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PROCESS FOR TREATING CELLULOSE-CONTAINING TEXTILES

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This invention relates to processes for treating cellulose-containing textiles and is a continuation in part of my U. S. A. application Ser. No. 459,842 filed September 26, 1942. More particularly the invention provides a process for rendering such textiles stable as to dimensions and at the same time giving them a good laundry-resisting finish. The process is especially useful in treating fabrics consisting of or containing a substantial percentage of regenerated cellulose artificial silk fibers such for example as viscose and cuprammonium silk fibers, including staple fibers thereof and mixtures of such fibers.

It is known that textiles made of natural or regenerated cellulose can be treated with formaldehyde at high temperatures in the presence of acid acting catalysts. This manner of treatment brings about mainly a reduction of the swelling property of the cellulose and an improvement of the shrinking resistance whereby these effects withstand many launderings. At the same time the high and often undesired stretching of rayon and staple fiber is reduced which effect is also permanent, so that these processes offer interesting possibilities especially for the treatment of rayon and staple fiber made of regenerated cellulose.

A disadvantage of this shrink-resistant finish is the limp feel or hand of the goods which can only be eliminated by a subsequent finish which, however, would not only entail an additional operation but furthermore would cause difficulties with respect to the stabilizing of fabrics to maintain their dimensions. A further disadvantage of these processes is that the resistance to abrasion of the textiles is considerably reduced as a result of the treatment with formaldehyde under the said conditions.

It has now been found that in both of these respects a considerable improvement can be obtained if the treatment of the cellulose-containing textiles is effected with formaldehyde solutions having a formaldehyde content of less than 10% but more than about 2%, in the presence of acid acting catalysts, at temperatures between about 70°–160° C. and in the presence of finishing agents having a stiffening or weighting action and consisting of vegetable or animal colloids or their colloidal film-forming conversion products, which are capable of reacting with formaldehyde to form condensation products which either swell only with difficulty in water or are insoluble therein.

By this process, not only is the abrasive resistance considerably improved but also in general the water-absorbing capacity of the fibers is further reduced. Another advantage consists therein that at the same time a good laundry-resisting finish is produced on the goods. Furthermore the properties which are due to the action of formaldehyde on the cellulose, as for instance the improved shrink resistance and the reduction of the stretch of textiles made from regenerated cellulose are maintained to their full extent. This was the more surprising as it was known from practical operation that the presence of finishing agents, as for instance starch, on the fiber rendered the action of formaldehyde on the cellulose more difficult.

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Suitable for the treatment are cellulose-containing textiles of any description such as fabrics, yarns, spun yarns and fiber material of natural or regenerated cellulose either alone or mixed with other fibers.

As acid catalysts one can use organic or inorganic acids of any kind which have a dissociation constant of at least about 10^{-4} to about 3×10^{-1}, and where such quantities are used as will not cause injury to the cellulose by disintegration (split-up of chemical structure); for instance depending on the strength of the acid, one may use up to 10 grams or more per liter of the impregnating liquid. Also acid salts of such acids can be used or salts which, on account of their dissociation in the presence of heat or their reaction with formaldehyde, have an acid reaction; such for instance as ammonium salts. Also mixtures of various catalysts can be used, for instance one may add buffer substances or substances which have a swelling action on cellulose as for instance zinc chloride.

The expression "acid catalyst" will be used herein to cover or define not only catalysts which are acids, but also substances which are acid-reacting or which liberate acid in solution or when exposed to the reaction conditions herein described.

As finishing agents having a stiffening or weighting action for the carrying out of the process, there can be used the customary vegetable or animal colloidal substances or their technically produced derivatives, as for instance, soluble starch, starch of every description, carob meal, gum tragacanth, gum arabic, dextrin, sugar and gelatin. It is also possible to add textile finishing agents, as for instance, softeners. The finishing agents are used in practical operation in quantities of for instance a few grams up to 100 grams and more per liter of impregnation liquid.

