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PROCESS OF MAKING REGENERATED CELLULOSE BALLOON FABRIC COMPRISING SHRINKING WITH STRONG ALKALI AND STEAM BLASTING AND PRODUCT PRODUCED THEREBY

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This invention relates to a process for treating fabric and is particularly directed to a process for treating regenerated cellulose compositions and to the compositions so treated. When regenerated cellulose compositions are treated according to the practice of this invention, greatly superior balloon cloth can be produced by coating the treated regenerated cellulose in the form of fabric with a rubbery composition.

It has long been a problem in the fabrication of lighter-than-air ships and balloons to prepare a fabric for the envelope which couples great strength and flex life with the ability of the fabric to withstand work. In order to increase the breaking strength of the fabric, heavier yarns have been used which in turn cause greater air permeability in the finished fabric. This is turn requires considerably more coating material so that the net result is a heavier bag-making material which results in less load-carrying capacity for a given bag volume. On the other hand, when the yarns which make up the fabric have been made smaller in an effort to get a closer weave, which in turn makes for less air permeability and less coating composition, the fabric breaking strength has been reduced.

Many attempts have been made to overcome these problems and to make a fabric which combines the optimum conditions of high breaking strength, long flex life, and great ability to absorb work coupled with a close weave which is comprised of small diameter yarns and a small amount of coating.

These difficulties have been largely overcome by the practice of this invention wherein enhanced strength, flex life and air permeability are obtained without increasing the weight by subjecting a regenerated cellulose fabric to a caustic treatment in order to increase the flex life by increasing the crimp of the yarns followed by a steam-blasting treatment which flattens the yarns by forcing a volatilized composition through the transverse plane of the fabric while the fabric is retained between spaced apart confining elements. When the treated fabric is coated with a rubbery cement, a superior balloon cloth is obtained.

It is a general object of this invention to improve the physical characteristics of regenerated cellulose yarns and fabrics. It is a further object of this invention to provide a process whereby the flex life and breaking strength of regenerated cellulose yarns and fabrics are improved without substantially increasing the gauge of the yarns and fabrics. It is a further object of this invention to provide a balloon fabric which has a low air permeability and thus can be coated with a minimum amount of coating composition.

This invention is concerned primarily with a process for treating regenerated cellulose compositions in the form of filaments, yarns or fabrics. Several different regenerated cellulose compositions are currently being marketed. Perhaps the most widely used of these materials is viscose

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rayon, which, as is well known, is made by treating cellulosic compositions with a caustic followed by a treatment with carbon disulfide which partially dissolves the cellulose and forms metallic cellulose xanthate and then treating the product thereof with a caustic solution in order to get all of the cellulose into solution. This composition is then spun or extruded into regenerating baths containing sulfuric acid, sodium sulfate, zinc sulfate and other chemicals which regenerate the cellulose in the form of filaments. The filaments are then stretched and washed preparatory to fabric construction.

Another type of regenerated cellulose is known as Fortisan. This composition is made by treating a cellulosic composition with acetic acid in order to obtain cellulose acetate. The cellulose acetate is then spun or extruded into threads. The threads or filaments are then stretched and saponified by a soap process which replaces the acetate radicals with hydroxyl radicals and thus regenerates the cellulosic material.

Still another regenerated cellulose is being marketed as X-36. This material is a high tenacity fiber which is similar to Fortisan. It is made by treating cotton linters or wood pulp with acetic anhydride in order to acetylate the cellulose to cellulose acetate. The cellulose acetate is dissolved in acetone and then extruded into air in the form of filaments. The filaments are then stretched and saponified, the acetate radicals being replaced with hydroxyl radicals, thus producing a regenerated cellulose.

There are various other regenerated cellulose compositions which are generally modifications of the above discussed materials. This invention contemplates the inclusion of any regenerated cellulose material.

The regenerated cellulose materials may be in the form of filaments, yarns (threads) or fabrics. Normally, the invention will be practiced with fabrics because of the ease and convenience of processing. Although any size yarn can be used, the yarn will normally be at least 180 denier and will have at least one turn per inch twist.

