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3,485,575

MODIFICATION OF LINERBOARD TO IMPROVE RETENTION OF STIFFNESS

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1 Claim

ABSTRACT OF THE DISCLOSURE

A hydrocarbon liquid such as xylene, benzene or toluene is added a composition of an organic polyisocyanate and dimethyl sulfoxide to improve the humidity resisting characteristics thereof with respect to felted paperboard, i.e. linerboard.

This invention relates to improvements in paperboard containers and relates in particular to a new and novel treatment of boxboard that materially enhances its stiffness retention properties.

In the handling and shipping of manufactured goods the most practical and frequently employed packaging material is paperboard or boxboard which is a sandwich-like construction composed of corrugated, felted fiber sheets positioned between and glued to felted sheets known as paperboard (sometimes referred to as linerboard). Containers constructed of this material possess the requisite strength and durability for ordinary handling during shipping. However, where the packaged goods are subjected to a highly humid environment, the pressed cellulosic fibers of the paperboard absorb moisture and swell. This action materially reduces the strength and stiffness retention properties of the paperboard and hence reduces the durability of the containers generally. Such moisture impregnated containers rapidly deteriorate and frequently disintegrated during handling exposing their contents to damage.

In the efficient distribution of manufactured goods in commerce, it is necessary to store packaged articles in warehouses where the economics of effective humidity control are prohibitive. Consequently, when such packaged goods are reshipped after being stored for relatively extended periods of time ranging from a week to several years, requisite stiffness and strength properties are found to have deteriorated markedly due to water absorption.

Further, when shipping folded boxboard packaged goods, the carrier is frequently subjected to such moist conditions brought on by ordinary precipitation that the containers are excessively soggy when they reach their destination.

Previous attempts to improve the stiffness retention properties of paperboard have been largely unsuccessful. Although impregnation with wax does improve both the stiffness and the stiffness retention properties of such materials, it causes other undesirable effects such as discoloration and poor scoreability. The use of resins has been largely unsuccessful for a variety of reasons. Only resins having low viscosity at temperatures which do not damage the paper may be employed at all. The resin may adversely affect the repulping characteristics of the paper or may interfere with the manufacture of the container by altering the compatibility of the paper with adhesives.

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We have discovered a new method for improving the stiffness and stiffness retention properties of paperboard that does not have the disadvantages of the prior known methods. Our method involves a treating of paperboard with a specific polyisocyanate-dimethylsulfoxide-organic solvent solution that provides surprising stiffness resistance to the effects of high humidity.

It is therefore the object of our invention to improve on the stiffness retention properties of paperboard and like materials.

It is also the object of the present invention to provide a method whereby the strength and stiffness retention properties of paperboard may be rendered substantially impervious to the effects of high humidity.

A further object of the present invention is to improve the stiffness retention properties of folded boxboard containers used to package manufactured goods that are shipped and warehoused during commercial distribution.

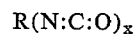
A still further object of the present invention is to treat paperboard and like felted materials with a polyisocyanate-dimethylsulfoxide-organic solvent solution that will improve the stiffness retention properties of such materials.

Other objects and advantageous features of the present invention will be obvious from the following description.

In general, the present invention consists of the discovery that when paperboard (textureboard-boxboard etc.) is contacted with a polyisocyanate-dimethylsulfoxide organic solvent solution that consists essentially of from 1 to 20 percent, by weight, of polyisocyanates and the solvent consists essentially of a mixture of dimethylsulfoxide and a second organic solvent within the ratio of from about 1:1 to 1:10 the paperboard acquires surprising stiffness and strength retention properties, even when exposed to a highly humid environment for extended periods of time.

The use of isocyanates, including di-isocyanates-solvent solutions to waterproof and stiffen cellulosic materials is well-known. Dimethylsulfoxide and benzene are known and useful solvents when applying isocyanates to cellulosic materials. Publications and patents such as U.S. Patents 2,339,913 and 3,007,763 reveal the use of these materials for waterproofing cloth.

Isocyanates are compounds that contain the univalent radical NCO which is an isocyano group united with oxygen. The generic formulation is the following:



R—an alkyl or aryl radical and
x—a number of from 1 to 3.

When isocyanates are applied to a cellulosic fiber, such as cotton cloth, in a solvent such as benzene or methylsulfoxide, to effect waterproofing, the terminal $\cdot N:C:O$ groups are believed to react with active groups on two adjacent polymer chains to effect cross linking. It is speculated that various groups on the organic chains of the fiber, such as hydrogen, hydroxyl and carboxyl groups are capable of reacting with the unsaturated linkages of the isocyanates. In any event, the cross-linking isocyanates, possibly coupled with hydrophobic organic radicals, impart the desired water resistance.