For formaldehyde it is most advantageous to

use the 40% technical or commercial formaldehyde solution or compounds which split off formaldehyde during the reaction, such as its polymers or hexamethylenetetramine. Quantitatively, the formaldehyde content of the impregnating bath should be below 10% but more than about 2%. A higher concentration causes a higher reaction speed, and furthermore a crease-resistant effect, which is not intended or desired in connection with the present invention, since a diminution of the abrasive resistance is caused thereby.

Preferably the formaldehyde, catalyst and finishing agent are added to the same impregnating bath and the goods are immersed therein at ordinary or elevated temperature. After a thorough soaking the excess liquid is removed, such for instance as by squeezing and the goods are pre-dried at about 60° C. After the pre-drying, which may be carried out at a higher or lower temperature, the actual condensation takes place between about 70–160° C., most preferably in a drying chamber or on a perforated drying drum, by strongly agitated air currents. Also other drying equipment which assures uniform heat is suitable, such for instance as drying with infra-red rays.

For the treatment of fabrics it is most important that these are brought to definite dimensions approximating those as customary in the trade, since the fabrics are to be stabilized or made shrink-proof at these dimensions, i. e., fixed to these dimensions. It is therefore essential that these dimensions are maintained during the heating or condensation treatment. For this purpose one can proceed so that the impregnated fabrics, after squeezing them out, are tensioned and pre-dried on a stenter frame to predetermined dimensions, i. e., to the length and width desired for the finished product, or suitably tensioned somewhat in excess of these dimensions, and then pre-dried. Thereafter with the fabric at these predetermined dimensions, the condensation is effected as described above. After rinsing the goods they are finished in the usual manner.

Fabrics thus treated will also, after repeated laundering, shrink only very little and have a durable full hand; they retain these characteristics also during further manufacturing manipulations and in the made up garment. The resistance to abrasion is good and the swelling property, i. e., swelling in water, is very much reduced. For artificial silk, including spun rayon fabrics, made from regenerated cellulose, the tensile strength of the wet material as well as the boiling fastness are improved. Simultaneously, the stretching property of these fabrics, which is troublesome during the manufacturing and while wearing the garment, is considerably reduced.

We have also found that a considerable amelioration especially of the abrasive resistance of the treated goods is obtained, if "colloids" are not added to the formaldehyde solution, but are first applied to the goods and the finished goods are then subjected to the formaldehyde treatment. It was surprising that this manner of proceeding would be efficient, because it was known, that the formaldehyde treatment requires thoroughly cleansed goods, to enable reaction between formaldehyde and cellulose.

Thus my process for treating cellulose containing fibers to reduce shrinkage and give a laundry resistant finish comprises, treating the fibers with "colloids" capable, when heated to react with formaldehyde to render the fibers insoluble or

only slightly soluble in water, drying and subjecting the fibers to a formaldehyde treatment (the formaldehyde being of the above content in the solution) in presence of an "acid" catalyst, having a dissociation constant of at least about 10^{-4} to about 3×10^{-1} at a temperature of from about 70° C. to 160° C. for a sufficient time to produce said reaction product and another reaction product between formaldehyde and cellulose thus giving to the fibers said properties of reduced shrinkage and a laundry resistant finish.

The "colloids" may be applied to the textile materials by means of a slop padding machine or a padding mangle or e. g. by a starching mangle with a starch-doctor. Filling materials and finishing agents, such as softeners may be added to the "colloids." Mostly it is of importance that the fabrics are brought to definite dimensions approximating those as customary in the trade after impregnation with the formaldehyde solution by tensioning them on a stenter frame. The fabrics are then dried and condensed maintaining those dimensions.

The following examples serve to illustrate only some of the many embodiments of the invention.

