**Title:** POLYUREA-REINFORCED FIBER-BASED MATERIALS

**Abstract**

Polyurea-reinforced fiber-based materials, and methods for their manufacture, are disclosed. A representative material is a sheetlike ply having on one or both faces thereof a polyurea-impregnated stratum. When the material has only one such stratum, the stratum has a thickness extending depthwise into the ply no greater than about half the ply thickness dimension. When the material has two such strata (one on each face), each stratum has a thickness no greater than about one-third the ply thickness dimension. In either case, a portion of the ply thickness dimension is unimpregnated. The material can comprise plural superposed plies, such as reinforced corrugated paperboard wherein at least one ply, such as the corrugated medium, has at least one polyurea-impregnated stratum. The present materials have, at a given compression strength, less brittleness (more foldability) than prior-art materials. The present materials are made by controllably applying a polyisocyanate resin to a fibrous web surface so as to prevent excess penetration of the resin into the web thickness dimension, then curing the resin. The materials are capable of being corrugated and folded after curing, and are useful for manufacturing cartons and other finished products.
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POLYUREA-REINFORCED FIBER-BASED MATERIALS

FIELD OF THE INVENTION

The present invention relates to reinforced fiber-based materials such as reinforced fiberboards and reinforced paperboards, and containers made therefrom.

BACKGROUND OF THE INVENTION

Fiberboards, including corrugated and non-corrugated paperboards are useful for an extremely wide variety of applications, but particularly for making containers such as packaging and shipping containers. Modern techniques for making such containers involve not only manufacturing the requisite fiberboard material but also cutting and shaping of one or more sheets of the fiberboard into "box blanks" that are folded into the corresponding container shape. Box blanks are typically designed with multiple scored lines and the like so that the blank can be readily formed into a container by merely folding the box blank in an ordered manner along the scored lines. Regardless of the container design, the forming of a substantially planar box blank into a corresponding three-dimensional container involves subjecting the fiberboard to a plurality of folds.

One drawback to many fiberboards, including paperboard, is their poor rigidity when wet. To overcome this shortcoming, manufacturers have tried various ways of reinforcing fiberboard and rendering the fiberboard nonabsorptive for liquids. Examples of such reinforcement include impregnating or coating the fiberboard with paraffin or other polymeric material.

While paraffin coating substantially decreases the tendency of the fiberboard to absorb water, making paraffin-reinforced corrugated paperboard popular for use in packaging vegetables and meats. Unfortunately, paraffin has the disadvantage of being readily softened by moderately elevated temperatures. Also, while paraffin coating can sometimes enhance the compressive strength of the fiberboard and resistance to puncturing, the enhancement may not be sufficient for
many uses. In view of the shortcomings of reinforcing fiberboard using paraffin, other polymeric resins, particularly various thermoset materials, have been considered for this purpose. Many cured thermosets have the advantage of being very rigid. As a result, fiberboards reinforced with cured thermosets tend to have high resistance to compression. Unfortunately, many currently favored thermosets are extremely brittle after being fully cured and fracture when subsequently creased or folded. Such fracturing of the thermoset reinforcing agent can readily extend to the fiberboard itself, thereby seriously reducing the integrity of the container made therefrom along edges and at corners.

Phenolics have received the greatest attention, particularly as a reinforcing agent for corrugated paperboard. Representative U.S. Patents disclosing use of phenolics include Patent Nos. 3,886,019, 4,096,935, 4,051,277 and 4,096,305 to Wilkenson et al. These patents disclose the application of a thin film of phenolic resin to surfaces of linerboards and corrugated medium that will be adhered together to form the corrugated paperboard. Since very little resin penetrates into the thickness dimension of the underlying paperboard, the outer surfaces of the corrugated paperboard are free of resin. After adhering together the linerboards and corrugated medium, the corrugated paperboard can be cut, scored, and slotted to make box blanks. Full curing of the resin is delayed until after the box blanks have been folded to make cartons.

Various thermoset blends of phenolics with other resins have also been tried in an attempt to reduce the brittleness of phenolic alone. Representative U.S. patents include Nos. 3,687,767 to Reisman et al. (phenol-aldehyde), 3,607,598 to LeBlanc et al. (phenol-aldehyde plus polyvinylalcohol), 3,616,163 to Reisman (phenol-aldehyde resole), 3,619,341 to Elmer (phenol-aldehyde resole), 3,619,342 to Burke (phenol-aldehyde resole), 3,697,365 to Reisman et al. (resole phenolic plus an organosilyl compound), 3,682,762 to LeBlanc (resole phenolic plus polyaminoalkyl substituted organosiloxane), 3,617,427 to LeBlanc (aminoplast-modified phenol-aldehyde resole), 3,617,428 to Carlson (aminoplast with phenolaldehyde resole), and 3,617,429 to LeBlanc (aminoplast plus phenol-aldehyde and polyvinylalcohol).
Despite these developments, even phenolic blends tend to be unacceptably brittle, which imposes certain limitations on manufacturing processes. For example, in all the phenolic-blend patents recited above, curing (thermosetting) of the resin is performed only after corrugating the medium fiberboard or even later such as after the corrugated paperboard is scored along fold lines. This means, for example, that resin-coated paperboard destined to become the corrugated medium cannot be cured before it is passed through a corrugating machine. As a result, conventional thermoset-impregnated medium paperboard cannot be made up and cured in one location and supplied to another location for corrugating and incorporation into corrugated paperboard using conventional machinery. Also, interposition of resin-applying and resin-curing machinery into existing production lines for manufacturing corrugated paperboard is expensive. These and other problems with existing methods can unacceptably increase the costs of products formed thereby, such as reinforced corrugated paperboard and cartons.

Another disadvantage inherent in using phenolic blends according to the above-cited references is that considerable amounts of resin must be used to obtain satisfactory reinforcement. Typical resin loading levels are 2 to 10 w/w percent resin per dry mass of linerboards and 5 to 15 w/w percent resin per dry mass of corrugated medium. Since these resins are expensive, it would be advantageous to have loading levels as low as possible, such as no greater than about 5 w/w percent.

SUMMARY OF THE INVENTION

According to one aspect of the present invention, a polyurea-reinforced fiber-based material is provided which comprises, at least, a single ply of a fibrous material impregnated with polyurea on at least one of the faces (i.e., major surfaces) of the ply. Each such impregnation, termed herein a "polyurea-impregnated stratum of fibers", extends depthwise from the corresponding face into the thickness dimension of the ply no greater than about one-half the thickness dimension. That is, the ply of fibrous material can have a polyurea-impregnated stratum on either or both faces. However, whether a stratum is located on either or on both faces, a
portion of the thickness dimension is left unimpregnated with polyurea. Therefore, if such a stratum is located on both faces, each stratum has a thickness dimension preferably no greater than about one-third the thickness dimension of the ply.

