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METHOD OF FORMING FIBER-RESIN MOLD PRODUCTS WHEREIN THE RESIN IS AN INTERMEDIATE STAGE THERMOSETTING RESIN

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This invention relates to products of high strength molded of fiber-resinous systems and it relates more particularly to the method of preparation of moldable fiber-resinous systems for use in the fabrication of such molded products and still more particularly to the method of preparation of such fiber-resinous systems into continuous webs from which products of high strength can be molded in a simple and efficient manner.

It is an object of this invention to provide a new and improved article of manufacture from which molded products of high strength can be fabricated and it is a related object to provide a method for the combination of resin and pulp fibers in a manner which enables the resin-pulp to be employed in conventional paper making processes and on conventional paper making machines for the formation of the resin-pulp system into continuous webs which can be used as a new and improved raw material in the manufacture of molded products and sheets of high strength wherein the resinous component is uniformly distributed in desired concentrations throughout the resin-pulp system and wherein the resinous component is incorporated with the pulp fibers without harmful effect on the length of the fibers thereby to provide a resin-pulp system from which molded products and sheets of high strength can be produced, and wherein the resinous system is capable of combination with the pulp fibers in various concentrations to produce combinations which can be processed in conventional paper making processes and machines as though no resinous component were present to cause sticking or other interferences ordinarily experienced where a resinous component or size composition is embodied with the pulp fibers, even in relatively low concentrations.

A more important concept of this invention resides in the discovery that certain resinous materials in a particularly selected intermediate stage of polymeric growth can be combined with pulp fibers to achieve uniform distribution in a wide range of concentrations without the necessity for subjecting the fibers to a beating action of the type which causes breakdown of the fibers with resultant lower strength in the final products, and that the described combination of resin and pulp fibers is free of tackiness to enable the combination of pulp and resin to be processed in conventional paper making processes and machines in the formation of the pulp and fiber into continuous webs from which sheets and molded products of high strength can be produced.

In accordance with the practice of this invention, use is made of a curable resinous material while the resinous material is in the intermediate stage of polymeric growth, often referred to in the art as in the A or B stage, and which will be more specifically defined hereinafter as in the water phase. While in this stage, the resinous component is capable of being introduced into the aqueous

dispersion of pulp fibers for intimate combination and uniform distribution with the pulp fibers responsive to a simple mixing action and without the necessity to beat the fibers before or after resinous addition to open the fibers for uniform distribution of the resin. Such beating action has been found to be undesirable since it breaks down the pulp fibers with the following results:

(1) The fibers remaining in the system have insufficient length for imparting mass integrity to the dried web that is formed with the result that the web cannot be handled in conventional paper making machines, it crumbles during handling of the web for molding, and the dried product is characterized by excessive volume per unit weight.

(2) The loss of the length of the pulp fibers from the beating action results in the corresponding loss in strength in the final product with the result that full utilization of the strength properties inended to be secured by the fibrous component cannot be developed.

(3) The cost is materially increased by reason of the additional equipment, additional space and additional processing required for beating the pulp fibers to open the fibers and incorporate the resinous component therein.

The resinous component, in the stage employed in the practice of this invention for combination with the aqueous system of pulp fibers, is substantially unlike the resinous materials or colloids of the type which are soluble in water and it is also unlike the water insoluble resinous materials or colloids which are incorporated in the aqueous system in a dispersed phase. The water soluble resins or colloids, when embodied in an aqueous system for combination with pulp fibers, operate materially to increase viscosity of the resulting system thereby to handicap the ability for incorporating substantial amounts of the water soluble resinous material or colloid with the pulp without materially affecting the ability of the pulp-resin system to be processed in ordinary paper making processes or machines. Further, the dissolved resinous material or colloid imparts adhesiveness or stickiness to the composition of the type which is effective quickly to clog the screen or coat the rolls or other pieces of paper processing equipment thereby to interfere with the correct and continuous operation thereof.

The use of water insoluble resinous materials dispersed in the aqueous pulp fiber system operates to reduce the freeness of the fibers whereby proper combination cannot be achieved between the resinous component and the fibers and the resultant increase in viscosity, even when low concentrations of resinous materials are incorporated, militates against the introduction of satisfactory amounts of resinous material and it further interferes with the abiltiy to run the resulting system on conventional paper-making machines.

