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3,189,404

TREATMENT OF CELLULOSIC FIBRE FABRICS
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The present invention relates to the treatment of fabrics containing cellulosic fibres to reduce their tendencies toward creasing and wrinkling.

It is well known that when a cellulosic fabric is impregnated and treated with formaldehyde in the presence of a strong acid, the tendency of the fabric to wet creasing may be reduced. However, the conventional formaldehyde-strong acid treatment has accompanied with various drawbacks, among which is that the treated fabric dries with a non-smooth or creased surface which looks like "ripple." Thus the fabric is not only unsightly but also too rough and stiff for the practical utility of the goods to be made therefrom. A further disadvantage in the conventional formaldehyde-strong acid treatment is in the fact that a satisfactory crease-proofing effect is obtained only with a considerable sacrifice of the mechanical strength such as tearing strength, tensile strength, etc. of the fabric. Still further drawback of the conventional formaldehyde-strong acid treatment is in the fact that it is extremely difficult to control the reaction involved in the treatment.

Therefore, it is a principal object of this invention to provide an improved process for treating cellulosic-fibre containing fabrics without accompanying undesirable "ripple" like appearance to reduce their tendency toward creasing and wrinkling or to assure a swift disappearance of wrinkles of the fabrics after wet treatment such as laundering.

Another object of this invention is to minimize a decrease in the mechanical strength of cellulosic fibre containing fabrics in the formaldehyde-strong acid treatment thereof.

It is a still further object of this invention to improve the formaldehyde-strong acid treatment of fabrics containing cellulosic fibres so that the reaction involved in the treatment is easily controlled.

Another object of this invention is to provide cellulosic fibre containing fabrics which are wet crease-proofing and yet have smooth hand feeling, lustrous appearance and soft handling.

Still another object of this invention is to combine the improved formaldehyde-strong acid treatment and a resin finish so as to provide cellulosic fibre containing fabrics which are assured of swift disappearance of wrinkles not only when wet but also during usage.

These and other objects of this invention are accomplished by a process which comprises immersing a cellulosic fibre containing fabric at the full or open width and for a short period of time, into a bath of an aqueous solution containing a strong acid in a concentration of from 30 to 60% by weight and formaldehyde in a concentration of from 5 to 20% by weight (or a substance which is capable of liberating free formaldehyde in a concentration from 5 to 20% in the solution) and maintained at a temperature below 40° C., removing the fabric from the bath, immediately thereafter leaving the fabric alone but at the full or open width for a period of time from 20 seconds to 5 minutes and immediately thereafter washing the fabric. It is preferable to slightly pretreat the fabric with an aldehyde or resin before the strong acid-formaldehyde treatment in order to facilitate control of the reaction involved in the strong acid-formaldehyde treatment. If dry crease resistance or crease resistance during usage is also desired it is preferable to subject the fabric, after the strong acid-

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formaldehyde treatment, further to an usual resin treatment.

As pointed out before, conventional strong acid-formaldehyde treatment has accompanied with various drawbacks. Most fatal drawback is in the fact that there is formed a non-smooth or creased surface which looks like "ripple." We have found that the formation of the ripple-like surface of the fabric is caused by the following phenomena, namely the latent internal strains which have been induced in the texture of the fabric by preceding processes such as knitting, weaving, preparative operations are enlarged when the fabric is swollen due to the impregnation with the strong acid-formaldehyde treating solution and are perpetuated or set as such enlarged state by a cross-linking reaction to become permanent strains which produce the "ripple" like appearance on the fabric surface. It has further been found that to avoid the undesirable phenomena it is necessary not only to immerse a fabric in a treating solution in such a short but effective period of time as to permit impregnation of the solution in the fabric but not permit swelling, but also to squeeze the fabric before swelling proceeds to an excessive extent followed by allowing the so squeezed fabric to rest in the air to proceed the desired reaction and immediately thereafter washing. It has further been found that to satisfy the above and to accomplish other objects of this invention a particular combination of various critical conditions which are hereinafter detailed is required.

The process of this invention is applicable to fabrics containing cellulose fibres (either natural or artificial alone or as mixtures of two or more in various proportions or as mixtures with other fibres. As natural cellulosic fibres, cotton, linen, hemp, etc., may be exemplified and among artificial cellulosic fibres are, for example, viscose rayon, cupra ammonium rayon and other regenerated cellulose. Other fibres which may be used with one or more of the above mentioned fibres are, for example, cellulose acetate, polyamide, polyester, polyacrylonitrile, polyolefine, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol fibres, etc. The fabric may be knit, woven or otherwise constructed fabric.

