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TREATMENT OF NONWOVEN CELLULOSIC FABRICS WITH UREA RESIN COLLOIDS

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1 Claim. (Cl. 117—65)

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This invention relates to the treatment of non-woven cellulosic fabrics. More particularly, it relates to a method for increasing the tensile strength of non-woven cellulosic fabrics wherein substantially all the fibers are oriented in one direction.

I have recently discovered that the application of cationic aminotriazine-aldehyde resin acid colloids such as, for example, an acetic acid colloid of methylated trimethylol melamine, to unwoven cellulosic fabrics increases their tensile strength. Processes for so treating unwoven cellulosic fabrics are described and claimed in my copending applications; Serial No. 123,792 filed October 26, 1949, entitled "Treatment of Non-Woven Cellulosic Fabrics with Weak Acid Aminotriazine Resin Colloids," and Serial No. 123,794 filed October 26, 1949, entitled "Treatment of Non-Woven Cellulosic Fabrics with Modified Acid Resin Colloids," and now abandoned.

It is an object of the present invention to provide a process for treating non-woven cellulosic fabrics wherein the fibers are substantially all oriented in one direction.

It is another object of the present invention to provide a process for treating non-woven cotton fabric in which substantially all of the cotton fibers are oriented in one direction.

Another object of the present invention is to provide a process for treating non-woven viscose fabric in which substantially all of the viscose fibers are oriented in one direction.

Still another object of the present invention is to provide a process for the treatment of non-woven fabrics containing a mixture of cotton and viscose fibers substantially all of which are oriented in a single direction.

A further object of the present invention is the production of a non-woven cellulosic fabric of increased tensile strength.

It is a further object of the present invention to increase the tensile strength of non-woven cellulosic fabrics in which substantially all of the fibers are oriented in one direction, the increase occurring both in the direction of the fibers and in the direction perpendicular to that of the fibers.

The above and other objects are attained by treating a fabric composed of substantially uni-

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directionally oriented, non-woven cellulosic fibers with a colloidal aqueous solution of a polymerized aldehyde condensation product of a carbamido compound such as urea.

The invention will be described in greater detail in conjunction with the following specific examples in which proportions are given in parts by weight unless otherwise noted. The examples are merely illustrative and it is not intended that the scope of the invention be limited by the details therein set forth.

EXAMPLE 1

A non-woven fabric known as cotton Masslinn is used in this and certain of the following examples. The cotton fibers in Masslinn are substantially all oriented in one direction, and the parallelized fibers are bonded together at intervals in a direction perpendicular to the direction of the fibers with a thermoplastic resin of the polyvinyl acetate type, the resin constituting generally from about 6%–10% of the weight of the fabric. Although the tensile strength of Masslinn will depend to a degree upon the way in which it is mechanically processed or treated, it will be apparent that the tensile strength perpendicular to the direction of the fibers is very low and several fold less than the tensile strength in the direction of the fibers.

Suitable samples of the Masslinn are placed in shallow vessels and covered with various resin colloid solutions. The wetted out samples are fed through squeeze rolls to remove excess resin solution and then dried at about 140° C. for 6–10 minutes.

The tensile strength of each of the resin-treated samples is then measured on a Suter tensile tester by the grab method using a three inch length.

Resin Designation	Resin Description
Resin A	Acetic acid colloid of ammonia modified urea-formaldehyde resin.
Resin B	Tetraethylenepentamine modified urea formaldehyde resin colloid.
Resin C	Bisulfite modified urea-formaldehyde resin colloid.

The tensile strengths observed are set forth in the following table:

Resin	Percent Add-on	Tensile Strength in lbs.	
		Warp	Fill
None		12	1
A	13	14	3
B	13		4
C	13		3

It is believed that the resin colloid solution extracts and/or redistributes the polyvinyl acetate resin binder present in Masslinn. This theory seems to be borne out by the fact, as will be demonstrated in a later example, that when non-woven fabric containing no resin binder is similarly treated with a resin colloid solution there appears to be a linear relationship between resin pick-up and increased tensile strength. Furthermore it is believed to explain the slight apparent decreases in warp tensile strength which are sometimes observed. In such instances, however, there is an over-all increase in tensile strength since that in the fill direction increases proportionately far more than that of the warp may decrease.

Similar treatment of Masslinn with non-colloidal dimethylol urea and an acid-liberating catalyst decreases the tensile strength of the fabric.

EXAMPLE 2

In this example a non-woven cotton material composed of substantially unidirectionally oriented fibers with no resin binder is used instead of Masslinn. Since the material has very little tensile strength in the dry state and even less when wet, it may be desirable to support it during the application of resin thereto.

Samples of the non-woven material are supported on sheets of tin plated soft steel 0.012 inch thick having a smooth surface and resin-colloid solutions are carefully poured thereover. The tin sheets with the so-wetted out samples are then passed through squeeze rolls as in Example 1. The material is stripped from the sheets and cured by heating for about 6–10 minutes at about 140° C.

