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POLYETHER-REINFORCED FIBER-BASED MATERIALS

FIELD OF THE INVENTION

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

CROSS-REFERENCE TO RELATED APPLICATION

10 The present application is a continuation-in-part of co-pending U.S. patent application Serial No. 07/770,587, filed on October 2, 1991.

BACKGROUND OF THE INVENTION

15 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
20 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
25 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
30 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 non-
35 absorptive for liquids. Examples of such reinforcement

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include impregnating or coating the fiberboard with paraffin or other polymeric material.

Paraffin coating substantially decreases the tendency of the fiberboard to absorb water, making
5 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
10 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
15 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
20 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.

25 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
30 patents disclose the application of thin films of phenolic resin to surfaces of linerboards and corrugated medium that will be adhered together to form the corrugated paperboard. After adhering together the linerboards and corrugated medium, the corrugated paperboard can be cut,
35 scored, and slotted to make box blanks. Because of the

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brittleness of the fully cured treated board, 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
5 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-
10 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),
15 3,617,427 to LeBlanc (aminoplast-modified phenol-aldehyde resole), 3,617,428 to Carlson (aminoplast with phenol-aldehyde resole), and 3,617,429 to LeBlanc (aminoplast plus phenol-aldehyde and polyvinylalcohol).

Despite these developments, even phenolic blends
20 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
25 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
30 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
35 production lines for manufacturing corrugated paperboard

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is expensive. These and other problems with existing methods can result in prohibitively high production and shipping costs.

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SUMMARY OF THE INVENTION

According to one aspect of the present invention, a polyether-reinforced fiber-based material is provided which comprises, at least, a single ply of a fibrous material impregnated with polyether on at least one of the
10 faces (i.e., major surfaces) of the ply. Each such impregnation, termed herein a "polyether-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.
15 That is, the ply of fibrous material can have a polyether-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 polyether. Therefore, if such a stratum is located
20 on both faces, each stratum has a thickness dimension preferably no greater than about one-third the thickness dimension of the ply.

Each polyether-impregnated stratum of fibers results in part from the application of a liquid resin
25 mixture to the corresponding face of the ply. The resin mixture comprises an epoxy resin (resin "A") and a hardening agent (resin "B"). Unlike conventional epoxy resin mixtures, the "resin mixture" used according to the present invention has a watery consistency as a result of
30 the "epoxy" molecules of resin "A" being in a substantially non-prepolymerized form.

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.
35 The fibers are preferably organized into a sheetlike web

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having a porosity sufficient to absorb a liquid epoxy resin mixture applied to the web for the purpose of forming a polyether-impregnated stratum. Most preferably, the wood pulp fibers are in the form of a paperboard.

5 Polyether-reinforced fiber-based materials according to the present invention exhibit high ring-crush strengths at low loading levels of polyether. For example, a polyether-reinforced paperboard according to the present invention contains a loading level of
10 polyether of about 5% w/w or less, yet exhibits a ring-crush strength greater than ring-crush strengths of other polymer-reinforced materials, such as phenolic-reinforced materials, having loading levels of polymer at least twice as high.

15 It has been unexpectedly discovered that the foldability of polyether-reinforced fibrous materials according to the present invention is excellent. All the reasons for such excellent foldability are not understood at this time. One important contributing factor is that
20 the resin mixture applied to the fibrous material according to the present invention is in a "substantially non-prepolymerized" form. As it cures, the molecules comprising resin "A" undergo less extensive crosslinking than conventional "epoxies," thereby producing a polyether
25 that has much less brittleness than polyethers produced using conventional epoxies.

Leaving a portion of the thickness dimension unimpregnated with polyether also contributes in part to the ability of the polyether-reinforced material according
30 to the present invention, despite the fact that the polyether is fully "cured," to be folded and creased without fracturing. This is in contrast to analogous prior-art materials that are generally so brittle that folding, and especially creasing, will cause fracture of
35 the material along the fold line. In fact, certain

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polyether-reinforced fibrous materials according to the present invention have exhibited foldabilities that are substantially no less than the foldabilities of corresponding fibrous materials without any polyether reinforcement. At a given ring-crush strength, the foldabilities of polyether-reinforced, fiber-based materials according to the present invention are much higher than the foldabilities of prior-art materials having equal ring-crush strengths.

10 According to another aspect of the present invention, the polyether-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 polyether-impregnated stratum. Hence, the present invention encompasses polyether-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 polyether-impregnated stratum. Preferably, but not necessarily, the corrugated medium contains one or more of the polyether-impregnated strata. Such corrugated paperboard can also be comprised of more than one corrugated medium, each sandwiched between and adhered to coextensive linerboards.

25 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 polyether-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 polyether-reinforced corrugated paperboard according to the present invention to be made at one location, then cut, scored, and folded to make cartons at another

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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,
5 methods are provided for manufacturing such polyether-reinforced fiber-based materials. In a representative embodiment, an epoxy resin mixture is applied to one or both faces of a fibrous web at a loading level that ensures that the resin mixture does not penetrate into the
10 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
15 nature of the web) is dictated by the necessity to leave a portion of the thickness dimension of the web unimpregnated with the resin mixture. Although heat and pressure are not required to cure the resin mixture, curing preferably occurs by application of heat and
20 pressure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 comprises plots of ring-crush strengths of polyether-reinforced paperboards according to the present
25 invention as a function of the amount of "hardener" (crosslinker) added to the resin mixture applied to the paperboards.

FIG. 2 shows plots of ring-crush strengths and foldabilities of prior-art polyether-reinforced
30 paperboards as a function of loading level.

DETAILED DESCRIPTION

In a method according to the present invention, a liquid epoxy resin mixture is controllably applied to
35 either the obverse face or the reverse face, or both

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faces, of a porous, sheetlike fibrous web. The resin mixture is subsequently cured to transform each epoxy-impregnated face into a polyether-impregnated stratum. Each polyether-impregnated stratum does not extend through
5 the thickness dimension of the web. In other words, even if the web possesses a polyether-impregnated stratum on both faces, the web still retains a non-impregnated stratum within the thickness dimension of the web.

