PROCESS FOR IMPROVING DRY STRENGTH AND DRAINAGE OF PAPER AND PAPERBOARD

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ABSTRACT

A process is provided of providing glyoxylated polymer additives to a paper making process which brings about improvements in drainage properties of a cellulosic pulp material along with the ability to increase the dry strength of a resulting paper product. The process uses concentrated glyoxal to generate a working solution of a glyoxylated polymer additive which can be generated on site in a paper mill and used within a 24 to 48 hour interval. The ability to glyoxylate polymers in a working solution concentration provides for a more active additive and which can be supplied in a more economical fashion than conventional glyoxylated polymers.
PROCESS FOR IMPROVING DRY STRENGTH AND DRAINAGE OF PAPER AND PAPERBOARD

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 60/646,341, filed on Jan. 24, 2005, and which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention is directed towards the manufacturing process of paper, paperboard, corrugated products, and other fiber-containing products such as gypsum board/drywall and fiber-based backing for vinyl flooring. This invention further relates to additives used in the wet end of a papermaking process to confer dry strength to the resulting product. An additional aspect of one aspect of the invention is a process which improves manufacturing efficiency by promoting increased drainage during fiber processing.

BACKGROUND OF THE INVENTION

[0003] Within the papermaking art, it is known to add cationic starches during fiber processing/manipulation so as to achieve an improved retention of cellulose fines, filler, and/or pigment within the fiber product and to also bring about an improved dry strength in the resulting paper.

[0004] Glyoxal is another additive which is frequently combined with a polyacrylamide polymer for incorporation into the wet end of a papermaking process. A glyoxylated resin additive is frequently used to obtain increased internal bond strength, greater dry tensile strength, improved modulus of elasticity, and improvements in sizing effectiveness.

[0005] Further, since the glyoxylated polymer additives may have cationic charges, the amount of cationic charge can be controlled so as to provide desired drainage and retention properties to the paper. Proper pH regulation avoids problems associated with excessive cationic charges such as flocculation of the fibers.

[0006] Heretofore, it has been the custom and practice within the papermaking industry to use bulk supplies of a low solids content of glyoxylated polymers having about 6% to about 11% solids. However, glyoxylated polymer solutions, even at the commonly used concentration levels, suffer a noticeable loss of efficiency following three to four weeks of storage. Further, if not used within a narrow time interval, the glyoxylated polymer will gel. Once gelling occurs, the glyoxylated polymer is no longer usable, and the equipment affected by the gelled glyoxylated polymer must be cleaned and reconditioned. In addition, the gel time of glyoxylated compositions is dependent upon ambient temperature. Accordingly, glyoxylated polymer degradation and gelling occurs more rapidly in warmer climates.

[0007] Since the traditional glyoxylated polymers employed within the papermaking industry have a limited storage life, it is common for the stored glyoxylated additives to be used for paper and paperboard products which do not require the higher strength parameters normally associated with the use of the strength additives. In other words, glyoxylated additives are frequently incorporated into products merely as a way of using up stored additive inventory before unacceptable gelling occurs.

SUMMARY OF THE INVENTION

[0008] Accordingly, there remains room for improvement and variation within the art.

[0009] It is one aspect of at least one embodiment of the present invention to provide for a paper manufacturing process in which a high solids content glyoxylated additive can be mixed into a cellulose pulp material by the incorporation of glyoxal and glyoxal-polymer reaction products into the cellulose pulp prior to formation of the paper product. Accordingly, a glyoxylated product may be added to an aqueous suspension of paper stock while the paper stock is in the head box recirculation loop, in the thick stock chest, the hydropulper, or at other points in the process prior to or after formation of a sheet. An example of the latter would be the spraying of a glyoxylated polymer solution between the plies of a multi-ply sheet.

[0010] It is yet another aspect of at least one embodiment of the present invention to provide for a process for introducing glyoxal to various reactive polymers, starches, gums, etc., to produce a cross-linked dry strength resin having excellent drainage properties and which can be applied in situ in a paper mill operation.

[0011] It is a further aspect of at least one embodiment of the present invention to provide for a process for introducing glyoxal to various reactive polymers, starches, gums, etc., to produce a cross-linked dry strength resin having excellent drainage properties and which can be applied in situ in a paper mill operation.

