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[54] **ABSORBENT PRODUCTS FROM WET
CROSS-LINKED WOOD PULPBOARD
AND METHODS OF MAKING THE
SAME**

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8/116.4

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[57]

ABSTRACT

A method of making a fibrous, cellulosic absorbent product from sheets of pulpboard which comprises: wet cross-linking sheets of pulpboard; grinding the wet cross-linked sheets of pulpboard to form a pulp fluff therefrom having improved wet resilience, increased fluid absorption and retention capacity, and low knot content; and forming an absorbent product utilizing the pulp fluff as a fluid absorption and retention material therein.

4 Claims, No Drawings

ABSORBENT PRODUCTS FROM WET CROSS-LINKED WOOD PULPBOARD AND METHODS OF MAKING THE SAME

The present invention relates to absorbent products for absorbing fluids, and more particularly, is concerned with fibrous cellulosic products having increased fluid absorption and retention capacities, improved wet resilience, and low knot content.

Absorbent products for absorbing and retaining body exudates and fluids such as sanitary napkins, diapers, hospital underpads, towels, compresses, combine dressings, pads, rolls, surgical dressings, tampons, and the like, usually contain fibrous absorbent materials of a cellulosic origin, usually wood pulp fluff. Other fibrous absorbent materials are often used but wood pulp fluff is normally preferred, particularly for economic reasons.

The wood pulp fluff is usually prepared by grinding sheets or strips of wood pulpboard in hammer mills or other commercial shredding or grinding devices and delivering the ground wood pulp in fluffed form to a production line where it is incorporated with other constituents in the particular absorbent product being manufactured. Such wood pulp fluff normally has excellent fluid absorption and retention properties and acceptable dry and wet resilience. Its low cost and other economic advantages, of course, do not need repeating.

Wood pulp fluff has been used in making absorbent products for many years with satisfactory results but it is always desirable to improve existing products and materials, no matter how satisfactory or acceptable they have been in the past.

For example, in recent years, there have been several efforts made in the direction of cross-linking cellulosic fibrous materials in order to improve their fluid-absorbency and fluid-retention properties, along with their dry and wet resilience, and other physical and chemical properties and characteristics.

Cross-linked cellulosic fibrous materials may be obtained by reacting cellulosic fibrous materials with cross-linking agents which are capable of combining with at least two hydroxyl groups in the cellulose molecule, or in adjacent cellulose molecules. The reactive groups of the cross-linking agent which combine with the hydroxyl groups may exist prior to the reaction with cellulose, as in the case of glyoxal, or they may be generated during the reaction with the cellulose, as in the case of the sodium thiosulfate derivative of divinyl sulfone. In order to cross-link cellulose, the cross-linking agent must be at least difunctional with respect to cellulose, e.g., it must react with at least two hydroxyl groups. Formaldehyde, for example, is monofunctional with regard to many substances; it is, however, difunctional with respect to cellulose. In many polyfunctional chemical compounds of the type that react with two or more hydroxyl groups, one reactive group of the polyfunctional chemical compound may react more rapidly than other groups. Consequently, within a given reaction time, not all of the reactive groups on a molecule of the polyfunctional chemical compound may react with the hydroxyl groups in the cellulose molecule to form cross-links; only one of the reactive groups may so react. As defined herein, cross-linking occurs when at least two of the reactive groups in a molecule of the polyfunctional material react.

Cellulose can be cross-linked in a number of ways and, in accordance with current concepts, may be dry cross-linked or wet cross-linked. The two types of cross-linking refer to the manner in which the cross-linking is done.

DRY CROSS-LINKING

Dry cross-linked cellulose is obtained when the cellulose fibers are in a collapsed state at the time of cross-linking. A collapsed state is obtained by removing most or all of the water from the fibers which causes the fibers to swell. In one known procedure, the cellulosic fibers are passed through a boric acid solution, dried, and then heated in a sealed tube in the presence of paraformaldehyde. The fibers are then washed

free of unreacted material. A more common technique is to apply the cross-linking agent and a catalyst to the cellulosic fibers in an aqueous bath, drive off the water in a drying step, and react the cross-linking agent with the cellulosic fibers in a subsequent curing step.

Dry cross-linking improves the properties and characteristics of cellulosic fibrous materials in many ways and particularly in both the dry resilience and wet resilience aspects. As a result of such improved properties and characteristics, dry cross-linking has been preferred in many areas and in many uses over wet cross-linking in which the improvement in dry resilience is not as marked.

