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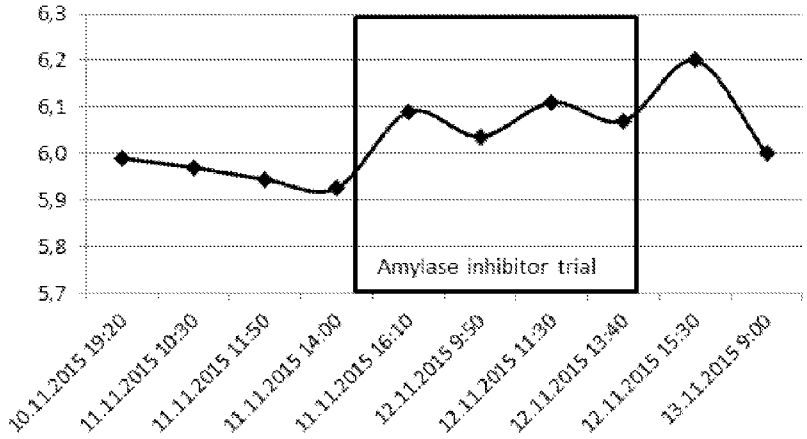



Fig. 4

(57) Abstract: This present invention relates to a method for stabilizing the pH in starch containing industrial aqueous fluid or slurry, use of an amylase inhibiting composition for stabilizing the pH and process for making paper or board.

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# METHOD FOR STABILIZING PROCESS PH IN STARCH CONTAINING INDUSTRIAL AQUEOUS FLUID OR SLURRY

## Field of the disclosure

This disclosure relates to a method for stabilizing the pH in starch containing industrial aqueous fluid or slurry, use of an amylase inhibiting composition for stabilizing the pH and a process for making paper or board.

## Background

Starch is a widely used additive within industry, such as in paper making. Actually, paper making is the largest non-food usage of starch. For example, in the wet end of a paper machine, starch is used to improve paper strength. In the dry end of a paper machine, starch is used for coating the paper in a process called surface sizing. This gives paper additional strength and better printing properties. In processes using recycled fibers the amount of starch varies typically between 10 to 50 kg / ton of dry fiber mass, i.e., the starch amount in the process is considerable.

Amylase is an enzyme that catalyzes degradation of starch. It is produced by many microorganisms, both fungi and bacteria. The microorganisms are not capable to utilize starch as such but excrete amylase enzymes outside the cells expecting them to degrade starch to glucose monomers and dimers which are suitable for cell intake and carbon metabolism. Amylase enzymes are divided into three groups: α-, β- and γ-amylases. They all hydrolyse α-1,4-glycosidic bonds that link together glucose units of starch molecule, β-amylase can break only the second α-1,4-glycosidic bond, yielding into two glucose units (maltose), α-amylase can attack any bonds in the starch molecule and thus is often faster acting than β-amylase. γ-amylase cleaves one glucose unit at the time and is most efficient in acidic environments.

Starch-containing process waters often contain microorganisms which can produce amylase enzymes. In paper industry starch degradation causes loss of the functionality of starch additive leading either to paper quality issues, or alternatively force paper makers to increase starch dosages thus creating unwanted additional costs. It is well known in the pulp, paper or board making industry to apply biocides to control microbial growth and one specific application of biocides is the control of starch degrada-

tion, both in starch containing slurries prior dosing to paper machine and in the starch containing process waters by inhibiting microbial growth.

WO 2012/025228 discloses a method for manufacturing paper, wherein a cellulosic material containing starch is treated with biocides, followed by adding an ionic polymer and an auxiliary ionic polymer, both polymers having different average molecular weight and different ionicity.

WO 2013/045638 teaches synergistic effect of Zn ions with one or more biocides in prevention or reduction of starch degradation by simultaneously inhibiting existing amylase enzymes and preventing the production of new amylase enzymes by microorganisms.

Microbial activity can decrease pH of the aqueous growth environment. This is due the organic acids produced in fermentation metabolism. Reducing pH of process water can lead to process and quality problems related to calcium carbonate or other calcium components. Decreasing pH dissolves calcium carbonate used as an additive in paper and/or board manufacturing. The dissolution increases the need for added calcium carbonate and causes problems such as calcium precipitates in water circulation and waste water treatment.

Circular economy requires effective utilization of raw materials such as starch in recycled fiber. There is a need for improved methods for preventing the starch degradation, stabilizing pH and preventing the dissolution of calcium components, especially calcium carbonates in pulp, paper and board making processes. This invention meets or at least relieves these needs.

## Summary

The present disclosure generally relates to pH stabilization in starch-containing industrial aqueous fluids and slurries. The inventors have surprisingly been able to demonstrate that introduction of amylase inhibiting compound(s) comprising zinc ions ($Zn^{2+}$) to such industrial aqueous fluid or slurry stabilized the system pH effectively and thereby provided several advantages to the process.

The first object of the invention is a method for stabilizing the pH in starch containing industrial aqueous fluid or slurry. According to the invention said method comprises adding an effective amount of an amylase inhibiting composition comprising zinc ions ($Zn^{2+}$) as active ingredient into said fluid or slurry.