The strong acid as contained in the aqueous treating solution may, for example, be sulfuric acid, hydrochloric acid, phosphoric acid, formic acid, etc. among which sulfuric acid is most preferred. The concentration of the strong acid in the aqueous treating solution should be within the range from 30% to 60%. If the concentration is lower than 30%, the desired wet crease resistance will not be attained, while should the concentration exceed 60% the treated fabric will come out harsh and dry with a "rippled" surface so that no useful product is obtained.

The concentration of formaldehyde in the aqueous treating solution should be within the range from 5% to 20%, and here again a concentration of less than 5% will be too weak to attain the desired wet crease resistance, while should it be higher than 20% the treated fabric will have coarse handling and be "rippled" upon drying. In carrying out the process of this invention not only formaldehyde but also substances which are capable of liberating formaldehyde under the treatment condition, such as paraform, urotropine, methylol hydantoin, etc. may be employed. The substance which is capable of liberating formaldehyde should be used in such amount that would liberate formaldehyde which satisfies the required concentration or a concentration within the range from 5% to 20% in the aqueous treating solution.

The aqueous treating solution composing of the strong acid and formaldehyde (or formaldehyde liberating substance) must be maintained at a temperature below 40° C. during the operation. Should the temperature be higher than 40° C. the mechanical strength of the fabric

would be impaired. A satisfactory result is obtained when the temperature is below 30° C.

A fabric to be treated is immersed or dipped in a bath of the above mentioned aqueous treating solution. In this case, it is essential that the fabric must be at the full or open width to avoid presence or formation of creases in the fabric. Throughout the whole stages inclusive the dipping stage and the subsequent stages care should be taken not to form creases. Once creases are formed at any stage of the process, they would be set or perpetuated and remain in the final goods even after finishing. Therefore, it is important to treat the fabric at the full or open width, free from creases, throughout the process.

The time of immersion should be sufficient to allow the impregnation of the fabric with the treating solution, but at the same time should be as short as possible to avoid undesired swelling of the fabric. The time may vary depending upon the particular fibre of the fabric, yarn denier, number of ply or twist of the yarn, construction of the fabric, etc. Generally, a time of immersion of from 1 to 3 seconds is satisfactory.

Immediately after taken out of the bath, the fabric is squeezed to remove an excess of the solution which otherwise may promote undesired swelling of the fabric. The squeezing rate (pick up after squeezing) may be from 70% to 90% (calculated as water) by weight based on the fabric. If the immersion time is too long, the fabric swells too much to effect satisfactory squeezing operation.

After squeezing the fabric with the treating solution as impregnated therein is left alone for a period of time within the range from 20 seconds to 5 minutes. A time shorter than 20 seconds will be insufficient to permit the desired reaction to proceed, while if the time is longer than 5 minutes it would result in a marked reduction in the mechanical strength of the fabric and in a considerable harshness (rough and stiff handling) of the fabric. Generally, the time for leaving the fabric to lie is preferable to be 30 seconds to 2 minutes. The temperature at which the fabric is left lying or subjected to reaction (cross-linking reaction) with formaldehyde should also be 40° C. or lower, preferably 30° C. or lower.

Throughout this reaction stage the fabric must be kept at the full or open width and free of creases. This is accomplished, for example, by supporting the both selvage edges on a stenter or passing the fabric through a plurality of guide rolls.

The concentration of the strong acid, the concentration of formaldehyde, the time of immersion, the reaction time (or the time for which the fabric is left lying) and its temperature and the bath temperature are correlated with each other. Generally, if the concentrations of the strong acid and formaldehyde are higher, the reaction time should be shorter. Similarly, when the bath and reaction temperatures are higher the reaction time should be shorter. In any event, the various factors should be selected within the particular ranges specified hereinbefore.

At the end of and immediately after the reaction, the fabric is promptly washed. The washing operation may be carried out in any suitable manner, but it is always preferred to remove the treating solution from the fabric as quickly as possible.

By the above treatment the wet crease resistance of the fabric is substantially improved without accompanying the formation of "ripple" like appearance on the surface and any undue loss of the mechanical strength. The surface of the treated fabric is smooth and lustrous.

If desired a nominal or slight aldehyde or resin pretreatment may be carried out on the fabric prior to the treatment with the strong acid-formaldehyde solutions. By this pretreatment an excessive swelling of the fabric in the strong acid-formaldehyde treatment is prevented and a control of the reaction involved in said treatment is facilitated.

