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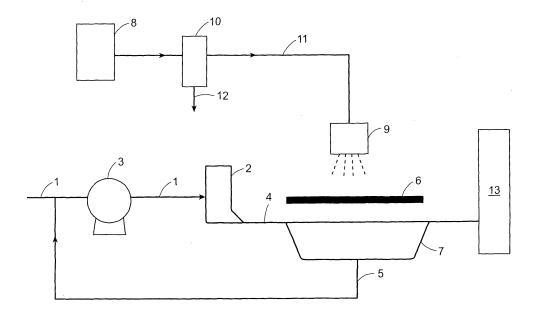
# (54) Multi-function starch compositions

- (57) A method of applying heat sensitive papermaking additives to paper during a papermaking process comprises the steps of:
  - a) providing a dry mix comprising an uncooked starch component and one or more heat sensitive papermaking additives;
  - b) adding the dry mix to water to form a slurry without

cooking the starch;

- c) providing a paper mat having a top surface and a bottom surface:
- d) applying the slurry to the top surface of the paper mat and allowing at least some of the slurry to permeate to the bottom surface of the paper mat; and e) heating the paper mat after applying the slurry to cook some or all of the starch.

FIG. 1



## **Description**

#### **BACKGROUND OF THE INVENTION**

## 5 Field of the Invention

**[0001]** The invention relates compositions comprising a starch component and papermaking additives, particularly heat sensitive papermaking additives. The invention further relates to the application of the compositions to a paper mat at the wet end of the papermaking process, a method for applying the composition to the paper mat by spraying and a process for making the composition.

## The Related Art

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**[0002]** Additives are generally used in making paper and board to provide desired properties to the paper and board. In some papermaking processes the additives are applied to the paper or board with cooked starch. This is particularly the case with additives having small particle sizes. The use of cooked starch and additives provides a colloidal suspension which facilitates uniform distribution of the additive in the paper product.

**[0003]** Colloidal suspensions of cooked starch and additive can be used in the paper pulp or for a coating. U.S. Patent No. 4,264,325 describes an example wherein an optical brightening agent is worked into a colloidal solution of cooked starch and water which is used as size liquor and coated onto paper prior to drying.

**[0004]** Certain papermaking additives, however, are sensitive to heat. These heat sensitive papermaking additives will lose some or all of their effectiveness and/or function when heated at elevated temperatures. When the papermaker desires to use a colloidal suspension of cooked starch and heat sensitive papermaking additives, the papermaker must cook the starch prior to incorporating the heat sensitive additive in the colloidal suspension to avoid losing effectiveness and/or function of the additive. This requires the papermaker to operate and maintain equipment to cook starch as part of the papermaking process.

**[0005]** A composition comprising uncooked starch and heat sensitive papermaking additives which can be applied to paper within the papermaking process without prior cooking of the starch, yet provide the benefits of the use of a colloidal suspension of cooked starch and heat sensitive papermaking additive, would be desired in the art. A method for applying the uncooked starch and heat sensitive papermaking additives that provides the benefits of application of cooked starch and heat sensitive papermaking additive without prior cooking of the starch would also be desired.

**[0006]** In the present Specification, all parts and percentages are on a weight-by-weight basis unless otherwise specified. "By weight based on the uncooked starch component" means the total amount of a particular component of the composition per the total amount of uncooked starch in the composition.

## **SUMMARY OF THE INVENTION**

**[0007]** The invention pertains to a composition comprising an uncooked starch component and papermaking additive, particularly a heat sensitive papermaking additive. The uncooked starch component and heat sensitive papermaking additive are dry blended. When used in the papermaking process, the composition is slurried with water and applied to the paper without cooking the starch component. After application, the paper may be heated which will cook the starch component; however, we have found that the heat sensitive papermaking additive is not adversely affected (e.g., does not lose significant, if any, effectiveness and/or functionality) by heating with the uncooked starch in the papermaking process, e.g., after being applied to the paper mat.