On the other hand, in the combination which makes use of curable resins in a water phase, the resinous component can be incorporated in various amounts with little, if any, effect on the viscosity of the resulting aqueous pulp system. As a result, it is possible to combine the resinous component and pulp fibers to provide a ratio ranging from 3 percent by weight of resin and 97 percent by weight of pulp fibers up to 60 percent by weight of resin and only 40 percent by weight of pulp fibers and still achieve complete and uniform incorporation of the resinous component with the pulp fibers without the necessity to beat the fiber-resinous system or otherwise subject the system to such attrition as would be encountered in

a rolling mill or Banbury of the type heretofore used to force resinous mixture with fibrous fillers.

When the resinous component is combined with the aqueous pulp while the resinous component is in the water phase described, the resinous component provides little, if any, stickiness to the resulting mixture with the result that the resinous system is completely and freely distributed with the pulp fibers in the system and the system can be processed in conventional paper making processes and on conventional paper making machines to form continuous webs. The combination of pulp and resin, even after being reduced to a dried state, can easily and quickly be reconverted into an aqueous slurry for processing in the manner of a conventional paper pulp through conventional paper making processes and machines without gumming up the rolls, screens, header or other elements of the paper making machines or without introducing complications into the beater or the like processing equipment for reforming the slurry.

Thus the system can be prepared merely by the admixture of the resinous component and pulp fibers while in an aqueous system followed by drying to produce a pulp-resinous product containing from 3 to 60 percent by weight of resin to 97 to 40 percent by weight of pulp and wherein the pulp fibers retain their original length with the resinous component uniformly distributed in combination therewith. Drying to produce the resin-pulp system can be effected in conventional equipment such as an air dryer, tunnel dryer, shelf dryer, spray dryer or the like at ambient temperature but preferably at an elevated temperature below the temperature of the advancement of the resinous component such as at a temperature below about 200° F. and preferably below about 150° F. The resulting dried resin-pulp combination can be easily redispersed in aqueous medium to form a paper making slurry.

The pulp fibers can be selected of such pulp forming fibrous substances as manila, jute, asbestos, bleached sulfate cellulose pulp, unbleached sulfate cellulose pulp, and bleached and unbleached sulfide pulp.

The resinous component comprises one of the class of materials capable of being arrested in various stages of polymeric growth including an A or B stage (water phase) and which can be carried on for cure to a C stage. Included are such condensation resinous systems as phenol formaldehyde resins, urea formaldehyde resins, melamine formaldehyde resins, alkyd resins and alkyd modified urea formaldehyde or phenol formaldehyde resins.

The following will be given by way of an example of the practice of this invention with a phenol formaldehyde resinous material. It will be understood that the following examples are given solely by way of illustration and not by way of limitation and that instead of the described phenol formaldehyde resin use can be made of any one of the resins listed above while in the water phase and which can subsequently be converted by heat and/or catalyst to a final cured or C stage.

EXAMPLE 1

Preparation of pulp

100 pounds of dry wet cellulose pulp is placed in a double arm mixer to which hot water is added to bring the temperature of the mass to approximately the temperature of the resinous system adapted to be incorporated therein from a separate kettle. Enough water is added to open the fibers of the pulp to prepare the pulp for receiving the resinous component. Use is made of a conventional double arm mixer which does not function to break down the fibers in the formation of the slurry upon the addition of the hot water.

EXAMPLE 2

Preparation of resin

94 pounds of U.S.P. phenol (42°) is combined with 81 pounds of 40% formaldehyde and 45 cc. of hydrochloric acid 22° Baumé, in a suitable reaction kettle. The materials are agitated in the kettle while being heated to a temperature of 97° C. and the heat is thereafter shut off until resin formation. Heat is again applied after the resin has been formed and the materials are brought to a boil at which temperature they are held for about 10 minutes with constant agitation of materials.

EXAMPLE 3

Preparation of fiber-resinous system

The resinous system produced in Example 2 is transferred from the kettle to the double arm mixer used in Example 1 which contains the heated and prepared pulp. The resin and pulp are kneaded in the mixer for about 20 minutes. Additions are made of about 1 pound of ethylene glycol and 2 ounces of stearic acid. 3 pounds of hexamethylene tetramine can be added to the mixture, at this stage, if it is desirable to make use of a curing agent to accelerate cure during subsequent molding. The mixture is thoroughly dried to a flocculent crumbly mass having a 50 percent resin content uniformly distributed in the pulp fibers.