[0012] It is a further aspect of at least one embodiment of the present invention to employ a metering system for a glyoxal stock solution and a base polymer to produce a freshly prepared glyoxylated polymer working solution of between about 4% to about 6% solids concentration. The working solution is useful for incorporation into a thick paper stock solution having between about 2% to about 5% solids and thereby achieve an increase in dry strength of the resulting paper product. The working solution can also be used to improve drainage properties in a thin paper stock having solids of less than about 1%.

[0013] It is a further aspect of at least one embodiment of the present invention to provide for a working solution of a glyoxylated additive in a papermaking process which reduces the tendency of the reaction product to form undesired gels.

[0014] It is yet another aspect of at least one embodiment of the present invention to provide for a process for introducing a glyoxylated additive, the proportion of glyoxal to polymer of which is varied, depending upon monitored production goals, such as sheet strength, stock drainage and drying rates, white water quality, and process variables which may include water properties, stock pH, fiber quality, fines content, and the type and amount of additional additives used in the paper making process.

[0015] It is yet a further aspect of at least one embodiment of the present invention to provide for an effective sulfide scavenger additive, or other sulfur compound, scavenging amount of free gly-
oxal in a working solution of a glyoxal additive which serves as a sulfide scavenger within a fiber furnish.

[0016] These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] A fully enabling disclosure of the present invention, including the best mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying drawings.

[0018] The FIGURE is a schematic view of a process of incorporating a high solid content glyoxylated polymer into the wet end of a papermaking process.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] Reference will now be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features, and aspects of the present invention are disclosed in the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions.

[0020] In describing the various FIGURES herein, the same reference numbers are used throughout to describe the same material, apparatus, or process pathway. To avoid redundancy, detailed descriptions of much of the apparatus once described in relation to a FIGURE is not repeated in the descriptions of subsequent FIGURES, although such apparatus or process is labeled with the same reference numbers.

[0021] In accordance with the present invention, it has been demonstrated that a high solids glyoxal will react with macromolecules such as polyacrylamide polymers and other polymeric agents in a cross-linking reaction. Glyoxal reacts with the polymeric agent to improve the paper properties, such as strength, upon drying of the paper. Generally, the amount of glyoxal resin is within the ratio of about 15 percent to about 25 percent by dry weight of the glyoxal to dry weight of a cationic polymer such as polyacrylamide.

[0022] In addition, glyoxal can promote improved drainage properties of a paper furnish. For purposes of improving drainage, the glyoxal resin is added within a ratio of about 5 percent to about 15 percent by dry weight of the glyoxal to cationic polymer such as polyacrylamide.

EXAMPLE 1

[0023] The effect of glyoxylation on polyacrylamides with varying chain lengths was determined with respect to drainage properties of a paper furnish. The laboratory conditions utilized are representative of a glyoxolation process that may be used on site in a paper mill. The following procedures were used and the results are set forth below.

[0024] Three types of polyacrylamide polymers supplied by Aquaserv, Memphis, Tenn., were selected as referenced in Table 1 below. As noted, samples PCV 005 and PCV 015 are nonionic polymers while the PCV 105 polymer has a 10% cationic charge. The polymers used were prepared using dry powders which were dispersed in deionized water at a 1.7% solids concentration. Thereafter, glyoxal supplied by Noveon, Charlotte, N.C., at a 40% solids concentration was slowly added to the polymer solution while stirring to produce a 25:75 glyoxal to polymer ratio, on a solids basis, for each reactant. The resulting solution was adjusted to a pH of between 7.8 to 8.0 using a dilute sodium hydroxide solution. The samples were continually mixed by stirring for 15 minutes and stored at room temperature.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Approx. Molecular Weight Range</th>
<th>Polymer Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCV 005</td>
<td>200,000 to 500,000</td>
<td>nonionic</td>
</tr>
<tr>
<td>PCV 015</td>
<td>1,000,000 to 1,250,000</td>
<td>nonionic</td>
</tr>
<tr>
<td>PCV 105</td>
<td>2,000,000 to 2,500,000</td>
<td>10% cationic</td>
</tr>
</tbody>
</table>

[0025] An appropriate paper furnish having a consistency of between about 0.8% to about 1.0% was provided by defiberization of a blend of paper stocks which included:

[0026] 98% old corrugated containers;
[0027] 1% office copy paper; and
[0028] 1% old newsprint.