Unfortunately, it has been found that such a dry cross-linking process, when applied to sheets of wood pulpboard, creates considerable problems in the subsequent shredding or grinding step and an unsatisfactory dry cross-linked wood pulp fluff is obtained which is not capable of being disintegrated properly and which contains severe fiber breakage in the final product. Another important objection is the very high hard fiber clump or knot content of the disintegrated dry cross-linked wood pulp fluff. Such hard fiber clumps or knots which are present sometimes rise as high as about 50-75 percent and render the dry cross-linked product completely unsuitable for many purposes.

In order to avoid such shortcomings, it has been proposed that the sheets of wood pulpboard be disintegrated first by grinding or shredding so that the resulting fibrous product will be in a substantially individually or loosely associated state and have a multiplicity of relatively large interconnected networks of voids and interfiber spaces at the time of a subsequent dry cross-linking reaction. In this way, it was hoped that the formation of hard fiber clumps and knots would be avoided. Unfortunately, the additional costs and economic disadvantages of such a system were believed to be too great and the search has continued for a better process and a better product.

WET CROSS-LINKING

Wet cross-linked cellulose is obtained when the cross-linking agent is reacted with the cellulose while the cellulose fibers are not collapsed but are in a swollen state. Ordinarily, the cellulose fibers are maintained in a swollen state by water which is present during the reaction. However, techniques have been developed whereby the cellulose fibers can be maintained in a swollen state in the absence of water by using in lieu thereof an inert, non-volatile substance. Cellulose fibers so treated have the properties of wet cross-linked cellulose even though the reaction takes place in the absence of significant amounts of water.

As mentioned previously, wet cross-linking does not materially improve all the properties and characteristics of cellulosic fibrous materials, such as its dry resilience, as much as dry cross-linking, and hence such wet cross-linking process has been ignored for use with certain products.

It has now been discovered that, even though wet cross-linking does not improve the dry resilience properties and characteristics of cellulosic fibrous materials, such process is admirably suited for use in producing fluid absorbent and retentive products, even though their dry resilience is not as high as could be obtained with dry cross-linking.

Of particular and outstanding merit, moreover, is the discovery that sheets of pulpboard may be wet cross-linked first whereby many of the desired properties and characteristics due to cross-linking may be obtained and that such sheets of wet cross-linked pulpboard may subsequently be ground or shredded without creating severe fiber breakage in the final product and without creating a high content of knots or hard fiber clumps.

These improved chemical and physical properties and characteristics are also obtained by processes described in greater detail in related copending patent application, Ser. No. 47,135, filed concurrently herewith. Such other processes

describe the application of cross-linking techniques to pulp slurries or dispersions at a time prior to their formation into pulpboard. However, there are many areas of related matter which exist between that copending patent application and this patent application.

The present invention will also be described in greater particularity in combination with the wet cross-linking reaction wherein the fibers are swollen and are not collapsed. The invention will also be disclosed specifically with reference to the use of formaldehyde as the wet cross-linking agent. This, however, is for purposes of illustration and it is to be appreciated that other wet cross-linking agents can be used. Additional wet cross-linking agents, for example, include: condensation products of formaldehyde with organic compounds, such as urea, or other chemical compounds which contain at least two active hydrogen groups, particularly dimethylolurea, dimethylol ethyleneurea and imidazolidone derivatives; dicarboxylic acids; dialdehydes such as glyoxal; diepoxides; diisocyanates; divinyl compounds; dihalogen-containing compounds such as dichloroacetone and 1,3-dichloropropanol-2; halohydrins such as epichlorohydrin; etc.

The principles of such wet cross-linking techniques are generally described in greater detail and greater specificity in U.S. Pat. No. 3,241,553 which issued Mar. 22, 1966 and reference thereto is made for particular aspects of the process which need not be repeated here.

The wet cross-linking process described herein using formaldehyde generally reaches a practical maximum of efficiency and cross-linking after about a 30-minute reaction time and levels off in practical effectiveness for reaction times beyond 30 minutes. Shorter periods of time, however, even as short as 5 minutes yield beneficial results and are of use. Additional cross-linking time beyond 30 minutes does not add materially to the cross-linking effect.

Subsequent to the wet cross-linking reaction, the wet cross-linked pulpboard may be immersed and washed in a basic or alkaline solution such as sodium carbonate, sodium bicarbonate, sodium hydroxide, etc. to neutralize the acidity of the materials due to the acidic nature of the wet cross-linking treatment and to remove excess or unreacted formaldehyde. Rinsing and washing then follow, preferably first in hot water and then in cold water. The washed and rinsed wet cross-linked wood pulpboard is then air dried at room temperature, or dried in a forced-air oven maintained at an elevated temperature of from about 210° F. to about 250° F.