Although the fibers comprising the ply can be any of a wide variety of fibers, including hydrophilic and hydrophobic fibers, they are preferably wood pulp fibers. In any event, the fibers should contain residual moisture in a concentration of about 3 to about 15% w/w relative to the dry mass of the fibers. The fibers are preferably organized into a sheetlike web having a porosity sufficient to absorb liquid polyisocyanate resin applied to the web for the purpose of forming a polyurea-impregnated stratum. Most preferably, the wood pulp fibers are in the form of a paperboard.

Polyurea-reinforced fiber-based materials according to the present invention exhibit surprisingly high ring-crush strengths at low loading levels of polyurea. For example, a polyurea-reinforced paperboard according to the present invention contains a loading level of polyurea of about 5% w/w or less, yet exhibits a ring-crush strength equal to ring-crush strengths of analogous polymer-reinforced materials known in the prior art having loading levels of polymer at least twice as high, about 10% or more.

Leaving a portion of the thickness dimension unimpregnated with polyurea contributes to the ability of the polyurea-reinforced material according to the present invention, despite the fact that the polyurea is fully "cured", to be folded and creased without necessarily fracturing. This is in contrast to analogous prior-art materials that are generally so brittle that folding, and especially creasing, will cause fracture of the material along the fold line. In fact, materials according to the present invention are sufficiently foldable that they can be passed through a corrugating machine without fracturing. At a given ring-crush strength, the foldability of polyurea-reinforced fiber-based materials according to the present invention is higher than the foldability of prior-art materials having equal ring-crush strengths.

Hence, to make a polymer-reinforced fiber-based material according to the present invention, less fiber and polymer are required to achieve a desired
ring-crush strength and foldability than are required to make analogous prior-art materials.

According to another aspect of the present invention, the polyurea-reinforced fiber-based material can comprise multiple web plies superposedly adhered together, wherein at least one of the faces of at least one of the plies has a polyurea-impregnated stratum. Hence, the present invention encompasses polyurea-reinforced "corrugated paperboard" comprising at least one "linerboard" and at least one "corrugated medium paperboard", wherein at least one of said plies has at least one polyurea-impregnated stratum. preferably, but not necessarily, the corrugated medium contains one or more of the polyurea-impregnated strata. Such corrugated paperboard can also be comprised of more than one corrugated medium, each sandwiched between and adhered to coextensive linerboards.

The crush resistance and foldability of materials according to the present invention permit the materials to be prepared at one location, including full curing, and used at a different location. For example, it is possible to manufacture polyurea-impregnated medium paperboard at one plant and ship the paperboard to a second plant at which the paperboard is corrugated for making into corrugated paperboard. It is also possible for fully cured polyurea-reinforced corrugated paperboard according to the present invention to be made at one location, then cut, scored, and folded to make cartons at another location. In other words, the end-user of the material does not have to be concerned with curing the material, in contrast to end-users of analogous prior-art materials.

As another aspect of the present invention, methods are provided for manufacturing such polyurea-reinforced fiber-based materials. In a representative embodiment, polyisocyanate resin is applied to one or both faces of a fibrous web at a loading level that ensures that the resin does not penetrate into the thickness dimension of the web more than about half the thickness dimension (if applied to only one face) or about one-third the thickness dimension (if applied to both faces). Hence, the maximal loading level (the magnitude of which will, of course, depend upon the particular nature of the web) is dictated by the necessity to leave a portion of the thickness dimension of the web unimpregnated with the resin. Although heat
and pressure are not required to cure polyisocyanate, curing of the polyisocyanate to form polyurea preferably occurs by application of heat and pressure.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a plot of the dry ring crush strength of polyurea-reinforced paperboards according to the present invention compared to prior-art reinforced paperboards.

FIG. 2 is a bar graph of the data of FIG. 1 together with plots of the foldability of polyurea-reinforced paperboards according to the present invention compared to prior-art reinforced paperboards.

**DETAILED DESCRIPTION**

In a method according to the present invention, a liquid polyisocyanate resin is controllably applied to either the obverse or the reverse faces, or both, of a sheetlike fibrous web. The polyisocyanate is subsequently cured to transform each polyisocyanate-impregnated face into a polyurea-impregnated stratum. Each polyurea-impregnated stratum does not extend through the thickness dimension of the web. In other words, even if the web possesses a polyurea-impregnated stratum on both faces, the web retains a non-impregnated stratum within the thickness dimension of the web.

As referred to herein, a "sheetlike fibrous web" can comprise woven or nonwoven fibers. Consistent with a sheetlike conformation, such a web has a length dimension, a width dimension, an obverse face, a reverse face parallel to the obverse face, and a thickness dimension extending between the obverse and reverse faces. As is typical with fibrous webs, the thickness dimension is porous.

Representative fibers, not intended to be limiting, comprising the web are hydrophilic fibers such as cellulosic fibers (e.g., cotton, wood pulp, rayon), carbohydrate fibers, polyvinyl alcohol fibers, substituted cellulosic fibers, glass fibers, mineral fibers, proteinaceous fibers (e.g., silk); and hydrophobic fibers such as sized wood pulp, cotton, or rayon fibers, polyethylene fibers, polypropylene fibers, polyester fibers, nylon fibers, polyvinylacetate fibers, treated glass fibers, and
aramid fibers; and mixtures of these fibers. If the fibers are synthetic polymeric fibers, the fibers can be spun-bonded or heat-bonded.

The fibrous web should contain about three to about fifteen percent moisture relative to the dry mass of the web. Such an amount of moisture is not necessarily sensed as "wetness". In fact, virtually all fibrous materials, especially hydrophilic materials, have a certain amount of moisture associated with the constituent fibers and fiber molecules. The stated range of about 3 to about 15 w/w percent moisture is a typical residual moisture range for most hydrophilic fibers such as cellulosic fibers. If the fibers are hydrophobic, they may not contain sufficient residual moisture. In that case, additional moisture may have to be added, such as by applying steam to the fibers or to the web made therefrom.

A "polyurea-reinforced fiberboard" is a product according to the present invention made from a sheetlike web of fibers. When the sheetlike web used to make the fiberboard is comprised substantially of wood pulp fibers, the product is referred to as a "polyurea-reinforced paperboard".

By way of example and not intended to be limiting, representative basis weights of webs comprising wood pulp fibers (i.e., "paperboards") range from about 10 to about 90 pounds per thousand square feet. It will be appreciated that, since different fiber materials have different specific gravity values and since webs made from different fiber materials may have different densities, suitable basis weight ranges for other types of fibers may be different from the stated range for wood pulp fibers.

