

PAPERMAKING PROCESSES USING COAGULANTS AND OPTICAL BRIGHTENERS

BACKGROUND OF THE INVENTION

[0001] This application claims the benefit under 35 U.S.C. §119(e) of prior U.S. Provisional Patent Application No. 60/761,913, filed January 25, 2006, which is incorporated in its entirety by reference herein.

[0002] The present invention relates to papermaking processes and products made from these processes. More particularly, the present invention relates to treating papermaking pulp with at least one charged starch, such as cationically-charged starches, and one or more optical brighteners.

[0003] Optical brighteners or optical brightening agents (OBAs) and Fluorescent Whitening Agents (FWAs) are typically used in certain papermaking processes in order to increase or improve the brightness of paper or paperboard and/or to increase or improve the paper fluorescence intensity. OBA/FWA products may be added at the size press with other additives. Other certain OBA/FWAs may be added in the wet end of the paper making process. The present invention relates, in part, to increasing the retention and/or the efficiency of OBAs/FWAs, whether present from wet end addition of OBA or OBA present in the broke (contains recycled paper), as well as not quenching or dulling the impact of OBA from any source, on the paper machine and in the final sheet of paper. Many consumers prefer paper with a high brightness, and the brightness of the paper is typically promoted as one important parameter to consumers of paper products. In order to achieve the brightness in paper, especially papers having a high brightness, such as over 80%, one or more optical brighteners or optical brightening agents are added during the papermaking process. These optical brighteners can be quite expensive and raise the overall cost of the paper product. This can be seen by any consumer purchasing paper. For instance, there can be a significant cost difference between a paper having a brightness of 80% compared to a brightness of 96%.

[0004] Typically, optical brightening agents are added to the wet end process, or to the size

press or to both the wet end and to the size press within the papermaking process. In typical papermaking processes, coagulants and flocculants are further used during the papermaking process in order to obtain desirable pulp characteristics, paper characteristics, and paper machine retention and runnability. Typically, coagulants neutralize system charge and assists the pulp fibers, fines, fillers and functional additives to electrostatically coagulate together retaining them in the sheet and to form a more uniform paper product. Traditional coagulants include polyaminoamido glycol, polyethylene imine, polyamine, polydadmec, alum and polyaluminum chloride. While coagulants are necessary to produce paper having suitable characteristics, many of these coagulants, unfortunately, affect in a negative way, the optical brighteners previously added. In particular, traditional coagulants can dull the affect of optical brighteners, thus reducing the paper ISO brightness and/or reducing the paper fluorescence intensity. As a result, paper manufacturers have typically added more optical brighteners, particularly in the wet end of the paper machine system, to compensate for this dullness occurring with the use of traditional coagulants.

[0005] The coagulants are also typically added at the wet end stage of the papermaking process either to a thick stock or a thin stock feed location.

[0006] Thus, there is a need for a new papermaking process that avoids this dulling effect caused by traditional coagulants. Further, there is a need to develop a process that will permit the use of optical brighteners without the need to provide an additional amount of optical brighteners to compensate for the use of coagulants during the papermaking process.

[0007] A feature of the present invention is to provide a method of making paper or paperboard which preferably does not dull the effects of optical brightening agents.

[0008] A further feature of the present invention is to provide a method which permits the reduction in the amount of optical brightening agents and yet achieves satisfactory brightness and/or paper fluorescence intensity in the paper or paperboard.

[0009] Additional features and advantages of the present invention will be set forth in part in

the description that follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

[0010] To achieve these and other advantages, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to a method of making paper or paperboard which involves introducing at least one ionically-charged starch (preferably with a degree of substitution above 0.045) and at least one optical brightening agent to a papermaking pulp to form a treated pulp. The treated pulp can then be formed into a paper or paperboard product. The ionically-charged starch and the optical brightening agent can be added in any order. For instance, the starch can be added to the thin stock and the optical brightening agent can be added to the thick stock, the OBA can be added to the thin stock, thick stock, or both, and/or the starch can be added to the thin stock, thick stock, or both.

[0011] The present invention further relates to a method of improving optical brightener performance by using at least one ionically-charged starch (preferably with a degree of substitution above 0.045) and at least one optical brightening agent and adding these components to a papermaking pulp to form a treated pulp and then forming the treated pulp into a paper or paperboard.

[0012] The present invention further relates to paper or paperboard which can be obtained by one or more of the methods of the present invention.

[0013] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention, as claimed.

[0014] The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate several embodiments of the present invention and together with the description, serve to explain at least one or more principals of the present invention.

BRIEF DESCRIPTION OF DRAWINGS

[0015] Figs. 1 and 2 are flow charts showing a papermaking process according to one or more embodiments of the present invention.

