschluss A die Signale empfängt, die den folgenden Parametern entsprechen, und diese an die Berechnungszentrale C überträgt; das Feststoffgehaltsverhältnis des ersten Verstärkers in Bezug auf das gemischte Erzeugnis (r), den Feststoffgehalt des ersten Verstärkers (α) und den Feststoffgehalt des zweiten Verstärkers (β), der pH-Wert des ersten Verstärkers (a) und den pH-Wert des zweiten Verstärkers (b), der eingestellte pH-Grundwert (δ_1), der pH-Zielwert, d. h. der Zielreaktionsindex (δ_2),

der Fluss des Endausgabeergebnisses (X) und

optional die tatsächliche Konzentration des gemessenen pH-Wert-Einstellers (C_2); und dann überträgt das Berechnungszentrum C den Fluss des pH-Wert-Einstellers, wie er gemäß dem Verfahren nach einem der Ansprüche 1 bis 11 berechnet wurde, in den Ausgabeanschluss B, wobei der Ausgabeanschluss B den Fluss des pH-Wert-Einstellers über eine Rohrleitung an den berechneten Fluss des pH-Wert-Einstellers und einer Flusssuereinrichtung anpasst, wobei der erste Verstärker aus einem aus Polyacrylamid-Verstärker und einem Dialdehyd-modifizierten Polyacrylamid-Verstärker ausgewählt ist, während der zweite Verstärker der andere ist und der pH-Wert-Einsteller eine organische oder anorganische alkalische Substanz mit einem pH-Wert im Bereich von 9 bis 14 ist.

11. Vorrichtung nach Anspruch 10, **dadurch gekennzeichnet, dass** die Formel (1) und die Parameter in Bezug auf K1-K4 und optional K5 wie k_1 , t , k_2 , k_2' , a_{ave} , b_{ave} , k_4 , C_1 und optional $C_{nominal}$ nach einem der Ansprüche 1 bis 5 im Voraus in der Berechnungszentrale C, wie etwa einem Taschenrechner, eingestellt und fixiert werden.

12. Verwendung des Verfahrens oder der Steuervorrichtung nach einem der Ansprüche 1 bis 11 in der Papier-, Wasseraufbereitungs-, Bergbau- und Mineralölindustrie.

Revendications

1. Procédé de réglage et de réaction en ligne pour la régulation du pH de la composition d'activateur binaire comprenant un premier activateur et un second activateur, comprenant les étapes suivantes :

1) la fourniture d'un premier activateur et d'un second activateur ainsi qu'un régulateur de pH du système de réaction,

2) le mélange du premier activateur et du second activateur, éventuellement après la dilution de chacun des deux avec de l'eau,

3) l'établissement d'une valeur de pH de base (δ_1) et d'une valeur de pH cible, c'est-à-dire d'un indice de réaction cible (δ_2),

4) l'ajout d'un régulateur de pH dans le mélange par l'intermédiaire d'une unité de réglage du pH et le mélange de ceux-ci pour obtenir le produit sortant final avec la valeur de pH cible ;

ladite unité de réglage de pH régulant la quantité de régulateur de pH en mesurant ou en entrant les paramètres suivants ;

a. le rapport de la teneur en solide du premier activateur par rapport au produit mélangé (r), ledit produit mélangé étant constitué du premier activateur et du second activateur,

b. la teneur en solide du premier activateur (α) et le teneur en solide du second activateur (β),

c. la valeur du pH du premier activateur (a) et la valeur du pH du second activateur (b),

d. la valeur de pH de base (δ_1) et la valeur de pH cible (δ_2) telle qu'établies à l'étape 3),

e. le flux du produit sortant final (X) qui est constitué d'un régulateur de pH, d'un premier activateur et d'un second activateur,

ledit premier activateur étant choisi parmi l'activateur de polyacrylamide et l'activateur de polyacrylamide modifié par un dialdéhyde, ledit second activateur étant l'autre, et ledit régulateur de pH est une substance alcaline organique ou inorganique avec une valeur de pH comprise dans la plage allant de 9 à 14, **caractérisé en ce que** ladite unité de réglage du pH régule le flux de régulateur de pH en acquérant au moins le paramètre associé K1, K2, K3 et K4 et en utilisant la formule suivante (1) :

$$\text{flux de régulateur de pH} = X \times (K1 - K2 + K3 + K4) \quad (1)$$

dans laquelle

X représente le flux de produit sortant final (X) qui est constitué du régulateur de pH, du premier activateur et du second activateur ;