As referred to herein, a "porous, sheetlike
10 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.
15 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),
20 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
25 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.

A "polyether-reinforced fiberboard" is a product
30 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 "polyether-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.

10 A "resin mixture" as used herein is a liquid formulation comprising a mixture of a resin "A" and a resin "B." Resin "A" is an epoxy resin comprising molecules having an aliphatic (straight or branched), alicyclic, aromatic, or aliphatic-aromatic core group. 15 The molecules have at least one terminal glycidyl ($-\text{CH}_2-\overline{\text{CH}}-\text{CH}_2\text{O}$) group. A wide range of such compounds are known in the art. Examples, not intended to be limiting, include glycidyl esters; glycidyl ethers such as butyl glycidyl ether and 2-ethylhexyl-glycidyl ether; diglycidyl 20 esters; and diglycidyl ethers such as 1,4-butanediol-diglycidyl ether and bis-phenol A-diglycidyl ether. Resin "A" can comprise a mixture of these various glycidyl compounds.

Resin "A," unlike the "resin" component of, for example, a conventional epoxy "cement," is substantially 25 non-prepolymerized. That is, the glycidyl compounds comprising resin "A" exist predominantly as monomers and short oligomers, such as dimers and trimers, rather than longer polymeric forms typical of conventional epoxy 30 cements. As a result, resin "A" has a watery viscosity in contrast to the syrupy consistency of epoxy "cement" resins.

Resin "B," which also has a watery consistency, comprises a "hardening" or "curing" agent for resin "A." 35 Resin "B" can be any of a wide variety of such agents

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known in the art for curing ("thermosetting") epoxies. Representative curing agents, not intended to be limiting, include polyamines, polyimines, phenols, carboxylic acids and anhydrides, mercaptans, and cationic photo-initiators
5 such as diaryliodonium salts and triarylsulfonium salts. Resin "B" can comprise a mixture of various epoxy thermosetting compounds. Preferably, polyamines such as diethylenetriamine ("DETA") or triethylenetetramine ("TETA") are used.

10 The resin mixture is prepared by combining resin "A" with resin "B" to yield a substantially homogeneous mixture thereof. Whereas virtually any amount of resin "B" can be added to resin "A," the best structural properties are obtained when the amount of resin "B" in
15 the mixture is no greater than the amount of resin "A" in the mixture. After combining resin "A" with resin "B," any of various known agitating or mixing means can be employed to create a substantially homogeneous mixture of the resins. Resins "A" and "B" can also be combined
20 together into a substantially homogeneous mixture by any of the various known continuous processes adapted for this purpose.

Mixtures of resins "A" and "B" have a watery consistency when prepared. That is, such mixtures have a
25 viscosity typically less than 500 centipoise and preferably 200 centipoise or less.

The resin mixture is preferably applied in a neat (undiluted) form to the web. Since the resin mixture is watery, it penetrates readily into virtually any porous
30 fibrous material. However, a diluent miscible with the resin mixture can be added thereto if required to facilitate penetration of the resin into unusually dense fibrous webs. Any organic liquid that is non-reactive with epoxies can be used as a diluent. Preferably, the
35 diluent is a low molecular weight monoepoxide such as a

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monoglycidyl ether or monoglycidyl ester, such as glycidyl butanoate. Other suitable diluents include, but are not limited to, propylene carbonate and phthalate esters. If used, the amount of diluent is generally within a range of
5 about 5 to 20% w/w, relative to the mass of the epoxy resin. As a diluent, propylene carbonate has certain beneficial characteristics including substantially odorless, colorless, low viscosity, low toxicity, low vapor pressure at room temperature, and low flammability
10 (boiling point: 242°C; flashpoint: 132°C).

Each polyether-impregnated stratum typically extends the length and width dimensions of the web parallel to the obverse and reverse faces of the web. When a polyether-impregnated stratum is located on only
15 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 polyether-impregnated stratum is located on both faces of
20 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 polyether.

Although fully impregnating the thickness
25 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 polyether, according to the present invention, provides a unique combination of crush strength and flexibility.
30 Accordingly, if too much of the thickness dimension is impregnated with polyether, the foldability of the fiber-based material may be less than desirable for certain uses. If too little of the thickness dimension is impregnated, the material may exhibit insufficient crush
35 resistance for certain uses.

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As the resin mixture is applied to the web, it absorbs rapidly into the pores of the thickness dimension of the web. The depth of absorption is controlled by precisely controlling the "loading" of the resin mixture on the surface of the web. As used herein, "loading" and "loading level" refer to the mass of resin mixture (or the mass of polyether, after the epoxy resin is cured) applied to a face of the web, relative to the mass of the web. Of course, a particular loading level of resin mixture will penetrate to different depths in the thickness dimensions of different webs, including webs made of different fibers. Hence, different webs can accommodate different loading levels before the requisite penetration limits are exceeded. By way of example, not intended to be limiting, most paperboards can be loaded with up to about 20% w/w resin mixture without the resin excessively penetrating the thickness dimension of the paperboard. Preferably, paperboards are loaded with 10% w/w resin mixture or less for maximal economy. For any type of web, simple cross-sectional examination of the thickness dimension of an impregnated web using a microscope or other suitable examination instrument 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 resin mixture in a manner whereby the mass of resin mixture applied per unit area of the web is precisely controlled. The resin mixture can be applied to the web by any of various liquid-application methods including, but not limited to, gravure printing, roller coating, and spraying using apparatuses having one or a plurality of spraying orifices. A preferred application method is gravure printing because it has been found that this method

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provides precise control of resin loading on the web surface.

It will also be appreciated that polyether-reinforced webs according to the present invention can be prepared by either a batch process or a continuous process. Since various apparatuses capable of performing either process are well known in the art, they will not be described further herein.