Example 1.—A cretonne-like fabric, in warp and filling consisting of spun viscose yarn, was cleansed by customary methods, slightly bleached and dried. Thereafter, it was impregnated on a padding machine with a solution containing per liter:

Solubia (soluble starch)	gr.	100
Formaldehyde 40% commercial	cc.	100
Zinc chloride pulverized	gr.	20
Potash alum	gr.	10

Thereupon it was well squeezed (wrung out), tensioned in warp and filling directions to 5% below gray dimensions and while at such dimensions pre-dried at a temperature of 70° C. Thereupon the goods were exposed in a heating chamber for 2 minutes to a temperature of 130° C., acidified with very dilute acetic acid, thoroughly washed, and tensioned in length and width to 6% below the gray dimensions and dried.

The fabric is considerably stiffened, and even after repeated laundering the stiffening is not materially reduced and the tendency of the goods to shrink is very slight. The resistance to abrasion is 62% higher than for similar goods analogously treated, but without the addition of Solubia to the formaldehyde. By reason of the addition of soluble starch the swelling property of the fiber material was further dimenished, as is proven by the following figures. The water absorption, in percent, based on the water absorption by similar goods which were only subjected to a preliminary cleaning, is as follows:

	Per cent
Fabrics treated according to the above example	58
Fabrics treated analogously, but without the addition of Solubia	73

The determination of the water absorption was carried out by the centrifuge method.

Example 2.—Mercerized, bleached cotton marquisette was impregnated on a padding machine with

Wheat starch	kgs.	5
Formaldehyde 40% comm.	litres	15
Aluminium rhodanide solution 17° Bé.	do.	4
Water, sufficient to make up to	do.	100

In making up the impregnating solution the

starch was made into a paste with a part of the water by strong stirring at boiling temperature, cooled off and then mixed in with the other components.

The goods after being well squeezed out were pre-dried at 60° C. while maintaining strong length and width tension therein; followed by heating for 20 minutes at 110° C.; thoroughly washed with cold water and soaped for a short time. The fabric is then dried while tensioned in both directions to about 4% below the gray dimensions.

By this treatment a good, materially stiffened marquisette finish is obtained which does not lose its character after laundering, and the tendency of the goods to shrink is very slight. The resistance to abrasion is considerably greater than in the case of goods treated similarly, but without the addition of wheat starch.

Example 3.—Spun rayon gabardine, dyed with dye-stuffs fast against the action of formaldehyde, was impregnated with a solution prepared according to the following directions: A 10% gum tragacanth solution was diluted with water with the addition of formaldehyde and hydrochloric acid to twice its original volume. The final solution contains per liter:

Gum tragacanth	g--	50
Formaldehyde 40% commercial	cc--	150
Hydrochloric acid conc	cc--	4

The goods were than tensioned in both directions to about 1% in excess of the commercially customary final dimensions and while so tensioned, dried at 60–70° C., thereupon heated in a heating chamber without tension for 8 minutes at 120° C., washed with cold water, passed for 10 minutes through a warm bath (40° C.) containing 0.1% of a commercial fatty alcohol sulphonate plus 0.05% sodium carbonate and after again rinsing with cold water, dried. This drying was carried out on a stenter frame maintaining a slight longitudinal pull whilst in the width the goods were tensioned to 6% below the width of the gray goods.

The goods obtained by this treatment have, characteristically, a fuller or more voluminous and firmer hand, the finished effect is not lost by laundering, and the tendency to shrink is considerably reduced. The resistance to abrasion is materially improved as compared with similar goods analogously treated with formaldehyde, but without the addition of gum tragacanth. Also in this instance the swelling properties of the fiber material are further diminished.

Example 4.—A well desized rayon taffeta of copper ammonium silk was treated with a solution containing per liter:

Gum arabic	gr--	100
Formaldehyde 40% comm	cc--	200
Zinc chloride	gr--	16
Acetic acid concentrated	cc--	2

and then squeezed out. The goods were then preliminarily dried at 65° C. while well stretched in length and width and then heated for 5 minutes at 135° C. Thereupon they were given a subsequent treatment with diluted acetic acid, washed, lightly soaped and again dried under tension. The final dimensions were fixed at about 1% below those dimensions obtained during the preliminary drying. The result was a stiff taffeta fabric which did not materially shrink after laundering. The resistance to abrasion as compared to goods similarly treated without the addition of gum arabic is improved by more than 30%.