K1 représente la quantité de régulateur de pH consommée lorsque la valeur de pH augmente de la valeur de pH initiale à la valeur de pH de base (δ_1) sous divers rapports de teneur en solide du premier ou du second activateur par rapport au produit mélangé (r), et satisfait $K1 = k_1 \times r + t$, k_1 étant la pente obtenue par ajustement

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linéaire et t étant le point d'intersection ;

K2 représente la quantité de régulateur de pH consommée en relation avec différentes valeurs de pH du premier activateur (a) et différentes valeurs de pH du second activateur (b) sous divers rapports de teneur en solide du premier activateur ou du second activateur en relation avec le produit mélangé (r), et satisfait $K2 = 2 \times r \times k_2 \times \Delta_{pH1} + 2 \times (1 - r) \times k_2' \times \Delta_{pH2}$,

k_2 et k_2' représentant une pente ou une pente moyenne obtenue par ajustement linéaire en traçant les quantités de régulateur de pH consommées avec une valeur de pH augmentant à partir de la valeur de pH limite inférieure, de la valeur de pH limite supérieure et de la valeur de pH moyenne de deux activateurs, dans laquelle lesdites valeurs limites inférieure et supérieure de pH sont respectivement les valeurs de pH minimale et maximale nominales de l'échantillon d'activateur, et Δ_{pH1} et Δ_{pH2} représentent la différence entre la valeur de pH inhérente du premier activateur, respectivement du second activateur ((a) ou (b)), et de la valeur de pH moyenne du premier activateur, respectivement du second activateur (($a_{ave.}$) ou ($b_{ave.}$)), c'est-à-dire représentent ($a - a_{ave.}$) et ($b - b_{ave.}$) respectivement, dans laquelle chacune desdites valeurs de pH moyennes (($a_{ave.}$) ou ($b_{ave.}$)) est une moyenne déterminée à partir des valeurs de pH de n échantillons du premier ou du second activateur et n est ≥ 50 , de préférence ≥ 70 ;

K3 représente l'effet de la différence entre l'indice de réaction cible ($\delta 2$) et la valeur de pH de base ($\delta 1$) sur la quantité de régulateur de pH sur la base de K2 et satisfait $K3 = (2 \times r \times k_2 + 2 \times (1 - r) \times k_2') \times (\delta 2 - \delta 1)$;

K4 représente l'effet de la teneur en solide variable (α) et de la teneur en solide (β) sur la quantité de régulateur de pH sous la valeur de pH de base ($\delta 1$) et satisfait $K4 = k_4 \times (r \times \alpha / (1 - r) \times \beta) - C_1$,

k_4 représentant une pente obtenue par ajustement linéaire en traçant les quantités de régulateur de pH consommées lorsque la valeur de pH est réglée jusqu'à la valeur de pH de base ($\delta 1$) par rapport à différents rapports de teneur en solide du premier activateur au second activateur,

C_1 étant une valeur calculée à partir de la formule $r_0 * \alpha_{theo} / ((1 - r_0) * \beta_{theo})$ dans le cas de la teneur en solide théorique du premier activateur ($\alpha_{theo.}$) et de la teneur en solide théorique du second activateur ($\beta_{theo.}$), dans laquelle r_0 est un rapport standard du premier activateur sur le produit mélangé et est établi comme 1/2.

