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TREATMENT OF PAPER

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1 Claim. (Cl. 117—65)

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This invention relates to the manufacture of paper products such as cardboard or paper board having a surface impregnated with urea-formaldehyde resin. This application is a continuation-in-part of my copending application S. N. 555,042, filed September 20, 1944, wherein I disclose that fibrous materials, particularly wood, may be impregnated with solutions of methylol ureas at a slightly alkaline pH, and that the resulting materials may be cured at elevated temperature and pressures to produce products having a hardened and dimensionally relatively stable surface.

It has been known for many years that fibrous materials, particularly paper, wood, and the like, may be impregnated with certain condensation products of urea and formaldehyde, and that urea-formaldehyde resins may be hardened within the fibrous material after impregnation (Pollak, U. S. Patent, 1,459,153). Since the time of this early disclosure several patents have described the manufacture of various molding compositions obtained by treatment of cellulose or shredded paper with urea-formaldehyde condensation products. Generally, these compositions could be molded under heat and pressure. Also, processes have been known for impregnation of paper with aqueous solutions of water-soluble urea-formaldehyde resins, generally in the presence of an acid-reacting catalyst, and in certain instances, in the presence of an excess of the formaldehyde reactant. In the conventional process for the impregnation of paper with urea-formaldehyde water-soluble resin, the resin is mixed with the fibers prior to the formation of the sheet. For example, this has been accomplished by employing a dilute solution of urea-formaldehyde resin in the beater, where the fibers are hydrated, after which the fibers are fed onto traveling wire screens and thereafter passed over rolls which form the stock into a sheet.

In contrast with the above processes the present invention is directed to the manufacture of paper products which are not merely impregnated throughout the mass of fibers with urea-formaldehyde resin, but which have a continuous impregnated surface which protects the mass of fibers in the interior. Thus, the present invention provides a novel process for preparing relatively thick sheets having a strong continuous resin-impregnated surface which prevents the passage of moisture into the interior of the sheet.

An object of this invention is to prepare paper products having improved resistance to dimensional changes produced by variations in atmospheric humidity. Another object is to prepare paper products having a surface or outer shell which is relatively impervious to moisture.

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These and other objects are accomplished in accordance with the invention by treating paper cards or sheeting with a solution of methylol urea at a slightly alkaline pH, and thereafter subjecting the surface of the treated article under conditions hereinafter described in detail to the action of heat and pressure.

In general to obtain the products of this invention relatively thick paper cards or sheeting (preferably having a thickness of at least about 0.005 inch) are treated with methylol urea solutions, preferably of about 10% to 50% concentration, for a period of time which may be as short as about 5 seconds or less, and the resulting product is heated at a temperature of about 240° to 320° F., preferably about 280° to 320° F. under a pressure of about 200 to 1000 pounds per square inch.

The methylol urea solutions which may be employed in the practice of this invention may be prepared by any suitable method, such as the process described in the Dittmar and Strain patent U. S. 2,321,544. The preferred solvent is water although organic solvents, such as methanol, ethanol, propanol, glycols, glycol ethers, dioxolane, dioxane, and the like, may be employed if desired. The pH should be within the neutral to slightly alkaline range, i. e. about 7.0 to 9.0, and preferably should not be substantially greater than 8.0. Buffers, such as diethanolamine, sodium polymethacrylate, hexamethylene tetramine, triethanolamine, monoethanolamine, sodium acetate, borax, and mono-sodium phosphate may be employed to keep the pH within the desired range and to prevent premature resinification of the methylol urea.

The methylol urea solutions may be prepared from urea and formaldehyde, or from the methylol ureas themselves. The desired molar ratio of combined formaldehyde to combined urea in the methylol urea solution may be obtained by adding appropriate quantities of monomethylol urea to formaldehyde or dimethylol urea to urea. For certain purposes, when maximum stability on storage is desired, the mixture of methylol ureas in solution may contain from about 25 mol per cent monomethylol urea and 75 mol per cent dimethylol urea to about 75 mol per cent monomethylol urea and 25 mol per cent dimethylol urea, i. e. the ratio of formaldehyde to urea is about 1.25 to about 1.75. For optimum hardness and dimensional stability the ratio of formalde-

hyde to urea in the dissolved methylol urea should be about 1.3 to about 1.6.

The treatment of preformed paper or cardboard with the methylol urea solution, in accordance with the invention, is accomplished either by coating a surface with the solution, or by dipping the paper or cardboard into the solution. In this manner the weight of resin taken up is generally about 5% to 15% based on the weight of the paper. The application of heat and pressure to the methylol urea treated paper is accomplished by heating the material in a press, such as a press containing heated platens. Alternatively, the heat and pressure may be applied by passing the methylol urea treated sheet between heated rolls. Only a short curing period is required, usually not more than about 5 minutes.

The invention is further illustrated by means of the following example.

Example.—Manila cards, 0.0067 inch thick, measuring about 8.30 centimeters across the machine direction, were dipped for 5 seconds in a 25% solution of methylol urea, having a urea: formaldehyde ratio of 1:5.1, at room temperature. The concentration of methylol urea solution was 25% by weight. Absorption of methylol urea solids was 11% by weight. The cards were dried and then heated at a pressure of 500 pounds per square inch at 300° F. for 5 minutes. The resulting product contained an infusible, insoluble, urea-formaldehyde resin-impregnated surface, but the resin did not penetrate the interior portions of the card. After the curing, the dimension of the cards, measured across the machine direction was 8.26 centimeters. The dimension change of the card with changes in relative humidity was 30% to 50% less than the corresponding dimension change of untreated cards, within the relative humidity range of 20% to 75%.

The cards used in this experiment were not appreciably penetrated by the methylol urea solution during the 5 second dip. This fact was further illustrated in a separate test in which two of the cards, 0.0067 inch thick, were pressed face to face and immersed in the methylol urea solution for 1 hour, after which it was found that the faces in contact had not been wetted.

While in the example given above the invention is illustrated as applied to the manufacture of dimensionally stable cards, it is to be understood that many different embodiments of the invention will occur to those skilled in the art. For

example, the invention may be used in the manufacture of various paper products which require a dimensionally stable surface, such as maps, paper employed in offset printing, graph paper, cards for business machines (perforated card type), and measuring devices of various kinds requiring precise control over the surface dimensions, and resistance to changes produced by variations in atmospheric humidity.

The invention is therefore not limited except as set forth in the following claim.

I claim:

A process for improving the dimensional stability of cardboard paper products adapted for use in making business machine cards of the perforated card type, which comprises dipping such cardboard having a thickness of at least 0.005 inch for not more than 5 seconds in a solution consisting essentially of water and methylolureas having a formaldehyde:urea mol ratio between about 1.3 and 1.6 at a pH of about 7.0 to 9.0, said solution having a concentration of about 10% to 50% by weight, withdrawing the said cardboard from the said solution when the cardboard has been only partially penetrated by the solution, drying the resultant impregnated cardboard and thereafter heating the resultant dried individual sheets of impregnated cardboard at a temperature of about 280° to 320° F. under a pressure of about 200 to 1000 pounds per square inch, whereby a cardboard product having a surface impregnated with infusible, insoluble urea-formaldehyde resin is obtained.

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