Fabrics made from regenerated cellulose yarns are known to be very strong, but also quite brittle. The strength of the fabric makes it a desirable material for many applications, e. g. for balloon fabric, but the brittleness often makes the fabric undesirable because it does not have sufficient resistance to repeated flexing. If the yarns are increased in diameter the porosity is increased, thus necessitating an excess amount of coating material when the fabric is used for purposes such as balloon cloth. This invention is concerned with the preparation of regenerated cellulose fabric which has enhanced resistance to flex cracking without increasing the gauge and which can be coated with a minimum amount of rubbery coating material because the porosity has been decreased without tightening the weave. These desirable qualities are added to regenerated cellulose fabrics by treating the fabric first with a caustic which greatly improves the resistance to flexing by increasing the crimp followed by a steam-blasting treatment which causes a reorientation of the yarn filaments which make up the fabric with a consequent closing of the interstices between the yarns without substantially tightening the weave.

The first step in the process of treating the regenerated cellulose materials of this invention is to immerse the material in a caustic solution. Any of the customary strongly alkaline materials such as the strong bases or caustics which have a high degree of ionization can be used in this process. These caustics are preferably used in the form of at least .1 N solutions. Strong bases such as sodium hydroxide, potassium hydroxide, lithium hydroxide, barium hydroxide and strontium hydroxide can be used. Also, the quaternary ammonium hydroxides, such as benzyl trimethyl ammonium hydroxide, are useful bases. However, the alkali metal hydroxides represent a preferred class of bases, particularly sodium hydroxide and potassium hydroxide. The length of treatment and the temperature of the treating baths are not critical but it is obvious that there will be a balance between the time and temperature of the treatment and the concentration of the caustic, an increase in one permitting a decrease in another. It has been found preferable to treat the materials for a period of about 2 minutes to 10 minutes and at a temperature of about 60° F. to 80° F.

When the regenerated cellulose is in the form of yarns or fabrics it must be treated in a relaxed state in order to obtain the maximum effect. Treatment of the regenerated cellulose with caustic in the absence of tension is critical. Treatment without tension allows the material to relax and shrink. This makes possible a substantial increase in crimp and elongation, important factors in improving flex life. Table 1 shows the significant increase in the very important crimp values. Crimp value is the difference in distance between two points on a yarn as it lies in a fabric and the same two points when the yarn has been removed and straightened, expressed as a percentage.

TABLE 1

Effect of tension on treated Fortisan fabric. Samples treated with 8.5% sodium hydroxide at 25° C. for 5 minutes

Treatment	Percent Crimp
1—None (from the bolt)	0-0.5
2—Treated and dried 150° F., relaxed	5.3
3—Treated and dried 150° F., stretched to original dimensions	2.8
4—Treated and dried 150° F., stretched 2% beyond original dimension in the warp	1.8

The importance of treating the regenerated cellulose while in a relaxed condition can be illustrated by further tests which are reported in Table 2. Samples of Fortisan fabric were treated at 78° F. for 5 minutes in a bath of 10% sodium hydroxide in water. One such fabric was treated in a relaxed condition and another under slight tension. These fabrics, after drying, were coated with a rubber coating composition. Thereafter, circular disks 4" in diameter were cut from each of the three coated fabrics. These disks were subjected to test in such manner that one half of each disk was alternately rotated 270° in opposite directions for 10 cycles. Each of these samples was shifted 45° until each quarter of each test sample had been subjected to rotation about the mid-point of the disk. Thereafter, each sample was subjected to a burst test which is described as test D76-49 on pages 45 and 46 of the A. S. T. M. standards for textile testing. The corresponding test disks which were not subjected to the rotation were subjected to the same burst test. Table 2 gives the data covering these comparative tests in percentage values which represent the relationship of the burst strength of the rotated samples with that of the nonrotated samples.