[0016] Fig. 3 is a bar graph comparing various hand sheet samples with optical brightening agents with or without cationic starches and measuring the resulting ISO brightness.

[0017] Fig. 4 is a photograph showing the fluorescence image of various hand sheet samples which contain an optical brightening agent with or without a cationic starch.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0018] The present invention provides methods of making paper or paperboard that use one or more optical brightening agents during the papermaking or paperboard making process. For purposes of the present invention, papermaking pulp will refer to pulp that can be made into paper or paperboard products.

[0019] In the present invention, one or more ionically-charged starches, such as cationic starch or starches preferably having a degree of substitution greater than 0.045, are added to the papermaking pulp along with at least one optical brightening agent. According to the present invention, the ionically-charged starch can be added to the pulp separately or in any combination. Paper and paperboard products made according to the methods of the present invention preferably exhibit increased paper brightness and/or paper fluorescence intensity compared to the same paper and paperboard being made by the same process but without the presence of cationic starch, having a degree of substitution greater than 0.045, and added to the wet end of the paper machine system.

[0020] In the present invention, the ionically-charged starch and the optical brightening agent can be added in any order of introduction, such as fed one after another into the papermaking pulp. The optical brightening agent and the starch can be added at the same stage of the papermaking process or it can be added at different stages of the papermaking process, as long as both

components are added prior to the size pressing stage of a papermaking process. For instance, the two components can be added within 50 minutes of each other, within 40 minutes of each other, within 20 minutes of each other, within 10 minutes of each other, or within 5 minutes of each other, or within 2 minutes of each other, or within 1 minute of each other, or even within seconds of each other into the pulp.

[0021] The starch, as stated, is an ionically-charged starch which is preferably a cationically-charged starch or cationic starch, preferably having a degree of substitution greater than 0.045. The charged state of the starch refers to the overall net charge of the starch. Two or more charged starches can be used, such as two or more cationic starches. When two or more starches are used, the starches can be added as a pre-blended composition, or they can be added at the same time, sequentially, or in any order to the pulp, alone or in combination with one or more optical brightening agents. When two or more starches are used, one of the starches can be a neutral starch. Preferably, at least one of the charged starches has a degree of substitution ranging from about 0.045 to about 0.5, such as from about 0.07 to about 0.45 or from about 0.10 to about 0.40, or from about 0.15 to about 0.4. Other degrees of substitution above and below these ranges can be used. Generally, a degree of substitution above 0.045 is preferred and can be used. The degree of substitution can be above 0.4 and higher degrees of substitution will benefit the present invention. Preferred cationic starches include, but are not limited to, potato starches, corn starches, and other wet-end starches, or combinations thereof. Specific examples of cationic starches that can be used in the present invention include, but are not limited to BUFLOC 5521 and BUFLOC 5567 products, both available from Buckman Laboratories International, Inc., Memphis, Tennessee. Other examples include, but are not limited to, Raifix, Raisiobond, and products supplied to the industry by CIBA.

[0022] With respect to the optical brightening agents, one or more optical brightening agents can be used, such as two or more or three or more. For purposes of the present invention, optical brightening agents include fluorescent whitening agents. For purposes of the present invention,

optical brightening agents are typically chemicals which are used to purify and/or increase the visible whiteness or brightness of paper fibers. Optical brightening agents can also be optical whitening agents and can include water-soluble dyestuffs. The optical whitening agents can be fluorescence dyes that absorb invisible UV light from daylight and re-emitted in the visible spectrum, thus enhancing the brightness with excellence of whiteness on the paper. When two or more optical brightening agents are used, as with the starch, they can be added as a pre-blend, sequentially, or in any order to the pulp. General classes of optical brightening agents include stilbenes, derivatives of stilbenes, distyrylbiphenyls, triazinylamino stilbene, and the like. For purposes of the present invention, an optical brightening agent includes tinting agents. Examples of OBAs include stilbene disulfonate, stilbene tetrasulfonate, stilbene hexasulfonate, 4,4' diamino stilene, 2,2' disulphonic acid, or stilbene derivatives. The OBAs described in U.S. Patent Nos. 5,873,913; 6,723,846; 4,025,507; and 6,464,832; and U.S. Publication Patent Application Nos. 2004/0077515; 2004/0074021 can be used and are incorporated in their entirety by reference herein. Examples of specific optical brightening agents include, but are not limited to, Blankophor, Leucophor, Tinopal, Catowhite OWA grades, Unipal, Palinil Brilliant White, Uvitex, Milkawhite, Fluolite, Kalbrite, OBA-C and W.