The second object of the invention is a use of an amylase inhibiting composition for stabilizing the pH in starch-containing industrial process waters.

The third object of the invention is a process for making paper or board. According to the invention said method comprises adding an amylase inhibiting composition into process fluid(s) and/or slurry (slurries) in an effective amount.

**Brief description of the figures**

**Figure 1.** shows pH values in RCF 20 h after additions of amylase inhibiting composition comprising zinc ions as active ingredient (0, 6, 12 and 24 mg/l)

**Figure 2.** shows Redox values (ORP, oxidation reduction potential) in RCF 20 h after additions of amylase inhibiting composition comprising zinc ions as active ingredient (0, 6, 12 and 24 mg/l)

**Figure 3.** shows Starch concentration in RCF 20 h after additions of amylase inhibiting composition comprising zinc ions as active ingredient, measured with iodine staining method

**Figure 4.** shows pH values after RCF tower before, during and after addition of amylase inhibiting composition comprising zinc ions as active ingredient to the aqueous slurry

**Detailed description**

Microorganisms can cause several problems in pulp, paper and board making processes. Without a proper control microorganism can grow on machine surfaces as slimy deposits (biofilms) that will cause paper defects (dirt spots, holes) or break paper web forcing the machine to stop for cleaning. Defects can cause costly quality complaints from end-users of the paper. Extra cleaning stops will cause production losses and lower the cost-efficacy of paper manufacturing. Fermentative activity of microbes may result in formation of volatile fatty acids (VFA), which can cause malodors in final paper or board, or even spoil air quality in the whole mill and neighboring city. VFAs are reducing pH of aqueous fluids and slurries (process water) and this can lead to process and paper quality problems related to calcium carbonate. Machines for paper and board production use biocides for controlling microbial growth and formation of VFAs (volatile fatty acids) and/or dose sodium hydroxide for pH control.

These chemicals are not satisfactory because of the high cost related to efficient microbe control or high dosing amounts of sodium hydroxide needed. It has been surprisingly found that by addition of an amylase inhibiting composition the pH of starch-containing aqueous fluids and slurries (process waters) from pulp, paper or board production remains at higher level and is more stable, although the addition of sodium hydroxide is reduced. pH decrease of starch-containing process waters from pulp, paper or board production can be effectively controlled by addition of an amylase inhibiting composition. Respectively, pH regulation is also needed in other starch containing aqueous process fluids and slurries.

The use of amylase inhibiting compounds comprising zinc ions ($Zn^{2+}$) has been surprisingly found out to be a more effective method than adding high doses of bases, such as NaOH, or dosages of toxic biocides normally used in paper mills, therefore being a safer method for stabilizing pH of aqueous fluids and slurries.

The present invention relates to a method for stabilizing the pH in starch containing industrial aqueous fluid or slurry. The method comprises adding an effective amount of an amylase inhibiting composition into said fluid or slurry.

As used herein an expression “industrial aqueous fluid or slurry” includes all water containing fluids used within industry. A term” slurry” refers especially to fluids containing solids (e.g. 1 - 10 % fibers). Within pulp and paper industry these fluids and slurries are generally called ”process waters”.

Stabilization of pH as used herein means that pH of the aqueous fluid or slurry in maintained at about same level within e.g. one process step or processing department (such as storage system for broke) or during certain period of time. Preferably delta pH is less than 0.6, more preferably less than 0.5; still more preferably less than 0.4 and most preferably less than 0.3.

In this connection an amylase inhibiting composition means a composition which decreases the activity of amylase enzyme in the same conditions in aqueous fluids and slurries (process waters). Activity of the amylase enzyme is preferably measured as degradation speed of starch using any method known within the field. When used in effective amount the decrease is at least 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 % or even 95 % compared to amylase activity without said inhibiting composition. Composition can comprise one or more active ingredients. Activity of amylase enzyme can be measured using methods known within the field and e.g. by defining the speed of

starch degradation. In this connection expression “amylase activity” refers to starch degrading amylase activities as such, without referral to a specific type of amylase.

The numerical values of effective amount to be used for the amylase inhibiting active ingredients depend on e.g. the starch-containing aqueous fluids and slurries to be treated, type of an active inhibiting ingredient and amount of starch, amount of starch degrading activities and process temperature. It is known that Zn ions can inhibit the enzyme amylase (Irshad et. al. 1981: Effect of $Zn^{2+}$ on plant a-amylases in vitro. Phytochemistry. 20:2123-2126).

In one embodiment the active ingredient of the amylase inhibiting composition comprises zinc ion ($Zn^{2+}$). In one embodiment zinc ions are derived from an inorganic zinc salt. In another embodiment zinc ions are derived from organic zinc salt. Preferably, an inorganic zinc salt is used as they do not introduce carbon usable by microbes to the process. In addition, as such they are not strongly acidic or alkaline and therefore do not have any direct effect on the pH. Zinc was found to be compatible with paper and board manufacturing processes. It was shown to be effective in concentrations that are not harmful for environment. Furthermore, use of zinc ions is improving safety of industrial process. Zinc ions are generally regarded as safe (GRAS) even in applications for human consumption (U.S: Food & Drug Administration; GRAS Substances Database (SCOGS)). In addition, zinc is inexpensive raw material.