2. Procédé selon la revendication 1, **caractérisé en ce que** la teneur en solide d'activateur de polyacrylamide (α ou β) est comprise dans la plage allant de 5 à 100 %, de préférence de 10 à 30 %, tandis que la teneur en solide d'activateur de polyacrylamide modifié par un dialdéhyde (α ou β) est comprise dans la plage allant de 5 à 100 %, de préférence de 6 à 20 %.
3. Procédé selon l'une quelconque des revendications 1 à 2, **caractérisé en ce que** la valeur de pH d'activateur de polyacrylamide (a ou b) est comprise dans la plage allant de 2 à 8, de préférence de 3 à 5, tandis que la valeur de pH d'activateur de polyacrylamide modifié par un dialdéhyde (a ou b) est dans la plage allant de 2 à 7, de préférence de 2 à 4.
4. Procédé selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** $\delta 2$ est de 7,5 à 11 et de préférence de 8,5 à 9,5.
5. Procédé selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** ledit premier activateur est un activateur de polyacrylamide.
6. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** la masse moléculaire moyenne d'activateur de polyacrylamide est comprise dans la plage allant de 500,000 à 5000,000 g/mol.
7. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce que** la masse moléculaire moyenne d'activateur de polyacrylamide modifié par un dialdéhyde est comprise dans la plage allant de 200,000 à 2000,000 g/mol.
8. Procédé selon l'une quelconque des revendications 1 à 7, **caractérisé en ce que** le paramètre K5 est introduit pour étalonner la concentration réelle du régulateur de pH,

$$K5 = C_{nominal} / C_2,$$

dans laquelle $C_{nominal}$ est la concentration nominale du produit et C_2 est la concentration réelle telle que mesurée.

9. Procédé selon la revendication 8, **caractérisé en ce que** le flux de régulateur de pH = $X \times (K1 - K2 + K3 + K4) \times K5$.

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10. Dispositif de réglage pour réguler automatiquement la valeur de pH, comprenant au moins un orifice d'entrée A, un orifice de sortie B et un centre de calcul C, dans lequel l'orifice d'entrée A reçoit les signaux correspondant aux paramètres suivants et les transmet dans le centre de calcul C ;
le rapport en teneur solide du premier activateur par rapport au produit mélangé (r), la teneur en solide du premier activateur (α) et la teneur en solide du second activateur (β), la valeur de pH du premier activateur (a) et la valeur de pH du second activateur (b),
la valeur de pH de base ($\delta 1$) telle qu'établie,
la valeur de pH cible, c'est-à-dire l'indice de réaction cible ($\delta 2$),
le flux du produit sortant final (X) et éventuellement une concentration réelle du régulateur de pH, telle que mesurée (C_2) ; et puis le centre de calcul C transmet à l'orifice de sortie B le flux de régulateur de pH tel que calculé selon le procédé tel que défini dans l'une des revendications 1 à 11, ledit orifice de sortie B adaptant le flux de régulateur de pH comme le flux calculé de régulateur de pH par l'intermédiaire d'une canalisation et d'un appareil de réglage de flux, dans lequel ledit premier activateur est choisi parmi un activateur de polyacrylamide et un activateur de polyacrylamide modifié par un dialdéhyde, ledit second activateur étant l'autre, et ledit régulateur de pH est une substance alcaline organique ou inorganique avec une valeur de pH comprise dans la plage allant de 9 à 14.
11. Dispositif selon la revendication 10, **caractérisé en ce que** la formule (1) et les paramètres relatifs à K1-K4 et éventuellement à K5 tels que k_1 , t , k_2 , k_2 , a_{ave} , b_{ave} , k_4 , C_1 et éventuellement $C_{nominal}$ tels que définis dans l'une quelconque des revendications 1 à 5 sont définis et fixés à l'avance dans le centre de calcul C tel qu'une calculatrice.
12. Utilisation du procédé ou du dispositif de réglage selon l'une des revendications 1 à 11 dans les industries de la papeterie, du traitement des eaux, minière et pétrolière.