"Curing" (or "hardening" or "thermosetting") an epoxy resin converts the molecules therein to a polyether which is a type of thermoset material. Curing of the resin mixture used according to the present invention occurs via crosslinking reactions of the glycidyl moieties in resin "A" with the molecules of hardening agent comprising resin "B."

Curing can occur at room temperature, but the time required (for self-cure) may be inconveniently long. 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 mixture, polyether, or web results. A general range for curing temperature is room temperature (25°C) up to about 200°C. A general range for curing pressure is zero up to about 1000 psig. With paperboards to which the resin mixture has been applied, curing is preferably conducted at about 150°C and about 800 psig for a time from about four seconds to about five minutes. The preferred curing time at 150°C and 800 psig is about 5 minutes. 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 by application of heat and pressure offers the additional benefit of compressing the web(s) during curing, which has been found to increase the crush

resistance of the polyether-reinforced material over the
crush resistance of similar material produced at the same
loading level but without application of heat and
pressure. Nevertheless, curing without compression tends
5 to produce polyether-reinforced materials according to the
present invention that exhibit better fold resistance than
materials cured with compression. Fold resistance is also
better with thinner materials (since fold resistance is a
measure of stiffness which is a function of Young's
10 modulus \times thickness. Young's modulus increases with
increased compression, but does not increase
proportionately with the decrease in material thickness
resulting from curing under compression.

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

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

A polyether-reinforced fiber-based material
according to the present invention can also be comprised
of multiple plies. In such multiple-ply materials, it is
35 not necessary that all the plies have a polyether-

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impregnated stratum. The present invention encompasses multiple-ply materials wherein only one ply thereof has at least one polyether-impregnated stratum. The present invention also encompasses multiple-ply materials wherein 5 multiple plies each have at least one polyether-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 10 different fibrous web. The webs need not all have the same basis weight, thickness, porosity, or texture.

When the polyether-reinforced fiber-based material is comprised of more than one ply, the plies are typically superposedly adhered together. Adhering the 15 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 polyether-impregnated faces.

20 One example, not intended to be limiting, 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 polyether-impregnated stratum. As used herein, a "corrugated paperboard" is a 25 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 30 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 35 linerboard(s) of a corrugated paperboard often have a

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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
5 interposed between plies of linerboards. Corrugated paperboards are widely used for making cartons and the like.

Since curing can occur at moderate temperatures, curing of the resin mixture applied to a paperboard could
10 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
15 curing and corrugation can be advantageous when making polyether-impregnated corrugated medium according to the 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
20 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 mixture has been applied passes through the corrugator, the resin mixture may
25 undergo curing simultaneously with impression of corrugations into the paperboard.

Curing can also occur at ambient temperatures. I.e., the resin mixture can undergo a "self-cure." As a result, it is not necessary to cure the resin mixture
30 on-line after applying the resin mixture to the web. For example, it is possible to apply the resin mixture to a paperboard, corrugate the paperboard, then allow the resin mixture to self-cure off-line.

As can be appreciated from the foregoing, the
35 polyether imparts a substantial reinforcement to a fibrous

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web, enabling the polyether-reinforced web to exhibit a crush-resistance strength that is greater than the crush-resistance strength of a corresponding non-reinforced web. Hence, with products made from a polyether-reinforced web
5 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
10 benefits such as wet strength.

It has unexpectedly been found that fiber-based materials reinforced with at least one polyether-impregnated stratum according to the present invention have excellent fold resistances. In fact, in certain
15 instances, the fold resistance of a polyether-reinforced web according to the present invention is as good as a non-reinforced web. Thus, the present invention makes it possible to substantially increase the crush resistance of a fiber-based material without adversely affecting the
20 fold resistance of the material. Furthermore, reinforcing a fiber-based material with polyether according to the present invention yields greater flexibility at a given crush strength than exhibited by prior-art reinforced fiber-based materials.

25 A key benefit of greater flexibility at equal strength is that it is possible for cartons and the like to be made from fully cured polyether-reinforced corrugated paperboard produced according to the present invention, including such operations as cutting and
30 folding, without the paperboard breaking along cut and fold lines.

Polyether-reinforced fiber-based materials according to the present invention can be adhered together using conventional adhesives. In part, this is because
35 the polyether impregnant is not present through the entire

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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 5 linerboards are polyether-reinforced according to the present invention) using conventional water-borne adhesives such as starch-based adhesives, latex-based adhesives, or latex-starch adhesives to adhere non-impregnated surfaces together. Alternatively, if desired, 10 conventional non-water-borne adhesives can also be used on either non-impregnated or impregnated surfaces. Such non-water-borne adhesives include, but are not limited to, hot-melt adhesives, polyurethanes, isocyanates, epoxies, rubber-based adhesives, various solvent-borne polymers, 15 mastics, and silicones.

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

(a) Wet resistance: the materials retain crush 20 resistance even when wet, which is of considerable benefit when the materials are employed in making shipping cartons.

(b) Resistance to fracture, even after being folded a number of times. Such resistance is due in part 25 to the unexpectedly superior flexibility of polyether (prepared from a resin mixture containing a substantially non-prepolymerized epoxy resin) as a reinforcing agent and in part to the fact that the polyether impregnant does not extend entirely through the thickness dimension of the 30 web. Hence, the non-impregnated portion of the web can serve as a hinge during folding, even after a lengthy series of folds. As stated above, the improved folding resistance is obtained, however, when resin "A" is not pre-polymerized. It has been found that conventional 35 "epoxy" reinforcing agents made with pre-polymerized

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resins do not yield good fold resistance, as disclosed in co-pending U.S. patent application Serial No. 07/770,587, incorporated herein by reference.