EXAMPLE 4

Web preparation

For preparation of a web from the dried resin-pulp system, the dried mixture is placed in a conventional beater of a conventional papermaking machine where it is wetted and brought to the required consistency to be run through the machine as in the ordinary papermaking process to form sheets of selected thickness.

EXAMPLE 5

Molded products

In the event that it is desired to produce a cured flexible sheet of the web that is formed on the papermaking machine, such molded sheet can be achieved by addition of the curing agent of hexamethylene tetramine previously described and by running the calender of the papermaking machine at a temperature above 200° F. whereby the web becomes a cured finished sheet wherein the resinous component is advanced to a cured and set stage.

Instead, the dried web that is formed on the paper making machine may be preformed into various shapes or otherwise introduced into molds of substantial contour for molding under heat and pressure to advance the resinous component and produce a cured product which is characterized by high strength by reason of the length of the pulp fibers present in the molded product and which is also characterized by a high degree of flexibility by reason of the fiber arrangement. The web produced by the paper making machine is characterized by sufficient mass integrity for handling the web in a manner similar to that for conventional paper for processing the web and preparing the web for subsequent molding under heat and pressure.

Instead of compression molding between mold dies at a temperature above 200° F., panels molded of single sheets or plural sheets laminated together may be secured by introduction of sufficient layers of the web between heated flat platens for integration and advancement of the resinous material under heat and pressure.

The invention is capable of various modifications to incorporate particular properties and characteristics into the molded product.

For example, by way of one modification, a firs resistant molded product can be fabricated by formulation of the resin-pulp system to include a volatilizable phosphate,

such as diammonium phosphate. The fire retardant can be incorporated into the system by solution in warm water for addition to the combination of resin-pulp in an amount within the range of from 2 to 20 percent by weight of the fire retardant based upon the dry weight of the resinous component. Addition of the diammonium phosphate or other fire retardant is preferably made to the pulp slurry at the time or after the resinous component has been incorporated or it can be added to the slurry that is formed of the dried resin-pulp system for use in the preparation of webs on the paper making machine.

By way of further modification, dyes, pigments, or other tinctorial agents may be incorporated into the resin-pulp system at the time of its original preparation or during redistribution of the dried system in aqueous medium for reconstitution of the paper making slurry whereby the coloring agent becomes uniformly distributed with the resin and pulp to impart a color which is uniform in cross-section in the product molded therefrom. For this purpose, it is sufficient to make use of an amount of pigment up to 5 percent by weight of the resin-pulp solids or an amount of dyestuff up to about 1 percent by weight of the resin-pulp solids.

By way of still further modification, a product of improved heat resistance, lubricity and water repellency can be produced by the formulation of the resin-pulp system to include an organo silicon compound in an amount within the range of 0.1 to 5 percent by weight of the resinous component. It is desirable to make use of an organo silicon compound while in a water soluble state. For this purpose, use can be made of water soluble organo silanes or silanols of the type which embody a solubilizing hydroxy group in a stabilizing aromatic group in the organic group attached to the silicon atom such as diphenol silicon dichloride, or diphenol silicane diol, phenol silicon trichloride or phenol silicon triol, or use can be made of the silane, its silanol hydrolysis product or polysiloxane condensation product which is solubilized by the presence of ammonia or an alkali metal cation to form the corresponding water soluble salts or polysiloxanolates, in which the organo silicon compound in its cured state may constitute a methyl polysiloxane, ethyl methyl polysiloxane, ethyl polysiloxane or mixtures thereof, and water soluble salts thereof. These organo silicon compounds can be incorporated into the resin and pulp in the original mixture or in the reformed slurry for use in the web formation. The described water soluble organo silicon compound in the form of the polysiloxanolate or the mono-, di- or trialkoxy or halo silane will become insolubilized upon drying and cure of the resinous components to the set stage.

It will be understood that the dried resin-pulp system is capable of use as a molding compound without reconstitution of the slurry to form a web and that cured products can be molded thereof in response to heat and pressure at a temperature in excess of 200° F.