In one embodiment, the source of the Zn ions can be inorganic or organic zinc compound, in particular an inorganic or organic zinc salt. Preferably, the zinc ion source is selected from $ZnBr_2$, $ZnCl_2$, $ZnF_2$, $ZnI_2$, ZnO, $Zn(OH)_2$, ZnS, ZnSe, ZnTe, $Zn_3N_2$, $Zn_3P_2$, $Zn_3As_2$, $Zn_3Sb_2$, $ZnO_2$, $ZnH_2$, $ZnC_2$, $ZnCO_3$, $Zn(NO_3)_2$, $Zn(ClO_3)_2$, $ZnSO_4$, $Zn_3(PO_4)_2$, $ZnMoO_4$, $ZnCrO_4$, $Zn(AsO_2)_2$, $Zn(AsO_4)_2$, $Zn(O_2CCH_3)_2$, or zinc metal, or a combination thereof. Preferred are $ZnCl_2$, $ZnBr_2$, $ZnSO_4$ and $Zn(O_2CCH_3)_2$. These salts are suitable e.g. as having high solubility in aqueous solution such as aqueous fluids and slurries (process water). More preferred are $ZnCl_2$, $ZnBr_2$, $ZnSO_4$. Most preferably $ZnSO_4$ or $ZnCl_2$ or a combination thereof is used.

In one embodiment an effective amount of zinc ions is at least 1 mg/l, preferably at least 2 mg/l, more preferably at least 3 mg/l, still more preferably at least 4 mg/l, still more preferably at least 5 mg/l and most preferably at least 6 mg/l (mg of Zn ions in l of the fluid or slurry). In one embodiment an effective amount of zinc ions is less than 40 mg/l, preferably less than 30 mg/l, more preferably less than 25 mg/l or 24 mg/ml, still more preferably less than 20 mg/l and most preferably less than 12 mg/l or even

less than 6 mg/l (mg of Zn ions in l of process water). In one embodiment an effective amount of zinc ions is 1 to 40 mg/l; preferably 4 to 30 mg/l; more preferably 6 to 20 mg/l, still more preferably 6 to 15 mg/l (mg of Zn ions in l of process water). In one embodiment an effective amount of zinc ions is 1 to 12 mg/l (mg of Zn ions in l of process water). In one embodiment an effective amount of zinc ions is about 6 mg/l (mg of Zn ions in l of process water). The need of zinc ions is dependent on conditions in process water, such as amount of starch and especially amount of starch degrading activities. Based on several pH stabilization experiments on aqueous fluid or slurries within paper and board manufacturing (initial starch content 200 to 1000 mg/l and non-inhibited degradation rates 2 wt-% per hour to even 21 wt-% hour, data not shown) it seems that 6 to 15 mg/l of zinc ions or 6 to 12 mg/l of zinc ions in process water and even lower amount of zinc ions is sufficient to prevent pH decrease in each condition but depending the conditions also much lower dosages provided a satisfactory pH stabilization.

In one embodiment delta pH after addition of an amylase inhibiting compound or composition, especially compound comprising Zinc ions, is less than 0.6, more preferably less than 0.5; still more preferably less than 0.4 and most preferably less than 0.3.

One embodiment of the invention, where zinc ion content is at least 2 mg/l, is shortly discussed below (data not shown). An amylase inhibiting composition comprising zinc ions as an active ingredient was used in 2 mg/l (calculated as total zinc in a fiber containing storage tower process water). After 12 hours it was surprisingly found that delta pH in storage towers was less than 0.4 units, delta Redox (ORP, oxidation reduction potential) in storage towers was less than 50 mV and pH remained was above 6.7 without addition of NaOH. In these conditions the concentration of soluble calcium was below 1500 mg/l. The pH of broke storage tower and/or pulp storage tower was at least 0.1 units higher and the concentration of soluble calcium was at least 5% lower than before treatment. This experiment clearly demonstrates the effect of zinc ions already in low amounts.

Amounts or quantities are herein defined in ppm or mg/l, wherein ppm (parts per million) means the same unit as mg/l, so that those units are interchangeably used. In the present disclosure ppm means weight of active ingredient per volume of the process water. Process water includes the solid matter such as fibers; fillers; starch; paper making additives such as retention aids, sizing chemicals, biocides, fixatives, colorants, defoamers; possible coating components such as latex, pigments, optical

brighteners etc.; wood pitch and other wood extractives; microorganisms and other process impurities. Due to retentive properties of the fibers the Zn ion content in fibrous fraction on process water is a usually higher than in just filtration water. As used herein an expression “process water(s)” refers to process water containing also the fiber fraction and can be used interchangeably with aqueous fluids or slurries within the process.

The amylases in process waters here discussed degrade the starch continuously unless the amylase activity is inhibited. Longer storage or process time without inhibiting composition results in increased degradation to saccharides serving as carbon source for microbial growth. In continuous process the amylase inhibiting composition can be added continuously or in desired intervals in order to maintain effective inhibitory concentration.