For best results, it is desirable to "swell" the cloth or fibrous structures to expose a greater surface of cellulosic

fibers to the effects of the isocyanates. This may be accomplished by pretreatment with water and an organic liquid and/or by the use of solvents such as benzene or dimethylsulfoxide as a carrier for the isocyanates.

Paperboard (or boxboard) may be waterproofed with isocyanates in the conventional manner, however, such waterproofing does not materially enhance the stiffness retention properties of this material, particularly when it is exposed to a highly humid environment for an extended period of time. Cardboard specimens waterproofed in the usual manner by impregnation with solutions of isocyanates in benzene or isocyanates in dimethylsulfoxide exhibit only slightly improved stiffness retention properties when compared to untreated specimens. However, where the isocyanate, dimethylsulfoxide-solvent solutions of the present invention are employed, the stiffness retention properties are significantly enhanced.

The isocyanates which we have found to be particularly effective in providing resistance to humid environments are the polyisocyanates. Polyisocyanates are commercially available materials usually found in a liquid form consisting of a polymer solution of a mixture of diisocyanates and triisocyanates plus small quantities of isocyanates and other impurities. We have found that treatment with solutions that are high in triisocyanate content provide optimum stiffness retention properties and hence the use of triisocyanates is a preferred embodiment of the present invention.

As set forth above, the isocyanates utilized in the solution and process of the present invention are preferably polyisocyanates. Some substantially pure triisocyanates are available commercially and we have found that best results are obtained with these. A minimum of at least one percent, by weight, of the polyisocyanate is a prerequisite in obtaining significant improved stiffness retention. As stated above, the polyisocyanates of the present invention may be alkyl or aryl polyisocyanates. Although there is no specific limit to the size or length of the radicals, it is preferred that the total number of carbon atoms of the isocyanate compounds not exceed about 33.

Dimethylsulfoxide (CH_3)₂SO is a well-known and powerful solvent which has exceptional penetrating powers. The low toxicity of this material reduces handling problems. It is a particularly good solvent for unsaturated hydrocarbons and aromatics such as the present isocyanates. As set forth above, isocyanate-dimethylsulfoxide waterproofing solutions employed for waterproofing cellulosic fibrous materials are well known, however, we have found that a second compatible solvent in amounts at least equal to the dimethylsulfoxide is necessary when such solutions are employed to impart significant humidity resistant stiffness to felted celulosic materials. The minimum preferred dimethylsulfoxide content, for the solvent is one-tenth of the compatible solvent.

The aforementioned compatible solvent may be any volatile organic liquid in which both the isocyanate and the dimethylsulfoxide are miscible and which is not reactive with either of these compounds. These requirements exclude the hydroxyl, amino, and carboxyl containing organic liquids since these reactive groups readily react with the unsaturated linkages of the isocyanates and/or the dimethyl-sulfoxide molecules.

The requisite of solvent volatility is met by nearly any organic solvent which will evaporate or volatilize at useable temperatures. It is, of course, preferred that volatilization occur at temperatures above that at which the isocyanates polymerize and bond to the felted cellulosic fibers within a reasonable period of time. Polyisocyanates polymerize and react with cellulosic fibers at room temperature, however, a reasonably rapid reaction requires temperatures within the range of from about 80° to 170° C. Thus, it is preferred that the compatible solvent possess a boiling point above the 80° C. minimum.

Preferred compatible solvents are the aromatic liquids such as benzene, toluene, xylene, and their derivatives that

are nonreactive with isocyanate and dimethyl-sulfoxide. Other particularly useful solvents are the aromatic ketones and esters.

The following specific examples illustrate the novelty of the method and composition of the present invention.

Six-by-ten-inch sections of 40 pound paperboard were treated by various strength isocyanate solvent solutions. Each section weighed approximately ten grams so that when treated with 10 grams of isocyanate-solvent solution the increase in weight (after drying) was an indication of the "add on" of isocyanates.

The specimens were contacted by the isocyanate-solvent solutions by immersing the 6 x 10" sections into the solutions in open glass trays or by positioning the specimens vertically and "drawing down" a glass rod over each surface on which the solution was deposited.

All specimens were dried in a forced draft oven for approximately one minute at about 160° C.

The treated samples or sections were cut into strips one-half inch wide and six inches long. These strips were stored for a minimum of one week under humid conditions (as indicated in the table below). One set of strips from each test solution was stored at 50 percent relative humidity, this being substantially a normal constant room temperature humidity. Other strips were stored for varying periods of time equivalent to or in excess of one week minimum time period.

Ring crush tests were performed on the specimens using the recommended practices specifications of the Technical Association of the Pulp and Paper Industry (TAPPI, 360 Lexington Ave., New York, N. Y. 10017).