Example 5.—Viscose voile was passed through an aqueous solution containing:

	Per cent
Potato starch	4
Formaldehyde	4.8
Soromin BS (a cation active softener)	1.0
Ammonium chloride	0.4

squeezed out, tensioned to approximately the gray dimensions and while so tensioned dried at 40–50° C. and thereafter heated at 120° C. for 2 minutes. The heating in this instance can be carried out to advantage on a so-called Airlay dryer. After thorough washing and a short subsequent soaping the goods were tensioned on a hand stenter frame to about 5% below the gray width and length and dried.

For the preparation of the impregnating fluid the potato starch was boiled with a part of the water for one hour while stirring vigorously. The paste thus obtained was allowed to cool off and thereupon there were stirred into it the other components such as formaldehyde, Soromin and ammonium chloride which were dissolved in the remaining part of the water.

The viscose voile was considerably stiffened by this treatment. The finished effect is quite laundry-proof. The swelling property of the fiber material is reduced to a far-reaching extent, which has an especially favorable effect on the wet strength.

The resistance to abrasion is 65% of that of the original goods. A sample of the same goods treated in the same manner, but only with the formaldehyde and the catalyst, shows a resistance to abrasion of only 32%.

Example 6.—A dyed lining material of viscose satin was impregnated with a solution having the following composition:

Carob kernel meal 2% aqueous solution	cc--	500
Formaldehyde 40% commercial	cc--	90
Tartaric acid	gr--	6

The goods were squeezed out and then subjected to a preliminary drying at 60–65° C. while maintained under a good tension in warp and filling directions, then calendered under strong pressure on a multi-roller calender, heated for 2 minutes at 140° C., washed well with cold water, lightly soaped and again dried under tension.

The goods thus treated attained a firm hand; were more resistant to the action of moisture and in subsequent use did not materially change their dimensions. The resistance to abrasion of goods thus treated as compared to that of similar goods finished in customary manner (i. e., without any formaldehyde treatment) is only very slightly decreased from a practical point of view (i. e., only about 2 to 3%) while similar goods treated according to this example but without the addition of the carob kernel meal, showed a decrease of nearly 50% in the resistance to abrasion.

Example 7.—Crêpe Georgette, consisting of viscose yarn both in the warp and filling, was desized in the customary manner, boiled, bleached and dried. Thereupon it was impregnated with a solution consisting of:

Gelatin	grams--	20
Formaldehyde 40% commercial	cc--	130
Ammonium sulfate	grams--	8
Water	cc--	970

The fabric was squeezed out and preliminarily dried at 40 to 50° C.; while stretched in the di-

rection of the warp and filling to about 10% below the gray dimensions. Thereafter the fabric was heated for 45 minutes at 120° C., thoroughly rinsed with cold water and lightly soaped, and finally dried under tension. As compared with the gray goods, the finished goods showed a shrinkage of 12% in length and width.

This treatment imparted to the goods a clear stiffening. Furthermore, they became more translucent and clearer and obtained thereby a character similar to a transparent-like crepe. This effect was not lost after several launderings and the usual strong tendency of crepe fabrics to shrink was in this instance greatly reduced. The resistance to abrasion of goods thus treated is 86% of that of the original goods, as compared to 58% for a sample of the same goods treated in the same manner but without the addition of gelatin.

Example 8.—A cretonne-(linen-)like fabric composed of regenerated cellulose staple fiber is boiled in the known manner, bleached, dried and treated with a starch paste of 20 g. potato-starch per kg. on a slop padding machine and dried. The so finished fabric is impregnated on the padding machine with a solution containing per liter

Formaldehyde conc. technical (40%)	cc	75
Zinc chloride technical	g	15
Potash alum	g	7.5

squeezed and then predried at a temperature of 70° C. while tensioning the fabric in both directions (weft and warp) at 4–5% below the original dimensions. The fabric is then heated in a heating room during 2 minutes at 140° C., acidified with strongly diluted acetic acid, washed out, stretched in length and width at 6% below the original dimensions and dried.