[0008] The invention further relates to a method for applying the composition comprising the uncooked starch component and the heat sensitive papermaking additive to the paper after the paper mat is formed. The uncooked starch component and papermaking additive can be sprayed onto the paper mat after the mat exits the head box. This type of spray method is described with respect to the application of starch and fiber mixtures in the co-pending application owned by the assignee, U.S. Patent Application Ser. No. 10/712,699, filed November 12, 2003 entitled "STARCH AND FIBER MIXTURE FOR PAPERMAKING AND METHODS OF MAKING PAPER WITH THE MIXTURE", which is incorporated by reference herein in its entirety.

### **DESCRIPTION OF THE DRAWINGS**

**[0009]** Fig. 1 is a flow chart showing a papermaking process comprising the application of the uncooked starch and heat sensitive papermaking additive to a paper mat.

**[0010]** Fig. 2 is a graph showing brightness gained from an optical brightening agent (y-axis) vs. amount of optical brightening agent in a handsheet (x-axis) where uncooked pearl starch and optical brightening agent are sprayed onto

the surface of a paper mat.

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#### **DETAILED DESCRIPTION OF THE INVENTION**

**[0011]** The composition comprising the uncooked starch component and heat sensitive papermaking additive composition comprises from about 90% to less than 100%, by weight, of an uncooked starch component and between more than zero to no more than about 10%, by weight, of a heat sensitive papermaking additive. When combined with water in the form of a slurry, the slurried composition comprises from about 0.01% to about 20%, by weight, uncooked starch component and about 0.01% to about 10%, by weight of the uncooked starch component, of one or more heat sensitive papermaking additives. The slurried composition may comprise about 8% to about 12%, by weight, uncooked starch component and about 0.1 % to about 5%, by weight of the uncooked starch component, of one or more heat sensitive papermaking additives. The dry mix and slurried composition may also comprise other papermaking additives that are not considered to be heat sensitive papermaking additives. The dry mix may consist essentially of or consist of uncooked starch and heat sensitive papermaking additives.

**[0012]** Both natural unmodified starch and modified starch can be used for the uncooked starch component in the composition, each providing equal or about equal performance. Modified starches may also be used as a dry strength agent in the heat sensitive papermaking additive component of the invention. Any starch appropriate for use in papermaking may be used and dextrin, as well as combinations of starch types, dextrin types and combinations of starches and dextrins. Also, maltodextrins and other forms of carbohydrates can be used as the starch component. The uncooked starch component comprises material selected from the group consisting of unmodified starch, modified starch, dextrin, maltodextrin and combinations thereof.

**[0013]** Unmodified starch is a commodity chemical produced from the root, stem or fruit from a number of plants. It is a high molecular weight carbohydrate polymer which is comprised of linear and branched polysaccharide polymers and it can have moisture content from about 8% to about 20%, most commonly from about 11 % to about 13%. Starches such as those derived from corn, wheat, barley, tapioca, rice, potato and/or other suitable plant source, and the like can be used, as well as hybrids. Blends of starches from various sources also can be used. Pearl starches and powdered starches may be used.

[0014] Modified starch can be mechanically, chemically or heat modified. Modified starches have different properties than unmodified starch, including differences in solubility, film forming, whiteness, gel strength, viscosity stability, adhesivity, resistance to shear and resistance to freeze-thaw degradation. Starches derived from other genetic forms of corn, such as high amylose and waxy corn, as well as sorghum varieties, would also be suitable. Chemically modified starches useful in the invention include modified oxidized starch such as hypochlorite-oxidized starch, acid thinned starches, cross-bonded starch, etherified starches, esterified-starches and others which have reduced molecular weight, high fluidity and/or functional sub groups. Examples of chemically modified starches which can be used in the invention and are commercially available are SUREBOND® Industrial Corn Starch or STABLEBOND® Industrial Corn Starch available from Corn Products International, Inc., Westchester, Illinois, USA ("Corn Products"). FOXHEAD® Cationic Starches available from Corn Products and Corn Products' oxidized starch may also be used in the invention.

