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(54) Title: HIGH STRENGTH PAPERBOARD AND METHOD OF MAKING SAME

(57) Abstract: A method of making high strength paper or paperboard is provided, comprising the steps of adding a high modulus filler to the aqueous pulp slurry prior and forming the pulp slurry into paper or paperboard. Preferably, the filler is glass fiber that has been coated with a thermosetting resin.



WO 2006/020089 A2

TITLE

HIGH STRENGTH PAPERBOARD AND METHOD OF MAKING SAME

BACKGROUND5 Field Of The Invention

 This patent relates to a high strength paperboard and a method of making the same by adding a high modulus filler and/or resin to the pulp slurry prior to forming the paperboard.

10 Description Of The Related Art

 Paper and paperboard generally are manufactured by preparing an aqueous pulp slurry; depositing a layer of the pulp slurry onto a moving screen or "wire"; draining water through the screen and away from the pulp stock, leaving a wet, weak fiber mat; and pressing and drying the mat to form sheets ready for finishing and cutting.

 During the pulping step, various ingredients may be added to affect the properties of the paper, including fillers such as titanium oxide and calcium carbonate for improving the optical properties of the paper. A number of references teach adding polymeric or resinous materials to pulp stock to enhance wet and/or dry strength. However, the inventors are aware of no reference that teaches adding high modulus fillers to pulp stock to enhance the dry strength of paper or paperboard.

 Daniel, Jr. U.S. Patent No. 2,601,598 teaches a method of making a formed cellulosic product, such as paper and paperboard, including the step of adding an

impregnating agent to the pulp-water slurry. A wide variety of impregnating agents are disclosed, including a number of thermoplastic resins. Thermoplastic phenol-formaldehyde resins are disclosed.

5 Rushmere U.S. Patent No. 4,798,653 teaches a papermaking stock comprising a two component combination of a colloidal silica sol compound and an anionic polyacrylamide. Together these two components increase the fines retention capability, and thus the resistance
10 to shear forces, during the papermaking process. Rushmere also teaches that clays, calcium carbonate, titanium oxide and/or recycled broke or other cellulosic waste may be added, but doesn't teach that they increase dry strength.

15 Degen et al. U. S. Patent No. 4,818,341 teaches a process for producing paper and paperboard of high dry strength. The dry strength enhancer is a mixture of a cationic polymer (a polymer having a positive charge) which contains as characteristic monomers copolymerized
20 units of diallyldimethylammonium chloride, N-vinylamine or an N-vinylimidazoline.

 Kokko et al. U.S. Patent No. 6,222,006 teaches a thermosettable wet strength resin comprising a type of polyaminamide-epichlorohydrin (PAE) resin.

25 Sears et al. U.S. Patent No. 6,270,883 teaches a composite containing cellulosic pulp fibers dispersed in a polymeric matrix for use as a plastic substitute.

 McCall et al. U.S. Patent No. 6,322,667 teaches

paper and paperboard that have improved mechanical properties due to their being treated with superheated steam during the drying step. McCall teaches using clay filler for improved optical properties, but notes that

5 "[a]dding fillers to paper has a detrimental effect on the strength properties."

Hjalmarson et al. U.S. Patent No. 6,391,156 teaches a process for making paper or paperboard including the step of using clay as a flocculating agent (to help

10 aggregate the cellulosic solids into clumps). Hjalmarson does not teach adding clay to pulp stock as a strengthening agent.

Pfohl et al. European Patent Publication No. 0146000 B1 teaches a process for making high dry strength paper including the step of adding an aqueous polymer solution

15 to the paper stock.

Hamaguchi et al. Japanese Patent Document No. 10025693 teaches using polyamidopolyamine-epihalohydrin resin as a wet paper strengthening agent.

Covarrubias International Application No. WO 0188267 teaches a method of making paper and paperboard including the step of adding fibrous cationic alumina microparticles and a polymer to the pulp to form a treated pulp having improved retention properties.

20 Secondary microparticles such as natural or synthetic hectorite, bentonite and zeolite can also be added. Covarrubias also teaches the use of calcium carbonate as a "filler", although its function is not stated.

25

Although the reference alludes to a need for "improved strength characteristics", nowhere in the document does Covarrubias teach that adding fibrous cationic microparticles to the pulp actually increases dry strength of paper or paperboard.

The primer Dry Strength Additives, published by Tappi Press (ed. Walter Reynolds, 1980), describes many wet and dry strength additives for paper and paperboard manufacture. Most commercial dry strength additives are hydrophilic water-soluble polymers added internally to the aqueous pulp slurry. The book divides dry strength agents into three categories: natural gums, natural and modified starches, and synthetic polymers.

