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CELLULOSE TREATED WITH DI-VINYL SULFONE TO SHRINKPROOF

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This invention relates to modified cellulosic products.

An object of the invention is to provide products derived from cellulose, regenerated cellulose, such as viscose and rayon, and the like, which products are dimensionally stable to water. A particular and outstanding object is to provide a method of reducing the shrinkage of cotton and regenerated cellulose textile materials and fabrics which are subject to washing. Another object is to provide fabrics having improved crease-resistance. Further objects will be apparent from the hereinafter description.

It is well-known that viscose and rayon are particularly subject to shrinkage during laundering and that a slight tension during laundering distorts and stretches the material. We have found that the treatment of the cellulosic fibres with vinyl sulfone in the presence of a basic catalyst substantially reduces the shrinkage of the rayon.

Although shrinkage is not so pronounced with cotton fabrics as with rayon, our process has definite application to cotton also. When a cotton fabric is creased and then treated, it takes on the surprising property of returning to the same creased condition when wet. Similarly, when a cotton or rayon fabric is pressed smooth and then treated, it subsequently tends to return to the same smooth condition during drying. Such effects can be applied in the manufacture of pleated or shaped fabrics, or in setting the twist in yarns. The treatment on both cotton and rayon is substantially permanent, and fabrics so treated retain the beneficial effects through normal conditions of laundering and wear. The treatment is applicable to the finished fabrics, either before or after dyeing, and to the yarns from which they are prepared, including staple, filament yarns, and filaments.

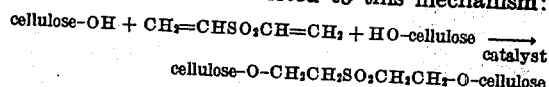
Broadly, the present invention is concerned with the treatment of cellulose and certain cellulosic derivatives which contain cellulosic hydroxyl groups, such as cotton, linen, viscose, cupra ammonium rayon, wood, saponified cellulose acetate, etc., including salts of cellulose xanthate.

In the preferred method, the fabric or yarn is moistened with an aqueous solution of vinyl sulfone, $(CH_2=CH)_2SO_2$, with or without a wetting agent, then is treated with an aqueous solution of the alkaline catalyst. The reaction is complete in a period ranging from a few seconds to about two hours, depending primarily upon the strength and concentration of the basic catalyst used. The reaction may be carried out from 0° C. to 100° C.

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and temperatures of 0-50° C. are preferred. At the end of the reaction period, the fabric or yarn is washed substantially free of catalyst and unreacted vinyl sulfone, and then dried. Alternatively, the catalyst may be removed as such, by neutralization by dilute acid which effectively stops the reaction.

We postulate the following reaction in the formation of vinyl sulfone-cellulose, although it is not desired to be restricted to this mechanism:



where cellulose —OH represents part of the cellulose or regenerated cellulose chain.

The treated cellulose and rayon no longer dissolve in the usual solvents for these materials, such as cupra ammonia, and the quaternary ammonium hydroxides. The treated fibres also swell less than untreated controls when immersed in water or alkali solutions.

A number of variations in the treatment are possible without departing from the spirit and scope of the invention. The reaction may be carried out under anhydrous conditions; also in the presence of suitable organic solvents, e. g., dioxane, benzene, chloroform. The fabric may first be treated with alkali followed by treatment with the vinyl sulfone. Alternatively, the sulfone and catalyst solutions may be pre-mixed and used for the treatment. Advisedly, this latter procedure is used when the pre-mixing and treatment are accomplished in a period of a few minutes. Also, since in the presence of aqueous alkali, the vinyl sulfone will react very slowly with water at room temperatures, e. g., 20-25° C., such temperatures are preferred.

As catalyst, we may employ any base or alkali which is unreactive with vinyl sulfone. Ammonia, and primary and secondary amines are reactive with vinyl sulfone. The catalyst should have a basic strength at least equivalent to that of sodium acetate. For practical purposes, however, we prefer to use stronger alkalies such as the phosphates, carbonates and hydroxides of sodium and potassium. Alkali earth metal hydroxides and quaternary ammonium hydroxides such as tetraethyl ammonium hydroxide and benzyl trimethyl ammonium hydroxide are also effective catalysts.

When a two-bath system is used, as for example, when the fabric is first run through the vinyl sulfone bath, and then through the catalyst solution, we find it convenient to dissolve the catalyst

in a concentrated salt solution. Any salt such as sodium chloride, sodium sulfate, sodium acetate, sodium phosphate may be used, the purpose being that this reduces the leaching of the sulfone from the fabric into the catalyst solution.