[0029] Lignin sulfonate solids were added to the suspension of fibers at a concentration of 200 ppm, based upon the lignin sulfonate solids to the wet paper stock weight. The addition of lignin sulfonate solids was used to provide a water/fiber suspension having properties of a closed mill water system. The lignin sulfonate retards drainage and duplicates conditions of a typical fiber furnish.

[0030] Furnish samples of the 0.8% to 1.0% consistency solution described above were prepared using 500 ml aliquots which were mixed in a Britt jar for 10 seconds. Following mixing, a corresponding amount of a freshly prepared glyoxylated polymer was added at levels equivalent to 5 pounds of polymer solids per ton of fiber solids. Following addition of this polymer, the material within the Britt jar was stirred for an additional 20 seconds and the furnish transferred to a Buchner funnel having a coarse filter (Whatman grade 202.15 cm diameter). Prior to transferring the furnish to the funnel, a vacuum was applied to the supporting filter flask. A 10 second vacuum interval was applied to the furnish at which time the vacuum was removed and the amount of water drained during the 10 second time interval was measured. Results are listed in
Table 2. The measurement of percent drainage improvement was calculated by the following equation:

\[
\text{Drainage Improvement} = \frac{\text{treated volume} - \text{blank volume}}{\text{blank volume}} \times 100
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. Drained, ml</th>
<th>Drainage Improvement, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>68</td>
<td>0</td>
</tr>
<tr>
<td>Gly. PCV 005</td>
<td>155</td>
<td>128</td>
</tr>
<tr>
<td>Gly. PCV 015</td>
<td>125</td>
<td>84</td>
</tr>
<tr>
<td>Gly. PCV 105</td>
<td>80</td>
<td>18</td>
</tr>
</tbody>
</table>

[0031] As seen from the results, low molecular weight glyoxylated polymers have a more significant impact upon furnish drainage than higher molecular weight polymers. This is true even when the higher molecular weight polymers have a cationic charge. Without wishing to be limited by theory, it is believed that the use of lower molecular weight polymers provide for an increased number of polymer molecules which are available for interaction. In other words, the lower molecular weight polymers result in enhanced uniformity of coverage of the polymeric species on the fiber and fines surfaces, resulting in a better distribution of chemical bonding between the additive and the cellulose.

[0032] In addition, when a glyoxylated solution is freshly prepared, there is a greater amount of free glyoxyl present within the solution. It is believed that the free glyoxyl serves as a scavenger for sulfide and other materials and which can bring about further improvements in drainage properties by scavenging materials that may otherwise contribute to reduced drainage.

**EXAMPLE 2**

[0033] The ability of freshly glyoxylated polymers to improve drainage properties of a commercial paper furnish having a clean, open water system was also evaluated. The polymer used to evaluate drainage improvements was a copolymer consisting of a 93 mol percent of dimethylallyl ammonium chloride (DADMAC) and a 7 mol percent of polyacrylamide. This copolymer was obtained in an aqueous solution, therefore, it did not require dispersion in water. The glyoxylation process used was otherwise identical to that described in Example 1.

[0034] The paper furnish used was obtained from the headbox of a commercial paper machine making kraft multi-wall bag paper material. The furnish composition was a mixture of 80% unbleached, refined virgin kraft Southern Pine pulp blended with 20% old corrugated containers.

[0035] The furnish was separated into four samples as set forth in Table 3. A portion of the furnish was introduced into a Britt jar at a propeller rotation of 800 rpm, and using a screen made from the paper machine’s forming fabric. As the level in the Britt jar dropped, additional furnish was added to maintain a volume of between 400 to about 600 ml. The effluent from the jar was collected and consisted of process water and fines, i.e., fibrous material capable of passing through the screen. Sample 3 was obtained by simply filtering a portion of the furnish. Sample 4 preparation began by collecting long fibers trapped by the screen which were subsequently thoroughly washed with tap water. The washed long fibers were then re-dispersed in filtrate from the headbox sample.

[0036] The drainage test procedure was set up as described in reference to Example 1 above. However, because of the much higher drainage rate of the filtrate (Sample 3) and the long fiber sample (Sample 4) a different evaluation measurement was obtained. As seen in reference to Table 3, the time required to completely evacuate free water was measured. All measurements set forth in Table 3 are set forth at a drainage rate of milliliters per second. The amount of glyoxylated polymer used to treat the samples was identical to that in Example 1. All samples were adjusted to have the same solids-to-water ratio as occurred in the original headbox sample, except for the filtrate, Sample 3, which had no suspended solids. The headbox sample consisted of a 65% long fiber and a 37% fines composition.