The ring crush test is regarded to be the most significant test for determining the stiffness resistance of paperboard to highly humid environments. This test was conducted on an Instron Testing Machine (manufactured by the Instron Engineering Corporation, Canton, Mass.) in accordance with the TAPPI specifications Code No. T472M-51 relating to the compression resistance of paperboard (ring crush test). In this test a standard size strip of paperboard is mounted along one edge in a circular track (or slot) in a flat surface of a holder, forming a cylindrical protrusion six inches in circumference and 1/4-inch in height. Approximately 1/4-inch of the cylindrically shaped paperboard extends above the holder. The holder is seated in the tester so that the cylindrical shaped paperboard sample extends upwardly with its axis vertically disposed. An anvil mounted to the apparatus presses downwardly on the cylinder of paperboard until the paperboard buckles. The force required to effect such buckling is measured and reported in terms of pounds of force. Each figure in the data of the following table is the mean of several determinations using samples cut both with, and across, the machine direction of the paper.

In carrying out the present testing, the following commercially available polyisocyanates were employed:

(1) Polymethylene polyphenylisocyanate sold under the trade name PAPI by the Upjohn Corporation.

(2) A polyisocyanate sold under the trade name Mondur MR by the Mobay Chemical Corporation.

(3) A polyisocyanate sold under the trade name Mondur E-246 by the Mobay Chemical Corporation.

(4) A blocked polyisocyanate sold under the trade name Mondur E-250 by the Mobay Chemical Corporation.

(5) A blocked polyisocyanate sold under the trade name Mondur S by the Mobay Chemical Corporation.

Each test result reported in the table represents several ring crush tests conducted on specimens exposed to the reported humid conditions for a minimum of one week. It was determined substantially all of the loss of stiffness resistance occurred during one week's exposure to humid conditions so that although some of the tests were conducted for periods longer than a week the comparative-ness of the data is valid.

Isocyanate-solvent-treatment	Ring crush after exposure			
	50% RH	Percent of control	100% RH	Percent of control
5 g. of 20%, by wt., PAPI in 1:5 DMSO, benzene ¹ ...	194	252	104	306
10 g. of 20%, by wt., PAPI in 1:5 DMSO, benzene....	218	283	121	356
10 g. of 10%, by wt., Mondur S in 1:1 DMSO, benzene ¹ ...	160	208	86	253
10 g. of 10%, by wt., Mondur MR in 1:5 DMSO, benzene.....	183	238	93	273
10 g. of 10%, by wt., Mondur E-246 in 1:5 DMSO, benzene.....	174	226	91	268
10 g. of 10%, by wt., Mondur E-250 in 1:5 DMSO, benzene.....	170	221	87	256
10 g. of 10%, by wt., PAPI in 1:5 DMSO, methyl isobutyl ketone ²	170	221	84	247
10 g. of 10%, by wt., PAPI in 1:5 DMSO, methyl isobutyl ketone.....	168	218	87	256
10 g. of 10%, by wt., Mondur S 1:5 DMSO, benzene ³ ...	110	143	54	159
10 g. of 10%, by wt., Mondur S 1:5 DMSO, benzene....	126	164	62	182
10 g. of a 10%, by wt., wax in benzene.....	72	95	38	112
10 g. of molten wax (paraffin).....	118	153	64	188
Control (no treatment).....	77	100	34	100

¹ Solution applied to sample by being drawn down over both surfaces with a glass rod. In all of the other tests the 10-gram samples were immersed in the solution in glass trays.

² This specimen was held at a highly humid environment (100% humidity) prior to treatment. All other specimens were treated from ambient (about 50% RH) storage.

³ The specimens were pretreated in formaldehyde to promote swelling.

It can be readily noted from the data of the above table that the stiffness retention properties of paperboard specimens exposed to extremely humid environments (100 percent relative humidity) for a minimum period of time of 1 week, which had been treated with polyisocyanates, far exceeded the stiffness resistance of the control specimens (no treatment) and wax impregnated samples. Samples showed from 200–300 percent greater stiffness retention when treated with 20 percent, by weight, triisocyanate (PAPI) in a 1:5 dimethylsulfoxide-benzene solvent solution when exposed to ordinary (50%, R.H.) humid conditions for periods of one week or greater and, more significantly, from about 300–350 percent greater stiffness retention when subjected to extremely high humid conditions (100 percent relative humidity). Specimens treated with wax exhibited stiffness retention property improvements under similar conditions of less than 200 percent. With the exception of one test wherein a formaldehyde pretreatment was employed, all of the polyisocyanate-dimethylsulfoxide-solvent treated specimens showed superior stiffness retention properties to the wax impregnated specimens.

What is claimed is:

1. In a method of imparting humidity resistant stiffness to felted cellulosic paperboard materials comprising impregnating said materials with a composition comprising an isocyanate compound of the formula $R(N:C:O)_x$, wherein R is an alkyl or an aryl group and x has a value of 1 to 3 and dimethylsulfoxide, the improvement comprising including in such composition a solvent in amounts by weight of at least equal to the amount of dimethylsulfoxide and selected from the group consisting of xylene, benzene and toluene.

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