The concentration of catalyst solution used depends upon the speed required in the reaction and upon the desire to avoid treatment by more concentrated alkali, which would tend to degrade the fabric. With cotton fabrics, concentrations of alkali, such as sodium hydroxide of 20 to 30%, may be employed satisfactorily with a reaction time of 15 seconds or less. A concentration of 0.5% will effect essentially the same reaction in a period of about 30 minutes. Concentrations ranging from 0.1% may be employed with somewhat longer reaction times. With fabrics containing regenerated cellulose, high concentrations of alkali are to be avoided, because of their tendering effect. With such materials, sodium hydroxide concentrations ranging from 0.1% to about 8% may be employed satisfactorily. Similar considerations hold for the other catalysts.

Compounds capable of forming vinyl sulfone in situ under the conditions of the reaction also are to be considered as operative.

The concentration of the vinyl sulfone employed will depend upon the textile material, yarn, or filament used, and also from the desired use for the treated fabric.

An observable effect is obtained with as little as 0.1% based on the weight of the cellulose, and preferred concentrations lie between about 1 and 10%, although concentrations up to 1 part of vinyl sulfone per part of cellulose, by weight, may be used.

As applied to fabrics, increasing concentrations of vinyl sulfone cause a progressive decrease in the tensile strength so it is desirable to keep the concentration as low as possible consistent with obtaining the desired effect. With regenerated cellulose, concentrations of vinyl sulfone between approximately 1 part and approximately 5 parts per 100 of the cellulose give satisfactory results with negligible tensile deterioration.

To obtain, for example, a 5% concentration of the sulfone on the fabric, it is convenient to dip the fabric into a 5% solution of the vinyl sulfone in water, and then pass it through rolls set at a tension to provide a wet pick-up of about 100%. The wet fabric is then passed through a solution of the basic catalyst in a concentrated aqueous salt solution and then through another set of rolls set to give a wet pick-up of about 120-200%. The fabric is allowed to stand until the reaction is substantially complete, and is then washed, dried, and finished according to normal textile finishing operations.

It has also been found that if the fabrics are impregnated or sized with textile sizing materials, such as starch, dextrin, methyl cellulose, carboxy methyl cellulose, polyvinyl alcohol, and various alkali soluble vegetable gums, such as gum arabic, and the like, that fabrics are obtained having permanent stiffness, improved hand, and in some cases improved crease-resistance, in addition to improved shrink resistance. This treatment is accomplished readily by simple procedures. For example, the fabric may be immersed in a solution or suspension of the sizing material and dried, leaving the fabric impregnated with the sizing. It is then treated with the vinyl sulfone according to the usual procedure. Part of the sulfone reacts with the cellulosic fabric and part

reacts with the sizing material. The reaction with the sizing material appears to give a water-insoluble, cross-linked resin. Alternatively, the sizing material may be added to the vinyl sulfone solution or to the catalyst solution, and the process carried out in the usual manner. When a sizing material is used, it is desirable to increase the vinyl sulfone concentration. It is often convenient to treat a sized fabric with vinyl sulfone, thus achieving stiffness and dimensional stability at the same time.

The following examples are given to illustrate our invention, but are not to be construed as limiting thereto.

EXAMPLE 1

A plain weave 100% viscose spun rayon fabric having a count of 54 x 53, a weight of 5.3 oz. per yard, and made of 16.3/1 warp and 16.4/1 filling of spun viscose staple fibre is passed through an aqueous impregnating solution containing 20 grams of vinyl sulfone in 1000 ml. of solution. The excess solution is removed by passing the rayon fabric through rolls set at such a pressure that the weight of the wet fabric is about twice the weight of the dry fabric, i. e., a 100% wet pick-up. The wet fabric is then immersed in an aqueous solution containing about 10 grams of sodium hydroxide and 200 grams of sodium sulfate in 1000 ml. of solution. The fabric is again passed through squeeze rolls, the pressure of which is less than that of the rolls mentioned above. The fabric is then allowed to stand for at least 30 minutes at or near room temperature (ca. 25° C.). At the end of this time it is immersed in an aqueous solution containing approximately 1% acetic acid to neutralize the alkali. The fabric is then washed in water and dried. Best results are obtained if the tension applied to the fabric during drying is sufficient only to hold it in the dimensions maintained during treatment. The following table gives the results of laundering tests run with ½% of mild soap at 160° F. for 15 minutes. The samples described as dried stretched are dried to their original dimensions after treatment, those described as dried relaxed, are dried hung on a line.

Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	8.4	7.7	10.8	9.7	14.6
Treated:					
Dried Stretched.....	1.0	0.7	2.8	2.1	4.2
Dried Relaxed.....	+0.3	+0.7	+0.7	0.3	2.1

NOTE.—The values for the "dried stretched" shrinkage mean that the sample after the treatment was dried in a stretched condition. After washing the drying was done relaxed. The + values denote stretching.

EXAMPLE 2

A 100% viscose rayon twill having a count of 97 x 51 and a weight of 6.5 oz. per yard and made of 19.8/1 warp and 19.8/1 filling of spun viscose staple fibre, is treated as described in Example 1, and the following table gives the percent warp shrinkage.

Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	5.9	9.7	14.9	26.4	31.9
Treated:					
Dried Stretched.....	3.8	4.9	4.5	3.5	6.2
Dried Relaxed.....	0	1.1	0.3	+1.4	2.8

The + value denotes stretching.

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EXAMPLE 3

A rayon twill, as described in Example 2, is impregnated with an aqueous solution containing 4% by weight of vinyl sulfone. The excess is removed to give a wet pick-up of about 100%, and the wet fabric is immersed in a 1% sodium hydroxide-20% sodium sulfate solution, for at least 30 minutes. The neutralization with acid, washing, and drying are similar to that in Example 1. The finished fabric is laundered in the same manner as the previous samples and the table below presents the shrinkage results.

Percent warp shrinkage

Washes	1	2	3	5	7
Untreated.....	5.9	9.7	14.9	26.4	31.9
Treated:					
Dried Stretched.....	2.1	2.1	2.8	1.4	2.8
Dried Relaxed.....	+1.4	+1.7	+1.7	+2.4	1.1

EXAMPLE 4

A viscose rayon fabric, as described in Example 1, is treated with vinyl sulfone and alkali, as described in Example 3. The table below presents the results of laundering tests:

Percent warp shrinkage

Washes	1	2	3	5	7
Untreated.....	8.3	11.8	15.3	18.0	13.9
Treated:					
Dried Stretched.....	1.1	1.4	0.3	0.7	0.3
Dried Relaxed.....	+1.4	+1.4	+0.3	+0.3	+0.3

EXAMPLE 5

A 15/1 all viscose spun rayon yarn wound on perforated tubes is impregnated with a 3% aqueous solution of vinyl sulfone in a package dyeing machine. The excess solution is allowed to drain off, and a 2% aqueous sodium hydroxide solution containing 20% sodium sulfate, is circulated through the yarn. The yarn is allowed to stand for 30 minutes, and the alkali is neutralized with dilute acetic acid. The yarn is washed, dried, and woven into a fabric. This fabric has much less shrinkage than a fabric woven from an untreated yarn.

EXAMPLE 6

A specially woven all cotton fabric with warp threads twisted into a coiled form, so that the material is highly elastic, is thoroughly wet with a freshly prepared aqueous solution containing 10 grams of vinyl sulfone and 0.5 gram of sodium hydroxide per 100 ml. of solution. The excess solution is allowed to drain off and the material kept 50° C. for about one-half an hour in a closed container. The reaction is stopped by neutralizing the alkali with an excess of dilute acetic acid and the fabric is then washed with water and dried.

A strip 3 inches wide in the fill direction is wet with water and loaded with the weights indicated in the table below. The percent elongation in the warp direction resulting from this load and the percent increase in length remaining after the load was removed is given for each loading. It can be seen from these figures that the treated fabric resists stretching to a much greater degree. It also returns to more nearly its original length after the load is removed than does

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the untreated piece. The percent elongation and the percent set of the dry fabrics were also measured and little difference was found between the values for the treated pieces and the controls, both of them being about the same as the treated piece when wet. This means that treatment of this elastic fabric with vinyl sulfone prevents any loss in modulus and resilience when the fabric is wet with water.

Load, grams.....	200	400	600	800	1,000	1,200	1,400
Per Cent Elongation, treated.....	9	15	21	27	31	35	38
Per Cent Elongation, control.....	25	39	49	57	63	70	76
Per Cent Set, treated.....	2	5	5	6	6	8	8
Per Cent Set, control.....	13	19	21	26	28	33	33

EXAMPLE 7

A plain weave cotton sheeting having a count of 80 x 80 and a weight of 3.1 oz. per yard and made of 30.6/1 warp and 42.6/1 filling cotton yarn is treated by the method as described in Example 1, except that a 4% aqueous solution of vinyl sulfone is used in place of the 2% solution specified there. The neutralization with acid, washing, and drying are the same as described in Example 1. The table below presents the results.

Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	5.3	6.6	7.0	7.6	7.9
Treated: Dried Stretched.....	1.1	1.4	1.1	1.7	1.4

EXAMPLE 8

Cotton sheeting of the same type as that used in Example 7 is folded and pressed with a hot iron to give a number of sharp creases about 1 cm. apart. The folded fabric is then immersed in a freshly prepared solution containing 10% vinyl sulfone and 0.5% sodium hydroxide in water. After 30 minutes the fabric is immersed in dilute acetic acid and then washed with water. It is then spread out and pressed with a hot iron until it is only slightly moist. When the iron is lifted, the fabric snaps back into the original folds, i. e., approximately 50% recovery. When pressing is continued to dryness, the fabric lies flat but the position of the original creases is still visible. When the flat fabric is sprinkled with water, it immediately snaps back to the original folded condition. This demonstrates how our treatment tends to "fix" the fabric in its original dimensions. A similar but less pronounced effect is observed with regenerated cellulose.

EXAMPLE 9

A viscose rayon fabric, as described in Example 1, is treated by the method described in that example except that a 4% aqueous solution of vinyl sulfone is used to first impregnate the cloth and a 5% aqueous sodium carbonate solution containing about 20% sodium sulfate, is used in place of the sodium hydroxide solution. The fabric is allowed to stand in contact with the vinyl sulfone and sodium carbonate for 45 minutes at room temperature. The neutralization with acid, the washing, and drying are carried out as previously described. The fabric is stretched to its original dimensions just previous to and during the final drying. The following table gives the results of laundering tests.

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Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	8.3	9.0	10.4	12.2	13.5
Treated.....	4.5	6.2	7.2	9.0	9.7

EXAMPLE 10

A viscose rayon fabric, as described in Example 8, is treated in the same way as described in that example, except that a 2% aqueous solution of benzyltrimethyl ammonium hydroxide, containing about 20% sodium sulfate, is used in place of the 5% aqueous sodium carbonate solution. The following table gives the results of laundering tests.

Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	3.3	9.0	10.9	12.2	13.5
Treated.....	2.8	2.8	5.2	4.9	3.5

EXAMPLE 11

A viscose rayon fabric, as described in Example 1, is immersed in an aqueous solution containing 2% sodium hydroxide and then squeezed between rolls so that the sodium hydroxide solution left in the fabric is equal to about the weight of the dry fabric. It is then placed in a 4% aqueous solution of vinyl sulfone for 30 minutes. At the end of that time it is washed in dilute acetic acid to neutralize all of the alkali in the fabric and then washed in water. It is stretched to its original dimensions and dried in this stretched condition. The finished fabric is subjected to a laundering test as in previous examples and the following table gives the results.

Percent warp shrinkage

Washes.....	1	2	3	5	7
Untreated.....	8.3	9.0	10.4	12.2	13.5
Treated.....	4.2	4.5	4.5	5.8	6.2

EXAMPLE 12

A piece of viscose rayon fabric is treated with 5% vinyl sulfone under the conditions of Example 11. At the end of the reaction the rayon does not dissolve in a 38% solution of benzyl tri-

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methyl ammonium hydroxide, while an untreated control dissolves in a few minutes.

EXAMPLE 13

A 4 oz. spun viscose rayon fabric is treated in the greige, without removing warp size, with a solution containing 3% vinyl sulfone and alkali catalyst, according to the procedure of Example 1. The treated fabric and a control are then laundered at 180° F. for 30 minutes, dried, and examined. The treated fabric shows only slight shrinkage and remains nearly as stiff as the original unwashed fabric, i. e., the size is not removed. The washed control shows much more shrinkage and is less stiff due to removal of the size.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A method which comprises contacting and chemically combining cellulose and derivatives of cellulose containing cellulosic hydroxyl groups with divinyl sulfone.

2. A method which comprises subjecting cellulose to chemical reaction with divinyl sulfone.

3. A method which comprises contacting and chemically combining cellulose and derivatives of cellulose containing cellulosic hydroxyl groups with divinyl sulfone in the presence of a basic compound unreactive to divinyl sulfone as a catalyst therefor, which basic compound is from the class consisting of alkali-metal, alkali-earth metal, quaternary ammonium hydroxides, and alkali-metal carbonates.

4. A product of reaction of divinyl sulfone and cellulose fibres in which the fibre form of the cellulose is retained in the modified cellulose, said modified cellulose fibres being more resistant to shrinking by water than the untreated cellulose fibres.

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