"Polyisocyanates" as used herein are liquid resins characterized as having at least two isocyanate (-NCO) groups per molecule, rendering the molecules polyfunctional and capable of covalently interconnecting with each other. Candidate polyisocyanates can be selected from a group consisting of aliphatic, aromatic, and alicyclic diisocyanates and other polyisocyanates generally known in the art as being capable of forming polyurea. The polyisocyanate resin can comprise a mixture of polyisocyanates. Preferred polyisocyanates are formulations known in the art as "PMDI" (a mixture of polyisocyanate oligomers) and an emulsifiable PMDI formulation known as "EMDI". EMDI generally reacts with water to form polyurea
at a faster rate than PMDI. This is because water is less soluble in PMDI than in EMDI. A representative PMDI formulation is "PAPI 2027" manufactured by the Dow Chemical Corp., Midland, Michigan. A representative EMDI formulation is "XI-242" supplied by ICI United states, Inc., Wilmington, Delaware.

The polyisocyanate used for treating webs according to the present invention can be in either a "neat" (undiluted) form or contain a diluent. Suitable diluents comprise organic solvents miscible with the polyisocyanate. If used, the amount of solvent is generally within a range of about 5 to 20% w/w, relative to the mass of the polyisocyanate. A preferred solvent is propylene carbonate, principally because it is substantially odorless, and colorless, has low viscosity, low toxicity, low vapor pressure at room temperature, and low flammability (boiling point: 242°C; flashpoint: 132°C). The high boiling of propylene carbonate is particularly advantageous because this solvent is thereby prevented from vaporizing under curing conditions of elevated temperature and pressure. Other organic solvents can also be used, so long as possible drawbacks of those other solvents, such as toxicity, low boiling point, or flammability, can be accommodated. Candidate alternative solvents include, but are not limited to, aromatics such as benzene, halogenated benzenes, nitrobenzenes, alkylnbenzenes such as toluene and xylenes, halogenated lower aliphatics, ethers, ketones, alkyl acetates, and other alkylene carbonates.

A benefit of diluting the polyisocyanate is reduced cost, since polyisocyanates such as PMDI are generally more expensive compared to the cost of the solvent. It has been found that diluting the polyisocyanate as described above generally does not cause any substantial corresponding increase in degree of reinforcement compared to neat polyisocyanate.

Adding solvent to the polyisocyanate tends to reduce the viscosity of the relatively viscous neat polyisocyanate, which can improve the rate or increase the depth of penetration of the resin into the web of a polyisocyanate at a particular loading level. These results can be advantageous especially in high-speed processes for producing reinforced fiber-based materials according to the present invention.

Each polyurea-impregnated stratum typically extends the length and width dimensions of the web parallel to the obverse and reverse faces of the web.
When a polyurea-impregnated stratum is located on only one face of the web, the impregnated stratum preferably has a thickness dimension no greater than about half the web thickness dimension and preferably between one-third and one-half the web thickness dimension. When a polyurea-impregnated stratum is located on both faces of the web, the strata each have a thickness dimension no greater than about one-third the web thickness dimension. In either case, a portion of the thickness dimension of the web is left unimpregnated with polyurea.

Although fully impregnating the thickness dimension of the web may yield a fiber-based material having even greater crush resistance, leaving at least a portion of the thickness dimension of the web without any polyurea, according to the present invention, provides a unique combination of crush strength and flexibility. Accordingly, if too much of the thickness dimension is impregnated with polyurea, the fiber-based material can become too brittle for certain uses. If too little of the thickness dimension is impregnated, the material may exhibit insufficient crush resistance for certain uses.

As the polyisocyanate resin is applied to the web, the resin usually absorbs rapidly into the pores of the thickness dimension of the web. The depth of absorption is controlled by precisely controlling the "loading" of polyisocyanate on the surface of the web. As used herein, "loading" and "loading level" refer to the mass of polyisocyanate resin (or the mass of polyurea, after the polyisocyanate is cured) applied to a face of the web, relative to the mass of the web. Of course, a particular loading level of polyisocyanate resin will penetrate to different depths in the thickness dimensions of different webs, including webs made of different fibers. Hence, different webs can accommodate different polyisocyanate loading levels before the requisite penetration limits are exceeded. By way of example, not intended to be limiting, a PMDI resin such as "PAPI 2027" when applied to paperboard at about a four to five percent w/w loading level will penetrate a maximum of about 1/3 the thickness dimension of the paperboard. When this resin is applied to paperboard at an eight percent w/w loading, the resin penetrates nearly the entire thickness dimension. When applied at twenty percent w/w, the paperboard becomes fully saturated with the resin. For any type of web, simple cross-sectional
examination of the thickness dimension of an impregnated web using a microscope will enable one to readily determine the particular loading level that will produce a particular depth of penetration of the resin.

It will be appreciated that controlling the loading level involves applying the polyisocyanate resin in a manner whereby the mass of polyisocyanate resin applied per unit area of the web is precisely controlled. The liquid can be applied to the web by any of various liquid-application methods including, but not limited to, gravure printing, roller coating, and spraying. The preferred application method is gravure printing because it has been found that this method provides more precise control of resin loading on the web surface than other methods.

"Curing" of a polyisocyanate resin in the presence of water (present as residual moisture in the web) converts the polyisocyanate resin to polyurea which is a type of thermoset material. Curing of polyisocyanate resin occurs via polyaddition and crosslinking reactions of the polyisocyanate molecules by reactions involving water as well as other molecules in the web that have -OH substituent groups available for reaction.

Curing can occur at room temperature, but the time required (several days) may be inconvenient. One way to increase the rate of curing is to increase temperature and/or pressure. However, the curing temperature must not be so high that damage to the resin, polyurea, or web results. A general range for curing temperature is room temperature up to about 232°C (450°F). A general range for curing pressure is from about zero up to about 1000 psig. With paperboards to which PMDI resin has been applied, curing is preferably conducted at about 204°C (400°F) and about 800 psig for a time from about four seconds to about five minutes. The preferred curing time at 200°C and 800 psig is about 40 seconds. Of course, since elevated temperature and pressure increase the rates of the curing reactions, the higher the temperature and/or pressure, the less time required to achieve the same degree of cure.

Curing at elevated temperatures and pressures can be effected in any of various devices adapted to controllably apply heat and pressure. Candidate curing devices include, but are not limited to, platen presses, continuous belt presses, and
autoclaves (steam). If necessary, curing can be performed by a regimen that includes two or more short applications of pressure rather than a continuous application for the entire time required to achieve full cure.

As is known in the art, curing of polyisocyanate can be accelerated by the addition of a catalyst to the resin. In general, any of various catalysts effective for use with polyisocyanates will work. Examples of catalysts, not in any way intended to be limiting, are dibutyltin dilaurate and "DABCO", which would be added to the resin in an amount ranging from about 0.1 to about 1.0% w/w relative to the mass of the polyisocyanate. However, we have determined that a catalyst is usually not required, especially if curing is effected by application of both heat and pressure.