TABLE 2

Untreated Control	Fortisan Treated in Relaxed State		Fortisan Treated under Slight Tension	
	In 10% Caustic Solution	In 8.5% Caustic Solution	In 10% Caustic Solution	In 8.5% Caustic Solution
Percent 71.3	*Percent* 91.2	*Percent* 94.5	*Percent* 67	*Percent* 67

This table thus shows the enhanced ability of the fabric to withstand work when it is treated with caustic in a relaxed condition. The control samples showed a relationship of 71.3% between the burst strength of the flexed sample and the burst strength of the nonflexed sample, the latter being taken as 100%. When the same Fortisan was treated with caustic according to this invention, either 10% or 8.5% solution being employed, the burst strength of the flexed samples, as compared with the nonflexed controls, increased markedly, thus showing the enhanced ability of the coated fabric to withstand repeated flexing such as encountered in actual service. It should be noted, however, that this improvement was obtained when the caustic treatment was applied to the fabric in the relaxed state. The third set of figures, which show the relationship between the burst strength of a flexed sample of Fortisan treated with caustic while under slight tension and the burst strength of a nonflexed sample of the same material, are lower even than the control. When the fabric was subjected even to slight tension burst strength fell off greatly, thus demonstrating that the caustic treatment must be conducted while the fabric is in a relaxed condition in order to achieve the desired result.

It has been found that the concentration of caustic in water may range from about 2% by weight of caustic to about 12% by weight of caustic. It is preferable that the concentration be maintained between about 3.5% by weight and 10% by weight. The importance of these conditions is illustrated in Tables 3 and 4.

TABLE 3

Effect of time of immersion in various concentrations of alkali on properties of Fortisan fabric

Concentration of Alkali, Percent	Time in Alkali					
	2 Minutes		5 Minutes		10 Minutes	
	Breaking Strength,[1] Pounds	Ultimate Elongation,[1] Percent	Breaking Strength,[1] Pounds	Ultimate Elongation,[1] Percent	Breaking Strength,[1] Pounds	Ultimate Elongation,[1] Percent
3.7	179	8.1	179	7.9	179	7.9
5	178	8.3	174	8.3	178	8.8
6	171	8.4	173	8.4	176	8.7
7	169	8.9	169	9.7	173	9.7
8.5	167	13	167	14	165	15
10	166	17	163	19	160	20
12	150	22				
None	178	7.5				
0 (Water Control)	179	7.6				

[1] Of 1" strip.

TABLE 4

Work factors of Fortisan fabric after various treatments with alkali

Concentration of Alkali, Percent	Time in Alkali		
	2 Minutes—Work Factor [1]	5 Minutes—Work Factor [1]	10 Minutes—Work Factor [1]
3.7	1,400	1,400	1,400
5	1,500	1,500	1,600
6	1,400	1,500	1,500
7	1,500	1,600	1,700
8.5	2,200	2,400	2,500
10	2,800	3,100	3,100
12	3,200		
None	1,300		
0 (Water Control)	1,300		

[1] The work factor is the product of the strength and the ultimate elongation of the yarns.

These tables illustrate that the alkaline treatment increases the ability of regenerated cellulose compositions to absorb work with a corresponding decrease in brittleness and consequent great improvement in flex resistance.

After the regenerated cellulose materials have been treated with the alkali, the excess alkali, if any, may be removed by any of the customary methods such as washing with water or by neutralizing with a weak water solution of an acid.

The chemical treatment can be handled on a batch basis or on a continuous basis. It is preferable to process the regenerated cellulose in the form of fabric on a continuous basis, maintaining the fabric in a relaxed state. This treatment greatly improves the elongation and the flex resistance but increases the air permeability of the fabric. This is illustrated by Table 5, which shows the results obtained on Fortisan fabric treated with alkali in the mill.

TABLE 5

Mechanical properties of Fortisan fabric, mill-treated with alkali

Sample No.	Alkali Conc., g./100 ml.	Finished Width, in.	Warp Ultimate Elongation, Percent	Air Permeability, ft.^{3}/min./ft.^{2}
Control	None	41	9.8	24.7
1	9.7	37	16.1	352
2	8.4	37	16.1	185

Coupled with the chemical treatment discussed above which makes possible the production of a fabric having greatly enhanced physical characteristics such as greater flex resistance, it has been found that a further treatment of the regenerated cellulose provides a fabric which approaches optimum conditions of strength, flex life and resistance to air permeability.

