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PROCESS AND PRODUCT OF RENDERING CELLULOSIC FABRICS AMENABLE TO MOLDING OPERATIONS

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6 Claims

ABSTRACT OF THE DISCLOSURE

A process for rendering a stressed woven or knit cellulosic fabric amendable to molding operations which comprises immersing said fabric while in a relaxed state in liquid ammonia maintained at a temperature from about -60° C. to about -30° C. for a period from about $\frac{1}{4}$ minute to about 5 minutes and drying the ammonia treated fabric under conditions of minimal moisture exposure.

This invention relates to presensitized cellulosic materials and more specifically to cellulosic materials which are rendered amendable to molding operations.

Cellulosic materials such as, for instance, paper, regenerated cellulosic films, and knitted and woven textile products composed wholly or partially of cellulosic fibers have been employed in operations which require the cellulosic materials to undergo a considerable degree of deformation. The deforming operations are operations such as, for instance, laminating, packaging, and molding and the like. While cellulosic materials have a certain degree of flexibility, it is found that for certain applications the cellulosic materials have insufficient strength and flexibility to undergo that degree of deformation which is a prerequisite to the utilization of cellulosic materials. Laminates of cellulosic textile materials and vinyl films are to be preferred, for instance, over laminates of thermoplastic textile materials and vinyl films due to the fact that the fabric texture of a cellulosic material does not strike through the vinyl film and the cellulosic material has a high degree of adhesion to the vinyl film. The inability of the cellulosic textile materials which have been heretofore known, however, to undergo deformations to which the laminates are subsequently subjected, has severely limited the use of cellulosic textile materials. It is also known, that while regenerated cellulosic films have certain advantages, appearancewise over thermoplastic film for use in packaging operations, the usage of the cellulosic materials have been severely limited by the inability of the cellulosic material to conform to the sharp deformations which are required in packaging operations.

It is therefore an object of this invention to provide a process for presensitizing cellulosic material to a condition wherein the treated material is more amendable to conformation with tortuous configurations.

It is another object of this invention to provide presensitized cellulosic materials which are amendable to conformation with tortuous configurations.

In accordance with this invention, it has now been discovered that it is possible to presensitize cellulosic materials so as to accept a subsequent conformation to a tortuous configuration by means of exposing the cellulosic material, while in a relaxed state, to the action of liquid ammonia. The liquid ammonia is preferably maintained at a temperature of from about -60° C. to below about -32° C., the exposure time being for an interval of from about one second to about five minutes. The liquid ammonia immersion operation is preferably followed by a

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drying operation wherein exposure to moisture is minimized. Minimal moisture exposure is obtained by rapid drying in normal atmospheres in a drying oven such as, for instance, a Fleissner drier or by drying at room temperatures under substantially moisture free conditions. The cellulosic material should be a cellulosic material which has been subjected to stresses in its manufacture. For purposes of this invention, a stressed cellulosic material may be considered as a material which when not subjected to external mechanical forces is capable of being reduced to a more relaxed state. Materials which meet the definition of a stressed cellulosic material are drawn sheets and filaments of cellulosic materials, knitted and woven textile materials, tension calendered paper and the like. Preferably the stressed cellulosic material should contain in excess of 80% alpha cellulose. The treatment converts substantial portions of the cellulosic molecule from a crystalline configuration to an amorphous configuration, the change being readily apparent from a viewing of the X-ray diffractogram before and after liquid ammonia treatment. The amorphous structure of the cellulose molecule has been found to be more amendable to conforming to a tortuous configuration than the crystalline structure. The amorphous structure is also a structure which may be readily reconverted to the initial crystalline structure. A reversion of the cellulosic material from an amorphous structure to a crystalline structure results in the permanent setting of a cellulosic material to that tortuous configuration to which it has conformed itself while in the amorphous state.