The amylase inhibiting compositions, such as composition comprising zinc ions can be continuously or sequentially added to the starch-containing waters to be treated.

In one embodiment the starch-containing aqueous fluid or slurry comprises aqueous fluid or slurry from pulp, paper or board production; or water-base drilling fluid in oil industry. Both processes involve pH stabilization.

Reduced starch degradation gains paper makers a significant saving in starch consumption as less new added starch is needed, reduce runability problems and increase paper quality. In addition, starch is not readily degraded to smaller sugars that microbes could use for their growth. In anaerobic conditions bacterial fermentation of these sugars could produce acids that lower system pH. Reduced quantity of such saccharides and reduced fermentation rate has positive effect on pH. In paper and board processes pH below 7.0 may result is dissolution of calcium carbonate used as filler or as a coating component, leading in difficulties in water circulation and downstream processing (e.g. precipitates in waste water treatment) and possibly also need of introducing new calcium carbonate to the process. These all reflect in process economy.

In one embodiment the starch-containing aqueous fluid or slurry is aqueous fluid or slurry from pulp, paper or board production, commonly named as ”process waters”. In general, the amylase inhibiting composition can be added to a position containing starch and including components that may degrade the starch. The amylase inhibiting composition can be added to the broke system, broke storage tanks, pulp system, pulp storage tanks, to the water entering the pulper, into the pulper or into the pulp

shortly after the pulper, water storage tanks, or pipe line before the broke or pulp storage tanks. Especially beneficial is to add the amylase inhibiting composition to the water entering the pulper or into the pulper. In one embodiment the amylase inhibiting composition is added the water entering to the pulper e.g. 5 to 30 minutes before water enters the pulper. In particular, the amylase inhibiting composition can be used in pulping of starch-containing recycled fiber and/or in broke systems. Without binding to the theory, adding the amylase inhibiting composition to composition to the water entering the pulper and especially to the water before it enters to the pulper allows amylase inhibition in the water before contact with the fiber containing material. Amylase inhibiting compositions may in some extent be adhered to the fibers thereby reducing the contact between amylase and amylase inhibiting composition.

In a specific embodiment the amylase inhibiting composition is mixed with dry starch before introducing it into paper or board manufacturing process. In another embodiment the amylase inhibiting composition is added to the paper or board manufacturing process simultaneously with starch. Amylase inhibiting compound can be mixed with dry starch or starch slurry or applied into the paper or board manufacturing process at the same time as the starch. This ensures that inhibitory activity is present from the beginning thereby enhancing pH stabilization. It is clear to a person skilled in the art that zinc ions can be added in connection with other process chemicals, e.g. together with polymeric fixatives or PAC, mixed together or separately, in same dosing point of the system.

According to one embodiment the amylase inhibiting compound is added into waters or slurries of pulp, paper or board production in an amount sufficient to maintain the pH of the process water at least on 6.8, preferably at least 7.0. pH above about 6.8 maintains calcium carbonate used as an additive in paper and/or board manufacturing in solid form and thereby reduces a need for added calcium carbonate and problems relating to calcium precipitates. In one embodiment delta pH within a process step or e.g. tank/container is being less than 0.6, more preferably less than 0.5; still more preferably less than 0.4 and most preferably less than 0.3. Suitable process steps or tanks/containers are e.g. broke system, broke storage tanks, pulp system, pulp storage tanks, the pulper, water storage tanks, pulp storage tanks. In another embodiment delta pH is less than 0.6, more preferably less than 0.5; still more preferably less than 0.4 and most preferably less than 0.3 during desired time.

The disclosure further relates to a method of inhibiting existing amylase activity, and/or preventing or reducing the production of new amylase by microorganisms in

starch-containing fluid, wherein the method comprises adding amylase inhibiting composition, preferably containing, zinc ions to process water. The zinc ions can be the same as defined above. The starch-containing fluid can be the same as the above-defined process water from pulp, paper or board production.

The present disclosure relates also to a use of an amylase inhibiting composition, especially composition comprising zinc ions as an active ingredient, for stabilizing the pH in starch-containing aqueous fluids or slurries. Suitable aqueous fluids or slurries are fluids or slurries from pulp, paper or board production or water-base drilling fluid. Said use comprises adding an amylase inhibiting composition into said fluid or slurry. The zinc ions can be the same as defined above. The starch-containing fluid or slurry can be the same as the above-defined, such as fluid or slurry from pulp, paper or board production. The advantages of an amylase inhibiting composition have been discussed above.

The present disclosure relates also to a process for making paper or board comprising adding an amylase inhibiting composition into fluid(s) and/or slurry (slurries). In one embodiment, in such a process an amylase inhibiting composition is introduced to the process simultaneously with dry starch or starch containing material. In one embodiment the amylase inhibiting composition is added to the paper or board manufacturing process simultaneously with starch. Amylase inhibiting compound can be mixed with dry starch or starch slurry or applied into the paper or board manufacturing process at the same time as the starch. This ensures that inhibitory activity is present from the beginning thereby enhancing pH stabilization.