**TABLE 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drainage Rate Without Polymer</th>
<th>Drainage Rate With Polymer</th>
<th>Drainage Improvement, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Sample</td>
<td>2.2 ml/sec</td>
<td>7.43 ml/sec</td>
<td>238</td>
</tr>
<tr>
<td>Fines in Process</td>
<td>2.3 ml/sec</td>
<td>6.00 ml/sec</td>
<td>200</td>
</tr>
<tr>
<td>Water Filtrate</td>
<td>15.0 ml/sec</td>
<td>63.10 ml/sec</td>
<td>321</td>
</tr>
<tr>
<td>Long Fiber in</td>
<td>88.2 ml/sec</td>
<td>90.10 ml/sec</td>
<td>2</td>
</tr>
<tr>
<td>Process Water</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[0037] As seen in the data set forth in Table 3, the glyoxylated polymer significantly enhances the drainage rate of all the samples with the exception of long fibers in the process water. In this latter example, the process water has been depleted of the primary material responsible for slow drainage, i.e., fines. In Examples 1 through 3, where fines, dissolved solids, and colloids are present, the freshly glyoxylated polymer brings about significant improvement in drainage rate.

**EXAMPLE 3**

[0038] The effect of the copolymer charge on drainage and floc formation was also evaluated using glyoxylated copolymers. As set forth in Table 4, the identified copolymers were used as the starting material and obtained in a liquid form. Glyoxal was added to the copolymer to achieve a 15:85 glyoxal to polymer ratio. The solution was adjusted to a pH of between 7.8 to 8.0 using dilute sodium hydroxide as described in Example 1 above. The glyoxylated copolymers were used at a level equivalent to 5 pounds of glyoxylated polymer per ton of fiber, though it is believed that a useful concentration of 3 to 5 pounds of glyoxylated polymer per ton of fiber is a useful range.

**TABLE 4**

<table>
<thead>
<tr>
<th>Polymer Identification</th>
<th>% Polyacrylamide</th>
<th>% DADMAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC 1070</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>PC 6050</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PC 6010</td>
<td>90</td>
<td>10</td>
</tr>
</tbody>
</table>

[0039] The paper furnish was prepared in a laboratory using defiberized paper stocks of 98% old corrugated con-
tainer and 2% old newsprint. The drainage test procedures set forth in Example 1 were used and the results set forth below in Table 5.

[0040] A determination of flocculation was made using qualitative assessments of furnish samples stirred in a Britt jar during the final 20 seconds of mixing. As observed from the data set forth in Table 5, the copolymer having a lower percentage of DADMAC, and hence less of a positive charge, produces very little floccing. In comparison, polymers having a higher percentage of DADMAC exhibited no additional improvement in drainage but produced moderate to severe floccing. Accordingly, with respect to freshly glyoxylated copolymers, it is believed that lower charged products which exhibit good drainage properties are preferable to higher charged products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observation of Floc Formation</th>
<th>Volume Drained, ml</th>
<th>Drainage Improvement, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Very little floccing</td>
<td>210</td>
<td>0</td>
</tr>
<tr>
<td>Gly. PC 1070</td>
<td>Moderate floccing</td>
<td>490</td>
<td>133</td>
</tr>
<tr>
<td>Gly. PC 6050</td>
<td>Severe floccing</td>
<td>505</td>
<td>140</td>
</tr>
<tr>
<td>Gly. PC 6010</td>
<td>Very little visible floccing</td>
<td>505</td>
<td>140</td>
</tr>
</tbody>
</table>

[0041] As seen in reference to the accompanying sole FIGURE, an overview of a representative process is set forth in which reacting polymers, starches, gums, etc., may be cross-linked to produce dry strength resins, serve as drainage aids, and enhance production efficiency within a paper mill.

[0042] The liquid reactants are generally stable for periods ranging between 6 months to 1 year and may be stored in bulk tanks equipped with metering pumps. For production of a batch product, pumps may supply the required ingredients at a programmed flow rate to a header. The required ingredients must be dispersed simultaneously, followed by static mixing.

