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FIBROUS PRODUCT AND METHOD OF MAKING THE SAME

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This invention relates to the treating of cellulosic materials, and more particularly unwoven cellulosic fibrous products by treating agents to give products of astonishingly great increase in wet and dry tensile and tear strength, resistance to water, and the like.

One object of the invention is to provide a product made of cellulosic fibrous material such as cotton fibers which are of unwoven character and which is of hitherto unknown properties of wet and dry strength.

Another object is to provide such an unwoven cellulosic material or sheet, produced by treating to give products of high strength equal to or adequately approximating the strength of textiles woven from such fibers while also providing or retaining desired flexibility, hand or feel within a wide range, including such characteristics as appear normally in the untreated cellulosic material or in commercial textiles, or other flexible materials such as leather or the like.

Another object is to provide such an unwoven, or random fiber arrangement, cellulosic material product or sheet which has hitherto unknown resistance to tearing, when dry or wet.

Still another object is to provide a process for producing such products.

Other objects and advantages of the invention will be apparent from the description and claims.

It has long been known that unwoven cellulosic fibrous materials, such as cotton wadding and sheeted and unwoven cotton, have little or substantially no tensile strength in any direction, whether wet or dry, whereas textiles woven from the same cotton fiber are known to have tremendously greater strength—the tensile and tear strength depending on the weave, the size of the thread, etc. We have discovered that such unwoven cellulosic material can be so treated, in the practising of this invention as to give tremendously and astonishing increased tensile and tear strength whether wet or dry. For purposes of simplicity of description herein, reference to resistance to water and wet strength as used in this application means the described capacity of the product of this reaction to retain its acquired strength and resistance to tearing and disintegration when in contact with water.

Since such hitherto available cellulosic materials of unwoven nature have had practically no tensile strength or wet strength they have proved unsatisfactory for commercial utilization where such properties are required although there were obviously many advantages such as, for example, simplicity of manufacture in that no weaving operation is required, relative economy of price and availability of raw materials.

And further, it has been found that the treated material, that is, the treated unwoven cellulosic material such as sheeting or batting of the pres-

ent invention has in addition and together with this tremendously increased tensile strength and wet strength or resistance to water, properties of flexibility and hand which are also truly remarkable. The properties of flexibility and hand generally relate to the pliability and to the feel of the material when it is crushed in the hand, a commonly employed test in practical commercial operations. It is extremely important for many commercial applications that cellulosic fibrous materials which have been processed to give adequate wet or dry strength should retain substantially the original flexibility and hand of the untreated material, and this applies importantly to materials such as the unwoven cellulosic sheeting or batting of the products of this invention. Generally, these cellulosic materials as originally obtained, and before weaving or former processing, are soft and pliable, and in very many applications in which they are employed, it is extremely important that such properties be retained. Generally these materials as originally obtained are soft and pliable, and in very many applications in which they are employed it is extremely important that such properties be retained. And it has now been found according to the present invention that a treated unwoven cellulosic material, even one having such random fiber arrangement as referred to, when produced according to the present invention may, if desired, be prepared in such manner that the properties of the treated material as regards flexibility and hand may be substantially unchanged from the originally untreated material while as described the tensile strength and wet strength are increased to a remarkable degree, in many instances from substantially no tensile and tear strength, dry or wet, up to strengths many times increased and even within the strength range of comparable textiles, i. e., textiles woven from similar fibrous materials of comparable thickness, porosity or quantity of fiber content whether the treated materials are tested wet or dry.

As illustrative of the practising and great advantages which flow from this invention, reference will be made to the tremendously increased tensile strength and resistance to tearing when in contact with water which results in practical operations with an available unwoven cellulosic material of a type commercially available and known to the trade as "Masslinn." This material which is a soft and pliable unwoven cotton fiber substance, generally available in the form of strips or sheets in which the cotton has been carded to effect rearrangement from the random fibers of the cotton to give a soft material with the fibers somewhat relatively arranged but still somewhat random in that they are in a relatively loose, substantially unrestrained or fluffy condition and not in any way woven and having a ten-