The liquid ammonia treatments also result in a shrinkage of the cellulosic material and a substantial increase in strength. While the cellulosic material of this invention may be maintained in an amorphous structure for substantial periods of time at temperatures of 25° C. or less, it is preferred to increase the stability of the amorphous structure by impregnation with a bond inhibitor. In general, these bond inhibitors fall into two groups which are liquid ammonia compatible polymers and liquid ammonia compatible plasticizers. The bond inhibitor may be employed by simply dissolving the inhibitor in the liquid ammonia treating bath. Inhibitors which are effective in accordance with this invention are compounds capable of interfering with or substantially preventing the formation of hydrogen bonds between adjacent molecular chains of cellulose. The polyhydric alcohols containing 2 to 6 carbon atoms or mixtures thereof have been found to be especially effective and preferably use is made of dihydric and trihydric alcohols exemplified by ethylene glycol, propylene glycol, glycerine, diethanolamine, triethanolamine, trimethylene glycol, butane dioles such as tetramethylene glycol, butane triol, pentane triol, diethylene glycol, dipropylene glycol and triethylene glycol.

Polymeric materials which are suitable for use as inhibitors are any of the polymeric materials which are soluble in liquid ammonia as well as any of the polymeric materials which are soluble in an organic solvent which is soluble in liquid ammonia. The term "polymeric material" as employed herein includes monomeric materials which may be cured in situ to a polymer. Polymeric materials which have been found to be especially suitable for purposes of this invention are phenol formaldehyde, melamine formaldehyde, urea formaldehyde, dimethylol ethyleneurea, dihydroxy dimethylol ethyleneurea, polyvinyl alcohol, polyethylene glycol, polyacrylic acid, polyvinyl acetate, the sodium salt of styrene-maleic anhydride copolymer and end blocked isocyanate containing polymers.

The inhibitor is effective over a range of proportions extending from about 50 to 150 parts by weight, preferably about 100 per 100 parts by weight of cellulose.

Where inhibitors are not employed, it should be understood that it is desirable to mold the ammonia treated cellulosic material immediately after removal from the ammonia treating bath. Apparently the swelling and lubricity provided by the presence of the ammonia is beneficial as well as the fact that broken hydrogen bonds have not had time to reform.

The crystalline properties exhibited by cellulose are largely attributed to the hydrogen bonding between cellulose chains. A moldable cellulose theoretically requires a condition in which a majority of the hydrogen bonds between cellulose chains are eliminated or prevented. One method of eliminating or reducing interchain hydrogen bonding is to interpose small molecules or groups between the cellulose chains. When crystalline cellulose is subjected to the action of liquid ammonia, an amorphous cellulose is obtained by the action of ammonia in rupturing of hydrogen bonds, a theory which is confirmed by X-ray diffraction patterns. Apparently, however, the ability of liquid ammonia to break the hydrogen bonds of cellulosic material is primarily an internal phenomenon and the process of this invention is preferably carried out on cellulosic materials having large surface areas which are readily penetrable by liquid ammonia such as, for instance, textile materials and sheets and films having thicknesses of 1/8 of an inch and less. If it is desired to treat materials of greater thicknesses, it is necessary to employ vacuum conditions in order to allow the liquid ammonia to penetrate substantially all pore spaces.

A better understanding of the invention may be had from the following examples. It should be understood, however, that the examples are given for purposes of illustration and should not be considered as limiting the spirit or scope of this invention.

EXAMPLE I

A high stretch all cotton knit fabric having a weight of 4.55 yards per pound knitted from singles twenty yarn on an eighteen inch diameter Camber machine so as to have 26 plus or minus 2 wales per inch and 24 plus or minus 2 courses per inch is immersed in a liquid ammonia bath. The liquid ammonia bath is maintained at approximately -33° C. and the fabric is subjected to an immersion time in this bath for about 2 minutes. The treated fabric is then removed from the bath and passed through a Fleissner drier at the rate of about 1 yard per minute, the rate subjecting the fabric to a total drying time of from about 4 1/2 minutes to about 5 minutes. The improvement obtained by the liquid ammonia treatment was determined by evaluating an untreated section of the previously identified fabric by means of a Scott Grab Tensile test and then evaluating a treated section in swollen state (area shrinkage-25%) of the previously identified fabric by means of the same test. The results being as follows:

Sample identification	Scott Grab Tensile			
	Brk. strength (lbs.)		Percent elongation	
	Wales	Courses	Wales	Courses
Control.....	28.4	16.6	64.3	257
Treated.....	42.6	26.4	103.9	313