The regenerated cellulose yarns or fabrics which have been treated while in a relaxed state with a strong caustic are subjected to a further treatment in order to substantially reduce the porosity of the treated fabrics which have been treated with the caustic while in fabric form or which have been woven from caustic treated yarns. This process, which is hereinafter generally referred to as "steam blasting," contemplates the substantially instantaneous application of heat at relatively high temperatures to a wet fabric while it is being confined or restrained in its cross-sectional dimension.

In the steam-blasting of fabric, according to the present invention, the liquid contained in the fabric is instantaneously converted into vapor by the heat applied to the fabric. Since the fabric is restrained on both surfaces, the expansive force of the vapor thus generated inside the fabric is concentrated in the longitudinal and transverse dimensions of the fabric. This force, which is in the nature of an explosion in each of the yarns, causes the fibers or filaments thereof to spread and close the weave. This spreading of the fibers or the filaments of the yarn and closing the interstices in the weave reduces the gauge and porosity of the finished fabric.

In the steam blasting of fabric, it is desirable that the spaced-apart opposed confining surfaces applied to both sides of the fabric be heated and rigid so as to insure that the quick volatilization of the liquid in the individual yarns of the fabric will produce internal forces in the yarns such that they will spread and become flattened. The opposed confining surfaces must also be capable of being adjustably positioned to a predetermined spacing.

It will be readily understood that the steam-blasting process of the present invention may be applied equally advantageously to a variety of different types of fabric construction or weave such, for example, as twill, sateen, plain weave, basket weave or others, as well as to a combination of different constructions. In practicing the invention, it is customary to use yarns of at least 180 denier for the fabric construction.

The steam-blasting process is applicable broadly to fabrics formed of multiple filament or fibrous yarns as opposed to the monofils and to the use of any type of liquid which will satisfactorily wet the yarn. Wetting of the yarn contemplates the complete permeation of the yarns by the liquid. Obviously, the selection of the liquid for application to the fabric to be treated should be such that the yarns composing the fabric will not be dissolved or otherwise deleteriously affected thereby.

Water alone has been found to be a satisfactory liquid since it is economical to use and creates no particular problem in connection with the venting of the gas or vapor formed as a by-product of the process. In the event that satisfactory penetration of the water into the yarn is not achieved with water alone, water solutions of various wetting agents, detergents, and the like can be employed to advantage. For example, water solutions of material can be used such as derivatives of the various fatty acids. Also, diisobutyl sodium sulfosuccinate, diamyl sodium sulfosuccinate and dioctyl sodium sulfosuccinate (Aerosol OT) can be used as a wetting agent. Various other volatilizable materials can be used as fabric saturants, either alone or in the form of a water solution.

The steam-blasting process of the present invention may be carried out by several different forms of apparatus. The preferred machine is a modified conventional calendering apparatus wherein the heating elements thereof will merely constrain the fabric to a predetermined gauge while it is being treated. For best results, it is necessary that at least one of the rolls have a metallic surface in contact with the saturated fabric as it passes between the rolls. Although more difficult to handle in production operations, metal-surfaced rolls to confine and constrain the fabric on both sides give the best results because more rapid volatilization of the saturant and greater uniformity of the gauge is thus made possible.

The rolls of the apparatus may be heated by any suitable medium such, for example, as high pressure steam circulated through tubes in the rolls, gas heated rolls or electrically heated rolls. Thermostatic controls may be employed to maintain the temperature of the rolls within certain predetermined limits and to prevent any marked fluctuation in the roll temperatures.

It is essential that at least one of the rolls be adjustably mounted in order to insure a predetermined degree of constraint upon the saturated fabric as it passes therebetween.

The direct result of the steam-blasting of fabrics is that a much more dense fabric is produced having a lower gauge. This treated fabric, when coated or subsequently processed, exhibits a much more satisfactory finished product in that a smaller quantity of coating compound will be required to produce the desired result.