[0043] As seen in reference to the sole FIGURE, Reactant A may be a polyacrylamide polymer, a copolymer of, for example, polyacrylamide and dimethyldialyl ammonium chloride, or any number of linear or branched polymers modified by appended anionically or cationically charged groups. Reactant B may be a liquid cationic starch solution, chitin, guar gum, or a hybrid product, such as a starch-cationic polymer complex with a high percentage (approximately 50 percent) of synthetic polymer Reactant C may be a glyoxal at 40% solids or another suitable cross-linking agent. Non-limiting examples include other dialdehydes, anhydrides, dianhydrides, polyfunctional amines, and polyamines. As the various reactants are mixed within a reactor, sodium carbonate may be added in small amounts to increase the pH of the mixed reactants to a desired range of between about 7.8 to about 8.0.

[0044] A typical reaction time of 15 to 30 minutes may be used in which the reactants are continually mixed by an agitator in the reactor or some other form of agitation.

[0045] The pH of the resulting reactant is monitored and adjusted with either sodium carbonate or sulfuric acid to maintain a desired pH. The product concentration in the reactor will typically be in a range of about 15% to about 35% solids. At this point, termination of the reaction and cross linking of product having proceeded, the reactant is diluted with water using a static mixer. The resulting working solution of freshly prepared glyoxylated polymer should be at a concentration of between about 4% to about 6% solids and which is then pumped to an accompanying storage tank. As seen in the exemplary FIGURE, two storage tanks may be employed to provide a continuous tank for operation.

[0046] From the storage tank, the reaction product necessary for the desired papermaking process may be metered via a metering pump. The metering pump is controlled by a distributed control system (DCS).

EXAMPLE 4

[0047] The effect of degree of glyxolation and age of glyoxylated polyacrylamide on drainage enhancement was evaluated.

[0048] Samples of glyoxylated polyacrylamide (PAM) were prepared under laboratory conditions similar to conditions for use within a pulp or paper mill environment. Specifically, a base polymer of a low molecular weight, 3 mol percent charge polyacrylamide, designated PAM and a 40% aqueous solution of glyoxal was used to obtain various degrees of glyxolation as measured relative to active PAM. The degrees of glyxolation are set forth in Table 6. The samples were prepared at ambient laboratory conditions with the pH adjusted to 7.8 using a dilute caustic followed by 15 minutes of vigorous stirring. During the stirring process, the pH typically drifts to the value of between 7.5 to 7.7, but no further pH changes were made.

[0049] Following the 15 minute stirring/reaction period, the viscosity of the sample was measured and an aliquot from each sample was used to prepare a 3% solids solution. From previous studies, it has been observed that solutions of 15% or higher glyoxal content result in the formation of gels in 24 hours or less unless the pH is reduced to 4.4 or lower. Similarly, it has been observed that 3% solutions will remain a pourable liquid at higher pH levels.

<table>
<thead>
<tr>
<th>TABLE 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

[0050] As set forth in Table 6, as discussed below, storage periods of 3 to 4 weeks for a 3% solution adversely affects the efficiency of the product. Such findings are consistent with observations from various pulp and paper mills that glyoxylated polymers experience various adverse effects upon storage which are dependent in part upon polymer concentration, temperature, and pH.

[0051] The samples described above were evaluated for their drainage efficiency in a recycled paper furnish product.
The furnish was prepared in the laboratory by re-pulping a mixture consisting of 80% corrugated container and 20% newsprint. The consistency of the furnish was 0.70% with a pH of 7.5.

[0052] The evaluation consisted of mixing 500 ml samples of furnish in a Britton jar using a stir rotation of 800 rpm in 15 seconds followed by the introduction of the respective sample or control by a syringe injection. A polymer product application amount corresponding to 3 lbs./ton was selected with the pounds of polymer product being on the solids basis and the tons being on an oven-dry fiber basis.

[0053] Following the polymer introduction, the samples were stirred for an additional 15 seconds at which time the furnish sample was poured into a Buchner funnel fitted with a fast, qualitative Whatman filter paper. Drainage occurred under vacuum for a period of 35 seconds at which time the vacuum was removed and the Buchner funnel was removed from the flask. The volume of water drained during the 35 second time interval was then measured, the results of which are set forth in Table 6. Samples 7 and 8 were polymers made 21 and 26 days, respectively, and stored under ambient laboratory conditions prior to use in the drainage test reported above. Samples 3 through 6 were prepared 24 hours prior to use.

[0054] As noted by the drainage improvement set forth in Table 6, as the percent increase of glyoxylation increases there is a significant increase in the drainage improvement properties. However, the rate of increase is not linear and less of a degree of improvement is noted as the percent glyoxal content increases.