A polyurea-reinforced fiber-based material according to the present invention comprises at least one fibrous sheetlike web. When the polyurea-reinforced fiber-based material is comprised of only web or "ply", the ply comprises at least one substantially continuous polyurea-impregnated stratum of fibers located within the thickness dimension of the web. The impregnated stratum can be located on either the obverse or reverse face of the web or on both faces.

A polyurea-reinforced fiber-based material according to the present invention can be comprised of only one ply or more than one ply. In such multiple-pl ply materials, it is not necessary that all the plies have a polyurea-impregnated stratum. The present invention encompasses multiple-ply materials wherein only one ply thereof has at least one polyurea-impregnated stratum. The present invention also encompasses multiple-ply materials wherein multiple plies each have at least one polyurea-impregnated stratum. Each stratum need not have the same loading level.

In multiple-ply materials according to the present invention, each ply can be made from the same or a different fibrous web. The webs need not all have the same basis weight, thickness, porosity, or texture.

When the polyurea-reinforced fiber-based material is comprised of more than one ply, the plies are typically superposedly adhered together. Adhering the plies together can be achieved by adhering non-impregnated faces to non-impregnated faces, non-impregnated faces to impregnated faces, and impregnated
faces to impregnated faces. The outermost faces of such multiple-ply materials need not be the impregnated faces.

One example of a multiple-ply material according to the present invention is a corrugated paperboard wherein at least one of the plies thereof has at least one polyurea-impregnated stratum. As used herein, a "corrugated paperboard" is a widely recognized product comprising at least two plies of paperboard adhered together, where at least one of said plies is corrugated in a manner known in the art. The corrugated ply is generally referred to as the "medium" paperboard. At least one of said plies is not corrugated and is used as a facing sheet for the corrugated paperboard. Hence, the non-corrugated ply is termed a "linerboard". Typical corrugated paperboards are comprised of a corrugated medium sandwiched between two linerboards adhered to the corrugated medium. The linerboard(s) of a corrugated paperboard often have a larger basis weight than the corrugated medium. Any suitable adhesive can be used to adhere the linerboards to the corrugated medium. A corrugated paperboard can also comprise multiple plies of corrugated medium separately interposed between plies of linerboards. Corrugated paperboards are widely used for making cartons and the like.

Since curing can occur at moderate temperatures, it has unexpectedly been found that curing of the polyisocyanate applied to a paperboard can be performed according to the present invention simultaneously with corrugation of the paperboard. This is because conventional corrugators impart a certain amount of heat and pressure to the paperboard as the paperboard passes through the corrugator. Simultaneous curing and corrugation is particularly advantageous when making polyurea-impregnated corrugated medium according to the compression strength of polyurea-reinforced material equal to prior-art reinforced material could be attained by using less fiber in the polyurea-impregnated material according to the present invention. Use of less fiber can substantially reduce production and shipping costs.

The data plotted in FIG. 1 is also presented in FIG. 2 in bargraph form.

Examples 1 through 16 were also subjected to folding endurance tests in order to assess the brittleness of the materials. Folding endurance tests as
described hereinbelow are a commonly used assessment of the brittleness of a material.

Folding endurance tests were performed on strips ½ inch wide and 6 inches long according to the TAPPI T511-OM-83 test procedure. Briefly, the folding endurance test comprises holding one end of a test strip in a stationary position and applying a one-kilogram weight to the other end. While applying the weight, the length of the strip between the ends is repeatedly flexed over a 270° arc until the strip breaks. Data is recorded as the number of flexes until break.

Fold-resistance data are plotted in FIG. 2. While PE/S exhibited the greatest fold resistance, the fold resistance of material treated with PMDI (polyurea-impregnated stratum) exhibited a fold resistance that was about the same as UF and substantially better than PF. These results also reveal that, as loading level increases, fold resistance decreases. Hence, a lower loading level of polyurea (relative to prior-art reinforcing agents) not only yields the same compression strength as prior-art reinforcing agents at substantially higher loading levels, such lower polyurea loading levels also provide better fold resistance at equal strength. Therefore, at a given compression strength, polyurea reinforced fiber-based materials actually have less present invention because conventional process machinery can be readily and inexpensively adapted to include a gravure coater, sprayer, or the like without the need to add a separate curing device. In such an instance, the gravure coater, sprayer, or the like is added to the process machinery upstream of the corrugator. As the paperboard to which the resin has been applied passes through the corrugator, the polyisocyanate undergoes curing simultaneously with impression of corrugations into the paperboard.

As can be appreciated from the foregoing, the polyurea imparts a substantial reinforcement to a fibrous web, enabling the polyurea-reinforced web to exhibit a crush-resistance strength that is greater than the crush-resistance strength of the corresponding non-reinforced web. Hence, with products made from a polyurea-reinforced web produced according to the present invention, lesser amounts of fibrous web are required to obtain a crush resistance equal to the crush resistance
of similar products made from non-reinforced web, which can yield considerable savings in cost and weight while adding other benefits such as wet strength.

It has been found that fiber-based materials reinforced with at least one polyurea-impregnated stratum according to the present invention actually have greater crush strength at lower loading levels than similar fiber-based materials impregnated with prior-art reinforcing resins. It has also been found that the flexibility of reinforced fiber-based materials according to the present invention is the same as or better than prior-art materials having the same loading level. Hence, at a given crush strength, reinforced fiber-based materials according to the present invention are more flexible than prior-art reinforced fiber-based materials.

A key benefit of greater flexibility at equal strength is that it is now possible for the first time, for example, to apply a polyisocyanate resin to paperboard according to the present invention and fully cure the resin to a polyurea before passing the paperboard through a corrugator. In contrast with known prior-art reinforced paperboards, corrugating a reinforced paperboard made according to the present invention will not cause the paperboard to crack along the corrugations. Hence, for the first time, paperboard destined to become corrugated medium can receive a fully cured polyurea stratum at a first location, be rolled and shipped to a second location remote from the first location, and be made into a corrugated material at the second location. Similarly, cartons and the like can now be made from fully cured polyurea-reinforced corrugated paperboard produced according to the present invention, including such operations as cutting and folding, without the paperboard breaking along cut and fold lines.

It has also been found that polyurea-reinforced fiber-based materials according to the present invention can be adhered together using conventional adhesives. In part, this is because the polyurea impregnant is not present through the entire thickness dimension of the web, as described above. For example, reinforced corrugated paperboards can be assembled from a corrugated medium and at least one linerboard (wherein at least one of the medium and linerboards are polyurea-reinforced according to the present invention) using conventional water-soluble adhesives such as starch-based adhesives, latex-based adhesives, or latex-
starch adhesives to adhere nonimpregnated surfaces together. Alternatively, if desired, conventional non-aqueous adhesives can also be used on either non-impregnated or impregnated surfaces. Such non-aqueous adhesives include, but are not limited to, hot-melt adhesives, polyurethanes, isocyanates, epoxies, rubber-based adhesives, various solvent-borne polymers, mastics, and silicones.