The result of tensile strength measurements on the samples of treated material are set forth in the following table:

Resin	Percent Add-on	Tensile Strength in lbs. Fill
None		0
A	4.5	0.5
A	9.5	1.5
A	11.2	2
A	20.2	3.2

It will be noted that the tensile strength of the non-woven material impregnated with resin A varies linearly with resin add-on at least up to about 20% resin pick-up which is close to the practical maximum pick-up.

Similar results are observed when other non-woven cellulosic fabrics such as all viscose Masslinn, Masslinn comprising viscose and cotton fibers in a 50:50 proportion, and cotton, viscose or cotton and viscose Masslinn from which the polyvinyl acetate resin binder has been extracted as, for example, by glacial acetic acid, are treated as described in the foregoing examples with urea resin colloids.

Preparation of resin A

60 parts urea (1 mol)
243 parts 37% aqueous formaldehyde (3 mols)
38.5 parts ammonium acetate (0.5 mol)

The formaldehyde is adjusted to a pH of about 8.5, the urea is dissolved therein, and the solution is heated at 70° C. for 10 minutes. The ammonium acetate is then added, and the reaction mixture is heated to boiling and boiled gently for 5 minutes. A noticeable viscosity increase occurs. The cationic resin colloidal solution obtained contains 31% resin solids.

Preparation of resin B

67.8 parts 37% aqueous formaldehyde
0.75 part triethanolamine
20.0 parts urea
2.0 parts tetraethylenepentamine
2.8 parts hydrochloric acid (specific gravity 1.19)
7.1 parts water
4.4 parts 10% aqueous sodium hydroxide

The formaldehyde and triethanolamine are charged into a kettle and well stirred. The urea is added and after mixing the solution, which has a pH of about 9.6–8.8, is heated by steam to 70° C. and held at that temperature for 15 minutes. As the reaction is exothermic some cooling water should be applied after the mixture attains 70° C. to keep the temperature. The solution is then cooled down by cooling water to 65° C. and tetraethylenepentamine is added followed by 3 parts of water. The temperature rises to about 70° C. during this addition due to the heat of dilution. It is again cooled down to 65° C. and a solution of the hydrochloric acid in 3 parts of water is added. The remaining water is also added. The temperature of the reaction is again brought to about 70° C. and maintained at that temperature for one hour. Ten minutes after the addition of the acid the pH of the mixture is about 2.4 and it gradually drops to 1.7–1.8. After the hour reaction the reaction product is cooled down by cooling water to 55° C. and immediately neutralized by slow addition of the sodium hydroxide solution. After further cooling to about 20–25° C. the pH of the resin is adjusted to 6.8–7.0. The resin syrup obtained in which the molar ratio of formaldehyde to urea is 2.5:1 contains about 45% resin solids. This value is based only on the resin-forming ingredients and ignores salts and minor ingredients.

Preparation of resin C

717.5 parts 37% aqueous formaldehyde
40.5 parts sodium metabisulfite
236 parts urea
2.8 parts 10% aqueous sodium hydroxide
1.1 parts 36% hydrochloric acid
2.2 parts triethanolamine

The sodium metabisulfite and urea are dissolved in the formalin and the pH of the solution is adjusted to 9.4–9.8 by the addition of the sodium hydroxide solution. The mixture is heated to reflux and refluxed for thirty minutes. Hydrochloric acid is then added to lower the pH of the solution to 3.0–3.5. In order to compensate for the heat of dilution of the acid it is advisable to cool the solution to about 80° C. before the acid is added. The reaction mixture is further refluxed for one hour, cooled to 75–85° C.

and maintained at that temperature. The viscosity of the resin syrup will increase steadily and when it reaches around 200 centipoises measured by the Gardner-Holdt method the reaction is stopped by addition of the triethanolamine. The resin is cooled to room temperature and additional triethanolamine is added if necessary to adjust the pH to 8.0–8.5.

The resin solution in which the formaldehyde-urea mol ratio is 2.25:1 contains about 54% resin solids. This figure is based on the resin-forming ingredients including the sodium metabisulfite and does not include salts and minor ingredients.

In general, whenever the monomer of a carbamide-aldehyde resin can be converted to a polymer which lends itself to the formation of a colloidal solution of the polymerized resin, the resin is found to impart an appreciable improvement in the tensile strength of non-woven cellulosic fabrics, both in the direction of the fiber and in the direction perpendicular to that of the fiber. Most of the resins which I have found useful are cationic in nature and since these appear to effect the largest increase in tensile strength they constitute the preferred embodiment of my invention. However, anionic type resins (Example 1, resin C) are also useful.

In addition to Resin B, other alkylene polyamine modified carbamide resins such as those modified with ethylene diamine, diethylene triamine, triethylene tetramine, etc., may be used. Moreover, colloidal solutions of guanidine modified carbamide resins, pyridine modified carbamide resins, carbamide resins modified with glycols, amino alcohols, etc., are also useful.