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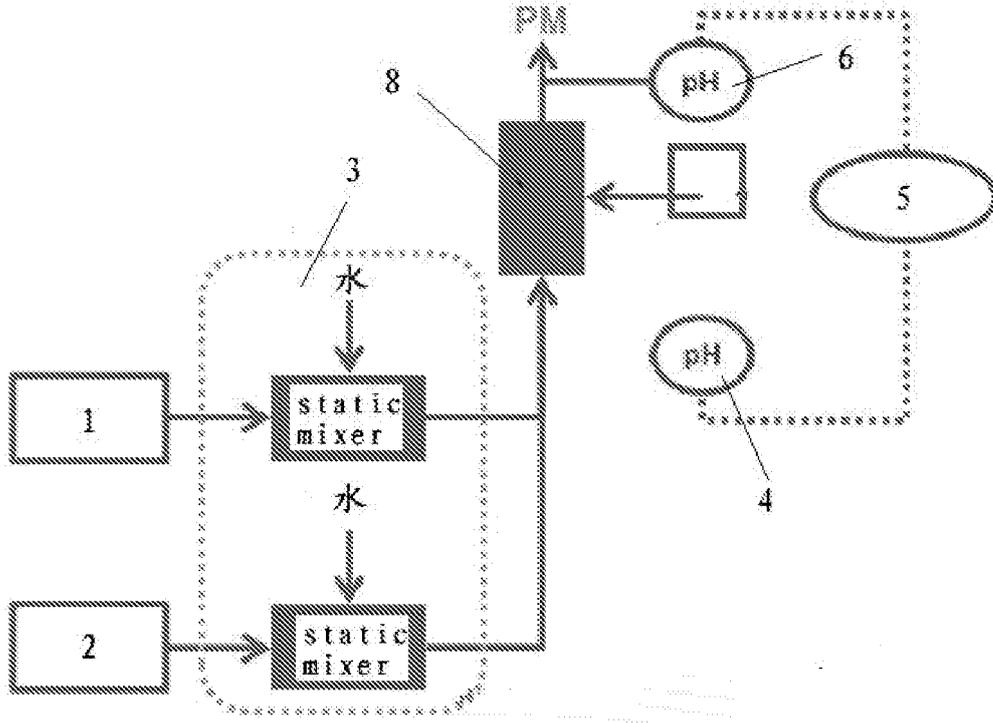


Fig. 1/Abs. Fig.