Aldehydes which may advantageously be employed in the pretreatment include aldehydes such as formaldehyde,

glyoxal, etc. as well as substances which are capable of liberating the aforementioned aldehydes under the pretreatment condition.

Among resins which can be employed in the resin pretreatment are, for example, thermosetting resins such as carbamide-formaldehyde precondensates (e.g. urea-formaldehyde, thiourea-formaldehyde, melamine-formaldehyde, ethyleneurea - formaldehyde, acetylenediurea - formaldehyde, uron-formaldehyde, triazone-formaldehyde precondensates), acetal, diepoxide, phenol-formaldehyde, ketone-formaldehyde precondensates, etc., and cellulose cross-linking agents including, for example, dichlorohydrine, divinyl sulfone, ethyleneimine compounds.

In carrying out the pretreatment the aldehyde, resin or other cross-linking agent is applied in the form of solution to the fabric. The concentration of the aldehyde, resin or other cross-linking agent in the solution and amount of the same to be deposited onto the fabric may vary depending upon the particular aldehyde, resin or other cross-linking agent. However in case of formaldehyde pretreatment it is preferable that the concentration of formaldehyde (37%) in the pretreating solution is from 1 to 10% and the amount of formaldehyde to be deposited on the fabric is from 0.05% to 0.3% by weight based on the fabric, while in case of thermosetting resin pretreatment it is preferable that the concentration of the resin in the pretreating solution is from 0.5 to 5% and the amount of the resin to be deposited on the fabric is from 0.5 to 3.0% by weight based on the fabric. Of course, a small amount of a well known catalyst is also added to the solution in case of the resin pretreatment.

Generally, the pretreatment is carried out in a conventional and usual manner which comprises impregnation of the fabric with the pretreating solution, squeezing, predrying, heat treatment, washing and drying. These operations and their conditions are conventional and well known in the art so that no detailed explanation would be required. Depending upon the type of cross-linking agent a wet process may be employed. If desired the predrying and heat treatment may be carried out concurrently. It is also possible to carry out the strong acid-formaldehyde treatment directly after the said heat treatment, thus omitting washing and drying stages.

By this pretreatment, the fabric is rendered to be somewhat less water absorptive without any appreciable decrease in the mechanical strength. Thus, for example, the water absorptivity of a cotton fabric is reduced from about 40% to 25-35%, while in case of a viscose spun rayon fabric the water absorptivity is reduced from about 80% (before the pretreatment) to 50-70% (after the pretreatment). However, if the water absorptivity is unduly reduced by this pretreatment, it would be difficult to adequately impregnate the fabric with the strong acid-formaldehyde treating solution in the subsequent treatment so that no sufficient or satisfactory wrinkle shedding properties of the fabric are obtainable. Accordingly, it is preferable to control the conditions of the pretreatment so that the fabric after the said pretreatment will still retain the above mentioned order of water absorptivity (25-30% for cotton and 50-70% for viscose rayon).

After this pretreatment, the previously explained strong acid-formaldehyde treatment is effected.

If crease resistance in the dry state is also desired, the fabric after the strong acid-formaldehyde treatment may further be subjected to a conventional resin treatment. The resins that may be employed for the last mentioned treatment are preferably such thermosetting resins as urea-formaldehyde, thiourea-formaldehyde, melamine-formaldehyde, alkyleneurea-formaldehyde, acetyleneurea-formaldehyde, uron-formaldehyde, triazone-formaldehyde, phenol-formaldehyde and other similar precondensates. The resin treatment may be carried out in a conventional manner and is well known in the art. By the combination of the strong acid-formaldehyde treatment and the subsequent resin treatment, there is obtained a fabric having

excellent wrinkle shedding properties, both wet and dry.

The important advantage of this invention, in addition to the advantages that an excellent crease resistance without unduly sacrificing other valuable properties of the fabric, is in the fact that the process can be carried out continuously and is therefore practically effective in enabling a mass-production with a relatively short period of time, in contrast to similar conventional processes which have been impossible to carry out continuously.

The invention will be further illustrated by reference to the following examples. In these examples various properties of fabrics have been determined by the following methods:

Tearing strength: By Elmendorf Method (ASTM D 1424-56 T).

Tensile strength (breaking strength): By ASTM D39-49 except that the width of sample was 2.5 cm. instead of 1 inch.

Wet crease resistance: By the method described in American Dyestuff Reporter, vol. 45, p. 472 (1956).

Dry crease resistance: By Monsanto Method wherein the load was 1½ lbs.