Additional benefits of polyurea-reinforced fiber-based materials according to the present invention include:

(a) Wet resistance: the materials maintain some crush resistance even when wet, which is of considerable benefit when the materials are employed in making shipping cartons.

(b) Printability: the materials can be printed on either impregnated surfaces or non-impregnated surfaces using conventional printing inks and methods.

(c) Resistance to fracture, even after being folded a number of times. Such resistance is due in part to the better flexibility of polyurea as a reinforcing agent and in part to the fact that the polyurea impregnant does not extend entirely through the thickness dimension of the web. Hence, the non-impregnated portion of the web can serve as a hinge during folding, even after a lengthy series of folds.

A polyurea-reinforced fiber-based material according to the present invention also has potential uses other than packaging and storage containers including, but not limited to, various laminates, skins, and facings for paneling, plywood, and other construction materials; wall coverings; and analogous uses.

In order to further illustrate the invention, the following examples are provided.

Examples 1-16

In these examples, the ring-crush strength (edgewise compression resistance) of a paperboard material treated according to the present invention (i.e., containing a polyurea-impregnated stratum) was compared to the ring-crush strength of similar paperboard material treated with various other resins known in the art for use as reinforcing agents. Ring-crush strength is an accepted measure of the crush
resistance of objects made from the respective material. The tests comprising these examples were performed according to the TAPPI T818 OM-87 standard test procedure.

The paperboard selected for these examples was a 42-pound basis weight Kraft linerboard. Separate sheets of the linerboard measuring 12 inches by 12 inches were treated individually on one face with the following resins and at the following loading levels:

<table>
<thead>
<tr>
<th>Example</th>
<th>Resin*</th>
<th>Loading Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMDI</td>
<td>3%</td>
</tr>
<tr>
<td>2</td>
<td>PMDI</td>
<td>4%</td>
</tr>
<tr>
<td>3</td>
<td>PMDI</td>
<td>8%</td>
</tr>
<tr>
<td>4</td>
<td>PMDI</td>
<td>20%</td>
</tr>
<tr>
<td>5</td>
<td>Urea-formaldehyde (UF)</td>
<td>3%</td>
</tr>
<tr>
<td>6</td>
<td>Urea-formaldehyde (UF)</td>
<td>4%</td>
</tr>
<tr>
<td>7</td>
<td>Urea-formaldehyde (UF)</td>
<td>8%</td>
</tr>
<tr>
<td>8</td>
<td>Urea-formaldehyde (UF)</td>
<td>20%</td>
</tr>
<tr>
<td>9</td>
<td>Phenol-formaldehyde (PF)</td>
<td>3%</td>
</tr>
<tr>
<td>10</td>
<td>Phenol-formaldehyde (PF)</td>
<td>4%</td>
</tr>
<tr>
<td>11</td>
<td>Phenol-formaldehyde (PF)</td>
<td>8%</td>
</tr>
<tr>
<td>12</td>
<td>Phenol-formaldehyde (PF)</td>
<td>20%</td>
</tr>
<tr>
<td>13</td>
<td>Polyester-styrene (PE/S)</td>
<td>3%</td>
</tr>
<tr>
<td>14</td>
<td>Polyester-styrene (PE/S)</td>
<td>4%</td>
</tr>
<tr>
<td>15</td>
<td>Polyester-styrene (PE/S)</td>
<td>8%</td>
</tr>
<tr>
<td>16</td>
<td>Polyester-styrene (PE/S)</td>
<td>20%</td>
</tr>
</tbody>
</table>

*The PMDI was "PAPI 2027" from the Dow Chemical Company, Midland, Michigan; the urea-formaldehyde was "SR 398B" from Borden Chemical, Columbus, Ohio; the phenol-formaldehyde was "RPLS 5460" from Georgia-Pacific, Atlanta, Georgia; the polyester-styrene was "33-402" from Reichold Chemicals, Inc., Pensacola, Florida, catalyzed with 0.6% methyl ethyl ketone peroxide.

The UF, PF, and PE/S resins were selected for comparison because they represent resins typically used in the art for reinforcing fiber-based materials such as paperboard.

The resins were applied to the sheets using a gravure coater. The PMDI resin was cured by heating the treated sheets at 204°C, 800 psig, for about
40 seconds. The urea-formaldehyde, phenol-formaldehyde, and polyester-styrene resins were cured by heating at 150°C and 800 psig for about five minutes.

After curing, the treated linerboards were cut into strips 1/2 inch wide and 6 inches long using a precision cutter. For each example, a representative strip from each example was rolled end-to-end into a cylinder and placed into a specimen holder manufactured by Sumitomo Corp., Chicago, Illinois. The holder with the test "cylinder" was then mounted on the lower platen of a conventional machine adapted for applying a compressive force. A progressively increasing axially compressive load was applied by the machine until the cylinder experienced compressive failure. The compressive force in pounds was recorded at time of failure. All tests were performed at 50% relative humidity. Experimental controls were similar compressive tests performed using the same but untreated linerboard.

Results of the ring-crush tests are shown in FIG. 1 wherein, at loading levels less than or equal to about eight percent w/w, the linerboard comprising a polyurea-impregnated stratum (treated with PMDI) exhibited substantially greater crush resistance than linerboards treated with UF, PF, or PE/S at the same loading levels. As can be seen, the ring-crush strength of the control was about 87 pounds. Of the linerboards treated with a three percent loading level, the PMDI-treated linerboard exhibited the greatest ring-crush strength (128 pounds for PMDI compared to 111 pounds for PE/S, 96 pounds for UF, and 94 pounds for PF). At a four-percent loading level, the PMDI-treated linerboard again exhibited the greatest ring-crush strength (139 pounds for PMDI compared to 113 pounds for PE/S, 108 pounds for PF, and 100 pounds for UF). At eight-percent loading, the PMDI-treated linerboard was again substantially better (154 pounds for PMDI versus 133 pounds for PF, 131 pounds for PE/S, and 124 pounds for UF).

FIG. 1 also indicates that the PMDI-treated linerboard at a three-percent loading level had a ring-crush strength after curing that was about equal to the ring-crush strengths of linerboards treated with eight percent UF, PF, or PE/S. Hence, the polyurea-reinforced fiber-based material prepared at a loading level less than half the loading level of the prior-art reinforced fiber-based materials exhibited about the same ring-crush strength as the prior-art fiber-based materials.
It is also evident from FIG. 1 that the ring-crush strength of linerboard treated with four-percent PMDI is even greater than the ring-crush strengths of linerboards treated with eight percent of PF, UF, or PE/S. Thus, again, polyurea will impart the same crush resistance to a fiber-based material at half (or less) the loading level of prior-art reinforcing agents. While it would be expected that increasing the loading level of any thermosetable resin in a fibrous web would yield corresponding increases in ring-crush strength for virtually any fibrous web treated as described with these resins, it was unexpected that polyurea at such low loading levels (particularly five percent w/w or less) would produce such dramatically improved compression strength over other reinforcing agents commonly known in the art.