sile strength too low to be measured with a Scott tester, a standard machine widely used for measurements of tensile strength, and on which measurements can be made as low as one pound per square inch tensile strength. Such material according to the described preferred embodiment of the present invention, having a thickness, when uncompressed, of the order of .01 inch, may be impregnated by dipping the sheet into an aqueous alkaline solution or dispersion of alkyl hydroxy cellulose, as for example ethyl hydroxy cellulose, prepared as described in detail on page 3 below. Following this immersion, the sheet may be removed therefrom and excess material removed as by passing the sheet through a set of squeeze rolls whereby excess of impregnating material above that necessary to secure successful results is removed from the sheeting. Following this step a number of methods are available for the final preparation of the treated material of the invention. For example, the treated or impregnated sheet may then be subjected to the action of heated water, and such may be satisfactorily accomplished in commercial practise by passing the treated or impregnated material through a bath which contains water at or near its boiling temperature. Subsequently the water remaining in the material may be removed by passing the latter through a drying oven, and by such operation a treated sheeting secured which has tremendously increased tensile strength as compared to the original untreated material and ranging up to 10 lbs. per square inch in tensile, and even higher. Also, the wet strength or resistance to tearing when in contact with water is similarly astonishingly advanced. And, in addition, to such remarkable increase in strength of the treated material such material may be caused to retain substantially its original characteristic softness, pliability and fine hand of the original untreated material.

Or, if desired, impregnated material after immersion in the aqueous alkaline solution or dispersion of alkyl hydroxy cellulose and subsequent removal of excess material as described may be treated by immersion in an aqueous solution of alkali to effect preparation of the treated sheet. And, in practical operation, the impregnated material obtained as described, may be immersed in a caustic solution of 45-55° Tw. (20-25% NaOH). Subsequently the material is washed with hot water to remove excess alkali material, and this removal may be both expedited and more definitely secured by washing with a dilute acid solution after the major portion of the excess alkali has been removed by the water washing followed by washing with water and drying as described to secure a product which is very soft and absorbent, and which has remarkably increased tensile strength, both wet and dry, when compared to untreated material.

Another method of effecting or preparing the final treated material, such as the "Masslinn" sheeting, is to effect the final step by immersion of the impregnated sheet material in an aqueous solution of an acid subsequent to impregnation with ethyl hydroxy cellulose as described. And one satisfactory method of effecting such treatment consists in immersion of the impregnated sheeting in an aqueous bath containing 5% of sulfuric acid. Other acids such as acetic or formic acids may likewise be employed, the particular acid chosen generally depending upon considerations of economy and availability and the amount of acid chosen to give comparable

conditions. Subsequently, the sheet is washed with water and with mild aqueous alkali or soda ash to remove the last traces of acid material, and the material then dried as described. As alkaline wash, there may be employed an aqueous 0.5% solution of sodium carbonate.

Very satisfactory results are also secured under the present invention by treating such an unwoven cellulosic fibrous material which comprises partial drying of the ethyl hydroxy cellulose-impregnated sheeting to remove about 50-75% of the water present from the impregnation treatment. Subsequently the semi-dried material is washed with water to remove alkali therefrom and dried as described. Such material obtained as described has excellent tensile strength both wet and dry, both properties being astonishingly greater when compared to the original material, such tensile strength ranging even up to 65 lbs. per square inch for the treated material being secured.

As illustrative of the remarkable increase in tensile strength in unwoven cellulose fibrous materials secured by practising the present invention, the tensile strength of several samples of "Masslinn" sheeting treated in accordance with the present invention are hereinafter given in the table. Measurements of tensile strength were made with the well-known Scott tester, in accordance with a standard method for measuring tensile strength of such materials.

Table

Sample	Method of coagulation	Deposit of alkyl hydroxy cellulose, percent by weight of "Masslinn"	Average tensile strength in lbs./sq. in.	
			Cross fiber	Fiber
"Masslinn"			Too low to be measured	
"Masslinn" and ethyl hydroxy cellulose.	Acid	18.2	7	23
Do	do	10.2	11½	3½
Do	do	17.8	52½	13
Do	do	16.05	6¼	18
Do	Semi-drying	18.2	12½	37½
Do	do	14.8	11¼	39
Do	do	12.5	7¾	13½
Do	do	35.6	17	63
Do	do	22.7	16	46
Do	Boiling water	6.5	1¼	9
Do	do	9.17	1	10½

Such sheeting as results from the preparation of a treated unwoven cellulosic article as described has greatly increased tensile strength, falling within the range of woven materials and comparing favorably with that secured with many comparable woven materials in regular commercial use. And in addition to such remarkably tensile strength, the material also has a very great resistance to the action of water, that is, it retains such increased tensile strength when in contact with water so that the wet strength of the treated material is likewise very great as compared to that of untreated material. Further the treated sheet material—treated as for example as above described—can be prepared in such manner that the flexibility or pliability and hand can be varied over a wide range depending upon the end use and upon the product characteristics desired for useful application. For example, in many instances it is extremely important to retain the initial pliability, softness and fine hand of the unwoven cellulosic sheeting or batting. By effecting treatment of the material as above described by immersion in alkyl hy-

droxy cellulose solution and subsequent treatment with boiling water, the initial properties of pliability, softness and hand of the unwoven cellulosic material are retained, and in addition thereto there is secured the valuable increase in tensile strength and in resistance to tearing when in contact with water. And such desirable properties of pliability and fine hand are secured by treatment as described, and without necessity for use of any plasticizing material.