Suitably modified aldehyde condensation products of carbamides including urea, thiourea, N-hydrocarbon substituted ureas and thioureas such as N-methyl urea, N-phenyl urea, N-benzyl urea, N-ethyl thiourea, N-phenyl thiourea, N-benzyl thiourea, etc., wherein each amino nitrogen atom contains at least one hydrogen atom attached thereto are contemplated as coming within the scope of the present invention.

Carbamide resins modified with amino sulfonic acids such as sulfanilic acid or with aminocarboxylic acids such as β-alanine or with hydroxycarboxylic acids such as salicyclic acid may be substituted for the bisulfite modified resin C.

The above resins are prepared by known methods as illustrated by the preparations of resins A, B and C set forth in detail.

Aldehydes other than the formaldehyde of the examples, such as formaldehyde-yielding materials including paraformaldehyde and hexamethlyenetetramine, benzaldehyde, furfural, acetaldehyde, paraldehyde, etc., may be used.

Resin colloids containing hydrochloric or other strong acid may not be used in the process of the present invention since they do not improve the tensile strength of the non-woven cellulosic fabrics.

In order to obtain the optimum effect of the present invention, the non-woven cellulosic fabric is so treated with the acid resin colloids that from about 0.5% to 25% by weight of resin solids, based on the dry weight of the fabric, will be deposited therein. Actually there is no real lower limit since incorporation of any small amount of the resin will increase the tensile strength to some degree but for practical purposes a lower pick-up than 0.5% will not increase the tensile strength appreciably. Higher pick-ups than 25%, however, produce undesirable properties such as excessive stiffness and harsh feel, and accordingly the upper limit is a real and practical one.

The invention is not limited to any particular method of impregnation of the non-woven fabric which may be immersed in a resin solution and the excess resin removed or which may be sprayed with a resin solution if necessary or if desired. In any event special care in handling must be taken in view of the extremely low tensile strength of the untreated non-woven fabrics, particularly when they are wet.

In the examples the resin-impregnated fabrics are dried and cured at about 140° C. for from 6–10 minutes. This is merely a matter of convenience since the acid colloid produces the same tensile strength increase at much lower curing temperatures. Even air drying is sufficient, and therefore little or no heat curing is really necessary in order to obtain in the fabric a resin polymer with desirable binding properties. Generally speaking, however, the impregnated fabric will be allowed to dry at temperatures ranging from about 65°–400° F.

Non-woven fabrics composed of substantially unidirectionally oriented cellulosic fibers, when treated according to the process of the present invention, are likely to possess a harsh and somewhat stiff hand, this effect being dependent upon the resin concentration and increasing with increased add-on or dry pick-up of the resin. There are several ways of improving the appearance and hand of the fabric.

In the first place, the acid colloid resins may be printed onto non-woven fabrics in much the same manner as the manufacturers of Masslinn apply the resin binder.

Another method involves lap calendering of dried non-woven fabrics treated with the resin colloids to soften the hand.

Moreover, the resin colloid treated non-woven fabrics may be hot calendered. A soft, yet firm, hand results.

A fourth remedy involves addition to the resin colloid of a textile softener such as, for example, the reaction product of from 5.5–6.5 mols of ethylene oxide with one mol of a mixture of the octadecylamine salt of N-octadecyl carbamic acid and the octadecyl guanidine salt of N-octadecyl carbamic acid as described in U. S. Patent No. 2,427,242. The softening agent appears to make the surface feel less harsh.

It is an advantage of the present invention that non-woven fabric which has been treated with a resin colloid may be dyed or pigment printed. Moreover, the treatment of the present process animalizes the fabric so that it may be dyed with acid dyestuffs.

The treated fabrics of the present invention may be coated to obtain interesting and useful articles. Other uses for my resin treated non-woven fabrics are as folows: towels, napkins, doilies, dish cloths, table cloths, drapery materials, wall covering, pipe covering, milk filters, cheese press cloths, ribbon, chemical filters, etc. If they are heat pressed to a stiffness, the fabrics are useful in the manufacture of lampshades, lintless wiping cloths, etc.

Use of my resin colloid treated non-woven fabrics as the plies of a laminate results in the production of a laminated product of improved flexural strength, flexural modulus, hardness and tensile strength and decreased water absorbency when compared with one made up of plies of untreated non-woven fabric.

I claim:

A process which consists of immersing a non-woven fabric composed of substantially unidirectionally oriented cotton and viscose fibers in equal proportions in a neutral colloidal aqueous solution of a cationic polymerized modified urea-formaldehyde condensation product prepared by reacting 67.8 parts of formalin, 20 parts of urea and 2 parts by weight of tetraethylenepentamine under acid conditions for more than 1¼ hours at 70 degrees centigrade and then neutralizing the reaction product, thereafter squeezing the wet fabric between squeeze rolls to reduce the amount of condensation product on the fabric to 13 percent of the dry weight of fabric, thereafter heating the fabric at 140° C. for between 6 and 10 minutes to dry the fabric and cure the condensation product to a water-insoluble state and lap calendering the dried fabric to soften the hand whereby the fill tensile strength of the fabric is substantially increased.

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