[0015] The heat sensitive papermaking additive may be selected from the group consisting of optical brightening agents, fluorescent agents, dry strength agents, filler particles, sizing agents, flame retardants, pigments and combinations thereof. Optical brightening agents that may be used in the invention include BLANKOPHOR® UW liquid and other BLANKOPHOR® optical brightening agents, available from Bayer Chemicals, Pittsburgh, Pennsylvania, USA and optical brightening agents from Clariant Corporation, Charlotte, North Carolina, USA available under the trade name LEUCO-PHOR®. Sizing agents useful in the invention include BASOPLAST® available from BASF Corporation, Mount Olive, New Jersey, USA. Useful flame retardants include SAFE-T-GUARD® available from FireTech Co., Canyon Country, California, USA, and useful dry strength agents include the FOXHEAD® modified starches from Corn Products. Pigments include conventional pigments as well as pigment types such as solid sphere plastic pigments and hollow sphere plastic pigments, which are commercially available, such as hollow sphere pigments from Dow Chemical, Midland, Michigan, USA.

[0016] The dry mix composition comprising starch and heat sensitive papermaking additive may be made by dry blending the uncooked starch component and heat sensitive papermaking additive. In one method for making the dry mix, the heat sensitive papermaking additive, and other optional additives, is added in liquid form into a pneumatic conveyance line. The liquid droplets are atomized as they enter the conveyance line for drying. The starch is blown into the pneumatic conveyance line and comes into contact with the heat sensitive ingredient after the heat sensitive ingredient, and other optional additives, is atomized in order to dry blend the components. The flow rate of the starch in the pneumatic conveyance line will determine the rate of addition of heat sensitive papermaking additive in the pneumatic conveyance line. In an embodiment of the invention, the air pressure in the pneumatic line is about 60 psi (about 4.2 kg/cm²) to about 100 psi (about 7.1 kg/cm²).

[0017] The composition is made up for use at the papermaking facility by adding the uncooked starch component and

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heat sensitive papermaking additive composition to water to form a slurry. The slurry is made by conventional means that would be understood by one skilled in the art. Generally, the slurry is made by adding the composition to water so that a homogenous slurry is obtained. The uncooked starch component and heat sensitive papermaking additives are mixed with water in sufficient quantities and for sufficient time to thoroughly wet out the starch. The dry mix of uncooked starch component and heat sensitive papermaking additive is mixed with water in any type of mixing apparatus at a temperature, such as ambient temperature, so that the starch is not cooked during the slurrying process.

**[0018]** The slurry comprising the uncooked starch component and heat sensitive papermaking additive can be applied as a coating to the paper by conventional means. The slurry can be applied to a surface of a paper mat, having a top surface and a bottom surface, during the papermaking process. For example, the uncooked starch component and heat sensitive papermaking additive slurry can be applied with spraying systems, as well as with spray bars, curtain coaters, blade coaters, rod coaters, air knife coaters, roll coaters, size presses, and the like.

[0019] In an embodiment of the invention, the slurry of the uncooked starch component and heat sensitive papermaking additive is sprayed onto a surface of the paper mat at the wet end of the papermaking process, such as prior to the nip of the press section. A papermaking process comprising means for applying the uncooked starch component and heat sensitive papermaking additive using spraying is shown in Fig. 1. A pulp and process water stream 1 is sent to a head box 2 by a first means for circulation 3 such as a pump, and the head box 2 deposits the pulp and process water onto the wire screen 4 where the paper web or mat 6, having a top surface 6a and bottom surface 6b, is formed. The pulp and process water is filtered through the mat forming the white water 5 which is collected in a tray 7 and recycled through the system with or without further processing.