In cases where different product characteristics with reference to pliability and hand are desired such results may be secured by varying the treatment of the wet material after impregnation in aqueous solution or dispersion of alkyl hydroxy cellulose. For example, if a material is desired which is less pliable and which is stiffer than the original untreated unwoven cellulosic material, such results may be accomplished by treatment of such material, after impregnation in aqueous solution or dispersion of alkyl hydroxy cellulose and removal of excess material as described, with dilute acid solution. When such is accomplished, and the excess water removed from the treated goods, a product is secured which is considerably stiffer and less pliable than the original unwoven cellulosic substance.

An extremely soft and absorbent finished material is obtained as by treatment of "Masslinn" sheeting as above set forth with aqueous alkaline solution of ethyl hydroxy cellulose with subsequent treatment with strong caustic solution, 20-25% aqueous sodium hydroxide for example. But where an end product with crisp, linen-like finish is desired, the semi-drying method above set forth may be used, wherein the impregnated sheeting is partially dried to remove 50% or more of the water present therein, and subsequently washed with water to remove excess alkali and thereafter dried. In all instances of treatment as above set forth, in addition to the product characteristics described, the material has the tremendously increased tensile strength and resistance to tearing when in contact with water which is characteristic of the products of the present invention. And it is astonishing that such variety of results in practise can be secured as regards pliability and hand without the use of any plasticizing or other agents. Treatment as described with alkyl hydroxy cellulose, as with ethyl hydroxy cellulose solution followed by further treatment by any of the subsequent steps described yields a finished product with the characteristics desired.

It is seen from the foregoing descriptive examples that the present invention contemplates the production of an unwoven cellulosic fibrous material of completely random fiber arrangement or controlled arrangement as described, and of tensile strength and wet strength hitherto unknown for such materials by impregnation of such material with an alkyl hydroxy cellulose, and further the product characteristics of such treated material of the present invention may be modified as desired with regard to flexibility or pliability and hand while retaining the increased tensile strength and wet strength, as described.

An alkyl hydroxy cellulose which is satisfactory in practising the present invention and illustrative of the general class of treating agents of the present invention is prepared as follows. One part of shredded fibrous cellulose, such as a purified wood pulp having a high alpha cellulose content, is converted to alkali cellulose by steeping it in a suitable quantity of an 18% sodium

hydroxide solution at 20-25° C. for a period of one hour. The alkali is then allowed to drain off, and the fibrous alkali cellulose is pressed to a weight approximately three times that of the dry cellulose originally taken. After pressing, the alkali cellulose is shredded for one hour at from 15 to 20° C. While still in the shredder, the alkali cellulose is treated with ethylene chlorhydrin in an amount 18.9% (equivalent to 10.33% of ethylene oxide) by weight of the cellulose, calculated on the basis of dry fibrous cellulose ($C_6H_{10}O_5$). This treatment is carried out with constant stirring at a temperature of from 15° to 20° C. for about one hour. There is now added to the reaction chamber, without permitting the ethylene oxide to escape, 0.3 part of amorphous cellulose, such as comminuted purified waste cellulose hydrate, in the gel state. The resulting mixture is now stirred at 15° to 20° C. for an additional period of three hours. The cellulose ether thus produced is then washed free of sodium chloride and sodium hydroxide with hot water. The washed material then is acidified then washed a second time and dried by centrifuging. The above outlined method, is that described in U. S. Patent 2,172,109, Reichel and Hindry, issued September 5, 1939, and produces an alkyl hydroxy cellulose satisfactory for practising the present invention. Other alkali soluble alkyl hydroxy celluloses, such as propyl hydroxy cellulose may also be utilized.

In preparing solutions of alkyl hydroxy cellulose for use in impregnation of the present invention, successful practical results have been secured using a 6% solution of alkyl hydroxy cellulose dissolved in 10% sodium hydroxide solution. More concentrated or dilute solutions may be employed, depending upon the use characteristics desired and amount of impregnation as described to be secured.

With "Masslinn" sheeting, the remarkable increase in tensile strength, both wet and dry, was secured by impregnation as described so that the amount of alkyl hydroxy cellulose remaining deposited in the sheeting was between 6 and 35% by weight of the original untreated material. And it has been found that the increase in wet and dry strength is related to the amount of alkyl hydroxy cellulose employed, generally increasing with increased amounts of impregnating agent utilized. Also, the characteristics of pliability, hand and absorbency of the treated substance will vary with amount of impregnant used, so that the end characteristics of product desired will govern the amount of impregnant used and the particular treatment employed.