[0055] Several factors were identified which influence the decrease in relative drainage improvement. First, the number of long chain polymer molecules within the samples decreases as the degree of glyoxylation increases. In other words, a larger percentage of the sample of polymer is now displaced with glyoxal. However, the polymers which are present are interacting through cross-linking activity which produces larger and more effective molecular structures.

[0056] Additionally, the storage of glyoxylated products results in a decrease of effectiveness as represented by the data set forth for samples 5, 7, and 8. As noted in Table 6, sample 5 of a 3% active solution with a 25% glyoxal content brings about a 61% drainage improvement. In comparison, samples 7 and 8, which have aged for 21 days as in sample 7 and 26 days as in sample 8, have a negative impact on desired properties. The use of freshly glyoxylated polymers improves drainage properties resulting in a more efficient paper manufacturing process. In addition, the freshly glyoxylated polymers can both increase the filtration efficiency of the furnish as well as prevent the formation of gels within storage and dispensing equipment used within the mill.

EXAMPLE 5

Improvement in Paper Dry Strength

[0057] In addition to the improvements in furnish drainage previously mentioned, it has been found that the dry strength of paper as measured by tensile strength, elongation at break, and tensile energy absorption of paper sheets are improved by incorporation of high solids glyoxylated cationic starch and high solids glyoxylated cationic polymer in the furnish. In addition, it is possible to improve the strength of the resulting paper product while simultaneously increasing the efficiency of drainage. In this manner, it is possible to achieve greater manufacturing efficiency using the glyoxylated products while also increasing the quality of the resulting paper product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basis Weight (lbs/MSF)</th>
<th>Drainage (ml/sec.)</th>
<th>Tensile Force (lb force)</th>
<th>Elongation At Failure (%)</th>
<th>TEA (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35.1</td>
<td>2.84</td>
<td>10.4</td>
<td>1.20</td>
<td>1.09</td>
</tr>
<tr>
<td>Glyoxylated Starch</td>
<td>36.7</td>
<td>8.20</td>
<td>12.6</td>
<td>1.71</td>
<td>1.94</td>
</tr>
<tr>
<td>Glyoxylated Polymer</td>
<td>37.1</td>
<td>8.93</td>
<td>12.8</td>
<td>2.64</td>
<td>3.18</td>
</tr>
</tbody>
</table>

[0058] The data set forth in Table 7 above is obtained from a commercial gypsum liner furnish which was treated with two types of glyoxylated product. Under laboratory conditions, furnish samples consisting of 500 m is of furnish were mixed in a Britton jar for 20 seconds followed by the injection of a polymer sample as noted in Table 7. Mixing continued for 20 seconds upon which the contents were transferred to a Buchner funnel attached to a vacuum flask. The time required to drain the water was measured. The fibrous furnish which was formed into a wet sheet was then air dried under restraint and without pressing, and the filter paper was peeled from the liner furnish sheet. The respective sheets were conditioned at TAPPI standards of 50% relative humidity and 73°F. and tested using an L&W tensile tester.

[0059] The three samples set forth in Table 7 were made using dosages equivalent to 5 lbs/ton on a solids basis in the treated samples. The base for the starch treatment, sample 2, is a commercial liquid cationic starch. The base for the polymer, sample 3, is a cationic low molecular weight solution polymer. The base samples were used to prepare a 30% glyoxal and 70% base reaction product. Glyoxylation was carried out at a pH of about 7.9 at 80°F. for a 15 minute period. This reaction process and timing simulates on-site production conditions within a paper or pulp mill.

[0060] The results are set forth in Table 7, and sets forth that tensile strength increases of about 23% may be obtained by using the glyoxylated polymers. Along with the improvements to tensile strength, the elongation break point also increases significantly as well as the tensile energy absorption. The tensile energy absorption data correlates with sheet toughness. As further noted, the drainage of the furnish also improved with the use of the glyoxylated products.

[0061] Further, the glyoxylated starch and the glyoxylated polymer as set forth in Table 7 can also be used at a similar dosage level of about 3 to about 5 lb/ton on a solids basis to be applied as a spray between ply layers on forming webs in a papermaking process. It is also envisioned that the strength additives can be sprayed onto forming webs prior to the drying of the webs to bring about improvements in dry strength.