As previously indicated herein, the steam blasting process effects changes inside the fabric itself. The liquid with which the fabric is saturated penetrates into the voids between the several fibers or filaments comprising the yarns which are woven into the fabric. When the heat is applied, instantaneously the liquid is volatilized and the suddenly formed vapor, since it is prevented from escaping except along the lateral or longitudinal dimension of the fabric itself, exerts a force which tends to rearrange the fibers or filaments of the yarns causing them to spread out.

This redisposition of the fibers or filaments in the yarns comprising the fabric is brought about by what corresponds to an explosive action of the liquid as it is changed into vapor form. Since, due to the restrictive action of the rigid surfaces above and below the fabric, the explosive action is confined to the plane of the fabric, the filaments can only move in that direction, hence the flattening effect.

The degree of porosity and gauge reduction is dependent upon the ratio of yarn diameter in the fabric to adjacent void spaces which may be closed by the steam-blasting of the yarn. Fabric porosity has been reduced by this process as much as 80%, and, in certain instances, has approached zero porosity. In some cases, the gauge of steam-blasted fabric has been reduced as much as 60%.

It should be explained also that the expression "plane of the fabric" as employed is intended to mean that area defined by the lateral (width) and longitudinal (length) dimensions of the fabric.

A steam-blasting process such as that disclosed herein is described in copending application Serial No. 308,223, filed September 6, 1952, now U. S. Patent 2,712,170, and is characterized by the instantaneous volatilization of a liquid saturant by means of heated calender rolls which are spaced at the ultimate gauge desired in the finished material. Because of the restraint on the top and the bottom, this treatment causes the filaments comprising the yarns to rearrange and this in turn causes a flattening of the yarns and consequent closing of the interstices which cuts down the air permeability of the fabric. Also, because of the volatilization of the saturant, the fabric comes from the steam-blasting apparatus in a substantially dry state. This results in a balloon fabric which is strong and flexible and can be coated with a thin coating of rubber or rubber-like material in order to provide a balloon cloth which approaches the optimum in the relationship of weight of the air bag to carrying capacity.

When the regenerated cellulose is in the nature of a fabric, the weave of the fabric is not critical. However, certain considerations regarding the fabric will enhance the optimum characteristics desired in the finished product.

Tests have been made to determine the reduction in porosity. These tests were conducted according to the A. S. T. M. standard test D–737–46 for determining porosity (air permeability). Table 6 illustrates the importance of steam-blasting in closing the interstices of the fabric. Sample 1, the control, was a 2 x 2 basket weave Fortisan fabric. Sample 2 was the same fabric after being treated with 8.5% caustic. Sample 3 was the same fabric tested after the caustic treatment and after steam-blasting. Samples 4, 5 and 6 illustrate the treatment of X–36 square woven fabric under the conditions outlined above.

TABLE 6

Sample	Wt., Ozs.	Gauge, Inches	Porosity
1—Control	3.67	0.007	17
2	3.91	0.009	119
3	3.83	0.0055	4
4—Control	4.42	0.0105	229
5	4.69	0.0105	259
6	4.66	0.0075	52

The following illustrative examples of the practice of this invention are not intended as limitations thereon.

EXAMPLE 1

A sample of 2 x 2 Fortisan basket weave fabric was treated in skein form by immersing it for 7 minutes at 25° C. in a solution of sodium hydroxide of 12.7° Baumé (97 grams per liter) concentration. The fabric was then neutralized with acetic acid, rinsed and dried at 250° F., all of these operations being performed with substantially no tension. The finished fabric showed a 65% increase in ultimate elongation, and after coating, the fabric demonstrated greatly enhanced flex resistance as compared with a corresponding fabric which has not been treated with alkali.

EXAMPLE 2

A sample of 2 x 2 Fortisan basket weave fabric was treated in open-width form by immersing it for 5 minutes at 25° C. in a solution of sodium hydroxide of 11.9° Baumé (90 grams per liter) concentration. The fabric was neutralized and rinsed as described above. It was then subjected to steam-blasting at a temperature of 250° F. Coated fabrics made from this material showed enhanced flex resistance, without increased thickness.