Laundry: Laundry was carried out by AATCC Tentative Test Method 88-1958, 2a.

EXAMPLE 1

In an aqueous solution containing 8% of formaldehyde and 55% of sulfuric acid and kept at 20° C., a sample of cotton poplin was immersed at its full width for three seconds. After squeezing to 120%, the sample was allowed to lie at the full width in the air at 20° C. for 40 seconds to proceed reaction. At the end of this period the sample was immersed in a water bath. Then washing and neutralization were alternately repeated until the sample was free from the treating solution. After drying the resulting fabric had a neat appearance, no ripples, and a tender hand. The tearing strength, breaking strength (tensile strength), and wet crease resistance of the sample as well as the laundry crease resistance of same were measured and the results given in Table 1, from which it will be noted that the treated fabric had improved wet crease resistance and laundry crease resistance with no appreciable reduction in the mechanical strength.

Table 1

Tearing strength, g., percent retentive	Breaking strength, kg., percent retentive	Wet crease resistance		
		Before treatment	After treatment	After 10 cycles laundering
942 g., 65%-----	32.5 kg., 81%-----	163	251	248

EXAMPLE 2

The product made according to Example 1 was immersed in a resin bath of the following composition:

10% triazon type resin precondensate (50%)
1% zinc nitrate (40%)
2% softener (solid form)

After the liquor was squeezed out and the fabric dried, the sample was heat-treated at 150° C. for three minutes, rinsed, and dried. Test results are summarized in Table

2, which shows the improved crease resistance, both wet and dry, of the resultant fabric which requires no ironing.

Table 2

Tearing strength, g., percent retentive	Breaking strength, kg., percent retentive	Crease resistance	
		Wet	Dry
884 g., 61%-----	25.2 kg., 63%-----	285	248

EXAMPLE 3

A solution of the following composition was prepared:

5% triazon-formaldehyde resin precondensate (50%)
0.4% triazon-formaldehyde resin precondensate (50%)

A sample of cotton poplin fabric was immersed in said solution and promptly squeezed. After drying, the sample was heat-treated at 140° C. for five minutes, rinsed and dried.

Results are shown in Table 3.

Table 3

	Resin deposited, percent	Water imbibition, percent	Crease resistance (warp and fillings)		Breaking strength (fillings), kg.	Tearing strength (fillings), g.
			Dry	Wet		
Pretreated with resin	1.0	34	160°	187°	22.1	950
Control		40	156°	143°	23.2	1,050

The pretreated sample was then immersed, at the open width, in an aqueous solution (adjusted to 20° C.) containing:

10% of formaldehyde
52% of sulfuric acid

After 3 seconds' immersion, the fabric was squeezed and allowed to lie, at the open width, in the air at 20° C. for 40 seconds. At the end of this time, the sample was thoroughly rinsed. After the treating liquor was completely removed, the fabric was dried. The resultant fabric had superior feeling and showed a less decrease in mechanical strength than the control sample which had not been subjected to the resin pretreatment. The product of this example also had a superior washability. Test results are summarized in Table 4.

Table 4

	Breaking strength, kg.	Tearing strength, g.	Wet crease resistance (warps and fillings)	Laundry (10 cycles)
Strong acid-formaldehyde after resin pretreatment	19.1	750	253°	248°
Strong acid-formaldehyde without resin pretreatment	18.0	700	229°	224°
Control	23.2	1,050	143°	150°

The laundry values are those of crease resistance measured after laundering.

EXAMPLE 4

The fabric made according to Example 3 was immersed in a resin bath of the following composition:

10% of dimethylolethyleneurea resin precondensate (50%)
0.75% of magnesium chloride (40%)
2% of silicone type softener (30%)

After squeezing and drying, the sample was heat-treated at 150° C. for three minutes, rinsed and dried.

Test results are given in Table 5. The sample had ex-

cellent crease resistance, both wet and dry, and requires no ironing.

Table 5

	Breaking strength (fillings), kg.	Tearing strength (fillings), g.	Crease resistance (warps and fillings)	
			Dry	Wet
Method of Example 4	13.8	700	261°	281°
Resin treatment after strong acid-formaldehyde	12.5	670	250°	270°
Resin treatment only	16.0	783	245°	225°
Control	23.2	1,050	150°	143°

Example 5

A sample of mercerized cotton poplin similar to the one employed in Example 3 was immersed in an epoxy resin bath or ketone-formaldehyde resin bath, whose compositions are given below respectively. The sample was squeezed, dried, heat-treated, rinsed and dried. Then, the sample was immersed in an aqueous solution, at 20° C., containing 15% of formaldehyde and 48% of sulfuric acid; squeezed to 100%, and allowed to lie, at the full or open width, in the air at 20° C. for 50 seconds. At the end of this period, the sample was washed with water, neutralized, washed again and finally dried. As shown in Table 6, the resulting fabric had a smooth surface, showed no appreciable decrease in mechanical strength, and had a superior wet crease resistance.