The wet cross-linked pulpboard is then ground or shredded to produce the pulp fluff. Such grinding may take place in any suitable grinding, shredding or comminuting device such as, for example, a Weber hammer mill. It is during this grinding operation that the wood pulp fluff is created which unfortunately contains undesirable clumps and knots to various degrees.

In this specification and particularly in the Examples, reference is made to the "knot content" of a particular sample of pulp fluff.

The knot content of the pulp fluff samples is determined according to the constant air-blowing technique. This involves placing a 5 gram sample in the bottom of a conventional 1,000 ml. burette and admitting air through the petcock at the bottom at a controlled constant flow rate of 3.5 cubic feet per minute to get a tumbling action of the sample. This causes the individualized fibers of the sample to rise and to escape through the open top end of the burette but leaves behind the heavier knots or fiber clumps at the bottom. The knots are then removed and weighed and the knot content (percent) determined.

As a result of using a wet cross-linking treatment on wood pulpboard prior to the grinding operation, the knot content is surprisingly not materially increased over the knot content of a pulp fluff derived from an untreated pulpboard. However, a comparison to a pulp fluff derived from a dry cross-linked pulpboard indicates a much higher knot content as compared to the untreated pulp fluff.

It is therefore seen that the wet cross-linking treatment yields substantially all the known desirable results of cross-linking over materials which are not cross-linked, such as minimized spreading of fluids, effective fluid transfer, low resistance to fluid flow, high fluid capacity, reduced material physical distortion in a wet state, high bulk in the wet state, high absorbency, etc., without any material increase in knot or fiber clump content.

The invention will be further described by reference to the following Examples wherein there are disclosed preferred embodiments of the present invention. However, it is to be appreciated that such Examples are illustrative but not limitative of the broader aspects of the inventive concept.

EXAMPLE I

Natchez wood pulpboard (Southern pine, kraft type, 8.5 percent hemicellulose) is washed in running water at room temperature for 60 minutes and is then air dried at room temperature. The wood pulpboard is then cut up into 1½ inch squares and ground in a Homoloid mill at 7,150 revolutions per minute. The 316-3A/187 screen (0.187 inch opening) is used. The knot content of the ground wood pulpboard which has not been cross-linked is determined for three samples by the hereinafter standard laboratory procedure. The results are as follows:

Water washed pulpboard control

21%
16%
18%

18.3% Average Knot Content

EXAMPLE II

Natchez wood pulpboard (Southern pine, kraft type, 8.5 percent hemicellulose) is wet cross-linked by being immersed at room temperature for 30 minutes in a solution containing (by volume) 20 percent Formalin (37 percent HCHO), 50 percent Hydrochloric Acid (37 percent HCl), and 30 percent water. The wood pulpboard is then neutralized by being immersed in an excess of 5 percent sodium bicarbonate solution. After bubbling ceases, the wood pulpboard is washed in running water at room temperature and then air-dried at room temperature. The wood pulpboard is then cut up into 1½ inch squares and ground in a Homoloid mill at 7,150 revolutions per minute. The 316-3A/187 screen (0.187 inch opening) is used. The knot content of the ground, wet cross-linked pulpboard is determined for three samples by the hereinafter standard laboratory procedure. The results are as follows:

Wet cross-linked pulpboard

24%
22%
18%

21.3% Average Knot Content

EXAMPLE III

Natchez wood pulpboard (Southern pine, kraft type, 8.5 percent hemicellulose) is dry cross-linked by being immersed at room temperature for 60 minutes in a solution containing (by volume) 10 percent Formalin (37% HCHO), 9 percent Hydrochloric Acid (37% HCl) and 81 percent Glacial Acetic Acid. The pulpboard is then neutralized by being immersed in an excess of 5 percent sodium bicarbonate solution. After bubbling ceases, the pulpboard is washed in running water at room temperature and then air-dried at room temperature. The pulpboard is then cut up into 1½ inch squares and ground in a Homoloid mill at 7,150 revolutions per minute. The 316-3A/screen (0.187 inch opening) is used. The knot content of the ground dry cross-linked pulpboard is determined for three samples by the hereinafter standard laboratory procedure. The results are as follows:

Dry cross-linked pulpboard

52%
56%
61%

56.3% Average Knot Content

The results of Examples I-III indicate that the wet cross-linking treatment does not materially increase the knot content of the ground wood pulp fluff over that of the water washed untreated control sample. On the other hand, the dry cross-linking treatment more than tripled the knot content of the ground wood pulp fluff over that of the water washed untreated control sample.