EXAMPLE 3

The efficacy of this invention has further been illustrated by semiproduction procedures. Twenty-five yards of regenerated cellulose fabric were treated for a period of 7 minutes in a caustic bath containing a water solution of sodium hydroxide wherein the sodium hydroxide was present in an amount of 97 gms. per liter. Thereafter, the fabric was removed from the caustic bath, the excess caustic was neutralized with acetic acid and the fabric was dried. All of the steps of this chemical treatment were performed without tension on the fabric. After the treated fabric was dried it was saturated with water. The saturated fabric, having a gauge of .009 inch, was then passed between the rolls of a steam-blasting apparatus, the rolls being set so that the final gauge of the fabric was about .0055 inch. After the interstices of the fabric had been substantially closed by the steam-blasting process, the fabric was coated with a rubber base coating composition. Physical tests have indicated that this coated fabric has greatly increased resistance to flex cracking and thus greatly increased ability to resist rupturing over comparable fabrics which were not treated according to the practice of this invention.

In the practice of this invention, any of the customary rubber, rubber-like or plastic coating compositions, conventionally compounded, can be used to coat the treated fabric. For example, natural rubber, the rubbery copolymers of butadiene and styrene, such as GR–S, polychloroprene, the polymerization products of a major proportion of a monoolefin such as isobutylene, and a minor proportion of a polyolefin, such as butadiene or isoprene, as exemplified by butyl rubber, polybutadiene, the rubbery copolymers of butadiene and acrylonitrile, polystyrene and other similar materials when suitably compounded, can be used as coating compositions in the practice of this invention where a coated fabric is desired.

Although this invention has been described in terms of "balloon" fabrics which are coated fabrics, both coated and uncoated treated regenerated cellulose fabrics are within the scope of the invention.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

We claim:

1. The process of making an improved fabric characterized by improved flex life and having improved air permeability comprising the steps of (1) immersing a fabric made from regenerated cellulose for a period of about 2 to 10 minutes at a temperature of about 60° F. to 80° F. in a caustic bath containing about 2% to about 12% by weight of a strong base selected from the group

consisting of sodium hydroxide and potassium hydroxide while the fabric is under substantially no tension and thereafter removing the excess base, (2) saturating the regenerated cellulose yarns which comprise the fabric with an inert volatilizable liquid which has a boiling point lower than the degradation temperature of the filaments which comprise the yarns, and (3) passing the saturated fabric between heated spaced-apart cylinder rolls, at least one of said heated cylinder rolls being constructed with a conductive metal surface, said rolls being adjusted to a predetermined opening which is substantially less than the original gauge of the fabric to be passed therebetween and adapted to readily heat the saturated fabric to a temperature sufficient to instantaneously volatilize the liquid fabric saturant so that the instantaneous conversion of the liquid to a vapor exerts a force which is concentrated in the longitudinal and transverse dimensions of the fabric to cause the yarns which comprise the fabric to be rearranged and flattened to bring about a reduction in the gauge of the fabric of from 60 to 80% of the original gauge and a substantial closing of the intersices of the fabric.

2. The process of making an improved fabric characterized by improved flex life and having improved air permeability comprising the steps of (1) immersing a fabric made from regenerated cellulose in a caustic bath containing about 2 to 12% by weight of a strong base selected from the group consisting of sodium hydroxide and potassium hydroxide for a period of about 2 to 10

minutes at a temperature of about 60° F. to 80° F., said immersion being characterized by the absence of tension on the fabric and thereafter removing the excess base, (2) saturating the regenerated cellulose yarns which comprise the fabric with an inert liquid which volatilizes at a temperature lower than that at which a deleterious effect is produced upon the yarns, (3) subjecting the saturated fabric to heat in excess of the boiling point of the liquid saturant in order to instantaneously volatilize the liquid saturant while constraining said fabric between heated spaced-apart confining surfaces in a direction normal to the plane of the fabric simultaneously with the heating so that the volatilization of the saturant exerts a force in the plane of the fabric which spreads the filaments comprising the yarns to cause the yarns to substantially close the interstices between the yarns.

3. The product of the process of claim 2.

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