EXAMPLE II

A high stretch all cotton knit fabric having a weight of 2 yards per pound prepared from singles eighteen yarn in a manner so as to have 27 plus or minus 2 wales per inch and 36 plus or minus 2 courses per inch is subjected to a liquid ammonia bath. The liquid ammonia is maintained at a temperature of about -33° C., the fabric being subjected to the liquid bath for about 2 minutes. The fabric is then removed and passed through a Fleissner drier at a rate of about 1 yard per minute, the rate being such as to subject the fabric to drying conditions or from about 4 1/2 to about 5 minutes. The improvement obtained

in fabric properties was determined by subjecting a sample of the previously identified fabric to a Scott Grab Tensile test and then repeating the test determinations on a sample of the above identified fabric which had undergone liquid ammonia treatment, the results being as follows:

Sample identification	Scott Grab Tensile			
	Brk. strength (lbs.)		Percent elongation	
	Wales	Courses	Wales	Courses
Control.....	51.6	41.9	67.3	126.7
Treated.....	76.5	59.4	159.3	218.7

EXAMPLE III

A high stretch jersey knit all rayon fabric having a weight of 4.05 ounces per square yard prepared from singles fifteen viscose rayon staple fiber yarn in a manner so as to have 16.4 wales per inch and 19.2 courses per inch is subjected to a liquid ammonia bath. The liquid ammonia bath is maintained at a temperature of about -33° C., the fabric being immersed in the bath for about 2 minutes. The fabric is then removed and passed through a Fleissner drier at the rate of about 1 yard per minute, the rate being such to subject the fabric to drying conditions for from about 4 1/2 minutes to about 5 minutes. The improvement obtained in treating the fabric with liquid ammonia is determined by testing an untreated sample of the previously identified fabric by means of a Scott Grab Tensile test and then repeating the test on a sample of the previously identified fabric which has undergone liquid ammonia treatment, the results being as follows:

Sample identification	Scott Grab Tensile			
	Breaking Str. (lbs.)		Percent elongation	
	Wales	Courses	Wales	Courses
Control.....	32.4	21.8	84.8	193.2
Treated.....	34.0	24.5	184.3	282.6

EXAMPLE IV

A single jersey stitch paper fabric yarn prepared from paper yarn produced by slitting 10 pound per ream kraft paper to 1/4 inch width and folding and crimping is subjected to the action of a liquid ammonia bath. The paper fabric prior to the liquid ammonia bath treatment is found to have 6 courses per inch and about 4 wales per inch. The liquid ammonia bath is maintained at a temperature of about -33° C., the fabric being immersed in a liquid ammonia bath for a period of about 2 minutes. The fabric is then removed and passed through a Fleissner drier at a rate of about 1 yard per minute, the rate being sufficient to subject the paper fabric to a drying time for a period of from about 4 1/2 minutes to about 5 minutes. A sample section of the previously described paper fabric is then subjected to a Scott Grab Tensile test, the test being repeated on a sample section of the previously described paper fabric which has undergone liquid ammonia treatment. A comparison of the test results of the Scott Grab Tensile test is found to show an improvement in percent elongation of the liquid ammonia treated fabric over the paper fabric which has not undergone liquid ammonia treatment.

EXAMPLE V

A cotton print cloth having 80 ends and 80 picks per inch prepared from singles forty yarn having a weight for a 39 inch width of 4 yards per pound is subjected to the action of a liquid ammonia bath, the liquid ammonia bath having glycerine dissolved therein in quantities of about 5% by weight. The liquid ammonia bath is maintained at a temperature of about -33° C., the fabric being immersed in the liquid ammonia bath for a period of about 2 minutes. The fabric is then removed and passed through a Fleissner drier at a rate of about 1 yard per minute, the rate being sufficient to subject the fabric

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to a drying time for a period of from about 4½ minutes to about 5 minutes. A sample section of the previously described cotton print cloth is then subjected to Scott Grab Tensile test, the tests being repeated on a sample section of the previously described cotton print cloth which has undergone liquid ammonia treatments. A comparison of the test results of the Scott Grab Tensile test is found to show an improvement in percent elongation and in tensile strength of the liquid ammonia treated fabric over the fabric which has not undergone liquid ammonia treatment.