Since compression strengths of fibrous materials treated with polyurea according to the present invention are substantially equal to such strengths of prior-art materials containing a loading level of reinforcing impregnant at least twice the loading level of polyurea, a brittleness (more flexibility) than fiber-based materials reinforced with prior-art agents such as PF, UF, or PE/S.

**Examples 17 and 18**

In these examples, webs made of thermoplastic fibers were treated with PMDI ("PAPI 2027") to produce a reinforced fiber-based material. The webs were a "55/50" Rayon/PET (polyethylene terephthalate) spun lace web, 2 oz/yd² (example 17) and a spun-bonded polypropylene web, 1 oz/yd² (example 8). These webs are paper-like in appearance but have "hand" characteristics similar to fabrics. The fibers comprising these webs are long compared to, for example, the fibers in a paperboard. Without reinforcement, these webs have no edgewise crush resistance at all. The PMDI loading level in each web was eight percent.

After curing, the treated webs were cut into strips and subjected to ring-crush tests at 50 percent relative humidity as described hereinabove.

The polyurea-reinforced "55:50" rayon/polyethylene terephthalate spun lace exhibited a ring crush strength of 4.4 pounds and the polyurea-reinforced polypropylene spun bonded web exhibited a ring crush strength of 1.9 pounds.
These results indicate that hydrophobic fiber-based materials can be reinforced with polyurea so as to substantially increase the crush resistance of these materials.

**Examples 19-37**

These examples comprise various paperboards treated on one side with PMDI according to the present invention. Also included are controls which received either no treatment (zero-present loading level) or PMDI loading levels greater than about 5% w/w.

The PMDI was diluted with 10% w/w propylene carbonate. The paperboards included 20 lb/1000 ft\(^2\) kraft bag paper (examples 19-22), 26 lb/1000 ft\(^2\) kraft linerboard (examples 23-25), 58 lb/1000 ft\(^2\) kraft linerboard (examples 26-31), 26 lb/1000 ft\(^2\) medium paperboard (examples 32-34), and 33 lb/1000 ft\(^2\) medium paperboard (examples 35-37). Untreated controls were examples 29, 23, 26, 32, and 35. After the resin was applied to the paperboards, the boards were cured as described in Examples 1-16. In examples 21, 22, 25, and 35, the resin was applied at loading levels greater than five percent. Ring-crush and foldability tests were performed as described in Examples 1-16. Data are presented in Table II.

**Table II**

<table>
<thead>
<tr>
<th>Example</th>
<th>Web</th>
<th>Loading</th>
<th>Crush</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>10 lb/1000 ft(^2) kraft bag paper</td>
<td>0%</td>
<td>29 lbs</td>
<td>956</td>
</tr>
<tr>
<td>20</td>
<td>&quot;</td>
<td>4.7%</td>
<td>33 lbs</td>
<td>876</td>
</tr>
<tr>
<td>21</td>
<td>&quot;</td>
<td>9%</td>
<td>33 lbs</td>
<td>904</td>
</tr>
<tr>
<td>22</td>
<td>&quot;</td>
<td>13%</td>
<td>42 lbs</td>
<td>674</td>
</tr>
<tr>
<td>23</td>
<td>26 lb/1000 ft(^2) kraft linerboard</td>
<td>0%</td>
<td>47 lbs</td>
<td>997</td>
</tr>
<tr>
<td>24</td>
<td>&quot;</td>
<td>3.9%</td>
<td>71 lbs</td>
<td>616</td>
</tr>
<tr>
<td>25</td>
<td>&quot;</td>
<td>9%</td>
<td>83 lbs</td>
<td>311</td>
</tr>
<tr>
<td>26</td>
<td>58 lb/1000 ft(^2) kraft linerboard</td>
<td>0%</td>
<td>113 lbs</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>27</td>
<td>&quot;</td>
<td>1%</td>
<td>163 lbs</td>
<td>967</td>
</tr>
<tr>
<td>28</td>
<td>&quot;</td>
<td>2.3%</td>
<td>196 lbs</td>
<td>937</td>
</tr>
<tr>
<td>29</td>
<td>&quot;</td>
<td>3.4%</td>
<td>212 lbs</td>
<td>416</td>
</tr>
<tr>
<td>30</td>
<td>&quot;</td>
<td>4.6%</td>
<td>218 lbs</td>
<td>421</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5%</td>
<td>219 lbs</td>
<td>269</td>
</tr>
<tr>
<td>----</td>
<td>---</td>
<td>-----</td>
<td>---------</td>
<td>-----</td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>26 lb/1000 ft²</td>
<td>0%</td>
<td>41 lbs</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>medium paperboard</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td>3%</td>
<td>47 lbs</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td>5.7%</td>
<td>51 lbs</td>
</tr>
<tr>
<td>35</td>
<td>33 lb/1000 ft²</td>
<td>0%</td>
<td>58 lbs</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>medium paperboard</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td>0.4%</td>
<td>65 lbs</td>
</tr>
<tr>
<td>37</td>
<td></td>
<td></td>
<td>4.3%</td>
<td>72 lbs</td>
</tr>
</tbody>
</table>

Referring to the untreated controls of Table II (examples 19, 23, 26, 32 and 35), it can be seen that each of the paperboards is quite different. The 20-lb kraft bag paper is a very flexible paperboard. Kraft linerboards are more rigid than bag paper (compare the ring-crush strength of example 23 to the ring-crush strength of example 19). Kraft medium paperboard is stiffer and more brittle than either bag paper or linerboard (compare, for example, the fold count of example 32 to the fold count of examples 19, 23, and 26). The data of Table II also show that, as PMDI loading increases, foldability (a measure of brittleness) decreases. Also, as loading increases, ring-crush strength increases. Finally, with lower basis-weight paperboards, the increase in ring-crush strength experienced with increased PMDI loading is less than the increase in ring-crush strength seen with increased PMDI loading of higher basis-weight paperboards.

While the invention has been described in connection with preferred embodiments and several examples, it will be understood that it is not limited to those embodiments. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the claims.
I CLAIM:

1. A polyurea-reinforced fiber-based material, comprising a first sheetlike web ply comprised of fibers, the first web ply having an obverse face, a reverse face parallel to the obverse face, a web thickness dimension extending between the obverse and reverse faces, and a polyurea-impregnated stratum of fibers located within said web thickness dimension, the stratum having a stratum thickness dimension no greater than about one-half the web thickness dimension such that a portion of the web thickness dimension is unimpregnated with polyurea.