[0023] The preferred amount of the ionically-charged starch, such as cationic starch, can be any amount effective to permit an improved optical brightener performance, such as improvement with respect to paper ISO brightness and/or paper fluorescence intensity. In the alternative, or in combination with this property improvement, the ionic starch, such as cationic starch, can be added in an amount of from about 0.25 to about 25 pounds per ton of dried pulp or a dry solids basis, or from about 1.0 pound to 20 pounds per ton of dried pulp on a dry solids basis, and more preferably from about 1 pound to about 6 pounds per ton of dried pulp on a dry solids basis. With respect to the optical brightening agents, conventional amounts are used, such as from about 1 pound to about 50 pounds per ton of dried pulp, and more preferably from about 2.0 to about 10.0 pounds per ton of dried pulp on a dry solids basis.

[0024] With respect to this process, this process is preferably used when making fine paper or paper that is coated or non-coated free-sheet, newsprint, specialty newsprint, supercalendered (SC), and light weight coated (LWC) grades. Non-coated free sheet paper is made from freely draining stock. Coated free sheet is a publication grade in which the coating raw stock generally contains no more than 10% by weight mechanical pulp. Supercalendered (SC) is off machine calendaring paper utilizing a stack having alternating chilled iron fiber rolls. LWC is coated papers of relatively low grammage. Newsprint machine-finished paper is composed mainly of mechanical pulp, commonly used for printing newspapers.

[0025] Preferably, the starch and brightening agent are introduced at or prior to the pulp entering a blend chest. In at least one embodiment of the present invention, the optical brightening agent and starch can be added at or prior to the pulp entering a machine chest. In at least one embodiment of the present invention, the starch and the optical brightening agents can be added to the pulp prior to the size pressing. The starch and the optical brightening agent can generally be added at any location of the paper making process and can be added prior to the whitewater silo in a paper making process or can be added prior to the machine chest or can be added prior to the blend chest or can be added prior to or after the first refiner.

[0026] The method of the present invention can be practiced on conventional paper making machines with modifications that can be easily made in view of the present invention. The method can employ many different types of paper making pulp or combinations thereof. For example, the pulp may comprise virgin and/or recycled pulp, such as virgin sulfite pulp, broke pulp, a hardwood kraft pulp, a softwood kraft pulp, mixtures of such pulps, and the like.

[0027] An enzyme composition can be optionally used for treating the pulp and may contain any conventional paper making pulp-treating enzyme that has cellulytic activity. Other conventional paper-making components can be present as long as these other components do not negatively affect the starch, or optical brightening agent. Preferably, the enzyme composition also exhibits hemicellulytic activity. Suitable enzymes and enzyme-containing compositions include

those described in U.S. Pat. No. 5,356,800 to Jaquess, U.S. Patent Application No. 09/031,830 filed Feb. 27, 1998, and International Publication No. WO 99/43780, all incorporated herein in their entireties by reference. Other exemplary paper making pulp-treating enzymes are BUZYME® 2523 and BUZYME® 2524, both available from Buckman Laboratories International, Inc., Memphis, Tenn. The cellulytic enzyme composition preferably contains from about 5% to about 20% by weight enzyme. The preferred enzyme composition can further contain polyethylene glycol, hexylene glycol, polyvinylpyrrolidone, tetrahydrofuryl alcohol, glycerine, water, and other conventional enzyme composition additives, as for example, described in U.S. Pat. No. 5,356,800. The enzyme may be added to the pulp in any amount, such as from about 0.001 to about 0.100% by weight enzyme based on the dry weight of the pulp, for example, from about 0.005 to about 0.05% by weight.

[0028] In one embodiment of the present invention, the enzyme composition contains at least one polyamide oligomer and at least one enzyme. The polyamide is present in an effective amount to stabilize the enzyme. Exemplary enzyme compositions containing polyamide oligomers and enzymes are described in International Published Application No. WO 99/43780, which is incorporated herein in its entirety by reference.

[0029] According to the present invention, the enzyme composition can include a combination of two or more different enzymes. The enzyme composition can include, for example, a combination of a lipase and a cellulase, and optionally can include a stabilizing agent. The stabilizing agent may be a polyamide oligomer as described herein.

[0030] A microparticle additive may be added to the pulp at any time during the process. The microparticle additive can modify the charge of the pulp or the charge of a component of the pulp. The microparticle additive can be, for example, a charging or modifying agent, a filler, a coagulating agent, and/or a retention aid. The microparticle additive can be a natural or synthetic hectorite, bentonite, zeolite, alumina sol, silica or any of conventional particulate additives as are known to those skilled in the art.

[0031] A biocide may be added to the pulp or treated pulp in accordance with conventional uses of biocides in paper making processes. For example, a biocide may be added to the treated pulp in a blend chest. Biocides useful in the paper making pulps according to the present invention include biocides well known to those skilled in the art, for example, BUSAN®1130, available from Buckman Laboratories International, Inc., Memphis, Tenn.