A polyether-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 1-23

In these examples, the ring-crush strengths (edgewise compression resistance) and foldabilities of paperboard materials treated according to the present invention (i.e., containing a polyether-impregnated stratum) were determined. Ring-crush strength is an accepted measure of the crush resistance of sheetlike objects. The ring-crush tests were performed according to the TAPPI T818-OM-87 standard test procedure.

Folding endurance tests were performed on strips $\frac{1}{2}$ inch wide and 6 inches long according to the TAPPI T511-OM-83 standard 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 are recorded as the number of flexes until break.

The paperboard selected for these tests 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 a resin mixture according to the present invention at a corresponding

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loading level as listed in Table I. Ten sample strips were ring-crush and foldability tested for each example; each datum in Table I represents a sample mean where $n = 10$.

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TABLE I

	Example	Resin "A"	Parts of Resin "A"	Resin "B"	Parts of Resin "B"	Load %	Ring Crush (lbs)	Folds	Caliper (mil)
10	1	Butyl glycidyl ether	99	DETA	1	5.2	112	2863	9.4
	2	"	97	"	3	5	110	1598	9.6
	3	"	90	"	10	7.2	117	2301	9.3
15	4	"	50	"	50	6	132	1564	9.3
	5	2-ethylhexyl glycidyl ether	99	"	1	4.9	101	2725	9.2
	6	"	97	"	3	4.8	103	2516	9.5
	7	"	90	"	10	4.5	97	2772	9.2
	8	"	50	"	50	6	110	2259	9.5
20	9	bis-phenol A diglycidyl ether	99	"	1	4.9	112	1648	9.8
	10	"	97	"	3	5	108	2736	9.4
	11	"	90	"	10	4.8	171	1229	9.3
	12	"	50	"	50	4.9	152	1662	9.4
25	13	1,4-butanediol diglycidyl ether	99	"	1	4.8	135	2122	9.3
	14	"	97	"	3	5.1	139	1846	9.5
	15	"	90	"	10	5.2	155	1670	9.6
	16	"	50	"	50	5.1	147	1724	9.3
30	17	49:34 bis-phenol A/1,4 butanediol diglycidyl ethers	83	"	3	5.6	126	1885	9.3
	18	"	43	"	50	5.3	152	1383	9.8
	19	25:18 bis-phenol A/1,4 butanediol diglycidyl ethers	83	"	3	5.6	119	1681	9.3
	20	"	43	"	50	4.7	164	1937	9.7
35	21	bis-phenol A diglycidyl ether	97	TETA	3	4.9	102	2299	9.5
	22	"	50	"	50	4.8	108	1547	9.6
	23	untreated control	0	-	0	-	85	2204	9.7

40

The resin mixtures were applied to the sheets using a gravure coater. The resin mixture was cured by heating the treated sheets at 150°C, 800 psig for about 5 minutes.

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After curing, the treated sheets were cut parallel to the machine direction of the sheets into strips $\frac{1}{2}$ -inch wide and 6 inches long using a precision cutter. For ring-crush testing of each example, 5 representative strips from each example were individually 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 10 adapted for applying a compressive force. A progressively increasing axially compressive force 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 15 humidity. The experimental control comprised similar compressive tests performed using the same but untreated sheets.

Results of the ring-crush and fold-resistance tests are tabulated in Table I. Ring-crush data are also 20 plotted in FIG. 1, showing ring-crush at 50% relative humidity as a function of percent amine crosslinker (i.e., resin "B"; DETA or TETA in these tests) in the resin mixture applied to the sheets.

Turning first to the ring-crush data, it can be 25 seen (FIG. 1 and Table I) that treating the paperboard sheets according to the present invention yielded polyether-reinforced paperboard sheets exhibiting appreciably greater ring-crush strengths than untreated controls (ring-crush data typically varied 1-5% from 30 sample means; loading levels were generally about 5%). With both monoglycidyl and diglycidyl ethers, increasing the amount of amine crosslinker in the resin generally resulted in greater ring-crush strength. However, the largest percentage increases in ring-crush strength over 35 the experimental control occurred with amine crosslinker

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contents up to about 10%. Above 10% amine crosslinker, further increases in ring-crush strength were comparatively small; in fact, increasing the DETA amine crosslinker content in the bis-phenol A and 1,4-butanediol diglycidyl ethers from 10% to 50% actually resulted in a slight decrease in ring-crush strength. These results indicate that 10% amine crosslinker (resin "B") in these resins may represent a practical upper limit to the amount of resin "B" actually needed for excellent ring-crush resistance, at least for polyether-reinforced paperboards. Of course, since higher amounts of amine crosslinker also work well, the user can modify the relative amount of resin "B" to resin "A" to achieve maximal strength at least cost.

It was also noted that generally greater crush resistance was obtained when resin "A" comprised a diglycidyl ether (examples 9-22) rather than a monoglycidyl ether (examples 1-8). The exception was bis-phenol A diglycidyl ether/TETA (examples 21-22), which yielded data similar to the monoglycidyl-ether compositions. The reason for this is unclear, but may be related to the use of TETA as a hardener in examples 21-22 rather than DETA. DETA mixed with bis-phenol A diglycidyl ether (examples 9-12) yielded ring-crush values that were appreciably higher.

It should be kept in mind that, in contrast with conventional epoxy resins, resin "A" as used according to the present invention is substantially non-prepolymerized. That is, resin "A" is not comprised of oligomers. Thus, large amounts of resin "B," up to about 50%, do not generally cause a significant decline in crush-strength. Thus, a cured mixture of resins "A" and "B," even mixtures containing 50% resin "B," appear to have a lower crosslink density than cured conventional epoxy resins.

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Turning now to the foldability data (Table I), it was noticed that individual data varied as much as 50% from the sample means. (Sample-mean data are presented in the "Fold" column of Table I.) Because of the variability
5 of the data, the only general conclusion that can be drawn is that reinforcing paperboard web with epoxy resin according to the present invention did not significantly degrade the foldability of the material, compared to the untreated controls.

