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(19) **United States**(12) **Patent Application Publication**
Duggirala et al.(10) **Pub. No.: US 2012/0073775 A1**(43) **Pub. Date: Mar. 29, 2012**(54) **METHOD FOR MONITORING ORGANIC
DEPOSITS IN PAPERMAKING**(76) Inventors: **Prasad Duggirala**, Naperville, IL
(US); **Sergey Sheychenko**, Aurora,
IL (US)(21) Appl. No.: **13/304,785**(22) Filed: **Nov. 28, 2011****Related U.S. Application Data**(63) Continuation-in-part of application No. 11/148,639,
filed on Jun. 9, 2005.**Publication Classification**(51) **Int. Cl.**
D21F 13/00 (2006.01)(52) **U.S. Cl. 162/198**(57) **ABSTRACT**

A method for monitoring the deposition of organic deposits from a liquid or slurry in a papermaking process is disclosed. Also disclosed is a method for measuring the effectiveness of inhibitors that decrease the deposition of organic deposits in a papermaking process. The method may involve monitoring the deposition of organic deposits of a liquid or slurry that simulates the conditions of a papermaking process. The methods may comprise the steps of monitoring the rate of deposition of organic deposits; adding an inhibitor that decreases the deposition of organic deposits from the liquid or slurry; and optionally re-measuring the rate of deposition of organic deposits from the liquid or slurry onto the quartz crystal microbalance, with the rates of deposition determined by measuring the vibration frequency of the quartz crystal microbalance.