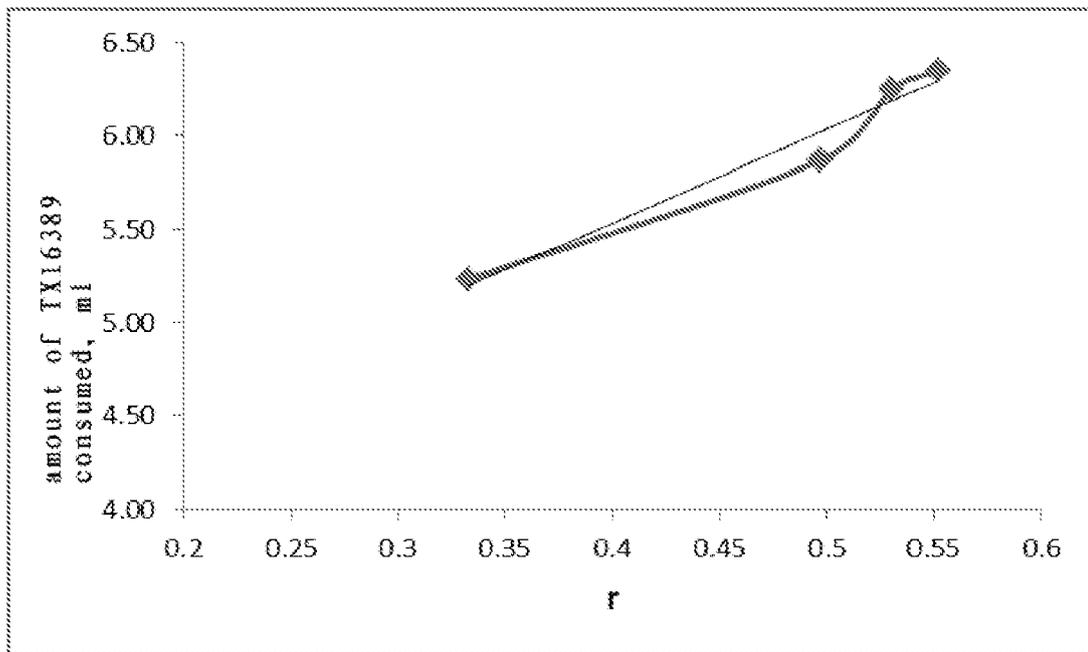


Fig. 2

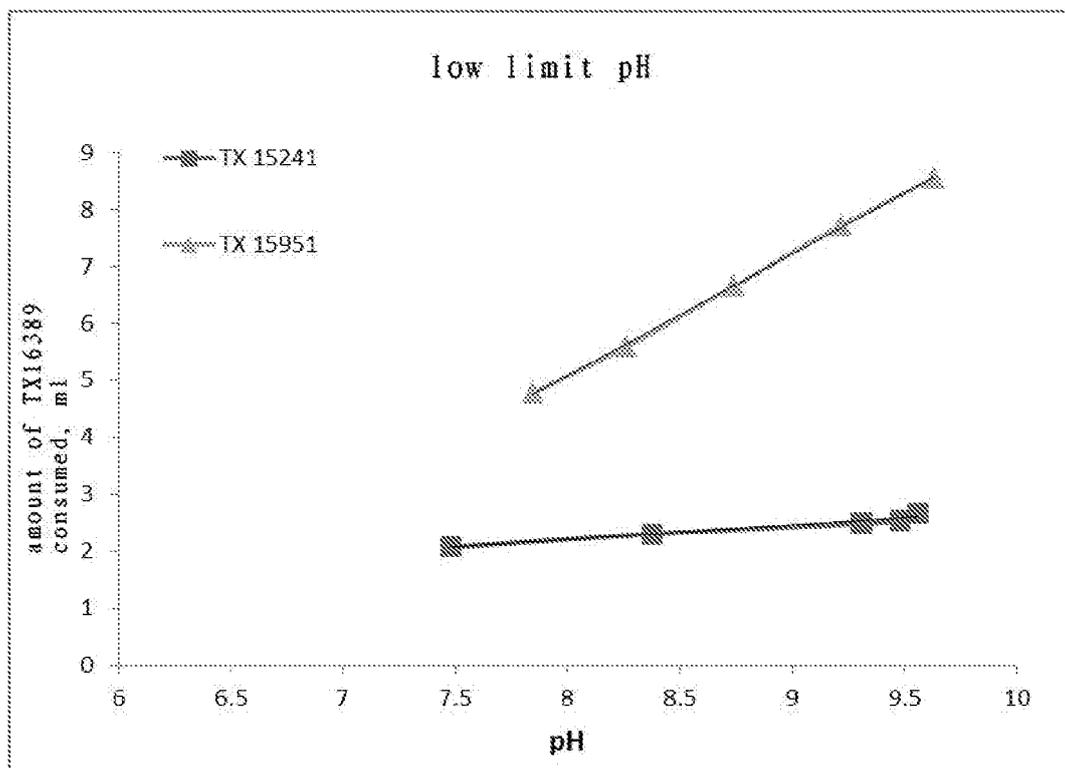


Fig. 3

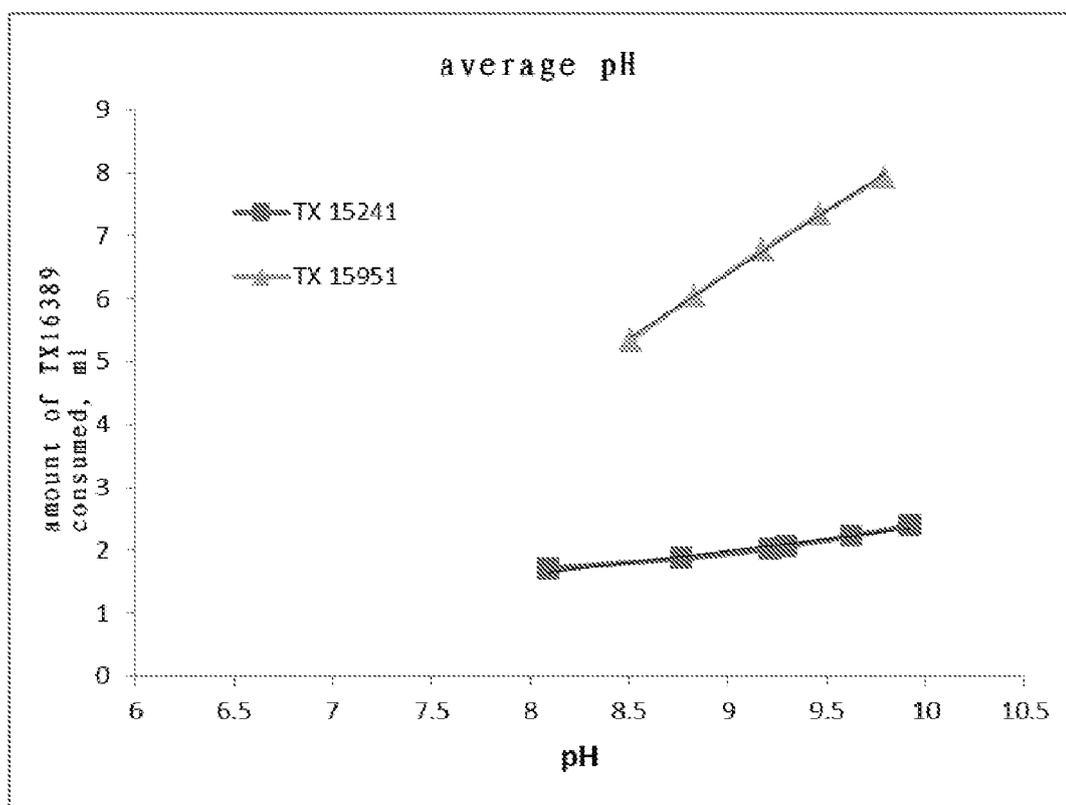