10 Thus, when the fold-resistance and crush-resistance data are considered in combination, the data of examples 1-23 indicate that reinforcing fiberboard webs with polyether according to the present invention yields not only an appreciable increase in crush resistance of
15 the web but also no significant decrease in fold-resistance over untreated controls. Use of a substantially non-prepolymerized resin "A" was important in achieving these surprising results. Foldability data (FIG. 2) obtained with similar webs treated with a bis-
20 phenol A glycidyl epoxy resin that had been pre-polymerized indicated that foldability decreased precipitously to zero even with only 3% loading. The ring-crush data of FIG. 2, however, indicates that crush resistance was about the same, at about 5% loading level,
25 as the data shown in FIG. 1.

Table I also includes a column containing "Caliper mL" data which pertain to measured thicknesses of the corresponding polyether-treated paperboards. Each datum represents a sample mean where $n = 10$. In view of
30 the fact that the untreated control (example 23) had a mean thickness of 9.7 mils, it appears that a small amount of compaction (compression) in the thickness dimension occurred with the polyether-treated samples (examples 1-22).

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Various polyether-treated paperboards from examples 1-23 were also investigated to determine how deeply the corresponding mixtures of resins "A" and "B" penetrated into the thickness dimensions of the paperboards. The penetration-depth values (expressed as a fraction of total thickness of the treated web) were determined by cutting the treated webs after the webs were cured and examining the cut edges using a light microscope. Data are presented in Table II.

10

Table II

Example	Resin "A" Parts				Resin "B" Parts		Penetration Depth	% Loading
	E1	E2	E3	E4	DETA	TETA		
15	3	90			10		1/3	7.2
	4	50			50		1/2	6.0
	7		90		10		1/4	4.5
	8		50		50		1/4	6.0
20	11			90	10		1/4	4.8
	12			50	50		<1/4	4.9
	13				99	1	1/2	4.8
	14				97	3	1/2	5.1
	15				90	10	1/3	5.2
25	16				50	50	1/4	5.1
	17			48.5	34	3	1/2	5.6
	18			48.5	34	50	1/4	5.3
	19			25	17.5	3	1/3	5.6
	20			25	17.5	50	1/4	4.7
30	22			50		50	<1/4*	4.8

E1 = Butyl glycidyl ether

E2 = 2-Ethylhexyl glycidyl ether

E3 = Diglycidyl ether of bis-Phenol A

35 E4 = Diglycidyl ether of 1,4-butanediol

DETA = Diethylenetriamine

TETA = Triethylenetetramine

*Thick layer of epoxy remained on surface

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The data of Table II indicate that adding more hardener (resin "B") causes the resulting mixture of resins "A" and "B" to penetrate a lesser distance into the thickness dimension of the web at a given loading level. This may be because a greater amount of hardener results in a more rapid rise in viscosity of the applied mixture of resins such that the mixture rapidly becomes too viscous after application to the fiberboard to readily penetrate further into the web. Also, TETA appears to cause more rapid curing than DETA. A comparison of examples 12 and 22 indicates that this is so, particularly since a thick layer of epoxy remained on the surface of the web in example 22.

While the invention has been described in connection with preferred embodiments and multiple 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 following claims.

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I CLAIM:

1. A 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
5 the obverse face, a web thickness dimension extending between the obverse and reverse faces, and a polyether-impregnated stratum of fibers extending parallel to the obverse and reverse faces and located within said web thickness dimension, the stratum having a stratum
10 thickness dimension less than the web thickness dimension such that a portion of the web thickness dimension is unimpregnated with polyether.
2. A fiber-based material as recited in claim 1
15 wherein the fibers of the first web ply are selected from a group consisting of woven and non-woven fibers.
3. A fiber-based material as recited in claim 1
20 wherein the fibers of the first web ply are selected from a group consisting of hydrophilic fibers, hydrophobic fibers, and mixtures of hydrophobic and hydrophilic fibers.
4. A fiber-based material as recited in claim 3
25 wherein the fibers of the first web ply comprise wood-pulp fibers.
5. A fiber-based material as recited in claim 4
30 wherein the first web ply is a paperboard.
6. A fiber-based material as recited in claim 1 wherein the stratum thickness dimension is no greater than about one-half the web thickness dimension.

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7. A fiber-based material as recited in claim 5 wherein the polyether-impregnated stratum comprises polyether at a loading level no greater than about 10 % w/w.

5

8. A fiber-based material as recited in claim 7 wherein the paperboard has a basis weight of about 42 pounds and the polyether-reinforced fiber-based material has a ring-crush strength greater than about 100 pounds at 10 50 percent relative humidity when tested according to TAPPI T818-OM-87.

9. A fiber-based material as recited in claim 8 having a foldability, when said material is tested 15 according to TAPPI T511-OM-83, substantially the same as an untreated control paperboard having a basis weight of about 42 pounds.

10. A fiber-based material as recited in claim 1 20 wherein the thickness dimension of the polyether-impregnated stratum extends from the obverse face into the thickness dimension of the web.

11. A fiber-based material as recited in claim 1 25 wherein the first web ply comprises a first polyether-impregnated stratum of fibers having a first-stratum thickness dimension extending from the obverse face into the thickness dimension of the web and a second polyether-impregnated stratum of fibers having a second-stratum 30 thickness dimension extending from the reverse face into the thickness dimension of the web.

12. A fiber-based material as recited in claim 11 wherein the first- and second-stratum thickness

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dimensions are each no greater than about one-third the thickness dimension of the web.

13. A fiber-based material as recited in claim 1
5 further comprising a second sheetlike web ply coextensive with the first web ply, wherein the second web ply is comprised of fibers and has an obverse face, a reverse face parallel to the obverse face, and a thickness dimension extending between the obverse and reverse faces,
10 and wherein the obverse face of the first web ply is adhered to the reverse face of the second web ply.