The first synthetic polymer specifically designed for dry strength without imparting wet strength was an acrylamide based anionic (negative charged) polymer (polyacrylamide resin) introduced in 1955. Other synthetic polymers used as dry strength additives include carboxymethyl cellulose (CMC), "melamine-formaldehyde" (MF), urea-formaldehyde (UF) and DAS.

Although adding dry and wet strength agents to paper and paperboard is well known, it has been heretofore unknown to add high modulus fillers either alone or coated with resin to the pulp slurry prior to forming the paperboard to obtain a high strength paperboard.

Thus it is an object of the present invention to enhance the modulus and strength of paperboard by adding a high modulus filler or a filler coated with resin to

the pulp slurry prior to forming the paperboard.

Another object of the invention is to provide a high strength paperboard for use in composite containers that can replace metal cans.

5 A further object of the invention is to provide a high strength paperboard that can be used in the manufacture of containers for holding foodstuffs such as ground coffee.

10 Further and additional objects will appear from the description, accompanying drawings, and appended claims.

SUMMARY OF THE INVENTION

The present invention is a high strength paperboard and method of making same. In a first embodiment of the invention, a high modulus filler ($E_f > 0.1$ GPa and preferably $E_f > 3$ GPa) is added to the aqueous pulp slurry prior to forming the modified pulp slurry into paper or paperboard. The addition of the high modulus filler increases the strength or modulus of the resulting paperboard.

In another aspect of the invention, a high modulus filler and a resin having a high glass transition temperature are added to the aqueous pulp slurry before the forming step. The resin promotes adhesion between the paper fibers and the high modulus filler to improve load transfer. In the preferred embodiment of the invention, glass fibers are coated with a hydrophilic resin and the coated filler is added to the aqueous pulp slurry. This may be accomplished by using a secondary reactor/mixer in which the high modulus filler is mixed and/or agitated with the resin matrix. The mixing/agitation enables the resin to wet or chemically react with the surface of the glass fibers, thus rendering the surface of the filler hydrophilic. The hydrophilic surface of the filler facilitates even distribution of the filler throughout the aqueous pulp slurry and improves the adhesion of the glass fibers to the paper fibers. After the coating step, the coated fibers are added to the aqueous pulp slurry.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

In the description that follows, a number of terms are used. In order to provide a clear and consistent understanding of the specification and claims, the following definitions are provided:

Aspect ratio: As used in paperboard making, the ratio of the length of the major axis (length) to the minor axis (diameter) of a fiber or other cylindrical filler.

Dry strength: The ability of a material to resist bursting stresses in its dry state.

Electrical glass (a.k.a. E-glass): The most commonly used and most economical glass fiber.

Structural or S-type glass has slightly higher strength and corrosion resistance. Filler: Any of a number of materials added to paper to enhance its properties. Examples include glass fibers, clay nanoplatelets and whiskers.

Glass transition temperature (T_b): The temperature at which a polymer becomes hard and brittle.

Hydrophilic: Water soluble.

Hydrophobic: Water repelling.

Isotropic: Having uniform properties in all directions.

Machine direction (MD): The direction in which the greater number of fibers of a sheet of paper tend to be aligned. Paper tends to be stronger in the machine

direction. Also called the "grain direction." The direction at cross angles to the machine direction is the cross direction (CD).

Modulus (a.k.a. tensile elastic modulus or Young's Modulus (E)): The force required to elongate (stretch) a material. Often measured in pounds force per square inch (psi) or in gigapascals (GPa (10^9 Pa)), where 1 psi = 6.895×10^{-6} GPa.

Orthotropic: Having at least two orthogonal planes of symmetry where material properties are independent of direction within each plane.

Paperboard: A broad term for a class of paper, the other class being paper (specific term), that is generally heavier, thicker and more rigid than paper, although the distinction is not a sharp one. Paperboard is used in the manufacture of tubes, cones, cores, packaging forms, containers and container partitions, among other items. When used herein, the term paperboard includes paper and vice versa.

Pascal (Pa): Unit of pressure. 1 Pa = 0.000145 lbf/square inch.

Polymer: A chemical compound or mixture of compounds, generally having a high molecular weight, formed by polymerization.

Pulp (a.k.a. pulp slurry, pulp stock): The mixture of fiber, water and other components extracted by chemical or mechanical means from plant material, mostly wood.