[0032] A flow chart of a paper making system for carrying out the method of the present invention is set forth in FIG. 1. It is to be understood that the system shown is exemplary of the present invention and is in no way intended to restrict the scope of the invention. In the system of FIG. 1, a supply of starch and a supply of optical brightening agent (OBA) are added at desired respective concentrations with a flowing stream of paper making pulp to form a treated pulp at any part of the front end of the wet process as shown. The supply of pulp shown represents a flow of pulp, as for example, supplied from a pulp holding tank or silo. The supply of pulp shown in FIG. 1 can be a conduit, holding, or mixing tank, or other container, passageway, or mixing zone for the flow of pulp. The supply of starch or OBA can be, for example, a holding tank having an outlet in communication with an inlet of the treated pulp tank.

[0033] The pulp treated with the starch and OBA can be passed from the treated pulp tank through a refiner, and then through a blend chest where optional additives including a biocide can be combined with the treated pulp. The refiner has an inlet in communication with an outlet of the treated pulp tank, and an outlet in communication with an inlet of the blend chest.

[0034] According to the embodiment of FIG. 1, the pulp treated in the blend chest is passed from an outlet of the blend chest through a communication to an inlet of a machine chest. The blend chest and machine chest can be of any conventional type known to those skilled in the art. The machine chest ensures a level head, that is, a constant pressure on the treated pulp or stock throughout the downstream portion of the system, particularly at the head box.

[0035] In the system of FIG. 1, drained pulp resulting from paper making in the headbox is recirculated to the white water silo.

[0036] In the embodiment shown in FIG. 2, a cationic starch and/or OBA are added to the refined treated pulp at the blend chest or up to the stuff box, and the system includes a conventional stuff box. Additional cationic starch may be added at the stuff box although not depicted in FIG. 2. The system of FIG. 2 has a second refiner between the machine chest and the stuff box. Other additives, including pH adjustment agents such as alum, may also be added at the stuff box. pH adjusting agents can be added at other points along the flow of pulp or treated pulp through the apparatus.

[0037] The apparatus of the present invention can also include metering devices for providing a suitable concentration of the OBA to the flow of pulp, for example, from about 0.05 to about 2.5 percent by weight OBA, based on the dried solids weight of the pulp. The apparatus can include a metering device for providing a suitable amount of the cationic starch to the flow of pulp, for example, from about 0.05 percent to about 1.5 percent by weight cationic starch, having a degree of substitution preferably greater than 0.045, based on the dried solids weight of the pulp. Other metering or dosing devices are preferably provided for the other additives and ingredients that may be used during the method.

[0038] A cleaner, for example, a centrifugal force cleaning device, can be disposed between, for instance, the fan pump and the screen, according to any of the embodiments of FIGS. 1-2 above.

[0039] The present invention further relates to a method of improving optical brightener performance by practicing one of the embodiments of the methods of the present invention which includes introducing at least one ionically-charged starch, such as cationic starch, and at least one optical brightening agent to a papermaking pulp to form a treated pulp and then forming the treated pulp into paper or paperboard. Preferably, the improved optical brightener performance includes an increase in paper ISO brightness and/or an increase in paper fluorescence intensity. These increases are compared to the same method using the same amount of optical brightening agents compared to the same method using the same amount of optical brightening agents, but without

any charged starch and/or any starch being added prior to the size pressing.

[0040] In the present invention, the present invention provides a method to avoiding the quenching of the optical brightening agent and/or retains the color or brightness achieved by using optical brightening agents.

[0041] The improvement in optical brightener performance can be measured by either paper ISO brightness or paper fluorescence intensity and can be on the order of at least 5% or more, such as 10% or more, or from about 5% to about 25% compared to the same paper being made in the same process with the same OBAs and amounts but without any charged starch being used prior to the size pressing.

[0042] Besides the above-mentioned benefits achieved with the present invention, the present invention can further achieve, as an option, excellent filler retention, such as PCC, TiO₂, clay, and the like. Further, higher ash retention is achieved, and can even be achieved with a decrease in filler amounts used in view of the ability of the present invention to increase the retention rate. Also, with the present invention, it is possible to achieve a reduced amount of sheet defects, such as measured by ULMA defects. Particularly, less dusting, for instance, in the early section of the dryers, can be achieved, holes reduced in all categories can be achieved (e.g., reduction in small holes, reduction in medium holes, reduction in small light spots). Further, with the present invention, increased drainage can be achieved, which allows speed increases and/or steam reduction. Further, with the present invention, the present invention can promote sizing retention and can increase FPR and/or FPAR. Also, the present invention can promote strength, such as improving fiber-to-fiber and fiber-to-filler bonding. Further, with the present invention, fewer breaks and/or improved paper machine runability is achieved. Also, with the present invention, a reduction in linting and dusting can be achieved. Also, with the present invention, a reduction in BOD (biological oxygen demand) and/or COD (chemical oxygen demand) can be achieved. One or more of those improvements can be achieved with the present invention, as compared to when no charged starch is used.