The invention is below illustrated by the following non-limiting examples. It should be understood that the embodiment given in the description above and the examples are for illustrative purposes only, and that various changes and modifications are possible within the scope the invention.

**Examples**

**Example 1.**

Sample of RCF (Recycled Cellulose Fiber) pulp from Mill 1 was taken on the 2nd of December 2015 and delivered to Kemira R&D Center in Espoo, Finland. The test was started on the following day. RCF was kept in a cool place during transportation. It was measured that the RCF contained about 80 mg/l soluble starch. Because starch

content was low, 500 mg/l cooked surface size starch (Corn starch, Merizet 170) was added into the pulp. RCF was divided into eight 50 ml portions and 0, 6, 12 or 24 ppm amylase enzyme inhibiting compound (Zinc ions from zinc sulfate, pH of the product 4-5) was added. Two replicates were made from each concentration. Samples were placed in +45 °C with shaking. Residual starch concentration, pH and Redox were measured on the following day, after approximately 20 hours of incubation. Starch was measured using conventional iodine staining method at 590 nm.

The results in Figure 1 and Table 1 show that the pH in reference samples without amylase enzyme inhibitor was 7.16 – 7.36. Samples treated with amylase enzyme inhibitor had clearly higher pH, between 7.7 and 8.1. Dosing of 12 mg/l zinc was enough in this experiment and higher dosage did not give any additional benefit.

The results in Figure 2 and Table 1 show that the Redox values in reference samples without amylase enzyme inhibitor were clearly negative, about -140 mV. Samples treated with amylase enzyme inhibitor had positive redox values. With 6 ppm redox was +95 – 100 mV, with 12 ppm 120 – 130 mV and with 24 ppm 140 mV.

The results in Figure 3 and Table 1 show that there was more starch left in the samples treated with amylase enzyme inhibitor than in samples without treatment. In the reference samples absorbance was 0.34 – 0.37. In five out of six treated samples absorbance was above 0.5, but already the lowest tested concentration, 6 mg/l, gave this benefit and no improvement was seen with higher concentrations.

**Table 1.** pH, Redox and starch amounts in RCF pulp samples 20 hours after the addition of amylase enzyme inhibitor.

| Amylase inhibitor concentration, mg/l | Measured values 20 h after addition of amylase enzyme inhibitor | | |
|---|---|---|---|
| | pH | Redox, mV | Starch, A590 |
| 0 | 7.161 | -147.1 | 0.337 |
| 0 | 7.362 | -137.9 | 0.367 |
| 6 | 7.712 | 99.9 | 0.519 |
| 6 | 7.899 | 95 | 0.572 |
| 12 | 8.106 | 129.6 | 0.573 |
| 12 | 7.998 | 121.9 | 0.554 |
| 24 | 7.985 | 141.5 | 0.554 |
| 24 | 7.859 | 141.9 | 0.464 |

**Example 2.**

Amylase enzyme inhibitor was tested at a board mill using recycled fiber raw material (Mill 2). Zinc sulfate as an amylase enzyme inhibiting compound was dosed for about 24 hours into RCF tank, which is located before RCF storage tower. Final amount was about 10 to 12 ppm zinc. No other changes were made into the process chemicals during the trial. We surprisingly observed that pH of the RCF tower was higher for the whole duration of amylase enzyme inhibitor trial. Before the trial the pH of RCF was just above 5.9 and during and after the amylase enzyme inhibitor treatment it was >6.0. The results are shown in Figure 4

**Example 3.**

Zinc sulfate as an amylase enzyme inhibiting compound was tested at a board mill using recycled fiber raw material (Mill 3). Amylase enzyme inhibiting compound was dosed for one week. Two dosing points were used: pulp stream after the RCF pulper, and another just before RCF storage tower. The mill used 50% sodium hydroxide (NaOH) solution for pH adjustment. Data from trial period (1 week) was compared to the data from reference period (before and after the trial, 3 months).

Table 2 shows that during amylase enzyme inhibitor trial pH in the process was higher, effluent tower calcium concentration was lower and still the mill was able to reduce the consumption of sodium hydroxide. Table 3 shows that the measured zinc concentrations. Before the treatment started, zinc concentration was 0.56 mg/l. During the trial, the concentration was 2.96 – 3.76 mg/l, except for one measurement with lower result.

**Table 2.** pH, $Ca^{2+}$ concentration and NaOH consumption during reference period and amylase enzyme inhibitor trial.

| | Reference period, average | Amylase enzyme inhibitor trial period, average |
|---|---|---|
| pH, Broke | 6.9 | 7.0 |
| pH, Broke Screen | 6.9 | 7.0 |
| pH, Short fiber dosing tank | 6.7 | 7.1 |
| Effluent tower $Ca^{2+}$, mg/l | 820 | 670 |
| NaOH addition, l/ton of board | 6.6 | 4.3 |

**Table 3.** Zinc concentrations during the trial

| | RCF, Pulper outlet | RCF tower, outlet |
|---|---|---|
| 4.7.2016, Before trial | 0.56 | |
| 5.7.2016 | 2.96 | 3.04 |
| 6.7.2016 | 3.76 | 1.0 |