2. A fiber-based material as recited in claim 1 wherein the first web ply is selected from a group consisting of woven and non-woven webs.

3. A fiber-based material as recited in claim 1 wherein the fibers of the first web ply are selected from a group consisting of hydrophobic fibers, hydrophilic fibers, and mixtures thereof.

4. A fiber-based material as recited in claim 3 wherein the fibers of the first web ply are hydrophilic fibers.

5. A fiber-based material as recited in claim 4 wherein the fibers of the first web ply are cellulose fibers.

6. A fiber-based material as recited in claim 5 wherein the fibers of the first web ply are wood-pulp fibers.

7. A fiber-based material as recited in claim 6 wherein the first web ply is a paperboard.

8. A fiber-based material as recited in claim 7 wherein the polyurea-impregnated stratum comprises polyurea at a loading level of no greater than about 5% w/w relative to the mass of the paperboard.

9. A fiber-based material as recited in claim 8 capable of being corrugated without fracturing.

10. A fiber-based material as recited in claim 8 wherein the paperboard has a basis weight of about 42 pounds and the polyurea-reinforced fiber-based material, after curing at 204°C and 800 psig for about 40 seconds, has a ring-
crush strength of at least 120 pounds at 50% relative humidity when tested according to TAPPI T818-OM-87.

11. A fiber-based material as recited in claim 10 capable, when cut to inch wide and 6 inches long, held fast on one end and gripped with a one-kg weight on the other end, and repeatedly folded over a 270º arc according to TAPPI T511-OM-83, of undergoing at least 500 folds before breaking.

12. A fiber-based material as recited in claim 1 wherein the first web ply has a first polyurea-impregnated stratum of fibers on the obverse face and extending depthwise into the web thickness dimension from the obverse face, and a second polyurea-impregnated stratum of fibers on the reverse face and extending depthwise into the web thickness dimension from the reverse face, each stratum having a stratum thickness dimension no greater than about one-third the thickness dimension of the first web ply such that at least one third of the thickness dimension of the first web ply between the first and second strata is unimpregnated with polyurea.

13. A fiber-based material as recited in claim 1 further comprising at least one additional sheetlike web ply coextensive with and adhered to the first web ply, each such additional web ply comprised of fibers and having an obverse face, a reverse face parallel to the obverse face, and a thickness dimension extending between the obverse and reverse faces.

14. A fiber-based material as recited in claim 13 wherein at least one of said additional web plies has at least one polyurea-impregnated stratum of fibers located within the thickness dimension of said additional web ply, each such stratum having a stratum thickness dimension no greater than about one-half the thickness dimension of the corresponding additional web ply, and wherein a portion of the thickness dimension of said additional web ply is unimpregnated with polyurea.

15. A fiber-based material as recited in claim 14 wherein each web ply comprises different types of fibers.

16. A fiber-based material as recited in claim 14 wherein the web plies comprise the same type of fibers.
17. A fiber-based material as recited in claim 16 wherein each web ply is a paperboard.

18. A fiber-based material as recited in claim 17 wherein each polyurea-impregnated stratum comprises polyurea at a loading level of no greater than about 5% w/w relative to the mass of the corresponding paperboard.

19. A fiber-based material as recited in claim 18 comprising two linerboards and a corrugated medium paperboard interposed between and coextensive with the two linerboards.

20. A fiber-based material as recited in claim 18 wherein at least one of said polyurea-impregnated strata is in the corrugated medium paperboard.

21. A fiber-based material as recited in claim 13 wherein each web ply comprises different types of fibers.

22. A fiber-based material as recited in claim 13 wherein the web plies comprise the same type of fibers.

23. A fiber-based material as recited in claim 22 wherein each web ply is a paperboard.

24. A fiber-based material as recited in claim 23 wherein the polyurea-impregnated stratum comprises polyurea at a loading level of no greater than about 5% w/w relative to the mass of the corresponding paperboard.

25. A fiber-based material as recited in claim 24 comprising two linerboards and a corrugated medium paperboard interposed between and coextensive with the two linerboards.

26. A fiber-based material as recited in claim 25 wherein the polyurea-impregnated stratum is in the corrugated medium paperboard.

27. A reinforced paperboard comprising:

a first paperboard ply having an obverse face, a reverse face parallel to the obverse face, and a ply thickness dimension extending between the obverse and reverse faces;

a second paperboard ply coextensive with and adhered to the first paperboard ply, the second ply having an obverse face, a reverse face parallel to the
obverse face, and a ply thickness dimension extending between the obverse and reverse faces; and

at least one of said plies having on at least one of the obverse and reverse faces thereof a polyurea-impregnated stratum coextensive with the corresponding face and having a stratum thickness dimension extending depthwise from the corresponding face into the corresponding web thickness dimension no greater than about one-half the corresponding ply thickness dimension, wherein a portion of the corresponding ply thickness dimension is unimpregnated with polyurea.

28. A reinforced paperboard as recited in claim 27 wherein each of said first and second plies has on at least one of said obverse and reverse faces thereof a polyurea-impregnated stratum coextensive with the corresponding face and having a stratum thickness dimension extending depthwise from the corresponding face into the corresponding ply thickness dimension no greater than about one-half the corresponding ply thickness dimension, wherein a portion of the corresponding ply thickness dimension is unimpregnated with polyurea.

29. A reinforced paperboard as recited in claim 27 wherein each of the obverse and reverse faces of one of said plies has a polyurea-impregnated stratum, each stratum having a stratum thickness dimension no greater than about one-third the corresponding ply thickness dimension such that at least one third of the corresponding ply thickness dimension between the strata is unimpregnated with polyurea.

30. A reinforced paperboard as recited in claim 27 wherein the first ply has a different basis weight than the second ply.

31. A reinforced paperboard as recited in claim 30 wherein the first ply is a linerboard and the second ply is a medium paperboard.

32. A reinforced paperboard as recited in claim 31 wherein the medium paperboard is corrugated.

33. A reinforced paperboard as recited in claim 27 further comprising a third paperboard ply coextensive with and adhered to the first paperboard ply.
34. A reinforced paperboard as recited in claim 33 wherein the first and third paperboard plies are linerboards and the second paperboard ply is a corrugated medium paperboard interposed between the first and third paperboard plies.

35. A carton blank made from the fiber-based material of claim 1.
36. A carton blank made from the fiber-based material of claim 14.
37. A carton blank made from the fiber-based material of claim 20.
38. A carton blank made from the fiber-based material of claim 26.
39. A carton blank made from the reinforced paperboard of claim 27.

40. A carton blank made from the reinforced paperboard of claim 34.

41. A carton made from the fiber-based material of claim 1.
42. A carton made from the fiber-based material of claim 14.
43. A carton made from the fiber-based material of claim 20.
44. A carton made from the fiber-based material of claim 26.
45. A carton made from the reinforced paperboard of claim 27.
46. A carton made from the reinforced paperboard of claim 34.