Fabrics so finished are distinctly stiffened. The stiffening resists repeated laundering and the tendency of the fabric to shrink on laundering is considerably reduced. The diminution of swelling is 33%, the diminution of the resistance to abrasion is only 37% relatively to the untreated fabric. A corresponding fabric, not pretreated with "colloids" shows a diminution of swelling of 35% and a diminution of the resistance to abrasion of 59%. The fastness to abrasion appears to be improved by more than 50%.

Example 9.—A coloured lining fabric of viscose-satin is padded with a solution containing 10 g. carob kernel meal per liter and predried. Subsequently the fabric is impregnated with the following solution:

Formaldehyde conc. technical (40%)	cc	180
Tartaric acid	g	10
Water	cc	820

and dried at 60–70° C. under remarkable tension in the directions of filling and warp, calendered, heated during 8 minutes at 130° C., washed out with cold water. after treated with 1 g./liter of a known fatty alcohol sulphonate at 30° C. during 10 minutes, rinsed and dried under tension. The fabric acquires a firm hand. It is more resistant to the influence of moisture and only slightly changes its dimensions on wearing. The fastness to abrasion of the fabric is improved by about 60% when compared with a fabric, showing about the same diminution of swelling, but not pretreated with the "colloids."

Example 10.—A regenerated cellulose staple fiber fabric, colour-printed in the well known manner is impregnated on a two-bowl-padding mangle with 20 g. gelatine per liter and dried on

a stenter frame at a temperature of 80°–90° C. Subsequently the fabric is impregnated with

Formaldehyde conc. technical (40%)	cc	100
Aluminium chloride cryst	g	3
Water	cc	900

dried at 60° C. under tension in the direction of filling and warp so that the fabric is stretched to 4% below the original gray dimensions and thereupon heated during 4 minutes at 140° C., washed well with cold water, lightly soaped and dried again.

The fabric shows a linen-like stiffening and only slightly shrinks on laundering. The finish resists to repeated laundering and the resistance to abrasion is the same as the untreated fabric, whilst a fabric not pretreated with the colloid shows a diminution of the resistance to abrasion of about 60%.

With respect to the carrying out of this process, as a general rule, the amount of the impregnating liquid retained in the fabric after squeezing should be about 80 to 100% compared to the weight of the dry goods. Also the drying of the fabric after the impregnation and prior to the baking should be uniform.

The products obtained following Examples 1–10 are characterized by the inherent quality of being insoluble but swellable in the usual cuprammonium hydroxide solutions and being recognized by the well known analytical methods as cellulose chemically combined with formaldehyde.

As stated above, a crease-resistant effect is not intended or desired to be produced by my process and, accordingly, the process is carried out until the fibers are proof against shrinkage and discontinued before they have been rendered substantially crease-proof and before they show any substantial resistance to swelling in the usual cuprammonium hydroxide solution. Conditions of time, temperature and concentration of the materials used are set forth specifically in Examples 1 to 10 to accomplish this end.

In the claims, where the expression "formaldehyde" is used, it is intended to include polymers of formaldehyde and compounds splitting off formaldehyde. Also, where the expression "colloid" is used, it is intended to include vegetable or animal colloids or their conversion products suitable as finishing agents and having a stiffening or weighting effect.

It may be mentioned that in most cases it is possible to treat fabrics finished in accordance with the foregoing examples, by a suitable mechanical shrinking process, for instance by "sanforizing" in such a way that even upon repeated washings, the changes in dimensions do not exceed 1%.