Resin: a. Any of various solid or semisolid amorphous fusible flammable natural organic substances. Examples include melamine, polyamide-polyamine-epichlorohydrin (PAE), polyvinyl acetate (PVA) and phenols. b. Any of a large class of synthetic products that have some of the properties of natural resins. c. Any of various products made from natural or synthetic resins or natural polymers.

Tensile strength: The ability to resist being ruptured when subjected to pulling.

Thermoplastic: Capable of becoming softened when heated and then rehardened when cooled. Any of numerous organic materials that are thermoplastic.

Thermosetting: Capable of becoming permanently rigid when heated or cured.

Wet strength: The ability of a material to resist bursting stresses in its wet state.

Whiskers: Short synthetic or organic fibers. Examples include carbon, silicon carbide and alumina.

The Invention

The invention is a high strength paperboard and method of making same. As used herein, strength may refer to compressive strength, tensile strength (i.e. modulus), tear resistance, folding endurance, etc.

The Young's modulus of the composite paperboard of the invention (paperboard with added filler and/or resin, E_c) may be calculated as:

$$E_c = K E_f V_f + K E_m V_m \quad (1)$$

where:

K = efficiency parameter ~ 1/5 to 3/8, depending on the randomness of the matrix throughout the composite

5 E_f = modulus of the filler

V_f = volume of filler

E_m = modulus of resin matrix

V_m = volume of resin matrix

10 Paperboard is an orthotropic material, and thus its mechanical properties are dependent on the direction in which they are measured. A sheet of paperboard may be thought of as having three orthogonal directions: machine direction (MD), cross direction (CD) and the direction orthogonal to the plane of the paperboard (ZD).

15 Paperboard fibers tend to be aligned in the MD direction during the manufacturing process. Paperboard typically has a modulus (E) of about 5.5 - 8.3 GPa (800,000 - 1,200,000 psi) in the machine direction (MD), 1.5 - 2.7 GPa (220,000 - 400,000 psi) in the cross direction (CD)
20 and 0.3 - 1.7 GPa (44,000 - 250,000 psi) in the z direction (ZD).

In a first embodiment of the invention, a high modulus filler ($E_f > 0.1$ GPa and preferably $E_f > 3$ GPa) is added to the aqueous pulp slurry prior to forming the
25 modified pulp slurry into paper or paperboard. The addition of the high modulus filler increases the strength or modulus of the resulting paperboard.

A number of high modulus fillers may be used for this purpose, including but not limited to polymers ($E = 0.1$ to 5 GPa), glass fibers ($E = 70$ to 110 GPa), clay nanoplatelets ($E = 110$ GPa), and various high strength whiskers.

The aspect ratio of the filler should be at least 50 to provide for efficient load transfer. Aspect ratio determines the efficiency of the load transfer from the filler matrix to the paper fibers. The larger the aspect ratio, the more efficient will be the load transfer.

In a second embodiment of the invention, a thermosetting resin having a high glass transition temperature is added to the paper pulp to improve the mechanical properties of the paperboard. Possible thermosetting resins include melamine, PAE, phenolic resins, phenol-formaldehyde, and anionic and cationic polymers.

Most of these resins have a glass transition temperature higher than that of polyvinyl acetate ($T_b = 85^\circ\text{C}$), a resin currently used in paperboard production. The use of resins having glass transition temperatures higher than the service temperature (so that the resins will always be in their glassy state) can lead to increased stiffness in the paperboard. Most polymeric resins above their glass transition temperature have tensile elastic moduli of about 3 GPa or about 435 ksi (kilopounds force per square inch). As noted earlier, paperboard typically has a Young's modulus of about 5.5 -

8.3 GPa in the MD, 1.5 - 2.7 GPa in the CD and 0.3 - 1.7 GPa in the ZD. Consequently, adding a thermosetting resin having a high glass transition temperature, and preferably higher than 85C, without a high modulus filler, will increase the modulus of a paperboard in the CD and ZD directions.

In a third embodiment of the invention incorporating both of the aforementioned aspects, a high modulus filler and a resin having a high glass transition temperature are added to the aqueous pulp slurry before the forming step. The resin promotes adhesion between the paper fibers and the high modulus filler to improve load transfer. Therefore, the resin should have a hydrophilic end (to adhere to the paper fibers) and a hydrophobic end (to adhere to the filler). The high modulus filler and the resin may be added separately or at the same time during the paper manufacturing process.