FIG. 1

Pulp Mill, #2 PO Filtrate, Organic Deposit
PP10-3074, 100, 50, 25-ppm dosages

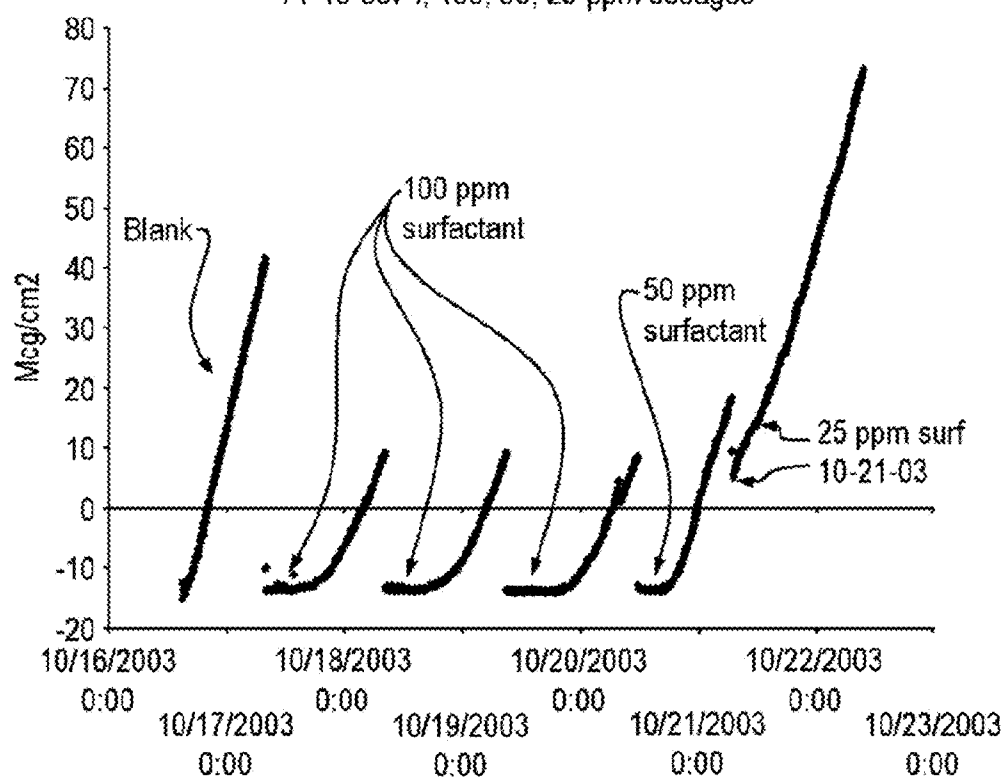


FIG. 2

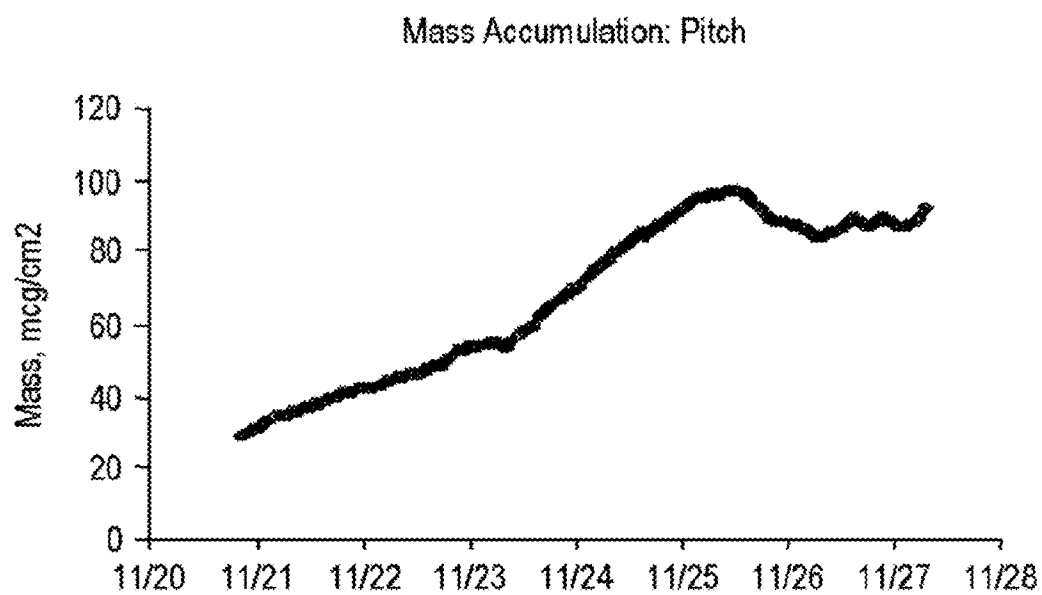


FIG. 3

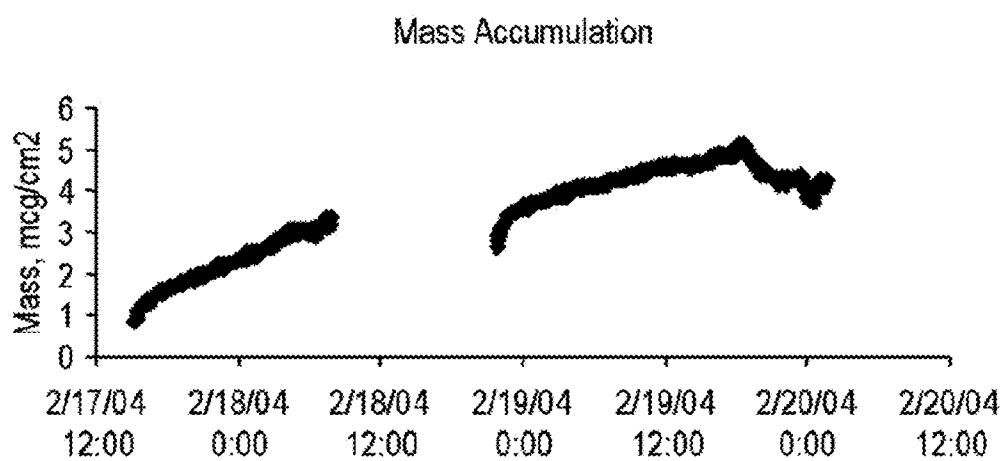


FIG. 4

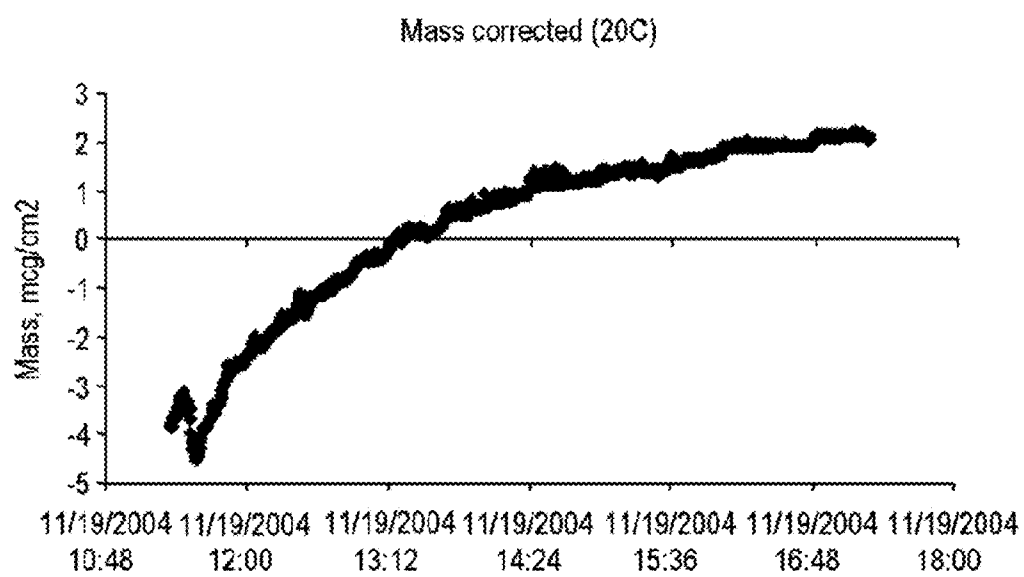


FIG. 5

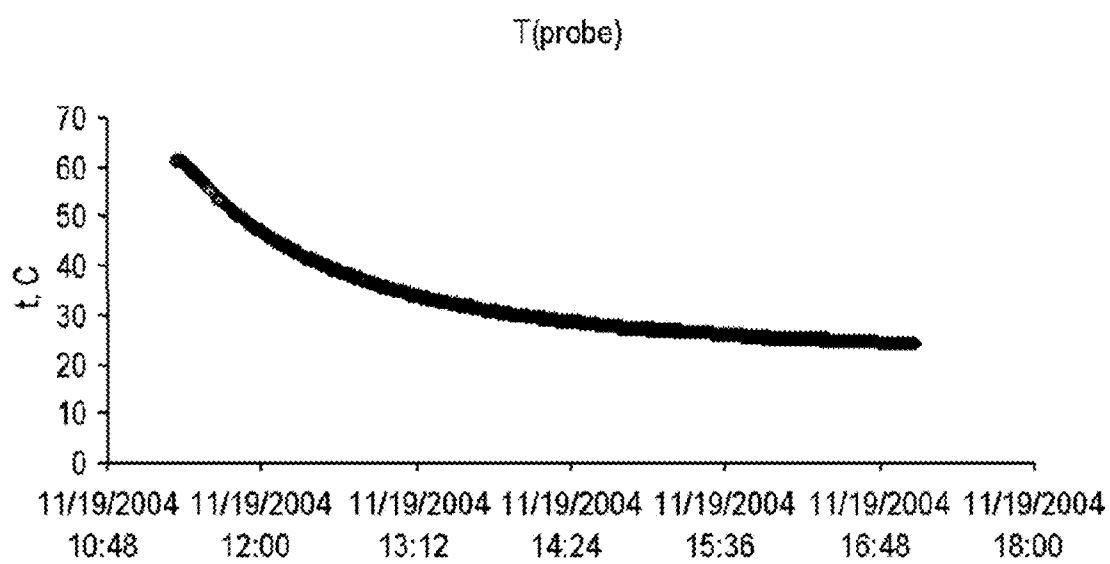


FIG. 6

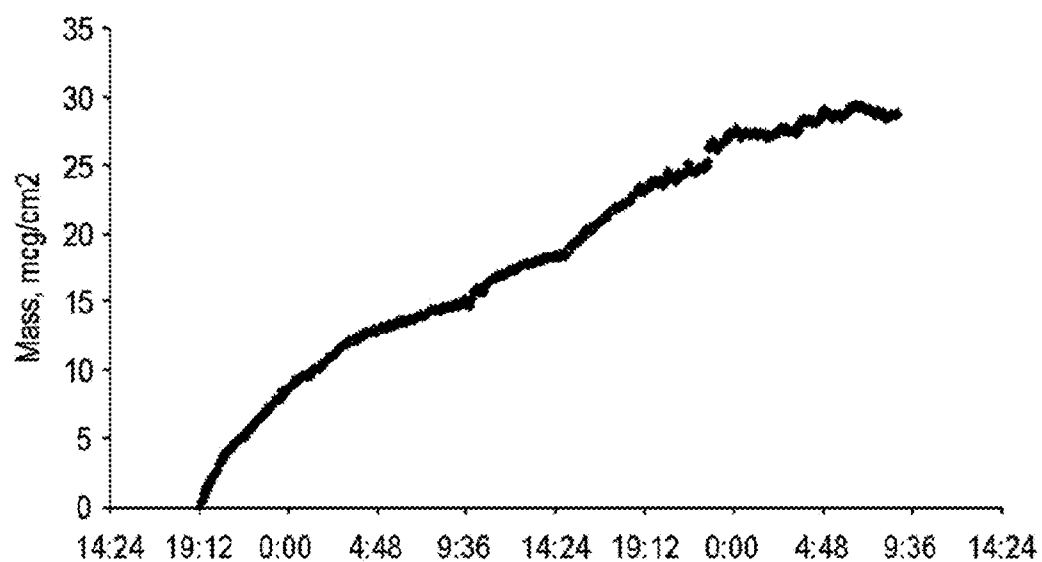


FIG. 7

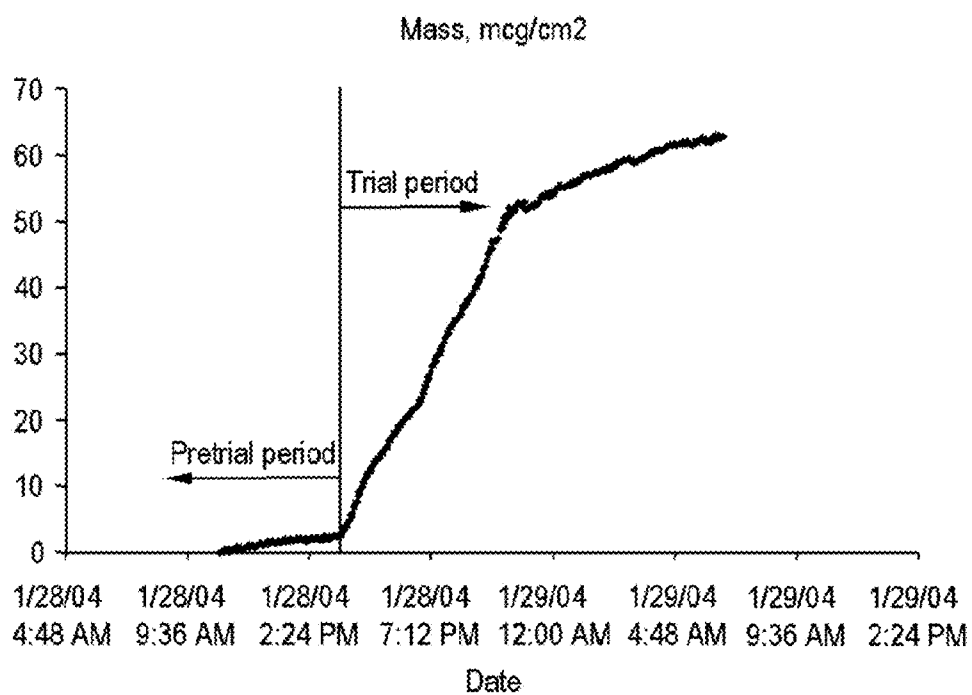


FIG. 8

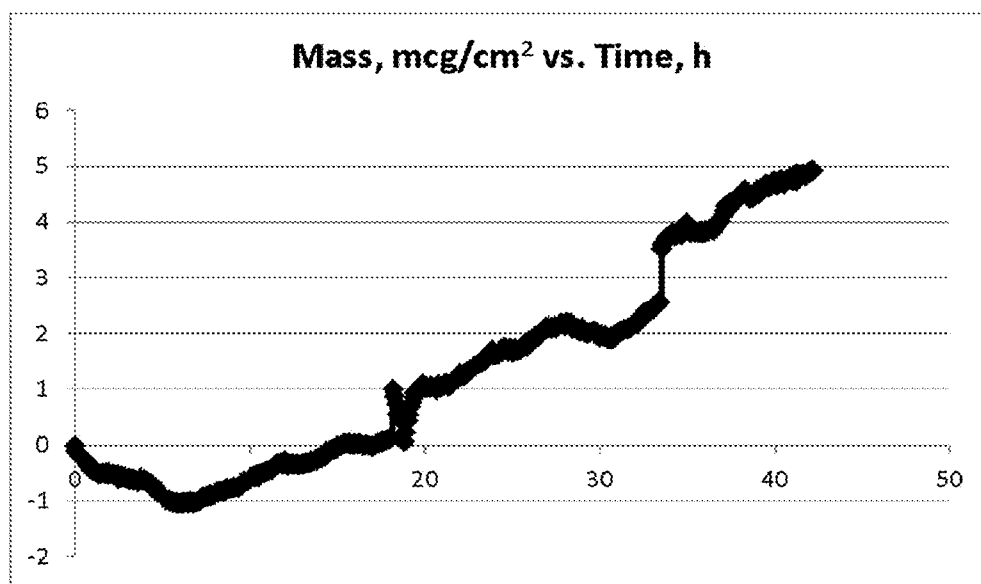


FIG. 9

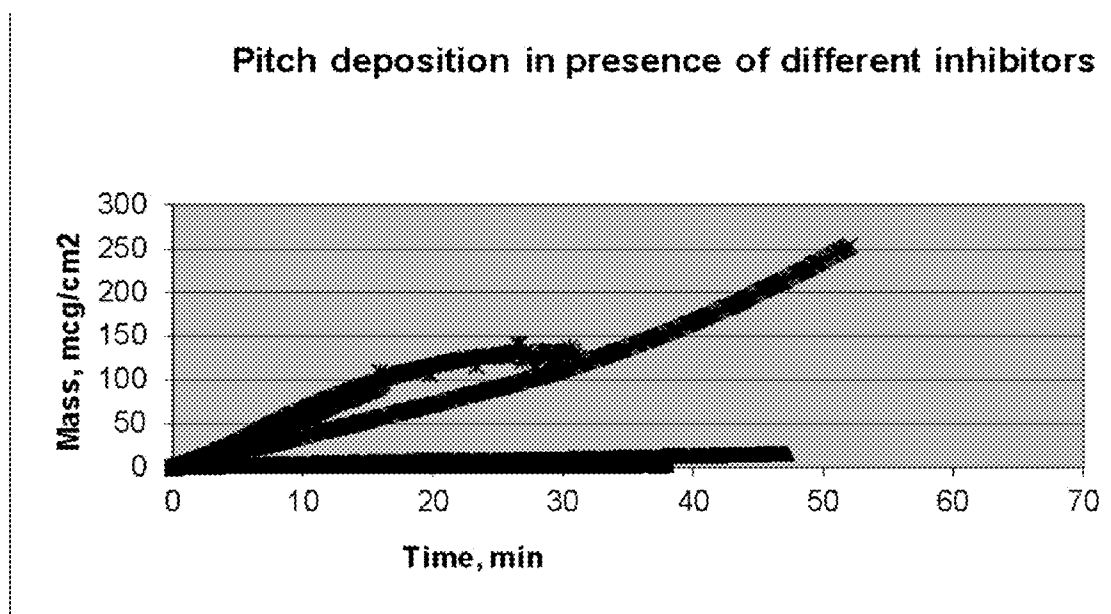


FIG. 10

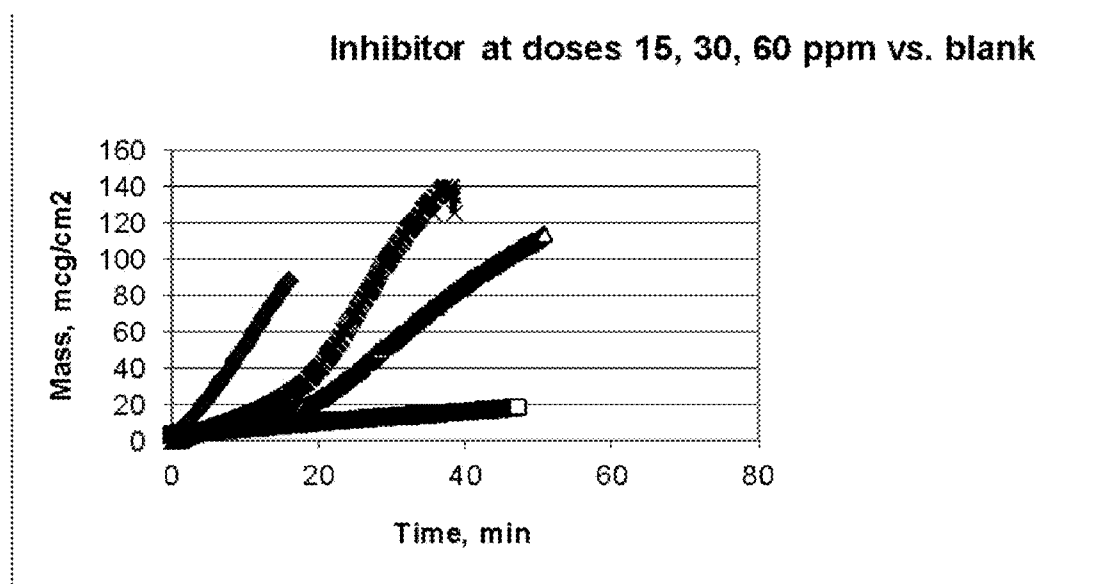
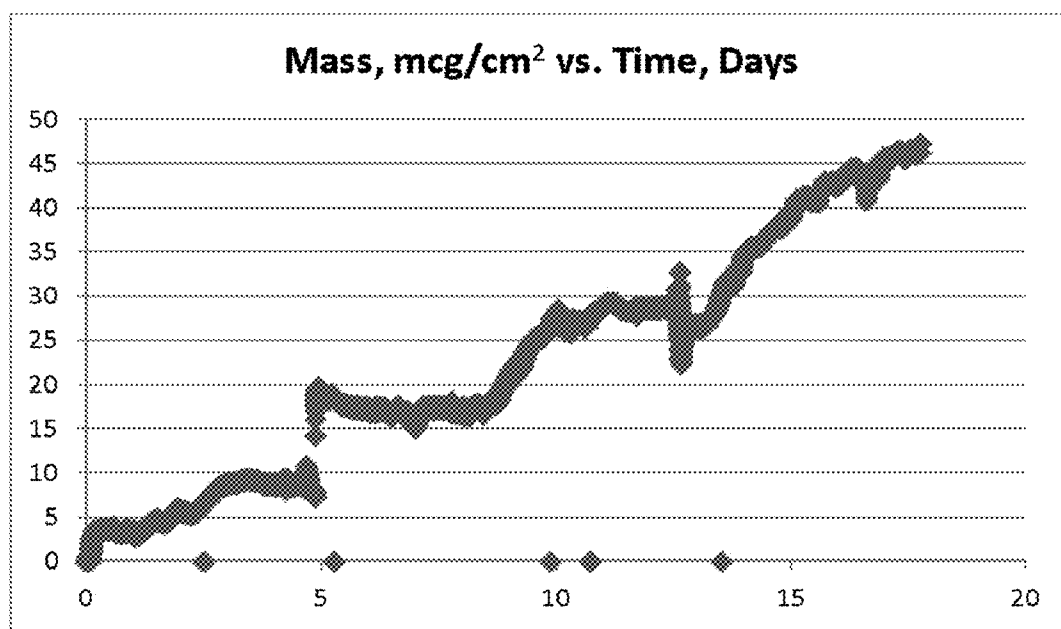


FIG. 11



METHOD FOR MONITORING ORGANIC DEPOSITS IN PAPERMAKING

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 11/148,639, filed Jun. 9, 2005, which is herein incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention is in the field of papermaking. Specifically, this invention is in the field of monitoring organic deposit formation in a papermaking process.