It will be further understood that any one or any combination of the described modifications may be employed in the resin-pulp system to produce final molded products embodying the various combinations of characteristics and that further changes may be made in the details of formulation, processing and molding without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In the method of producing a moldable pulp-resin product wherein the resin is capable of advancement to a cured stage during molding consisting of the steps of dispersing the pulp fibers in an aqueous system uniformly to distribute the pulp fibers and open the pulp for receipt of the resinous material, introducing a thermosetting resinous material in an intermediate stage of polymeric growth and in a water soluble state for solution in the aqueous material without noticeable increase in viscosity and adhesiveness of the resulting aqueous system, and then drying the mixture at a temperature below 200° F. to a crumbly, flocculent mass of pulp fibers without advancement of the resinous material beyond an intermediate stage of polymeric growth with the resin uniformly distributed therein and in which the resinous material is introduced in an amount within the range of 3 parts by weight of resin to 97 parts by weight of pulp fibers as a minimum to 60 parts by weight of resin and 40 parts by weight of pulp fibers as a maximum.

2. In the method of producing a moldable pulp-resin system wherein the resin is capable of advancement to a cured stage during molding consisting of the steps of, dispersing the pulp fibers in an aqueous system uniformly to distribute the pulp fibers and open the pulp for receipt of the resinous component, introducing a thermosetting resinous material in an intermediate stage of polymeric growth and in a water soluble state for solution in the aqueous medium without noticeable increase in viscosity and adhesiveness of the resulting aqueous system, introducing the pulp-thermosetting resinous material into the beater of a paper making machine to form an aqueous slurry which can be run over the wire of the paper making machine and processed through the machine without sticking to the wire and parts of the machine and with sufficient freeness for drainage of the aqueous medium from the pulp-resinous material, running the slurry over the wire of the paper making machine to separate out the dispersed resin-pulp to form a web on the wire surface of pulp fibers having the resinous material still uniformly distributed therein in an uncured and non-tacky stage and in which the resinous material is introduced in an amount within the range of 3 parts by weight of resin to 97 parts by weight of pulp fibers as a minimum to 60 parts by weight of resin and 40 parts by weight of pulp fibers as a maximum.

3. The method as claimed in claim 1 in which the pulp fibers are selected from the group consisting of manilla, jute, asbestos, bleached sulfate cellulose pulp, unbleached sulfate cellulose pulp, bleached sulfite cellulose pulp, and unbleached sulfite cellulose pulp.

4. The method as claimed in claim 1 in which the thermosetting resinous material comprises the reaction product of phenol and formaldehyde reacted at a temperature of about 97° C. in an acidic medium.

5. The method as claimed in claim 1 which includes the step of introducing a volatilizable phosphate as a fire retardant to the aqueous dispersion of pulp fibers and resinous material and in which the phosphate is added in an amount within the range of 2–20 percent by weight of the resinous component.

6. The method as claimed in claim 5 in which the phosphate is diammonium phosphate and in which the diammonium phosphate is dissolved in warm water for addition to the dispersion of the pulp fibers and resinous material.

7. The method as claimed in claim 1 which includes the step of introducing an organo silicon compound to the pulp fibers and resinous materials to impart heat resistance, lubricity and water repellency to the molded product and in which the organo silicon compound is introduced in an amount within the range of 0.1 to 5 percent by weight of the resinous component.

8. In the method of producing a moldable pulp-resin system wherein the resin is capable of advancement to a cured stage in molding consisting of the steps of dispersing the pulp fibers in a heated aqueous system with agitation uniformly to distribute the pulp fibers and open the pulp fibers for receipt of a resinous material, introducing a thermosetting resinous material in an intermediate stage of polymeric growth and in a water soluble state for solution in the aqueous material without noticeable increase in viscosity and adhesiveness of the resulting aqueous system, and in which the thermosetting resinous material is introduced in an amount within the range of 3 parts by weight of resin to 97 parts by

weight of pulp as a minimum to 60 parts by weight of resin and 40 parts by weight of pulp as a maximum, drying the mixture of pulp and resinous material at a temperature below 200° F. without advancement of the resinous material to a cured stage, redispersing the dried pulp and resinous material into aqueous medium in the beater of a paper making machine to form an aqueous slurry having sufficient freeness and non-tackiness for processing through the paper making machine and over the wire to form a web, running the slurry over the wire of the paper making machine to separate out the dispersed resin-pulp to form a web of pulp fibers having the resinous material uniformly distributed therein in an uncured and non-tacky stage, drying the web, and then subdividing the web, and then molding the subdivided web under heat and pressure to advance the resinous component to the cured stage to form a molded product.

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