**Example 4.**

Effect of amylase enzyme inhibiting compound was tested on the pH of RCF pulp. Table 4 shows that without treatment, pH decreased 0.55 unit during 24 h storage. With NaOH the initial pH could be increased, but it had no effect after the storage time, and pH change was even bigger than without NaOH. Zinc sulfate as an amylase

enzyme inhibiting compound reduced pH drop, with 6 – 24 mg/l the pH drop was 0.29 – 0.39 units. Amount of soluble calcium was 187 mg/l at the beginning of the test. In untreated sample and in the sample “NaOH” calcium concentration increased to 244 or 245 mg/l, *i.e.* 30%. With zinc, the increase in the calcium concentration was smaller, and in one sample measured soluble calcium even decreased.

**Table 4.** pH in recycled fiber pulp after 24 h with and without treatment. The pH of the pulp was 7.2 at the beginning of the test. In the sample "NaOH" pH was adjusted to 7.5 with sodium hydroxide. After that and Zn additions, samples were incubated 24 h at +45°C and pH values were measured again.

| | pH | | | Ca, mg/l, | | |
|---|---|---|---|---|---|---|
| | 0 h | 24 h | Δ pH | 0 h | 24 h | Δ Ca |
| no additions | 7.20 | 6.65 | 0.55 | 187 | 244 | 57 |
| NaOH | 7.50 | 6.66 | 0.85 | 187 | 245 | 58 |
| Zinc 6 mg/l | 7.20 | 6.81 | 0.39 | 187 | 197 | 10 |
| Zinc 12 mg/l | 7.20 | 6.82 | 0.38 | 187 | 229 | 42 |
| Zinc 24 mg/l | 7.20 | 6.91 | 0.29 | 187 | 154 | -33 |

**Example 5.**

Effect of amylase enzyme inhibiting compound was tested on the pH of RCF pulp. Table 5 shows that without treatment, pH decreased 0.55 unit during 48 h storage. In this experiment 6 mg/l zinc was not enough, and in this sample pH drop was similar to the non-treated reference. With 12 mg/l the pH drop was significantly lower, only 0.22 pH units.

**Table 5.** pH in recycled fiber pulp after 48 h with and without treatment. The pH of the pulp was 7.15 at the beginning of the test. After Zn additions (zinc sulfate), samples were incubated 24 h at +45°C and pH values were measured again.

| | pH | | |
|---|---|---|---|
| | 0 h | 48 h | Δ pH |
| no additions | 7.15 | 6.60 | 0.55 |
| Zinc mg/l | 7.15 | 6.56 | 0.59 |
| Zinc mg/l | 7.15 | 6.93 | 0.22 |

**Example 6.**

White water from a machine producing fluting and liner from recycled fiber was collected and tested on-site at the mill. First, 7 mg/l zinc was dosed into the white water and the amount of soluble zinc was measured after 15 min. Then, 40 g/l OCC (old corrugated carton, type of recycled fiber) was pulpered into the water. The amount of soluble zinc was measured again after 5 min and 25 min.

In the second part of the test, 40 g OCC was first pulpered into 1.0 l of the white water. Then, 7 mg/l zinc was added into the pulp and the amount of soluble zinc was measured 5 min and after 25 min after the pulpering.

Zinc was measured using Hach ZincoVer kit according to manufacturer's instructions and Hach DR-900 spectrophotometer.

Table 6. Amounts of soluble zinc in the tests.

| Test | Soluble Zn, mg/l | | |
|---|---|---|---|
| | From water, 15 min after addition | From pulp, 5 min after pulpering | From pulp, 25 min after pulpering |
| Test 1: Zinc into water | 1.65 | 1.27 | 0.73 |
| Test 2: Zinc into pulp | | 0.61 | 0.60 |

The results in Table 6 show that when zinc was added into the water before the fibers, there was 1.27 mg/ soluble zinc available 5 min after the addition of the fibers. After 25 min, the amount was 0.73 mg/l. In the second test, zinc was added into the pulp only after the fibers had been pulpered. In this case the amounts of soluble zinc were lower, after 5 min 0.61 mg/l and after 25 min 0.60 mg/l. Because soluble zinc ions react with amylase enzyme, this experiment shows that it is beneficial to add zinc into water before cellulose fibers from OCC, i.e. into the dilution water of recycled fiber pulper.