[0062] Without wishing to be limited by theory, it is Applicant's belief that use of freshly glyoxylated compounds results in greater efficiencies in paper drainage and paper strength as opposed to comparable strength solutions
which have been stored long term. Further, the ability to provide, on-site, freshly prepared working solutions of glyoxylated polymers provides substantial cost savings. For instance, at the diluted working solutions used, it is not economical to ship large volumes of the glyoxylated polymers. Further, such shipments, while prohibitively expensive, would also suffer from disadvantages Applicant believes exist with using the working solutions of glyoxylated polymers that are not freshly prepared and used within about a 24 to 48 hour interval.

Likewise, there are disadvantages of the conventional techniques used within the papermaking industry of shipping large quantities of more concentrated glyoxylated polymers. At conventional shipping concentrations used within the paper industry, the solutions have a very short shelf life. As a result, gel formations within the product can lead to costly equipment cleaning and downtime. Further, the use of aged glyoxylated polymer solutions makes it difficult to standardize production techniques, in that age induced loss of efficiency introduces undesired variability into the manufacturing process. Such variability can be eliminated by using glyoxal stock solutions to prepare fresh glyoxylated polymers which are used within a time interval not exceeding 48 hours. In this manner, a consistent level of reactivity can be assured from one process to another, reducing one source of variability that can result in uneven paper quality.

The enhancements in the quality of the glyoxylated polymer strength and drainage additives are best achieved using the preparation methods described above in which the appropriate material quantities are combined and through control of the solution pH, mixing time, and post-reaction dilution control, allows for a high level of control over the quality and reactivity of the glyoxylated polymer additives. The automation overcomes problems in the prior art dealing with gelation, loss of efficiency through storage and shipping, sensitivity to temperatures, along with age-dependent variability in the reactivity of the glyoxylated polymer additives.

Although preferred embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those of ordinary skill in the art without departing from the spirit or the scope of the present invention which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged, both in whole, or in part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.

That which is claimed:

1. A method of improving drainage properties of fibers in a papermaking process comprising:

   providing a stock solution of glyoxal at a concentration of between about 25% to about 40%;

   adding a quantity of said stock solution of glyoxal to a polyelectrolyte polymer to produce a solids working solution of a glyoxylated polyacrylamide polymer, said glyoxal being present at about 15% to about 25% by dry weight relative to the dry weight of said polymer;

   adjusting said pH of said working solution to between about 7.8 to about 8.0;

   metering said pH adjusted working solution into an aqueous suspension of a cellulosic pulp at a loading level of at least about 3 lbs of glyoxylated polyacrylamide per ton of fiber solids; and,

   mixing said cellulosic pulp and said metered pH adjusted solution, thereby increasing the drainage properties of said cellulosic pulp.

2. A method of improving the dry strength of a paper product comprising:

   providing a stock solution of glyoxal at a concentration of between about 25% to about 40%;

   adding a quantity of said stock solution of glyoxal to a strength additive selected from the group consisting of cationic starch, PAM, and combinations thereof, to produce an about 4% to about 6% solids working solution of a glyoxylated polyacrylamide polymer, said glyoxal being present at about 30% by dry weight relative to the dry weight of said strength additive;

   adjusting said pH of said working solution to between about 7.8 to about 8.0;

   metering said pH adjusted working solution into an aqueous suspension of a cellulosic pulp at a loading level of at least about 3 lbs of glyoxylated polyacrylamide per ton of fiber solids; and,

   mixing said cellulosic pulp and said metered pH adjusted solution, thereby increasing the strength properties of cellulosic sheets made from said cellulosic pulp.

3. A method of improving the dry strength of a paper product comprising:

   providing a stock solution of glyoxal at a concentration of between about 25% to about 40%;

   adding a quantity of said stock solution of glyoxal to a strength additive selected from the group consisting of cationic starch, PAM, and combinations thereof, to produce an about 4% to about 6% solids working solution of a glyoxylated polyacrylamide polymer, said glyoxal being present at about 30% by dry weight relative to the dry weight of said strength additive;

   adjusting said pH of said working solution to between about 7.8 to about 8.0;

   spraying said working solution onto a surface of a paper web at a dosage of about 3 to about 5 pounds of glyoxylated polyacrylamide on a solids basis to a ton of dry paper; and,

   drying said paper web and said working solution, thereby increasing the strength properties of the resulting dried cellulosic product.

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