RESIN PRETREATMENT BATH COMPOSITIONS

- (1) 4% of epoxy resin (Epikote 562)
1.4% of tartaric acid
Heat-treatment: 5 minutes at 150° C.
- (2) 10% of dimethylolacetone
1% of potassium carbonate
Heat-treatment: 5 minutes at 140° C.

Table 6

	Breaking strength (fillings), kg.	Tearing strength (fillings), g.	Crease resistance (warps and fillings)	
			Dry	Wet
Strong acid-formaldehyde after epoxy resin pretreatment	19.2	700	285°	178°
Strong acid-formaldehyde after ketone-formaldehyde pretreatment	18.1	750	263°	170°
Strong acid-formaldehyde only	17.5	680	240°	154°
Control	24.2	1,000	146°	155°

Example 6

In an aqueous solution, at 20° C., containing 7% of formaldehyde and 30% of hydrochloric acid was immersed a sample of blended poplin made of 70% cotton and 30% viscose spun rayon, for 3 seconds. The sample was squeezed to 120%, and allowed to lie, at the full or open width, in the air at 20° C. for 60 minutes. At the end of this time, the fabric was subjected to a few cycles of washing and neutralization, after which it was dried. The properties of this sample are summarized in Table 7. The fabric had a lasting wet crease resistance and a superior hand.

Table 7

	Tearing strength, g., percent retentive	Breaking strength, kg., percent retentive	Wet crease resistance		
			Before treatment	After treatment	After 10 cycles laundering
730 g., 80%-----	29.4 kg., 84%----		231	161	229

EXAMPLE 7

A sample of viscose spun rayon fabric was treated in the same manner as in Example 3. The resulting fabric had as good wet crease resistance as the sample of Example 3.

What we claim is:

1. A process of treating cellulosic fiber-containing fabric to improve the crease and wrinkle resistance thereof, which comprises pretreating said fabric with resin so that the resin is deposited on the fabric in an amount of from 0.05 to 3.0% by weight based on the fabric, immersing the resultant fabric for 1 to 3 seconds in an aqueous solution containing sulfuric acid in a concentration of from 30 to 60%, based on the weight of the aqueous solution, and formaldehyde in a concentration of from 5 to 20%, based on the weight of the aqueous solution, the temperature of said solution being maintained at a temperature below 40° C., removing the fabric after 1 to 3 seconds and leaving the fabric in contact with air for from 30 seconds to 2 minutes, and then immediately washing and drying said fabric.

2. A process of treating cellulosic fiber-containing fabric to improve the crease and wrinkle resistance thereof, which comprises pretreating said fabric with resin selected from the group consisting of carbamide-formaldehyde, acetal, diepoxide, phenol-formaldehyde and ketone-formaldehyde precondensates, so that the resin is deposited on the fabric in an amount of from 0.5 to 3.0% by weight based on the fabric, immersing the resultant fabric for 1 to 3 seconds in an aqueous solution containing sulfuric acid in a concentration of from 30 to 60%, based on the weight of the aqueous solution, and formaldehyde in a concentration of from 5 to 20%, based on the weight of the aqueous solution, the temperature of said solution being maintained at a temperature below 40° C., removing the fabric after 1 to 3 seconds and leaving the fabric in contact with air for from 30 seconds to 2 minutes, and then immediately washing and drying said fabric.

3. A process of treating cellulosic fiber-containing fabric to improve the crease and wrinkle resistance thereof, which comprises pretreating said fabric with resin selected from the group consisting of dichloromethylene, divinyl sulfone and ethylene imine, so that the resin is deposited on the fabric in an amount of from 0.5 to 3.0% by weight based on the fabric, immersing the resultant fabric for 1 to 3 seconds in an aqueous solution containing sulfuric acid in a concentration of from 30 to 60%, based on the weight of the aqueous solution, and formaldehyde in a concentration of from 5 to 20%, based on the weight of the aqueous solution, the temperature of said solution being maintained at a temperature below 40° C., removing the fabric after 1 to 3 seconds and leaving the fabric in contact with air for from 30 seconds to 2 minutes, and then immediately washing and drying said fabric.

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