**CLAIMS**

1. A method for stabilizing the pH in starch containing industrial aqueous fluid or slurry comprising adding an effective amount of an amylase inhibiting composition comprising zinc ions ($Zn^{2+}$) [as active ingredient] into said fluid or slurry.
2. The method of claim 1, wherein the zinc ions are derived from an inorganic or organic zinc salt.
3. The method of claim 2, wherein the inorganic or organic zinc salt is selected from: $ZnBr_2$, $ZnCl_2$, $ZnF_2$, $ZnI_2$, ZnO, $Zn(OH)_2$, ZnS, ZnSe, ZnTe, $Zn_3N_2$, $Zn_3P_2$, $Zn_3As_2$, $Zn_3Sb_2$, $ZnO_2$, $ZnH_2$, $ZnC_2$, $Zn(NO_3)_2$, $Zn(ClO_3)_2$, $ZnSO_4$, $Zn_3(PO_4)_2$, $ZnMoO_4$, $ZnCrO_4$, $Zn(AsO_2)_2$, $Zn(AsO_4)_2$, $Zn(O_2CCH_3)_2$), zinc metal, and any combination thereof.
4. The method of any of the preceding claims, wherein Zinc ions are added to obtain amount of at least 1 mg/l, preferably at least 2 mg/l, more preferably at least 3 mg/l, still more preferably at least 4 mg/l, still more preferably at least 5 mg/l and most preferably at least 6 mg/l (mg of Zn ions in l of the fluid or slurry).
5. The method of any of the preceding claims, wherein Zinc ions are added to obtain amount less than 40 mg/l, preferably less than 24 mg/ml and more preferably less than 12 mg/l (mg of Zn ions in l of process water). The method of any of the preceding claims, wherein the starch-containing aqueous fluid or slurry comprises
    a. aqueous fluids or slurries from pulp, paper or board production; or
    b. water-base drilling fluid.
6. A method of claim 5, wherein said aqueous fluid or slurry is aqueous fluid or slurry from pulp, paper or board production.
7. The method of claim 6, wherein the amylase inhibiting compound is added in an amount sufficient to maintain the pH of the process water at least on 6.8, preferably at least 7.0.
8. The method of any of the preceding claims, wherein the delta pH after addition of the amylase inhibiting compound within a process step or tank or container is less than 0.6, more preferably less than 0.5, still more preferably less than 0.4 and most preferably less than 0.3.

9. The method of claims 7 or 8 wherein the amylase inhibiting composition is added to water located in the broke system, broke storage tanks, pulp system, pulp storage tanks, to the water entering the pulper or, into the pulper, water storage tanks, or pipe line before the broke or pulp storage tanks, preferably to the water before it enters the pulper.

10. The method of any of the claims 7 to 9, wherein the amylase inhibiting composition is mixed with dry starch before introducing it into the paper or board manufacturing process or wherein the amylase inhibiting composition is added to the process simultaneously with starch.

11. Use of an amylase inhibiting composition comprising zinc ions ($Zn^{2+}$) for stabilizing the pH in starch-containing industrial process waters, such as process waters from pulp, paper or board production or water-base drilling fluid.

12. A process for making paper or board comprising adding an amylase inhibiting composition comprising zinc ions ($Zn^{2+}$) into process fluid(s) and/or slurry (slurries) in an effective amount.

13. The process of claim 12, wherein said amylase inhibiting composition is introduced to the process simultaneously with dry starch or starch containing material.


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12
12
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Amylase enzyme inhibitor, mg/l

Fig. 1

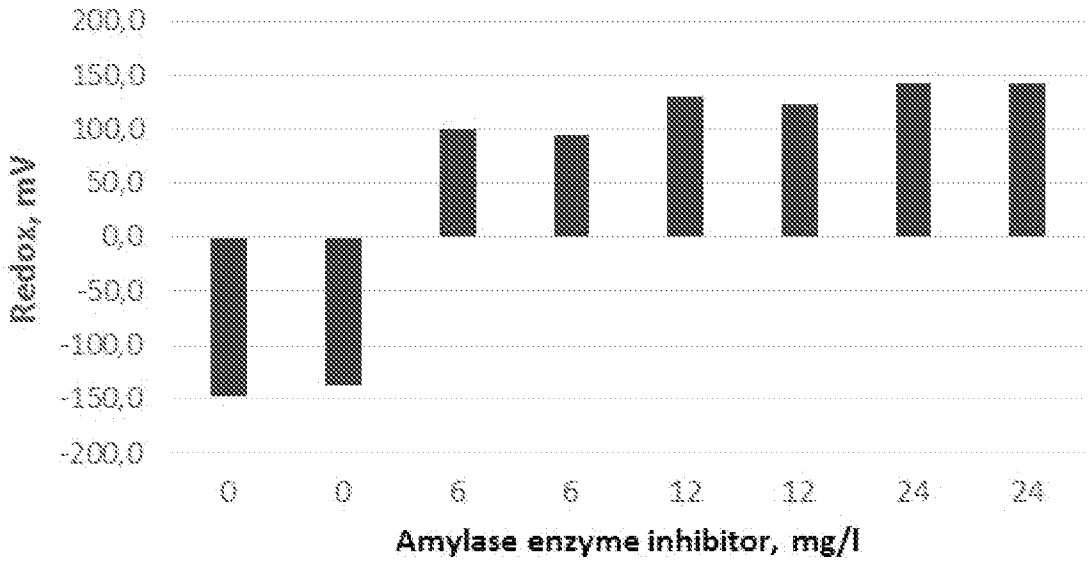

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50,0
0,0
-50,0
-100,0
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-200,0
Redox, mV
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0
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6
12
12
24
24
Amylase enzyme inhibitor, mg/l