EXAMPLE IV

The procedures of Example I-III are carried out substantially as set forth therein except that a Weber hammer mill is used instead of a Homoloid mill and different types of wood pulpboard are used to prepare the wood pulp fluff. The results are as follows:

	KNOT CONTENT		
	Untreated Control	Wet Cross-Linked	Dry Cross-Linked
Buckeye Regular (Southern pine, kraft type, 8.5% hemicellulose)	2	3	37
Natchez (Southern pine, kraft type)	14	13	100*
Natchez (Southern pine, kraft type)	14	13	45
Buckeye Holocellulose (Southern pine, kraft type, 15.2% hemicellulose)	51	54	75

*Resin-forming cross-linking agent (Permafresh 183, imidazolidone derivative, cured at 150° C.).

Again, such values show that the knot content of the wet cross-linked wood pulp fluff is not materially different than the knot content of the water-washed untreated control sample. However, in all cases, the knot control of the dry cross-linked wood pulp fluff is materially increased over the knot content of the water washed untreated control sample.

EXAMPLE V

The water-washed untreated Natchez pulpboard of Example I is ground and formed into catamenial tampons which are soaked for five minutes in a standard test solution at room temperature and a pressure of 24 inches of water. More specific details of such test procedures are to be found in U.S. Pat. No. 3,241,553. The following results show the absorbent fluid capacities of such tampons:

	Tampon Weight (grams)	Tampon Density (grams per cc)	Tampon Capacity (cc per gram)
1	3.79	0.403	2.64
2	3.76	0.391	2.74
3	3.78	0.609	2.03
4	3.76	0.600	2.01
5	3.76	0.387	2.41
6	3.76	0.382	2.57

EXAMPLE VI

The wet cross-linked Natchez wood pulpboard of Example II is ground and formed into catamenial tampons which are soaked for five minutes in a standard test solution at room temperature and a pressure of 24 inches of water. The following results show the absorbent fluid capacities of such tampons:

	Tampon Weight (grams)	Tampon Density (grams per cc)	Tampon Capacity (cc per gram)
1	3.76	0.354	3.03
2	3.74	0.384	3.31
3	3.76	0.547	2.87
4	3.73	0.504	2.73
5	3.76	0.388	3.10

6 3.73 0.389 2.97

The results of Examples V-VI indicate that the fluid absorptive and retentive capacity of a catamenial tampon containing wet cross-linked wood pulp fibers represents a substantial increase at comparable densities and weights over the fluid absorptive and retentive capacity of a catamenial tampon containing water-washed wood pulp fibers which are not wet cross-linked.

EXAMPLES VII-VIII

The improvement in the wet resilience of the wet cross-linked wood pulp fluff over the wet resilience of water-washed wood pulp fluff which is not cross-linked is established by the following Examples.

In these Examples, samples of selected wood pulp fluff are placed in Petri dishes containing sufficient water to saturate the samples which are permitted to remain there for several minutes before testing begins.

The wet control wood pulp fluff sample (not cross-linked) is derived from 4.3 percent hemicellulose wood pulpboard which is not cross-linked. This sample collapses to 55 percent of its original bulk volume upon being wetted and then, upon the application of a pressure of 200 grams per square centimeter, collapses even farther to 10 percent of its original bulk volume. Upon removal of the pressure, the sample recovers only to 23 percent of its original bulk volume.

The wet cross-linked wood pulp fluff is also derived from 4.3 percent hemicellulose wood pulpboard. This sample collapses only to 67 percent of its original bulk volume upon being wetted and then, upon the application of a pressure of 200 grams per square centimeter, collapses farther only to 14 percent of its original bulk volume. Upon removal of the pressure, the sample recovers well to 31 percent of its original bulk volume.

These examples show the improvement in wet resilience properties due to the wet cross-linking treatment.

A comparison of the samples obtained in Examples VII and VIII indicates that the wet cross-linked wood pulp fluff can be made into an absorbent pad for a sanitary napkin which is considerably more resistant to deformation in the wet state than an absorbent pad for a sanitary napkin made from untreated wood pulp fluff.