[0020] Referring again to Fig. 1, the slurry of the uncooked starch component and heat sensitive papermaking additive is made up in a mixer 8 and sent to a means 9 for applying the slurry of the uncooked starch component and heat sensitive papermaking additive to the paper mat 6, such as a surface of the paper mat like the top surface 6a. A spray bar or spray nozzle may be used as the means 9. As shown in Fig. 1, the slurry may be sent through a means for separation 10, such as a filter or pressure screen to remove any large particles, e.g., starch contaminants. Filters available from RPA Process Technologies USA, Portage, Michigan, USA may be used. The filter must be properly sealed to prevent pressure drop, particularly during the cleaning cycle, to provide continuous flow to the means 9 for applying the slurry of the uncooked starch component and heat sensitive papermaking additive to the paper mats. The accepts 11 from the means for separation 10 are sent to the means 9 for applying the uncooked starch component and heat sensitive papermaking additive slurry and the rejects 12 are discarded. The uncooked starch component and heat sensitive papermaking additive slurry is applied to the paper mat 6 after the mat is formed on the wire screen but before the paper mat is further processed (shown graphically as block 13 in Fig.1) such as by drying and pressing, like prior to the nip of the press section.

**[0021]** During the application method, the uncooked starch component and heat sensitive papermaking additives permeate through the paper mat (e.g., move through the paper mat from the top surface to the bottom surface) such that at least some of the slurry permeates to the bottom surface of the paper mat. In this manner, the uncooked starch and heat sensitive papermaking additive becomes absorbed in the paper mat. The uncooked starch component prevents the heat sensitive papermaking additive from completely running through the paper mat. The uncooked starch component also uniformly, or substantially uniformly, distributes the heat sensitive papermaking additive within the paper mat and, thus within the finished paper product at the end of the papermaking process.

[0022] During the process for drying the paper mat, the starch component is cooked and gelatinizes, however, because the drying process does not provide as much direct heat to the heat sensitive papermaking additive as would occur if the combination of the uncooked starch component and heat sensitive papermaking additive were directly heated to cook the starch, the heat sensitive papermaking additive ingredient is not negatively affected during the heating process and does not loose any or significant effectiveness and/or function. The papermaker achieves the benefits of the combination of a cooked starch component and a papermaking additive without the need to separately cook the starch before adding a heat sensitive papermaking additive. The papermaker does not need to maintain equipment for cooking the starch and can eliminate a separate starch cooking step in the papermaking process.

# **EXAMPLE 1**

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**[0023]** Handsheets of paper were made from 100% softwood fibers that were refined in a valley beater (lab/pilot scale) from Voith Sulzer, Appleton, Wisconsin, USA to about 400 Canadian Standard Freeness ("CSF"). The brightness of the handsheets, without application of an uncooked starch component and optical brightening agent composition, was determined to be 75.6 using a Micro S5 brightness/opacity/color meter from Technidyne Corporation, New Albany, Indiana, USA using the testing procedures described in the operations manual for the Micro S5 meter.

**[0024]** A 15% starch slurry was dosed with 5 grams optical brightening agent (BLANKOPHOR® UW liquid from Bayer Chemicals) per 1000 grams of starch (3005 Pearl Starch from Corn Products). This slurry was thoroughly mixed and applied to handsheets (made as described above) using a VEEJET® 8006 spray nozzle from Spraying Systems Co.,

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Wheaton, Illinois, USA at 275.78 kilopascal (40 psi). The spray nozzle was swept back and forth across the handsheets (making 2 passes in about 1 second) as soon as the level of the water dropped below the forming screen of the handsheet mould. Two sheets of blotter paper and a roll were then used to press the handsheets. The outer sheet of the blotter paper was then discarded. The handsheet and remaining blotter paper were then placed in the press felt and run through the roll press. The felt and blotter paper were removed and the handsheet alone was run through the roll press a final time. The handsheets were twice run through the roll dryer at 115.56°C (240°F) to cook the starch and dry the handsheet. [0025] A 15% starch slurry was dosed with 10 grams of optical brightening agent (BLANKOPHOR® UW liquid from Bayer Chemicals) per 1,000 grams of starch (3005 Pearl Starch from Corn Products). This slurry was applied to a handsheet and the handsheet was finished and dried in accordance with the procedure discussed above with respect to the 5 gram dose.