[0043] In one or more embodiments of the present invention, the present invention can improve one or more of the following properties:

- (a) an increase in filler retention compared to no charged starch being present;
- (b) an increase in sheet ash content in the paper compared to when no charged starch is used;
- (c) an increase in drainage compared to when no charged starch is present;
- (d) an increase in sizing retention compared to when no charged starch is present;
- (e) a reduction in breaks compared to when no charged starch is present;
- (f) a reduction in linting and/or dusting compared to when no charged starch is present.

[0044] With respect to one or more of these property improvements, the improvement can be on the order of at least 2%, at least 5% or more, such as 7% or more, 10% or more, 25% or more, 50% or more, 75% or more, 100% or more, such as from 2% to 100%, from 5% to 75%, from 10% to 50%, and any ranges or values within these ranges, wherein the percent improvement is compared to the same paper being made in the same process with the same OBAs and amounts, but without any charged starch being used prior to the size pressing. The particular numerical improvements detailed in the examples can be achieved herein, in general, with respect to other embodiments of the present invention, meaning other OBAs, other charged starches, and/or process conditions.

[0045] The present invention further relates to pulp and paper obtained from the present invention. In particular, the present invention relates to a pulp or pulp slurry containing pulp, one or more optical brightening agents, and at least one cationic charged starch, preferably having a degree of substitution of greater than 0.045. The charged starch can have any degree of substitution described above. The amounts can be the amounts described above. The pulp can further contain other conventional ingredients, such as at least one filler, at least one biocide, at least one microparticle, at least one enzyme, at least one polymer, other starches, or any combinations thereof. Similarly, the present invention relates to a paper or paperboard obtained

from the present invention. In particular, the paper or paperboard can be any type of paper, such as the paper grades mentioned above, and the paper or paperboard contains pressed cellulose fibers, at least charged starch, preferably having a degree of substitution of greater than 0.045, and at least optical brightening agent. The degree of substitution for the charged starch, such as a cationic starch, can have the various degrees of substitution mentioned earlier. As stated, the paper can be fine paper or paper that is coated or non-coated. The paper can be newsprint, specialty newsprint, super calendered, or light-weight coated grades. The paper made from the pulp can be from recycled and/or virgin pulp.

[0046] The present invention will be further clarified by the following examples, which are intended to be exemplary of the present invention.

EXAMPLES

[0047] **Experimental:** The pulp suspension used in this example contained 70% by weight bleached hardwood and 30% by weight bleached softwood with a CSF of 380 mL. Optical brightener used was Tinopal. Both BFL 5521 and BFL 5567 (from Buckman Laboratories International, Inc.) were cationic starches with different charge densities.

[0048] During the handsheet preparation, 15 lb/ton (as received) OBA was first added to the thick pulp stock (consistency 2.2%) followed by the cationic starch. Afterwards, the pulp stock was diluted to 0.4% and the handsheets were prepared by the standard Tappi method T205.

[0049] Figure 3 shows the brightness results of the prepared handsheets. The introduction of OBA increased the paper ISO brightness from 64.0 to 65.2. Upon the addition of 7 lb/ton (as received) cationic starches of BFL 5521 and BFL 5567, the brightness further increased to 65.2 and 66.0 respectively.

[0050] Figure 4 shows the fluorescence image of the prepared paper samples. In this experiment, small paper pieces were cut from the handsheets and taped on the fluorescence lamp. The picture was taken in a dark room using a digital camera. As can be seen, the introduction of

cationic starches increased the fluorescence intensity (samples 3 and 5). In addition, the samples with higher cationic starch dosages (samples 4 and 6) displayed higher fluorescence intensity.

[0051] Thus, cationic starches, such as BFL 5521 and BFL 5567 starch compositions, improved optical brightener performance by increasing both the paper ISO brightness and the paper fluorescence intensity (excited by UV).

[0052] In a further experiment, the effects of the starch based coagulants of the present invention were compared against other coagulants which are conventionally used, namely polyamine and a polyDMDAAC. In this particular experiment, as shown in the table below, the fluorescence and brightness were measured for handsheets made from a pulp having 70% by weight bleached hardwood and 30% by weight bleached softwood. The pulp further had an OBA (Leucophor OBA) present in the amount of 15 pounds per ton of dried pulp, based on a dry solids basis. In one of the samples, no coagulant was present. In two other samples, a cationic starch, pursuant to the present invention, was present in the wet pulp in an amount of 4 pounds per ton of dried pulp based on a dry solids basis. Both of these cationic starches are available from Buckman Laboratories International. The remaining four samples contained a conventional coagulant in the pulp, namely polyamine or polyDMDAAC, in an amount of 2 pounds per ton or 4 pounds per ton of dried pulp based on a dry solids basis.