BACKGROUND OF THE INVENTION

[0003] Formation of deposits of organic substances (wood extractives and related natural materials in virgin raw material, stickies, wax and microbiological components in recycled material) is a common problem in papermaking. For paper grades, these materials can become both undesirable components of papermaking furnishes and troublesome deposits on all mill equipment.

[0004] The nature of the organic deposits differs from process to process and from mill to mill. Most often, they are mixtures of organic insoluble salts, unsaponifiable organics, wood fibers and/or poorly soluble polymeric paper additives. In absence of adequate chemical control, they form simultaneously with microbiological deposits. Thereby, their deposition during the production process is a quite complex matter due to these many possible potential causes.

[0005] An express method for organic deposit monitoring and prediction of the activities of deposit control programs is of great value to the industry. Currently, there is no such method in the market.

SUMMARY OF THE INVENTION

[0006] The present invention is directed toward methods of using a quartz crystal microbalance in a papermaking process and in benchtop testing of deposit control chemistries. The quartz crystal microbalance of the invention has a top side in contact with the liquid or slurry and a bottom side that is isolated from the liquid or slurry.

[0007] The present invention provides for a method for monitoring the deposition of organic deposits from an actual or model liquid or slurry in a papermaking process comprising measuring the rate of deposition of organic deposits from the liquid or slurry on to a quartz crystal microbalance having a top side in contact with the liquid or slurry and second bottom side isolated from the liquid or slurry.

[0008] The present invention also provides for a method for measuring the effectiveness of inhibitors (biocides in case of microbiological deposits) that decrease the deposition of organic deposits in a papermaking process comprising monitoring the deposition of organic deposits from a liquid or slurry in a papermaking process comprising measuring the rate of deposition of organic deposits from the liquid or slurry on to a quartz crystal microbalance having a top side in contact with the liquid or slurry and second bottom side isolated from the liquid or slurry; adding an inhibitor that decreases the deposition of organic deposits to the liquid or slurry; and re-measuring the rate of deposition of organic deposits from the liquid or slurry on to the quartz crystal microbalance.