**[0026]** The handsheets having the 5 gram and 10 gram dosages of optical brightening agent were allowed to condition for a minimum of 24 hours, and were then tested for brightness using the testing procedures described in the operations manual for the Micro S5 meter from Technidyne Corporation. Results for brightness are set forth in Table 1. Figure 2 provides a graph of the brightness gained in the handsheet as a result of the addition of optical brightening agent, based on the average brightness of 75.6 for sheets made from the same pulp as those in the example, but without having the uncooked starch and optical brightening agent slurry sprayed on the sheet.

Table 1

| Brightness  | Optical Brightening Agent (5 grams) | Optical Brightening Agent (10 grams) |  |  |  |  |
|-------------|-------------------------------------|--------------------------------------|--|--|--|--|
| UV included | 80.44                               | 82.58                                |  |  |  |  |
| UV excluded | 76.37                               | 76.21                                |  |  |  |  |
| FL comp     | 4.08                                | 6.38                                 |  |  |  |  |

[0027] In Table 1, "UV (ultra Violet) included" is the brightness of the paper when exposed to a light source that contains a fluorescent component. "UV excluded" is the brightness of the sample when exposed to a light source that has no UV radiation. "FL Comp" is the amount of brightness added by the inclusion of UV light to the sheet (the difference between UV Included and UV Excluded).

## Claims

- A method of applying heat sensitive papermaking additives to paper during a papermaking process comprising the steps of
  - a) providing a dry mix comprising an uncooked starch component and one or more heat sensitive papermaking additives;
  - b) adding the dry mix to water to form a slurry without cooking the starch;
  - c) providing a paper mat having a top surface and a bottom surface;
  - d) applying the slurry to the top surface of the paper mat and allowing at least some of the slurry to permeate to the bottom surface of the paper mat; and
  - e) heating the paper mat after applying the slurry to cook some or all of the starch.
- 2. The method of Claim 1 wherein the slurry comprises the uncooked starch component in an amount of from about 0.1 % to about 20%, by weight, and about 0.01 % to about 10%, by weight of the uncooked starch component, of the heat sensitive papermaking additives.
- 3. The method of Claim 1 or Claim 2 wherein the heat sensitive papermaking additives are selected from the group consisting of optical brightening agents, fluorescent agents, dry strength agents, filler particles, sizing agents, flame retardants, pigments and combinations thereof.
  - **4.** The method of any one of Claims 1 to 3 wherein the uncooked starch component is selected from the group consisting of unmodified starch, modified starch, dextrin, maltodextrin and combinations thereof.
  - **5.** The method of Claim 4 wherein the unmodified starch or modified starch are derived from a source selected from the group consisting of corn, wheat, barley, tapioca, rice, potato and combinations thereof.

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- 6. The method of Claim 4 wherein the unmodified starch or modified starch is pearl starch.
- 7. The method of any one of Claims 1 to 6 wherein the slurry is applied to the paper mat by spraying the slurry onto the top surface of the paper mat with a spray bar.
- **8.** The method of any one of Claims 1 to 6 wherein the slurry is applied to the paper mat by spraying the slurry onto the top surface of the paper mat with a spray nozzle.
- 9. The method of any one of Claims 1 to 6 wherein the slurry is applied to the paper mat by means selected from the group consisting of curtain coaters, blade coaters, rod coaters, air. knife coaters, roll coaters and size presses.
  - **10.** The method of any one of Claims 1 to 9 wherein the paper mat is formed by sending pulp and process water to a head box, having the process water deposited from the head box onto a wire screen and removing the paper mat from the wire screen.
  - **11.** The method of Claim 10 wherein the slurry is applied to the paper mat after the paper mat is removed from the wire screen.
  - **12.** A process for making paper comprising the method of any one of Claims 1 to 9.
  - **13.** A process for making paper comprising the method of Claim 10 or Claim 11.
  - 14. Paper made by or obtainable by the process of Claim 12 or Claim 13.