As pointed out "Masslinn" sheeting of unwoven cellulosic fibers and treatment thereof have been described as illustrative of a satisfactory manner of practising the present invention to produce certain very desirable end products. Other unwoven or such random fiber arrangement cellulosic fibrous materials, such as cotton batting and paper of comparable loose and open or fluffy formation however come within the present invention and show the comparable excellent and astonishing increase in tensile strength and wet strength or resistance to disintegration when in contact with water, when treated in accordance with the present invention, such paper for example may have substantial dry strength to be measurable on the instrument above described but no measurable wet strength and yet may be changed to have high wet and dry strength when treated in accordance with

the present invention without any objectionable filling up of the large percentage of voids or formation of an objectionable surface film or layer.

While the above sets out the preferred embodiments of the invention, it will be understood that the invention is not intended to be limited thereto, but is as defined in the appended claims.

What is claimed is:

1. As a new product, unwoven carded cotton cellulosic fibrous material impregnated with an alkali soluble alkyl hydroxy cellulose.

2. As a new product, unwoven carded cotton cellulosic fibrous material impregnated with ethyl hydroxy cellulose.

3. As a new product, unwoven carded cotton cellulosic fibrous material bonded with an alkali soluble alkyl hydroxy cellulose modified by precipitation while within the fibrous material and having greatly increased strength in the resulting product as compared to the untreated fibrous material.

4. As a new product, unwoven carded cotton cellulosic fibrous material bonded with an alkali soluble alkyl hydroxy cellulose modified by precipitation while within the fibrous material and having greatly increased wet strength in the resulting product as compared to the untreated fibrous material.

5. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, subsequently removing excess impregnating solution, and subsequently treating said impregnated material with heated water, whereby a treated material with substantially the same pliability and hand as the said unwoven cellulosic fibrous material is secured.

6. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of ethyl hydroxy cellulose, subsequently removing excess impregnated material with heated water, whereby a treated material with substantially the same pliability and hand as the said unwoven cellulosic fibrous material is secured.

7. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, subsequently removing excess impregnating solution, and subsequently treating said impregnated material with aqueous alkali.

8. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of ethyl hydroxy cellulose, subsequently removing excess impregnating solution, and subsequently treating said impregnated material with aqueous alkali.

9. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, subsequently treating said impregnated material with aqueous acid.

10. The process of imparting increased tensile

strength and wet strength to unwoven carded cotton cellulosic fibrous materials, which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, subsequently treating said impregnated material with aqueous acid.

11. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials which comprises impregnating said fibrous material with an alkaline solution of alkyl hydroxy cellulose, thereafter removing excess impregnating material from said impregnated fibrous material, thereafter removing from said impregnated material at least 50% and less than 100% of water contained therein, thereafter removing from said impregnated material excess alkaline material by means of water and thereafter drying said impregnated material.

12. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous materials which comprises impregnating said fibrous material with an alkaline solution of ethyl hydroxy cellulose, thereafter removing excess impregnating material from said impregnated fibrous material, thereafter removing from said impregnated material at least 50% and less than 100% of water contained therein, thereafter removing from said impregnated material excess alkaline material by means of water and thereafter drying said impregnated material.

13. The process of treating an unwoven carded cotton fibrous material having substantially negligible tensile strength to produce a treated product having wet and dry tensile strength within a range up to 65 pounds per square inch, which comprises impregnating said unwoven fibrous material with an aqueous alkaline solution of an alkyl hydroxy cellulose and bonding the unwoven material by precipitating said alkyl hydroxy cellulose in situ.

14. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous material, which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, subsequently removing excess impregnating solution, and subsequently treating said impregnated material with an aqueous solution containing approximately 20 to 25% sodium hydroxide.

15. The process of imparting increased tensile strength and wet strength to unwoven carded cotton cellulosic fibrous material which comprises impregnating said fibrous material with an aqueous alkaline solution of alkyl hydroxy cellulose, thereafter removing excess impregnating material from said fibrous material, thereafter removing from said impregnated material approximately 50 to 75% of the water contained therein, thereafter removing from said impregnated material excess alkaline material by means of water, and thereafter drying said impregnated material.

16. As a new product, unwoven carded cotton cellulosic fibrous material, bonded with an alkali soluble alkyl hydroxy cellulose modified by precipitation with acid while within the fibrous material, and having greatly increased strength in the resulting product as compared with the untreated fibrous material.

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