[0009] The present invention also provides for a method for measuring the effectiveness of inhibitors that decrease the deposition of organic deposits in a papermaking process comprising measuring the deposition of organic deposits from a model liquid or slurry that simulate a liquid or slurry found in a papermaking process comprising measuring the rate of deposition of organic deposits from the model liquid or slurry on to a quartz crystal microbalance having a top side in contact with the liquid or slurry and second bottom side isolated from the liquid or slurry; repeating the measuring process under the same conditions in presence of an inhibitor that decreases the deposition of organic deposits to the liquid or slurry; and comparing the rates of deposition of organic deposits from the liquid or slurry on to the quartz crystal microbalance in the blank experiment in presence of the inhibitor. The present invention is also directed toward a method for monitoring and controlling a rate of deposition of organic deposits from a liquid or slurry in a papermaking process. The method comprises the steps of providing a crystal quartz microbalance; monitoring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency; and adding an inhibitor to the liquid or slurry. The inhibitor decreases the rate of deposition of the organic deposits from the liquid or slurry, and the adding is based upon the monitoring.

[0010] The present invention is also directed toward a method for measuring the effectiveness of at least one inhibitor that decreases a rate of deposition of organic deposits in a papermaking process. The method comprises the steps of providing a quartz crystal microbalance; monitoring the deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency; adding the at least one inhibitor that decreases the deposition of the organic deposits from the liquid or slurry; and re-measuring the rate of deposition of the organic deposits from the liquid or slurry onto the quartz crystal microbalance by measuring the vibration frequency.

[0011] The present invention is also directed toward a method for measuring the effectiveness of at least one inhibitor that decreases a rate of deposition of organic deposits in a papermaking process simulation. The method comprises the steps of providing a quartz crystal microbalance; monitoring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency; adding the at least one inhibitor to the liquid or slurry based on the monitoring; and re-measuring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency.

[0012] These and other features and advantages of the present invention will be apparent from the following detailed description, in conjunction with the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1. Formation of organic deposits in the post-oxygen brownstock washer line: mass accumulation determined by measuring vibration frequency of a quartz crystal microbalance.

[0014] FIG. 2. Deposition of wood resins and glued fines in the paper machine (white water line) determined by measuring vibration frequency of a quartz crystal microbalance. The deposition stops upon adding an inhibitor at 11/25 moment.

[0015] FIG. 3. Deposition of wood resins and glued fines in the paper machine (white water line): mass accumulation determined by measuring vibration frequency of a quartz crystal microbalance.

[0016] FIG. 4. Wax (temperature-dependent adhesives) monitoring in headbox furnish repulped at 60° C. and gradually cooled down (benchtop experiment): mass accumulation determined by measuring vibration frequency of a quartz crystal microbalance, with the mass corrected for changes in temperature. Notice slowing down the deposition when temperature decreases with time (see FIG. 6).

[0017] FIG. 5. Wax monitoring in headbox furnish repulped at 60° C. (benchtop experiment, FIG. 5): temperature.

[0018] FIG. 6. Mixed organic/inorganic deposition in D100 filtrate discharge lines of a bleach plant, mass accumulation determined by measuring vibration frequency of a quartz crystal microbalance.

[0019] FIG. 7. Mixed aluminum-calcium salt of a polymeric organic acid (a scale inhibitor overdose, diagnostics in deposit control program applications) in a white water line in the broke repulper: mass accumulation determined by measuring vibration frequency of a quartz crystal microbalance.

[0020] FIG. 8. Wood pitch deposition at a bleached Kraft pulp mill (headbox).

[0021] FIG. 9. Synthetic pitch accumulation under mild acidic conditions in presence of four pitch control chemicals at 60 ppm: benchtop test, SRM.

[0022] FIG. 10. Synthetic pitch accumulation under mild acidic conditions in presence of a pitch control chemical at doses 15-60 ppm.

[0023] FIG. 11. Monitoring microbiological growth at a recycle board and packaging mill.

DETAILED DESCRIPTION OF THE INVENTION

[0024] “QCM” means quartz crystal microbalance.

[0025] “IDM” means independent deposition monitor. The instrument is available from Nalco Company, Naperville, Ill. It is a portable instrument that records actual deposition and, from the application standpoint, differs from conventional coupons by its high sensitivity and ability to continuously follow deposition and assess the nature of the deposit. Data are collected continuously at intervals ranging from minutes to hours and then downloaded from the IDM to a personal computer. All plumbing is generally accomplished using stainless steel tubing with compression fittings. This includes the system’s sample inlet and outlet. The flow rate in a continuous operation (the probe connected to a process line through a slipstream arrangement) is normally 2-4 gallons per minutes. The instrument also allows data collection from a batch system, where the instrument probe is immersed into the test liquid stirred using a mechanical or magnetic stirrer.

[0026] “DRM” means deposit rate monitor. The instrument is available from Nalco Company, Naperville, Ill. It is an instrument similar to IDM but without pressure compensation.

[0027] “SRM” means scale rate monitor. The instrument is available from Nalco Company, Naperville, Ill. It is a benchtop instrument based on QCM technology.

[0028] While the present invention is susceptible of embodiment in various forms, there is shown in the drawings and will hereinafter be described a presently preferred embodiment with the understanding that the present disclo-

sure is to be considered an exemplification of the invention and is not intended to limit the invention to the specific embodiment illustrated.

[0029] It should be further understood that the title of this section of this specification, namely, “Detailed Description of the Invention,” relates to a requirement of the United States Patent Office, and does not imply, nor should be inferred to limit the subject matter disclosed herein.