14. A fiber-based material as recited in claim 13 wherein the second sheetlike web has a polyether-
15 impregnated stratum of fibers extending parallel to the obverse and reverse faces of the second web and located within the thickness dimension of the second web such that a portion of the thickness dimension of the second web is unimpregnated with polyether.

20

15. A fiber-based material as recited in claim 13 wherein the first web ply is a medium paperboard and the second web ply is a linerboard.

25

16. A fiber-based material as recited in claim 13 wherein the first web ply is corrugated.

17. A fiber-based material as recited in claim 16 further comprising a third web ply coextensive with and
30 adhered to the reverse face of the first web ply, wherein the third web ply is a linerboard.

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18. 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; and

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

19. A reinforced paperboard as recited in claim 18 wherein each of said first and second plies has on at least one of said obverse and reverse faces thereof a polyether-impregnated stratum 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 polyether.

20. A reinforced paperboard as recited in claim 19 wherein the first ply is a linerboard and the second ply is a medium paperboard.

21. A reinforced paperboard as recited in claim 20 wherein the medium paperboard is corrugated.

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22. A reinforced paperboard as recited in claim 18 further comprising a third paperboard ply coextensive with and adhered to the first paperboard ply.

5

23. A reinforced paperboard as recited in claim 22 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.

10

24. A carton blank made from the fiber-based material of claim 1.

15

25. A carton blank made from the fiber-based material of claim 18.

20

26. A carton made from the fiber-based material of claim 1.

27. A carton made from the fiber-based material of claim 18.

28. A polyether-reinforced fiber-based material, comprising a first sheetlike web ply comprised of cellulosic 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 polyether-impregnated stratum of fibers extending parallel to the obverse and reverse faces and located within said web thickness dimension, the stratum having a stratum thickness dimension less than the web thickness dimension such that a portion of the web thickness dimension is unimpregnated with polyether,

25

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wherein the stratum comprises polyether at a loading level of greater than zero up to about 20 percent w/w.

29. A method for manufacturing a reinforced
5 fiber-based material, comprising:

(a) applying a curable liquid resin mixture comprising a substantially non-prepolymerized epoxy resin and a hardening agent for said epoxy resin to at least one face of a porous, sheetlike fibrous web having an obverse
10 face, a reverse face parallel to the obverse face, and a thickness dimension between the obverse and reverse faces, wherein the liquid is applied at a loading level at which the resin mixture does not penetrate completely through the thickness dimension, thereby forming an epoxy-
15 impregnated stratum on the corresponding face while leaving a portion of the thickness dimension unimpregnated with the resin mixture; and

(b) curing the resin mixture in each epoxy-
impregnated stratum to form a polyether-reinforced fiber-
20 based material.

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

(a) applying a curable liquid resin mixture
25 comprising a substantially non-prepolymerized epoxy resin and a hardening agent for said epoxy resin to at least one face of a porous, sheetlike fibrous web having an obverse face, a reverse face parallel to the obverse face, and a thickness dimension extending between the obverse and
30 reverse faces;

(b) allowing the resin mixture to penetrate into the thickness dimension from the corresponding face while leaving a portion of the thickness dimension unimpregnated with the resin mixture, thereby forming an epoxy-
35 impregnated stratum on the corresponding face; and

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(c) while leaving a portion of the thickness dimension unimpregnated with the resin mixture, curing the resin mixture in each epoxy-impregnated stratum to form a polyether-reinforced fiber-based material.

5

31. A method as recited in claim 30 wherein the curable liquid resin mixture has a viscosity of less than 500 centipoise.

10

32. A method as recited in claim 31 wherein the curable liquid resin mixture has a viscosity of 200 centipoise or less.

15

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

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

20

(b) applying a curable liquid resin mixture comprising a substantially non-prepolymerized epoxy resin and a hardening agent for said epoxy resin to at least one of the faces of the web at a loading level at which the resin mixture does not penetrate completely through the thickness dimension so as to form an epoxy-impregnated stratum on the corresponding face of the web while leaving a portion of the thickness dimension unimpregnated with the resin mixture, thereby forming an epoxy-treated web; and

25

30

(c) curing the epoxy in the epoxy-treated web to form a polyether-reinforced fiber-based material.

34. A method as recited in claim 33 wherein the step of curing the epoxy comprises allowing the epoxy to self-cure at ambient temperature.

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35. A method as recited in claim 33 wherein the step of curing the epoxy comprises applying heat and pressure to the epoxy-treated web.

5

36. A method as recited in claim 35 wherein the step of curing the epoxy comprises heating the epoxy-treated web to a temperature within a range of about 25°C to about 200°C at a pressure within a range of zero up to
10 about 1000 psig for a time period within a range of about four seconds to about five minutes.

37. A method as recited in claim 33 wherein the substantially non-prepolymerized epoxy resin comprises
15 molecules selected from a group consisting of glycidyl ethers, glycidyl esters, diglycidyl ethers, and diglycidyl esters, and mixtures thereof.

38. A method as recited in claim 33 wherein the
20 hardening agent is selected from a group consisting of polyamines, polyimines, phenols, carboxylic acids, carboxylic acid anhydrides, mercaptans, and cationic photo-initiators.

25 39. A method for manufacturing a reinforced fiber-based material, comprising:

(a) providing a porous, sheetlike fibrous web having an obverse face, a reverse face parallel to the obverse face, and a thickness dimension between the
30 obverse and reverse faces;

(b) providing a liquid resin mixture of a resin "A" comprising a substantially non-prepolymerized epoxy resin and a resin "B" comprising a thermosetting agent for resin "A";

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(c) applying the resin mixture to at least one of the faces of the web at a loading level at which the resin mixture does not penetrate completely through the thickness dimension, thereby forming an epoxy-impregnated stratum on the corresponding face while leaving a portion of the thickness dimension unimpregnated with the resin mixture, thereby forming an epoxy-treated web; and

(d) curing the epoxy-treated web to form a polyether-reinforced fiber-based material.