[0053] As can be seen in the table below, the samples containing the cationic starch with OBA had a significantly higher brightness and a significantly higher fluorescence compared to the control sample, as well as to the samples containing conventional coagulants that further contained an OBA. It is clear that the present invention provides superior brightness and fluorescence properties and that the OBA is not quenched or diminished by the presence of the cationic starches.

1.2gram handsheet
70% Bleached hardwood
30% Bleached softwood

pH=8.0

15 #/ton OBA

<i>Non Gloss Side</i>		<i>Glossy Side</i>		
Minolta Flourescence	Tappi Brightness	Minolta Flourescence	Tappi Brightness	Coagulant
6.22	75.2	6.11	75.1	No coagulant
9.53	78.8	8.12	78.8	4#/t BFL 5521
9.98	80.6	9.4	80	4#/t BFL 5567
5.03	73.1	5.15	73	2#/t Polyamine
5.43	73.8	5.21	73.7	2 #/t PolyDMDAAC
4.43	69.4	4.67	69	4#/t Polyamine
4.55	70.8	4.71	70.2	4 #/t PolyDMDAAC

Example 2

[0054] In an experiment, a five-day experimental trial on a paper machine was conducted to determine the effects of using a cationic starch along with an optical brightener. In particular, BUFLOC 5567 organic coagulant was used. More specifically, BUFLOC 5567 coagulant was introduced into the thin stock stage starting at an amount of 0.5 lb/ton, which was gradually increased to 2 lb/ton, and then increased to 3 lb/ton, and then increased to 4 lb/ton for the remainder of the trial. The dosage was then decreased by 1 lb/ton every reel until the trial was finished.

[0055] From this experiment, it was noticed that the breaks on the machine dropped from an average of 2.4 breaks per day (based on a one month average) to an average of 1.6 breaks per day during the trial. The breaks on the machine is a term understood to those skilled in the art and refers to the paper that is formed on the machine does not break prior to it being rolled up.

[0056] Furthermore, during the experiment, there were no significant impacts on the headbox charge with the addition of BUFLOC 5567 coagulant at any dose. Also, the ULMA holes (purple only) were not impacted significantly during the experiment.

[0057] Furthermore, during the experiment, it was determined that the threading of the size

press was quicker and easier, which may be due to the better fiber-to-fiber bonding or better sizing achieved with the use of the BUFLOC 5567 coagulant.

[0058] Furthermore, during the experiment, retention gains were realized, and even during a five-day trial, retention and distribution of fillers and other functional additives in the paper were achieved. It is believed that a thirty-day experiment would show even greater increases in the retention percentage.

[0059] With respect to the OBA carry-over (optical brightening agent carry-over), the brightness and fluorescence level were not significantly effected through the use of the BUFLOC 5567 coagulant. On 92 bright grade production, the average brightness from one week before and one week following the experiment was 91.8 and the average fluorescence was 2.4. During the experiment, the average brightness was about 91.3 and the fluorescence was about 2.2. More importantly, the optical brightening agent usage significantly dropped and yet, average brightness and average fluorescence were maintained as described above. More specifically, prior to the experiment, the OBA usage was around 750-950 ml/m per side. However, during the experiment with the use of BUFLOC 5567, a significant reduction in OBA was obtainable. Specifically, the OBA used during the experiment was around 450-550 ml/min. to meet optical specifications. This is an overall reduction of approximately 500-700 ml/min. The hardwood level chest based loading remaining constant at about 0.73 pounds per ton. Thus, with the present invention, the amount of OBA can be significantly reduced and yet brightness levels and fluorescence levels maintained at acceptable levels.

[0060] It was also determined at one point, that the pitch control additive could be eliminated with no effects on the overall paper quality.

[0061] Further, there was a significant reduction in dusting when the BUFLOC 5567 coagulant was used.

Example 3

[0062] In this experiment, a forty-five day experimental trial was run on a paper machine to determine the longer term effects of using BUFLOC 5567 coagulant in view of OBA efficiency. Specifically, during a forty-five day period, BUFLOC 5567 coagulant was used in the amount of 2.6 lbs/ton. As stated, an OBA was also present. The following observations were made from the experiment:

- Break time on the machine was reduced by 13 to 17 minutes per day when the 45 days of usage were compared to the 104 days without BUFLOC 5567.
- The draw between the 2nd press and 1st dryer section was reduced by 4 to 5 feet with the added drainage from BUFLOC 5567.
- First pass ash retentions increased a minimum of 11% with the added usage of BUFLOC 5567.
- ULMA Small Holes decreased from 3.8 small holes per 1,000,000 lineal feet to 0.75 small holes per 1,000,000 lineal feet with BUFLOC 5567.
- ULMA Medium Holes decreased from 5.9 medium holes per 1,000,000 lineal feet to 0.4 medium holes per 1,000,000 lineal feet with BUFLOC 5567.
- ULMA Small Light Spots decreased from 210 small light spots per 1,000,000 lineal feet to 40 small light spots per 1,000,000 lineal feet with BUFLOC 5567.