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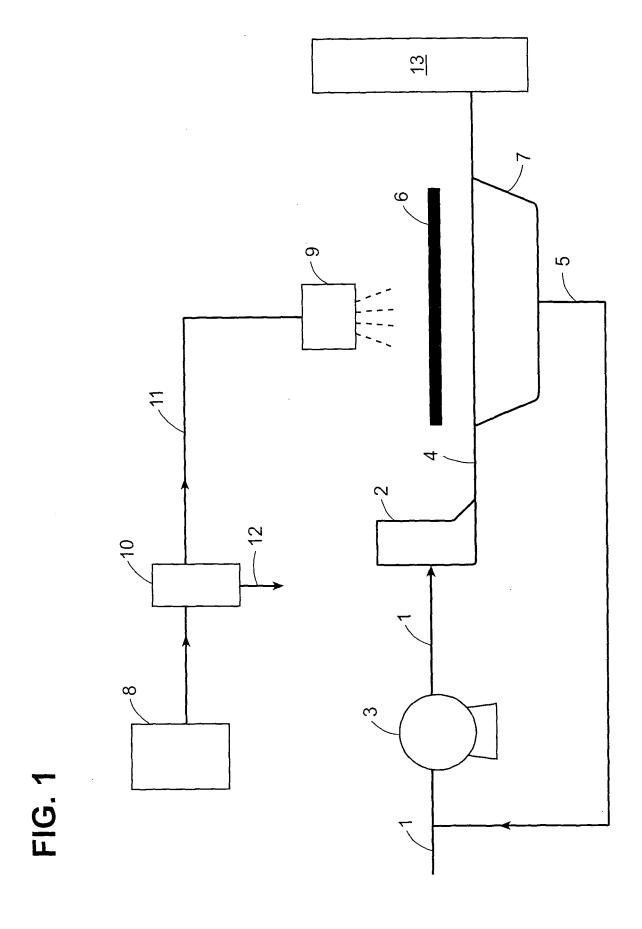
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- 25 **15.** A dry mix composition that can be applied to a paper mat in the form of a slurry for distribution of one or more heat sensitive papermaking additives within the paper mat comprising from about 90% to less than 100% of an uncooked starch component and between more than zero to no more than about 10% of a heat sensitive papermaking additive.
- 16. The composition of Claim 15 wherein the heat sensitive papermaking additives are selected from the group consisting of optical brightening agents, fluorescent agents, dry strength agents, filler particles, sizing agents, flame retardants, pigments and combinations thereof.
  - **17.** The composition of Claim 15 wherein the uncooked starch component is selected from the group consisting of unmodified starch, modified starch, dextrin, maltodextrin and combinations thereof.
  - **18.** The composition of Claim 17 wherein the unmodified starch or modified starch are derived from a source selected from the group consisting of corn, wheat, barley, tapioca, rice, potato and combinations thereof.
  - 19. A paper mat comprising a slurry of the dry mix composition of any one of Claims 15 to 18 and water.
  - 20. A process for making a dry mix composition comprising the steps of blowing starch into a pneumatic conveyance line having an air pressure of about 60 psi to about 100 psi and adding heat sensitive papermaking additive and optional additive in liquid form into the pneumatic conveyance line wherein the heat sensitive papermaking additive and optional additive are atomizied as the heat sensitive papermaking additive and optional additive enter the conveyance line.



0.5

0,4

OBA % in handsheet

FIG. 2

Brightness gained from 3

Color 1

Color 2

Color 2

Color 3

Color 3

Color 3

Color 3

Color 3

Color 3

Color 4

Color 4

Color 4

Color 5

Color 4

Color 5

Color 6

Color 6

Color 7

Color

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Application Number EP 05 25 4229

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FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82