Fig. 4

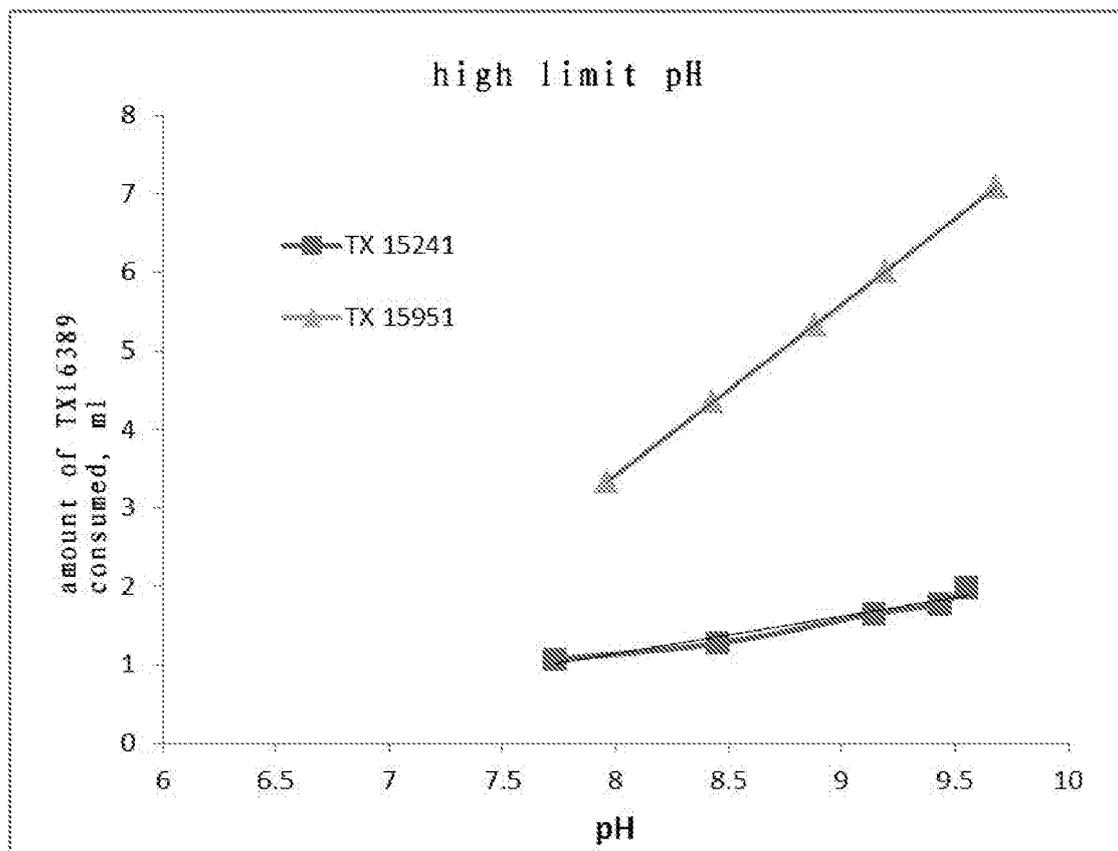


Fig. 5

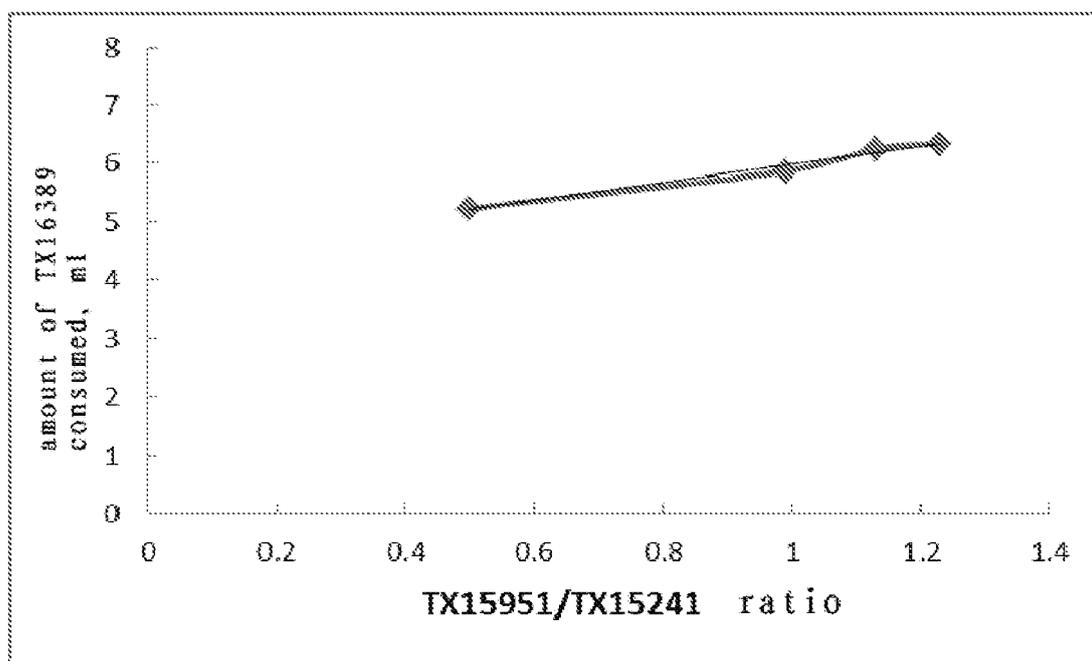


Fig. 6

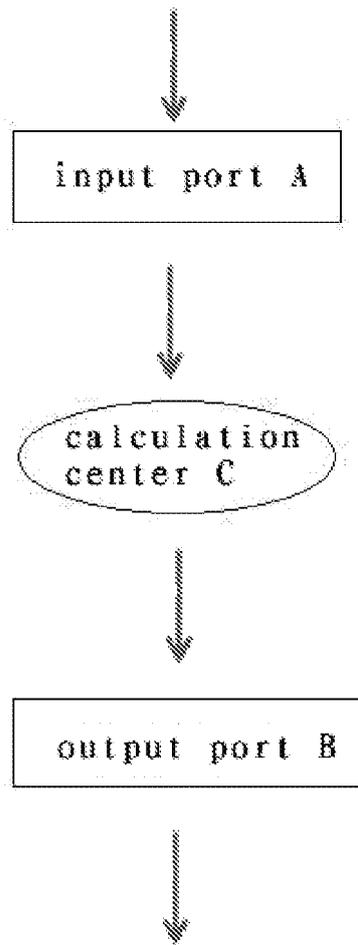


Fig. 7

REFERENCES CITED IN THE DESCRIPTION

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