Break Time Data

	Without BUFLOC 5567	With BUFLOC 5567	Difference
Days	104	45	
Total Minutes	149,760	64,800	
Total Break Time Minutes	5753	1703	
Break Time, %	3.841%	2.628%	1.213%

Break Location Data

	Wet End Breaks per Day	Size Press Breaks per Day	Reel Breaks per Day	Total Breaks per Day
104 Days without BUFLOC 5567	0.26	1.34	0.27	1.87
45 Days with BUFLOC 5567	0.20	1.00	0.18	1.38
Break Difference per Day	0.06	0.34	0.09	0.49
Avg Minutes per Break per Location	43.66	28.93	11.89	28.67
Total Minutes Saved per Day	2.60	9.74	1.09	13.43

[0063] During the course of the evaluations performed with BUFLOC 5567, as it was introduced to the system, the couch vacuum would decrease and the size press moisture would decrease until the 6th section steam control brought it back to target. As the evaluations took place, the draw between the 2nd press and 1st dryer section was reduced with this added drainage. At equal refiner loadings, press loadings, filler loadings and equivalent couch vacuum, the draw was reduced by 4 to 5 feet with 2.6 lbs./T of BUFLOC 5567. The Couch Vacuum decreased from 17.78" to 17.25" with the introduction of BUFLOC 5567. The Size Press Moisture decreased from 3.0% to 2.8% until effect of 6th sxn steam controller. The 6th section steam pressure dropped from 59.5 psig to 52.5 psig.

[0064] The effect of BUFLOC 5567 on retentions is more pronounced with first pass ash retentions (FPAR) in comparison to overall retentions. The introduction of BUFLOC 5567 during the trials indicated an overall increase in first pass retention (FPR) of 2% to 5%. An 11% to 20% increase in FPAR was observed with the introduction of BUFLOC 5567.

[0065] Evaluation on 92 BCP (brightness copy paper) APAM (1.15 lbs./T, Microparticle (1.35 lbs./T) and Filler Usage (16%) at 2.850 lbs./T of BUFLOC 5567, FPR increased 7% and FPAR increased 22%.

[0066] BUFLOC 5567 usage of 3.0 lbs./T, APAM (0.7 lbs./T, Microparticle (1.0 lbs./T) and Filler Usage Constant (15%), 2-4% increase in FPR and 11-13% increase in FPAR.

[0067] During the introduction of BUFLOC 5567 to the fan pump suction, there was

evidence from the filler and weight reading that indicated BUFLOC 5567 was having an effect on fines and filler retention. Each time it was introduced, the filler reading and weight would increase until their respective controllers brought everything back to target. The following is a summary of the filler trends. An ABB scanner was used for measurements.

[0068] During the use of BUFLOC 5567, ULMA defects were reduced. The improvements in ash retentions as stated above should lead to a reduction in defects. Also, as noted during the evaluations, a reduction in dusting was observed in the early main section dryers. This would also lead to reduction in ULMA defects. The following is a summary of the historical data reviewed:

- ULMA Small Holes decreased from 3.8 small holes per 1,000,000 lineal feet to 0.75 small holes per 1,000,000 lineal feet with BUFLOC 5567.
- ULMA Medium Holes decreased from 5.9 medium holes per 1,000,000 lineal feet to 0.4 medium holes per 1,000,000 lineal feet with BUFLOC 5567.
- ULMA Small Light Spots decreased from 210 small light spots per 1,000,000 lineal feet to 40 small light spots per 1,000,000 lineal feet.
- The only negative trend occurred with ULMA Large Dark Spots. It is unclear as to why this occurred with all the positive results observed in the other defect categories. ULMA Large Dark Spots increased from 19 to 44 dark spots per 1,000,000 lineal feet.

[0069] During the initial evaluation of BUFLOC 5567, a 7.2% increase in fluorescence was observed at the same OBA usage. This indicated that BUFLOC 5567 was helping retain the OBA. The OBA usage decreased from 163 oz./T to 149 oz./T on 92 BCP to reach target fluorescence.

Example 4

[0070] In an additional experiment, the effects of the present invention were studied in a

whitewater system containing an OBA. Prior to the introduction of the BUFLOC 5567 coagulant, the base line for the paper having a brightness of 92, was a fluorescence of 2.5, and the base line for the paper having a brightness of 96, was a fluorescence of 6.0.