[0030] The monitoring system is based on the QCM that is the main part of the instrument’s probe. Basic physical principles and terminology of the QCM can be found in publications: Martin et al., Measuring liquid properties with smooth- and textured-surface resonators, Proc. IEEE Int. Freq. Control Symp., v.47, p. 603-608 (1993); Martin et al., Resonator/Oscillator response to liquid loading, Anal. Chem., v.69 (11), 2050-2054 (1997); Schneider et. al., Quartz Crystal Microbalance (QCM) arrays for solution analysis, Sandia Report SAND97-0029, p. 1-21 (1997). In the QCM, a flat quartz crystal is sandwiched between two electrically conductive surfaces. One surface (top side) is in a continuous contact with the tested medium while the other (bottom side) is isolated from the tested liquid or slurry. The QCM vibrates when the electrical potential is applied (piezoelectric effect). The oscillator frequency is connected to the amount of the deposit on the top (open to the medium) side of the QCM. The vibration frequency is, generally, linearly proportional to the mass of a deposit on the metal surface of the QCM. Measuring the frequency thus provides a means to monitor real-time deposition. The oscillator frequency also is affected by the properties of the aqueous phase such as a temperature and viscosity. Therefore, uniform conditions should be maintained through every experiment.

[0031] In one embodiment, the papermaking process occurs at location selected from the group consisting of: a pulp mill; a papermaking machine; a tissue making machine; a repulper; water loop; wet-end stock preparation; and deinking stages.

[0032] In another embodiment, the organic deposits are selected from the group consisting of: wood; extractives; redeposited lignin; defoamers; surfactants; and stickies. In another embodiment, the surfactants are silicon surfactants.

[0033] In another embodiment, the stickies are selected from the group consisting of: sizing chemicals; and adhesives.

[0034] In another embodiment, the continuously flowing slurry is a pulp slurry.

[0035] In another embodiment, the organic deposits are silicon surfactants and the papermaking process is a tissue repulping process.

[0036] In another embodiment, the top side of the quartz crystal microbalance is made of one or more conductive materials selected from the group consisting of: platinum; titanium; silver; gold; lead; cadmium; diamond-like thin film electrodes with or without implanted ions; silicides of titanium, niobium and tantalum; lead-selenium alloys; mercury amalgams; and silicon.

[0037] In another embodiment, the top side of the quartz crystal microbalance is coated with any one or more conductive or uncondutive materials selected from the group consisting of: polymeric films; monolayers; polylayers; surfactants; polyelectrolytes; thiols; silica; aromatic sorbates; self-assembled monolayers; and molecular solids.

[0038] In an embodiment, if an inhibitor is added to the liquid or slurry but the vibration frequency of the quartz

crystal microbalance does not decrease as desired, the invention may add more of the inhibitor until the vibration frequency decreases accordingly.

[0039] The following examples not meant to limit the invention unless otherwise stated in the claims appended hereto.

EXPERIMENTS

Example 1

[0040] The IDM instrument was directly connected (a slipstream connection) to a filtrate line to assure a continuous flow of the solution. The deposition was directly recorded and the data is embodied in FIG. 1. Formation of "light" organic deposits in a post-oxygen brownstock washer line was monitored on-line with the IDM. Steady mass accumulation was observed. In several experiments, the addition of Nalco chemical PP10-3095 led to deposit removal followed by complete suppression of deposition (100-50 ppm) or slowing the deposition down (25 ppm).

Example 2

[0041] The IDM instrument was directly connected (a slipstream arrangement) to the white water line in the paper machine (0.3-0.5% pulp fines). The deposition of wood resins and glued fines was directly recorded and the data is embodied in FIG. 2. The deposition stopped when Nalco chemical PP10-3095 was applied at 100 ppm (note that the chemical did not remove the material from the surface of the QCM).

Example 3

[0042] The IDM instrument was directly connected (a slipstream arrangement) to the white water line in the paper machine (0.3-0.5% pulp fines). The deposition of wood resins and glued fines was recorded and the data is embodied in FIG. 3. The deposition stopped when Nalco chemical PP10-3095 was applied at 50 ppm and 100 ppm (the chemical did not remove pitch from the surface of the QCM).

Example 4

[0043] Silicon oil surfactants from facial tissue repulping process (3% pulp, beaker, 400 rpm, room temperature, SRM instrument). In this benchtop application, linear accumulation of the organic deposit was observed, at a rate dependent of presence of deposit control agents in the system.

Example 5

[0044] Wax (temperature-dependent adhesives) monitoring. A sample of headbox furnish (100% recycled OCC box) was repulped at 60° C. The slurry was transferred in a 1-L beaker with a magnetic stirrer. The IDM probe was placed vertically on a stand and the data is embodied in FIGS. 4 and 5. The slurry was stirred at a constant rate 400 rpm at room temperature and allowed to cool down. The data are corrected to 20° C. using the temperature-frequency linear correlation formula obtained for the IDM instrument in a separate experiment. Mass accumulation could be unambiguously ascribed to an organic material that deposits at a noticeable rate while the solution is still warm, later deposition slowed down.

Example 6

[0045] Mixed organic/inorganic deposits. This gives an example of using the technique as both a monitoring and diagnostic tool. In a paper mill, the IDM was installed, consecutively, in filtrate discharge lines (pH 3.5-3.8, 60-66° C.) where mixed barium sulfate/calcium oxalate scale was thought to be depositing. However, microphotographs of the deposit also indicated that the scale is mixed, predominantly containing an organic component (likely, trapped fibers and possibly viscous organic). The instrument recorded deposition as illustrated in FIG. 6.

Example 7

[0046] Mixed aluminum-calcium salt of a polymeric organic acid (a scale inhibitor overdose, diagnostics in deposit control program applications). The IDM instrument was directly connected (a slipstream arrangement) to the white water line in the broke repulper (0.3-0.5% pulp fines). The deposition initially was inorganic. The solution contained very high concentrations of metal ions, especially aluminum and calcium. Application of an excess of a scale control agent into the IDM line via peristaltic pump that was a polymeric organic acid in its nature resulted in a surge of deposition of a mixed aluminum-calcium salt of a polymeric organic acid due to scale inhibitor overdose (FIG. 7).