While the invention has been described in detail according to the preferred manner of carrying out the same, it will be obvious to those skilled in the art after understanding the invention, that changes and modifications may be made therein without departing from the spirit or scope of the invention, and it is intended in the appended claims to cover all such changes and modifications.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent, is:

1. A process for treating cellulose fibres, which comprises, impregnating the fibres with a formaldehyde solution having a formaldehyde content of less than 10% but more than about 2% in the presence of an acid catalyst having a dissociation constant of at least 1×10^{-4} to about 3×10^{-1}

and in the presence of an aldehyde-reactive agent selected from the group consisting of animal and vegetable colloids and their colloidal film-forming conversion products capable, when heated with formaldehyde, of forming reaction products insoluble or slightly soluble in water, heating the so-treated fibres at about 70°–160° C. until the fibres are proof against shrinkage, and discontinuing the treatment before the fibres have been rendered substantially crease-proof and before they show any substantial resistance to swelling in the usual cuprammonium hydroxide solution.

2. A process for treating a fabric containing cellulose fibres, which comprises, impregnating the fabric with a formaldehyde solution having a formaldehyde content of less than 10% but more than about 2% in the presence of an acid catalyst having a dissociation constant of at least 1×10^{-4} to about 3×10^{-1} and in the presence of an aldehyde-reactive agent selected from the group consisting of animal and vegetable colloids and their colloidal film-forming conversion products capable, when heated with formaldehyde, of forming reaction products insoluble or slightly soluble in water, removing the excess liquid, adjusting the fabric to predetermined dimensions and, with the fabric at approximately said dimensions, heating the so-treated fabric at about 70–160° C. until the fabric is proof against shrinkage, and discontinuing the treatment before the fabric has been rendered substantially crease-proof and before it shows any substantial resistance to swelling in the usual cuprammonium hydroxide solution.

3. Cellulose fibers, chemically combined with formaldehyde coated with a formaldehyde starch compound and which are shrink-resistant but have no substantial crease-proof character, but showing substantially no resistance to swelling in the usual cuprammonium hydroxide solution.

4. Cellulose fibres combined with formaldehyde coated with reaction products of formaldehyde with an aldehyde-reactive agent selected from the group consisting of animal and vegetable colloids and their colloidal film-forming conversion products, said coated fibres being shrink-resistant but having no substantial crease-proof character and showing substantially no resistance to swelling in the usual cuprammonium hydroxide solution.

5. A process for treating fabrics containing cellulose which comprises, preliminarily impregnating the fabrics with an aldehyde-reactive agent selected from the group consisting of animal and vegetable colloids and their colloidal film-forming conversion products capable when heated with formaldehyde of forming reaction products insoluble or slightly soluble in water, drying the fabric so treated and subjecting the same to a formaldehyde solution having a formaldehyde content of less than 10% but more than about 2% in the presence of an acid catalyst having a dissociation constant of at least 1×10^{-4} to about 3×10^{-1}, heating the so-treated fabric at about 70°–160° C. until the fabric is proof against shrinkage, and discontinuing the treatment before the fabric has been rendered substantially crease-proof and before it shows any substantial resistance to swelling in the usual cuprammonium hydroxide solution.

6. A process for treating fabrics containing cellulose which comprises, preliminarily impregnating the fabrics with an aldehyde-reactive agent selected from the group consisting of animal and vegetable colloids and their colloidal film-forming conversion products capable when heated with formaldehyde of forming reaction products insoluble or slightly soluble in water, drying the fabric so treated and subjecting the same to a formaldehyde solution having a formaldehyde content of less than 10% but more than about 2% in the presence of an acid catalyst having a dissociation constant of at least 1×10^{-4} to about 3×10^{-1}, removing the excess liquid, adjusting the fabric to predetermined dimensions and, with the fabric at approximately said dimensions, subjecting it in dry condition to a temperature of from about 70°–160° C. until the fabric is proof against shrinkage, and discontinuing the treatment before the fabric has been rendered substantially crease-proof and before it shows any substantial resistance to swelling in the usual cuprammonium hydroxide solution.

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