In a fourth, preferred embodiment of the invention, a high modulus filler (preferably glass fibers) is primed (coated) with a resin that is hydrophilic (to adhere to the paper fibers), and then the coated filler is added to the aqueous pulp slurry. This may be accomplished by using a secondary reactor/mixer in which the high modulus filler is mixed and/or agitated with the resin matrix. The mixing/agitation enables the resin to wet or chemically react with the surface of the filler, thus rendering the surface of the filler hydrophilic which facilitates even distribution of the filler throughout

the aqueous pulp slurry and improves the adhesion of the filler to the paper fibers. After the coating step, the coated filler is added to the aqueous pulp slurry.

In the foregoing four embodiments, because the filler and/or resin are dispersed throughout the paperboard (instead of just coating a surface), they improve the out-of-plane strength of the paperboard, which is typically low.

EXAMPLES

In the examples that follow, the paperboard modulus is measured in the MD direction.

Example 1

Demonstration that adding a high modulus filler to the pulp slurry increases the paperboard modulus

In a first example, E-glass fiber filler having a modulus of 72 GPa was added to an aqueous pulp slurry in varying concentrations prior to forming the paperboard. The results are summarized in Table 1 below:

Table 1

Effect of E-glass Filler Volume on Paperboard Modulus

Volume % E-glass filler	Paperboard Modulus (psi)	Paperboard Modulus (GPa)
0	406,500	2.80
5	454,000	3.13
10	425,400	2.93
15	442,700	3.05
20	508,900	3.51

As shown in Table 1, the modulus in the MD direction was greatest (3.51 GPa) at 20 volume % E-glass. This represented a 25 % increase in modulus in the MD

direction over the unmodified paperboard. However, the observed modulus was not as high as would be expected from equation (1) at lower filler concentrations. It is expected that increases in modulus would be observed at
5 filler concentrations greater than 20 %.

Example 2

Demonstration that adding resin coated glass fibers to the pulp slurry increases the paperboard modulus

In a second example, E-glass fibers ($E_f = 72$ GPa) were wetted with a resin matrix ($E_m = 5.5 - 11.7$ GPa) to
10 form coated glass fibers, then the coated glass fibers were added to an aqueous pulp slurry prior to forming the paperboard. The volume of filler was approximately 20% and the volume of resin was approximately 10%. The
15 modulus of the composite paperboard increased 20% in the MD (from 0.9 GPa to 1.1 GPa) and 100% in the CD (from 0.25 GPa to 0.5 GPa).

Other modifications and alternative embodiments of
20 the invention are contemplated which do not depart from the spirit and scope of the invention as defined by the foregoing teachings and appended claims. It is intended that the claims cover all such modifications that fall within their scope.

WE CLAIM AS OUR INVENTION:

1. A method of making high strength paper or paperboard comprising the steps of:
adding a high modulus filler to an aqueous pulp slurry to form a modified pulp slurry; and
forming the modified pulp slurry into paper or paperboard.
2. The method of claim 1 wherein the filler has a modulus of at least 0.1 GPa.
3. The method of claim 1 wherein the filler has a modulus of at least 3 GPa.
4. The method of claim 2 wherein the filler is selected from the group consisting of polymers, glass fibers, clay nanoplatelets, carbon fibers, silicon carbide fibers and alumina fibers.
5. The method of claim 2 wherein the filler has an aspect ratio of at least 50.
6. The method of claim 1 wherein a thermosetting resin is also added to the aqueous pulp slurry prior to the forming step.

7. The method of claim 6 wherein the resin has a glass transition temperature higher than the service temperature.
8. The method of claim 6 wherein the resin has a glass transition temperature of at least 85C.
9. The method of claim 6 wherein the resin is selected from the group consisting of melamine, PAE, phenolic resins, phenol-formaldehyde, and anionic and cationic polymers.
10. A paperboard made according to the method of claim 2.
11. A paperboard made according to the method of claim 3.
12. A paperboard made according to the method of claim 7.
13. A paperboard made according to the method of claim 8.
14. A method of making high strength paper or paperboard comprising the steps of:
 - coating a filler with a resin matrix;
 - adding the coated filler to an aqueous pulp slurry to form a modified pulp slurry; and
 - forming the modified pulp slurry into paper or paperboard.

15. The method of claim 14 wherein the filler has a modulus of at least 0.1 GPa.

16. The method of claim 14 wherein the filler has a modulus of at least 3 GPa.

17. The method of claim 16 wherein the filler is glass fiber.

18. The method of claim 14 wherein the resin is hydrophilic.

19. A paper or paperboard made according to the method of claim 14.