10

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

(a) providing at least 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;

(b) applying a curable liquid resin mixture of a substantially non-prepolymerized epoxy resin and a hardening agent for said epoxy resin to at least one face of at least one of said webs, thereby forming an epoxy-impregnated stratum on each corresponding face to which the epoxy resin is applied, wherein the resin mixture is applied at a loading level at which the resin mixture penetrates depthwise from the corresponding face into the thickness dimension of the corresponding web to a depth that leaves a portion of said thickness dimension unimpregnated with the resin mixture, said depth of penetration of the resin mixture being no greater than about one-half said thickness dimension of the corresponding web;

(c) curing each epoxy-impregnated stratum to convert each said epoxy-impregnated stratum to a polyether-impregnated stratum; and

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(d) coextensively adhering a face of the first web to a face of the second web to form a polyether-reinforced fiber-based material.

5 41. A method as recited in claim 40 wherein, in step (d), the face of the first web is adhered to a face of the second web using a non-water-borne adhesive.

10 42. A method as recited in claim 40 wherein the first and second webs have no more than one polyether-impregnated stratum formed thereon, leaving at least one non-impregnated face on each web.

15 43. A method as recited in claim 42 wherein, in step (d), a non-impregnated face of the first web is adhered to a non-impregnated face of the second web using a water-borne adhesive.

20 44. A method as recited in claim 40 wherein the step of providing first and second fibrous webs comprises providing a first linerboard as the first web and providing a medium paperboard as the second web.

25 45. A method as recited in claim 44 including the step, after step (c) but before step (d), of corrugating the second web.

30 46. A method as recited in claim 45 wherein step (a) further comprises providing a third fibrous web having an obverse face, a reverse face, and a thickness dimension between the obverse and reverse faces, wherein the third fibrous web is a linerboard.

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47. A method as recited in claim 46 wherein step (d) further comprises coextensively adhering a face of the third web to a second face of the first web.

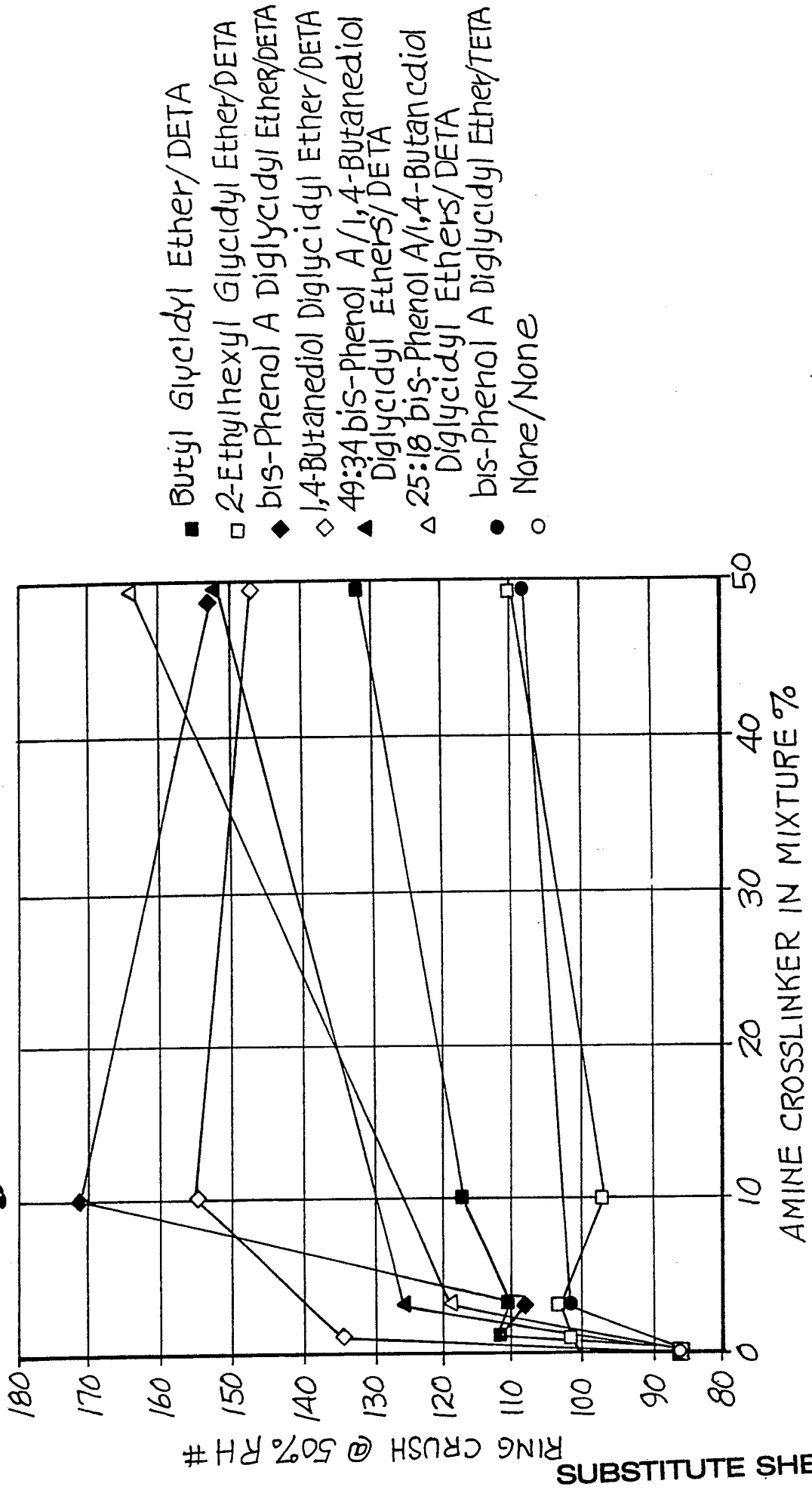
5 48. A method for manufacturing a reinforced carton comprising:
 cutting and scoring the polyether-reinforced fiber-based material of claim 1 to form a carton blank;
 and
10 folding the carton blank to form a carton.