47. A method for manufacturing a reinforced 30 fiber-based material, comprising:

providing a fibrous web having an obverse face, a reverse face parallel to the obverse face, and a thickness dimension between the obverse and reverse faces;

applying a liquid polyisocyanate resin to one of the obverse and reverse faces of the web at a loading level at which the resin penetrates from the corresponding face into the thickness dimension to a depth no greater than about one-half the thickness dimension so as to form a polyisocyanate-impregnated stratum on the face of the web while leaving a portion of the thickness dimension unimpregnated with the resin, thereby forming a polyisocyanate-treated web; and

curing the resin in the polyisocyanate-impregnated stratum to form a polyurea-reinforced fiber-based material.
48. A method as recited in claim 47 wherein the step of curing the resin comprises applying heat and pressure to the polyisocyanate-treated web.

49. A method as recited in claim 47 wherein the polyisocyanate resin is selected from a group consisting of PMDS and EMDI.

50. A method as recited in claim 47 wherein the polyisocyanate resin comprises a mixture of a polyisocyanate with a solvent miscible with the polyisocyanate, the solvent present at a concentration within a range of about 5% to about 20% w/w relative to the mass of the polyisocyanate.

51. A method as recited in claim 47 wherein the step of providing the web comprises providing such a web having a moisture level of about three to about fifteen percent w/w, relative to the dry mass of the web, before applying the resin to the web.

52. A method as recited in claim 47 wherein the step of providing the web comprises providing a nonwoven web.

53. A method as recited in claim 52 wherein the step of providing the web comprises providing a paperboard.

54. A method as recited in claim 53 wherein the polyisocyanate resin is applied to the face of the paperboard at a loading level of no greater than about five percent w/w relative to the mass of the paperboard.

55. A method as recited in claim 53 wherein the step of curing the resin comprises heating the polyisocyanate-treated web to a temperature within a range of about 90°C to about 230°C at a pressure within a range of about 0 psig to about 1000 psig for a time period within a range of about 4 seconds to about 80 seconds.

56. A method as recited in claim 53 wherein the step of curing the resin comprises passing the polyisocyanate-treated web through a corrugator.

57. A method as recited in claim 53 including the step of corrugating the polyurea-reinforced fiber-based material.

58. A method as recited in claim 47 further comprising the step of also applying the liquid polyisocyanate resin to the other of said obverse and reverse faces of the web, thereby forming a polyisocyanate-impregnated stratum on each of
said faces, the polyisocyanate resin applied to each face at a loading level at which
the resin penetrates from the corresponding face into the thickness dimension to a
depth no greater than about one-third the thickness dimension so as to leave a portion
of the thickness dimension unimpregnated with the resin.

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59. A method for manufacturing a multiple-ply reinforced fiber-
based material, comprising:

providing first and second fibrous webs each having an obverse face,
a reverse face parallel to the obverse face, and a thickness dimension between the
obverse and reverse faces;

10
treating at least one of the obverse and reverse faces of the first web
by applying a liquid polyisocyanate resin to each face to be treated, thereby forming
a polyisocyanate-impregnated stratum on each of said treated faces, the resin applied
to each treated face at a loading level at which the resin penetrates depthwise from
the treated face into the thickness dimension of the first web to a depth that leaves
15
a portion of the thickness dimension of the first web unimpregnated with the resin,
said depth of penetration of the resin from each treated face being no greater than
about one-half said thickness dimension of the first web;
curing the polyisocyanate-treated first web to convert each
polyisocyanate-impregnated stratum on said web to a polyurea-impregnated stratum;

20
and

doextensively adhering a face of the first web to a face of and the
second web to form a polyurea-reinforced fiber-based material.

60. A method as recited in claim 59 wherein the step of providing
first and second fibrous webs comprises providing a medium paperboard as the first
web and providing a linerboard as the second web.

61. A method as recited in claim 60 including the step of
corrugating the first web after curing said web but before adhering together the first
and second webs.

62. A method as recited in claim 60 wherein the 5 step of curing
the first web comprises passing said web through a corrugating machine.
63. A method as recited in claim 60 including the steps, before adhering together the first and second webs, of:

- treating at least one of the obverse and reverse faces of the second web by applying the liquid polyisocyanate resin to each face of the second web to be treated, thereby forming a polyisocyanate-impregnated stratum on each of said treated faces of the second web, the resin applied to each treated face of the second web at a loading level at which the resin penetrates from the treated face into the thickness dimension of the second web to a depth that leaves a portion of the thickness dimension of the second web unimpregnated with the resin, said depth of penetration of the resin from each treated face of the second web being no greater than about one-half the thickness dimension of the second web; and

- curing the polyisocyanate-treated second web to convert each polyisocyanate-impregnated stratum on said web to a polyurea-impregnated stratum.

64. A method as recited in claim 61 including the step of providing a third fibrous web, the third fibrous web being a linerboard.

65. A method as recited in claim 64 including the step, after curing the polyisocyanate-treated first web, of coextensively adhering a face of the third web to the first web.

66. A method as recited in claim 64 including the steps:

- treating at least one of the obverse and reverse faces of the third web by applying the liquid polyisocyanate resin to each face of the third web to be treated, thereby forming a polyisocyanate-impregnated stratum on each of said treated faces of the third web, the resin applied to each treated face of the third web at a loading level at which the resin penetrates from the treated face into the thickness dimension of the third web to a depth that leaves a portion of the thickness dimension of the third web unimpregnated with the resin, said depth of penetration of the resin from each treated face of the third web being no greater than about one-half the thickness dimension of the third web; and

- curing the polyisocyanate-treated third web to convert each polyisocyanate-impregnated stratum on said web to a polyurea-impregnated stratum.

67. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 1 to form a carton blank; and
folding the carton blank to form a carton.

68. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 14 to form a carton blank;
folding the carton blank to form a carton.

69. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 20 to form a carton blank;
folding the carton blank to form a carton.

70. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 26 to form a carton blank;
folding the carton blank to form a carton.

71. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 27 to form a carton blank;
folding the carton blank to form a carton.

72. A method for manufacturing a reinforced carton comprising:
cutting and scoring the polyurea-reinforced fiber-based material of claim 34 to form a carton blank;
folding the carton blank to form a carton.
# INTERNATIONAL SEARCH REPORT

## I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

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## II. FIELDS SEARCHED

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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US, A, 5 008 359 (HUNTER) 16 April 1991 see the whole document</td>
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<td>WO, A, 9 209 645 (WEYERHAEUER COMPANY) 11 June 1992 see the whole document</td>
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- "Y": Document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "A": Document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search: 04 December 1992

Date of Mailing of this International Search Report: 30 December 1992

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: SONGY Odile

Form PCT/ISA/210 (second sheet) 1 January 1993
ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9208236
SA 65481

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