Fig. 2

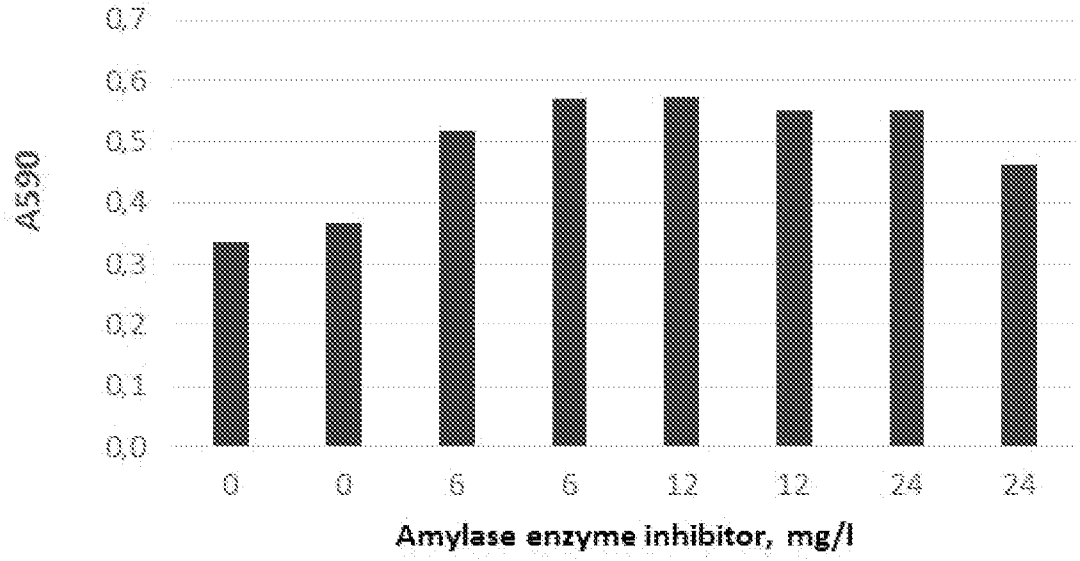

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12
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24
24
Amylase enzyme inhibitor, mg/l

Fig. 3

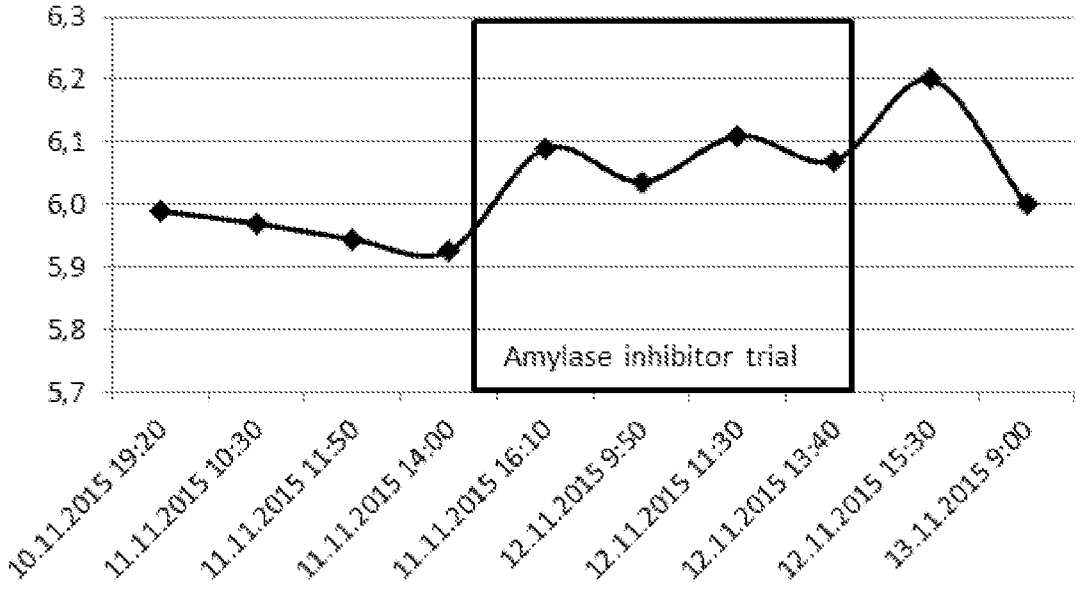

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Amylase inhibitor trial
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13.11.2015 9:00

Fig. 4

# INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2018/050279

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H17/28 C02F1/66 C12N9/99 D21H17/00 D21H21/36
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21H C02F C12N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | WO 2013/045638 A1 (KEMIRA OYJ [FI]; KOLARI MARKO [FI]; EKMAN JAAKKO [FI]; IKAEVALKO SATU) 4 April 2013 (2013-04-04)<br>cited in the application<br>page 5, line 10 - page 6, line 2<br>page 11, line 4 - line 22; claims;<br>examples | 1-13 |
| X | WO 2013/124542 A1 (KEMIRA OYJ [FI])<br>29 August 2013 (2013-08-29)<br>page 11, line 11 - page 12, line 12;<br>claims; example 3 | 1-13 |

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

☒ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 7 June 2018 | 14/06/2018 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Koegler-Hoffmann, S |

1

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