[0071] When the BUFLOC 5567 coagulant was introduced at a rate of 1.5 kg/t, the fluorescence averaged 3.2 for the 92 brightness grade paper, and when BUFLOC 5567 coagulant was introduced at a rate of 2.0 kg/t, the fluorescence averaged 2.6 for the paper having a brightness of 92. In this study, the BUFLOC 5567 was introduced on the suction side of the screens.

[0072] Also, with respect to the paper having a brightness of 96, OBA consumption was reduced to achieve comparable brightness. In particular, historically, the amount of OBA was 3700-4300 ml/min per side. During the use of BUFLOC 5567 coagulant, at a rate of 1.5 kg/t, the OBA averaged an amount of 2400 ml/min per side, which was an average of a 40 percent reduction in OBA consumption with no major swing in the brightness of the paper.

[0073] In addition, dusting studies were made based on no BUFLOC 5567 coagulant being present compared to BUFLOC 5567 coagulant at a dosage rate of 1.5 kg/t and a dosage rate of 2.0 kg/t. The following table provides the results.

	Dusting Measurement (doses per carton)
Base line	12.53
BUFLOC 5567 (1.5 kg/t)	12.09
BUFLOC 5567 (2.0 kg/t)	8.87

[0074] From these results, it can clearly be seen that the charged starch coagulant can be used in all grades of paper to improve brightness and fluorescence efficiency, as well as improve retention, drainage, de-watering, and/or formation. Further, as shown in the studies, the use of charged starch coagulant significantly improved the retention and distribution of fillers and other functional additives while reducing dusting, linting, sheet defects, and/or holes, and allows

superior paper machine runability and sheet quality.

[0075] Applicants specifically incorporate the entire contents of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0076] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

WHAT IS CLAIMED IS:

1. A method of making paper or paperboard comprising introducing
 - a) at least one charged starch, having a degree of substitution greater than 0.045, and
 - b) at least one optical brightening agent, in any order, and at the same time or at a different time, to a papermaking pulp to form a treated pulp and then forming the treated pulp into paper or paperboard.
2. The method of claim 1, wherein said charged starch is a cationic starch.
3. The method of claim 1, wherein said charged starch is a blend of two or more charged starches.
4. The method of claim 1, wherein at least two charged starches are introduced.
5. The method of claim 1, wherein said optical brightening agent is a stilbene compound or a distyrylbiphenyl compound.
6. The method of claim 1, wherein the optical brightening agent is a dyestuff.
7. The method of claim 1, wherein said charged starch has a degree of substitution of from about 0.01 to about 0.5.
8. The method of claim 1, wherein said charged starch has a degree of substitution of from about 0.15 to about 0.42
9. The method of claim 1, wherein said charged starch has a degree of substitution of from about 0.12 to about 0.3.
10. The method of claim 1, wherein said method forms fine paper or coated or non-coated free-sheet, newsprint, specialty newsprint, supercalendared, or light weight coated grades of paper.
11. The method of claim 1, wherein at least one charged starch and said at least one optical brightening agent are introduced at or prior to said pulp entering a blend chest.
12. The method of claim 1, wherein said at least one charged starch and said at least one optical brightening agent are added at or prior to said pulp entering a machine chest.

13. The method of claim 1, wherein said least one charged starch and said at least one optical brightening agent are introduced prior to a size press.

14. The method of claim 1, wherein said charged starch is added in an amount of from about 1 to about 20 pounds per ton of dried pulp.

15. The method of claim 1, wherein said charged starch is added in an amount of from about 0.25 to about 5 pounds per ton of dried pulp.

16. A method of improving optical brightener performance comprising introducing

a) at least one charged starch, and

b) at least one optical brightening agent, in any order, at the same time, or at a different time, to a papermaking pulp to form a treated pulp and then forming the treated pulp into paper or paperboard.

17. The method of claim 16, wherein improving said optical brightener performance includes an increase in paper ISO brightness compared to the same method but with no charged starch being added prior to any size press.

18. The method of claim 16, wherein said optical brightener performance includes an increase in paper fluorescence intensity as compared to the same method being practiced, but with no charged starch being added prior to any size press.

19. The paper or paperboard obtained from the method of claim 1.

20. A pulp composition comprising pulp, at least one charged starch having a degree of substitution of greater than 0.045 and at least one optical brightening agent.

21. The pulp composition of claim 20, wherein said charged starch is a cationic starch and has a degree of substitution of greater than 0.045 to about 0.5.

22. The method of claim 16, wherein at least one of the following properties is improved:

(a) an increase in filler retention compared to no charged starch being present;

(b) an increase in sheet ash content in the paper compared to when no charged

starch is used;

- (c) an increase in drainage compared to when no charged starch is present;
- (d) an increase in sizing retention compared to when no charged starch is present;
- (e) a reduction in breaks compared to when no charged starch is present;
- (f) a reduction in linting and/or dusting compared to when no charged starch is

present.