Example 8

[0047] The DRM was installed at a bleached Kraft pulp mill in the side stream of the primary screener headbox before the dryer, with pulp flow at 1.5% consistency. The deposition of wood pitch was recorded and the data is embodied in FIG. 8.

Example 9

[0048] To simulate pitch deposition, model pitch solution was added to a 0.5% suspension of bleached Kraft pulp at pH 10.6, in presence of inhibitors, when needed. A small amount of concentrated solution of calcium chloride was added. Then the pH was decreased to 2.5 with HCl, and subsequent pitch deposition was recorded using an SRM instrument. The results are presented in FIGS. 9 and 10.

Example 10

[0049] The DRM was installed at a recycle board and packaging mill in the side stream of the headbox before the dryer, with pulp flow at 0.5% consistency. Due to the lack of a microbio control program and heavily contaminated water, the mill has been experiencing microbiological growth problems that interfered with the deposition data. While no fiber is accumulating in the flow cell, bio-related slime (identified upon inspection of the DRM probe) was building up in the cell. Monitoring microbiological growth is illustrated in FIG. 11.

[0050] All patents referred to herein, are hereby incorporated herein by reference, whether or not specifically done so within the text of this disclosure.

[0051] In the present disclosure, the words "a" or "an" are to be taken to include both the singular and the plural. Conversely, any reference to plural items shall, where appropriate, include the singular.

[0052] From the foregoing it will be observed that numerous modifications and variations can be effectuated without departing from the true spirit and scope of the novel concepts

of the present invention. It is to be understood that no limitation with respect to the illustrated specific embodiments or examples is intended or should be inferred. The disclosure is intended to cover by the appended claims all such modifications as fall within the scope of the claims.

What is claimed is:

1. A method for monitoring and controlling a rate of deposition of organic deposits from a liquid or slurry in a papermaking process, the method comprising:

providing a quartz crystal microbalance, the quartz crystal microbalance having a top side in contact with the liquid or slurry and a bottom side isolated from the liquid or slurry, the quartz crystal microbalance measuring a vibration frequency;

monitoring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency; and

adding an inhibitor to the liquid or slurry, the inhibitor decreasing the rate of deposition of the organic deposits from the liquid or slurry, wherein the adding is based upon the monitoring.

2. The method of claim 1 wherein the top side of the quartz crystal microbalance comprises at least one conductive material selected from the group consisting of: platinum, titanium, silver; gold; lead; cadmium; diamond-like thin film electrodes with or without implanted ions; silicides of titanium, niobium and tantalum; lead-selenium alloys; mercury amalgams; and silicon.

3. The method of claim 1 wherein the method is performed at a location selected from the group consisting of: a pulp mill; a papermaking machine; a tissue making machine; a repulper; water loop; wet-end stock preparation; and a deinking stage.

4. The method of claim 1 wherein the organic deposits are selected from the group consisting of at least one of the following: wood extractives; related natural materials in virgin raw material; redeposited lignin; defoamers; surfactants; mixtures of organic insoluble salts; unsaponifiable organics; wood fibers; poorly soluble polymeric paper additives; waxes; stickies, optionally wherein the stickies are selected from the group consisting of sizing chemicals and adhesives; and microbiological deposits.

5. The method of claim 1, wherein the liquid or slurry is a pulp slurry.

6. A method for measuring the effectiveness of at least one inhibitor that decreases a rate of deposition of organic deposits in a papermaking process, the method comprising:

providing a quartz crystal microbalance, the quartz crystal microbalance having a top side in contact with a liquid or

slurry and a bottom side isolated from the liquid or slurry, the quartz crystal microbalance measuring a vibration frequency;

monitoring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency;

adding the at least one inhibitor that decreases the rate of deposition of the organic deposits to the liquid or slurry, wherein the adding is based upon the monitoring step; and

re-measuring the rate of deposition of the organic deposits from the liquid or slurry on to the quartz crystal microbalance by measuring the vibration frequency.

7. The method of claim 6 wherein the papermaking process occurs at location selected from the group consisting of: a pulp mill; a papermaking machine; a tissue making machine; a repulper; water loop; wet-end stock preparation; and deinking stages.

8. A method for measuring the effectiveness of at least one inhibitor that decreases a rate of deposition of organic deposits in a papermaking process simulation, the method comprising:

providing a quartz crystal microbalance, the quartz crystal microbalance having a top side in contact with a liquid or slurry and a bottom side isolated from the liquid or slurry, the quartz crystal microbalance measuring a vibration frequency; the liquid or slurry simulating that of a liquid or slurry found in a papermaking process;

monitoring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency;

adding the at least one inhibitor to the liquid or slurry, wherein the adding is based upon the monitoring; and re-measuring the rate of deposition of the organic deposits from the liquid or slurry by measuring the vibration frequency.

9. The method of claim 4, wherein the surfactants are silicon surfactants and optionally wherein the organic deposits are silicon surfactants and the papermaking process is a tissue repulping process.

10. The method of claim 1 wherein the top side of the quartz crystal microbalance is coated with at least one material selected from the group consisting of: polymeric films; monolayers; polylayers; surfactants; polyelectrolytes; thiols; silica; aromatic sorbates; self-assembled monolayers; and molecular solids.

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