Sample identification	Scott Grab Tensile			
	Breaking Str. (lbs.)		Percent elongation	
	Warp	Fill	Warp	Fill
Control.....	50.2	36.0	9.5	18.9
Treated.....	69.1	35.0	30.4	43.2

EXAMPLE VI

A 1 inch by 6 inch sample of untreated regenerated cellulose film having a thickness of .001 inch is immersed in a liquid ammonia bath containing 5% by weight diethylene glycol. The liquid ammonia bath is maintained at approximately -33° C. and the regenerated cellulose film is subjected to an immersion time of about 2 minutes. The ammonia treated film is then removed and allowed to dry at room temperatures under substantially moisture free conditions. The improvement obtained by the liquid ammonia treatment of film was determined by evaluating an untreated 1 inch by 3 inch sample of the previously identified film by placing the lengthwise end of the film in the jaws of an Instron machine. The test was then repeated by placing the ends of the short axis of the sample in the jaws of the Instron machine. Comparable tests were then run on the treated regenerated cellulose film sample with the overall result being as follows:

Sample identification	Instron break test	
	Lengthwise	Widthwise
Control.....	9.5	4.5
Treated.....	17	12

EXAMPLE VII

A cotton broadcloth of 136 x 64 construction prepared from single thirties fill yarns and single forties warp yarns is subjected to the action of a liquid ammonia bath, the liquid ammonia bath containing 5% based on the weight of the ammonia of dihydroxy dimethyl ethyleneurea. The fabric is maintained in the bath for 4 minutes and then removed and immediately molded on a brassiere cup molding device, the mold being maintained at a temperature of 253° F. The molded fabric was found to retain its dimensional stability and to be durable to washing.

EXAMPLE VIII

An all rayon challis fabric of 68 x 62 construction prepared from single thirties rayon staple yarn in both warp and fill directions is immersed for 4 minutes in a liquid ammonia treating bath containing 5% by weight based on the weight of the liquid ammonia of urea formaldehyde. The fabric is then removed and passed through a Fleissner drier at the rate of about 1 yard per minute, the rate being sufficient to subject the fabric to a drying time for a period of from about 4½ minutes to about 5 minutes. The dried fabric is then placed in a brassiere cup mold, the mold being maintained at a temperature of about 253° F. The molded product is found to retain its dimensional stability and to be durable to washing.

The Scott Grab Tensile test which has been called for in the previous examples is a standard method of tests

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for breaking load and elongation of textile fabrics and is set forth in ASTM designation D1682-64. In general, the Grab test is a test in which only part of the width of the specimen is gripped in the clamps of the testing equipment. For example, in the specimen which is 4 inches and the width of the gripping device 1 inch, the specimen is gripped centrally in the clamp. The Grab method is applicable whenever it is desired to determine the "effective strength" of the fabric in use, that is the strength of the yarn in specific width together with the additional strength contributed by adjacent yarn.

As previously stated, the cellulosic materials of this invention lend themselves to molding operations and especially to the molding operations wherein the cellulosic material retains its dimensional stability by itself or as part of a laminate such as, for instance, a cellulosic fabric-vinyl film laminate. Where the cellulosic material is to retain its molded configuration without undergoing laminating operations, it is preferred that the cellulosic material be treated with a liquid ammonia bath containing a thermosetting resin. The molding operations may be any of the molding operations well known to the art such as vacuum molding operations and pressure molding operations.

Having thus disclosed the invention, what is claimed is:

1. A process for rendering a stressed woven or knit cellulosic fabric amenable to molding operations which comprises immersing said fabric while in a relaxed state in a bath consisting essentially of a thermosetting resin and liquid ammonia maintained at a temperature from about -60° C. to about -30° C. for a period from about ¼ minute to about 4 minutes and drying the ammonia treated fabric under conditions of minimal moisture exposure.

2. A process according to claim 1 wherein the drying is performed in an oven.

3. A process according to claim 1 wherein a polyhydric alcohol containing from 2 to 6 carbon atoms is incorporated in the liquid ammonia.

4. A process according to claim 1 wherein the fabric is immersed in liquid ammonia for a period from about ¼ minute to about 2 minutes.

5. A stress relieved woven or knit cellulosic fabric prepared according to the process of claim 1.

6. A stress relieved woven or knit cellulosic fabric prepared according to the process of claim 3.

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