 49. A method for manufacturing a reinforced carton comprising:
 cutting and scoring the polyether-reinforced
15 fiber-based material of claim 17 to form a carton blank;
 and
 folding the carton blank to form a carton.

 50. A method for manufacturing a reinforced
20 carton comprising:
 cutting and scoring the polyether-reinforced fiber-based material of claim 18 to form a carton blank;
 and
 folding the carton blank to form a carton.

25 51. A method for manufacturing a reinforced carton comprising:
 cutting and scoring the polyether-reinforced fiber-based material of claim 23 to form a carton blank;
30 and
 folding the carton blank to form a carton.

Fig.1



- Butyl Glycidyl Ether/DETA
- 2-Ethylhexyl Glycidyl Ether/DETA
- ◆ bis-Phenol A Diglycidyl Ether/DETA
- ◇ 1,4-Butanediol Diglycidyl Ether/DETA
- ▲ 49:34 bis-Phenol A/1,4-Butanediol Diglycidyl Ethers/DETA
- △ 25:18 bis-Phenol A/1,4-Butanediol Diglycidyl Ethers/DETA
- bis-Phenol A Diglycidyl Ether/TETA
- None/None

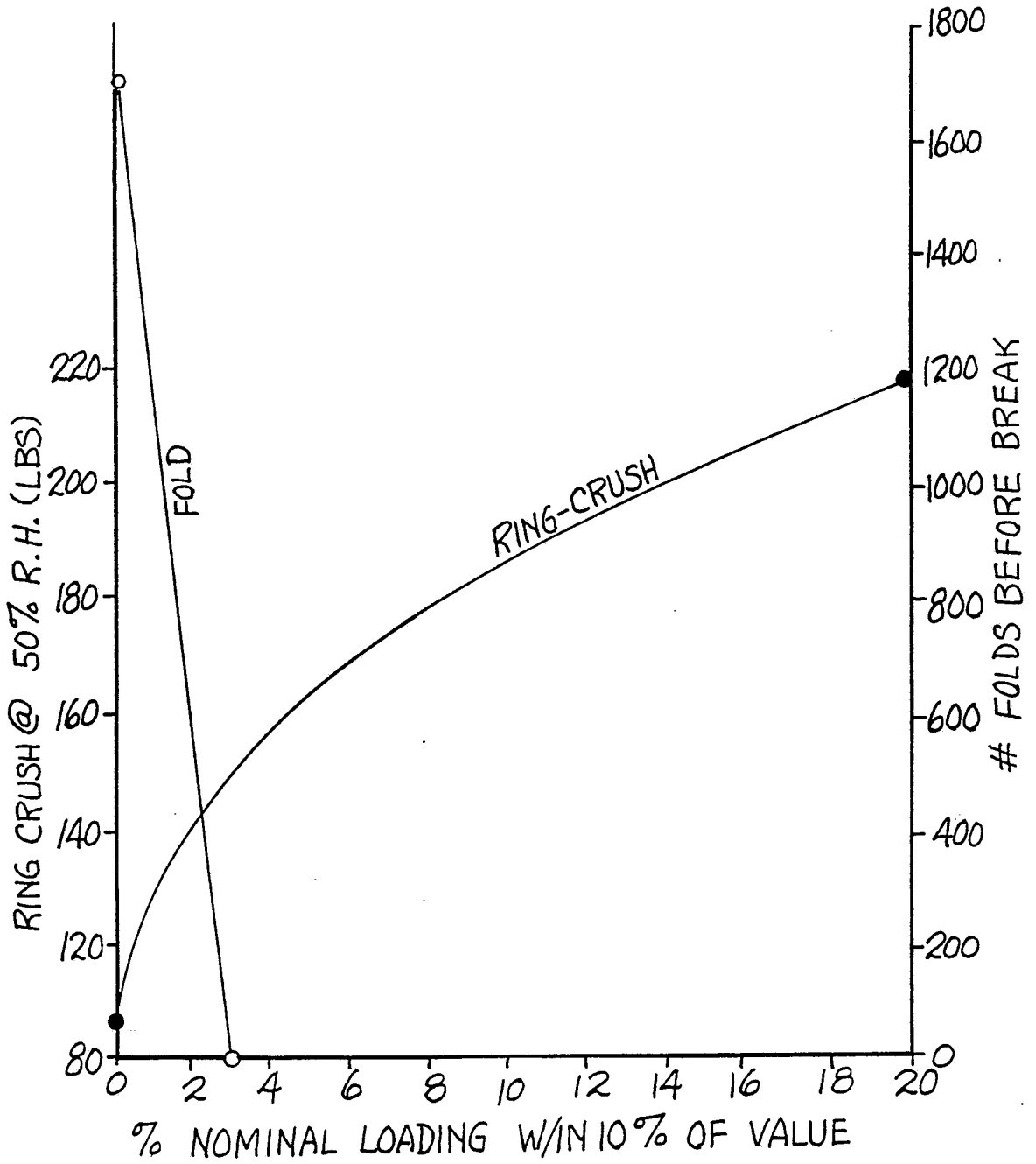


Fig. 2
PRIOR ART

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02327

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D21H27/30;	D21H17/52;	D21H17/53; B65D5/00
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,5 008 359 (HUNTER) 16 April 1991 see the whole document ---	1-51
Y	FR,A,2 087 423 (LINCRUSTA) 31 December 1971 see the whole document ---	1-51
A	US,A,3 129 133 (DOYLE et al.) 14 April 1964 ---	
P,Y	WO,A,9 209 645 (WEYERHAEUSER COMPANY) 11 June 1992 see the whole document -----	1-51
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
14 JUNE 1993		08.07.93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		SONGY Odile

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302327
SA 71586

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 14/06/93

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