The pulpboard used in the above Examples is preferably used in the form of sheets of various sizes, lengths, thicknesses and widths, depending upon the shape and size of the absorbent product in which it will be incorporated subsequent to grinding. Ribbon sheets as narrow as about 2 or 3 inches or less may be used or strip sheets as wide as about 20 or 24 inches or more may be utilized. Such pulpboard is normally available commercially in densities of from about 0.5 to about 0.6 grams per cubic centimeter and in basis weights as low as about 130 pounds per 1,000 square feet up to as high as about 160 pounds per 1,000 square feet.

Although the specification has referred in places to specific types of pulpboard derived from a particular type of pulp, it is to be appreciated that such is merely for illustrative purposes and that the principles of the present invention are equally applicable to pulps derived from any of the presently known processes, or combinations thereof. Examples of pulps derived from known processes are: sulfite pulps in which the cooking liquor, calcium bisulfite, is acid, or sodium sulfite which is neutral or slightly alkaline; soda pulps in which the cooking liquor, caustic soda, is alkaline; sulfate pulps in which the cooking liquor, sodium hydroxide and sodium sulfide, is alkaline; etc. Semichemical, mechanical, and groundwood pulps are also of use.

Although the present invention has been described with particular reference in the preceding examples and in the specification to pulpboard and cellulose fibers derived from wood, it is to be appreciated that the principles are equally applicable to other cellulosic fibrous materials. Examples of such other fibrous materials include bamboo, esparto grass, straw,

rayon, reclaimed papers, rags, cotton linters, rope, jute, flax, bagasse, and the like, as well as industrial waste products such as cotton seed hulls, corn cobs, corn stalks, peanut shells, pineapple stalks, banana stalks, bamboo stalks, etc.

It is not necessary that the wet cross-linked cellulose fibers be used as the sole constituent of the absorbent portion of the product involved. It may be blended, if desired, in proportions as low as 10 percent by weight up to 90 percent with other fibers or other fibrous materials, depending upon the requirements of the particular product. Such other fibers and other fibrous materials include cotton fibers, cotton linters, rayon, wood pulp which has not been wet cross-linked, cotton batting, synthetic fibers, such as cellulose esters notably cellulose acetate, polyesters from dihydric alcohols and terephthalic acid such as "Dacron" and "Kodel," acrylics containing at least 85 percent by weight of acrylonitrile such as "Acrilan" and "Orlon," modacrylics containing less than 85 percent but at least 35 percent of acrylonitrile such as "Dynel" and "Verel," polyamides such as nylon 6 and nylon 6/6, polyolefins such as polyethylene and polypropylene, spandex fibers derived from polyurethane such as "Lycra" and "Vyrene," fluorocarbons such as "Teflon" TFE and FEP, etc.

The blending of such materials need not be uniform and the cross-linked cellulosic materials may be used as the top or an intermediate layer in a laminated structure such as in a sanitary napkin, diaper, or the like; as the centrally located, internal, concentric core or the hollow cylindrical externally positioned wrapping sheath in a composite tampon construction; or the like.

Other changes, variations, and modifications apparent to a person skilled in the art may be resorted to, without departing from the scope of the present invention which is defined in the following claims.

What is claimed is:

1. A method of making a fibrous, cellulosic absorbent product from pulpboard which comprises: providing a pulpboard sheet wet cross-linking said pulpboard; grinding said wet cross-linked pulpboard to form a pulp fluff therefrom having improved wet resilience, increased fluid absorption and retention capacity; and low knot content; and forming an absorbent product utilizing said pulp fluff as a fluid absorption and retention material therein.
2. A method of making a fibrous, cellulosic adsorbent product as defined in claim 1 wherein the pulpboard is wood pulpboard.
3. A method of making a fibrous, cellulosic absorbent product from pulpboard which comprises: providing a pulpboard sheet wet cross-linking said pulpboard; washing the wet cross-linked pulpboard; drying the wet cross-linked pulpboard; grinding the wet cross-linked pulpboard to form pulp fluff therefrom having improved wet resilience, increased fluid absorption and retention capacity, and low knot content; and forming an absorbent product utilizing the pulp fluff as a fluid absorption and retention material therein.
4. A method of making a fibrous, cellulosic absorbent product from wood pulpboard which comprises: providing sheets of wood pulpboard wet cross-linking said sheets of wood pulpboard; neutralizing said wet cross-linked wood pulpboard; washing said wet cross-linked wood pulpboard; drying said wet cross-linked wood pulpboard; grinding said wet cross-linked wood pulpboard to form a wood pulp fluff therefrom having improved wet resilience, increased fluid absorption and retention capacity, and low knot content; and forming an absorbent product utilizing said wood pulp fluff as a fluid absorption and retention material therein.

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