PROCESS OF CREASEPROOFING CELLULOSE FIBERS WITH BOTH GLYOXAL AND FORMALDEHYDE


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7 Claims. (Cl. 8—116.4)

This invention relates to the modification of fabrics containing cellulose fibres and other forms of cellulose fibres by reaction with dialdehydes.

It has been proposed to modify the properties of cellulose by reaction with a dialdehyde, for example, glyoxal or glutaraldehyde. Thus the crease-resistant properties of the fibres may be increased and the water-imbibition reduced. However, we have found that a drawback associated with most of these treatments is that the beneficial effect of the modification diminishes with successive washes and that the cellulose material is frequently discoloured and tendered. These latter defects are particularly noticeable when more than 4 percent of glyoxal is taken up by the fibres.

We have now found a method of improving the wash fastness of the properties derived from the treatment with dialdehydes and, where it is important, mitigating the tendering and the discolouration of the fibres treated with glyoxal, even when 4 percent or more of dialdehyde is retained by the fibres.

According to the present invention, a process for modifying cellulose fibres comprises impregnating the fibres with a dialdehyde and a compound having 1 or 2 functional groups capable of converting a hemiacetal into an acetal, and subsequently drying and heating the fibres to a temperature above 100° C.

We consider that dialdehydes react with cellulose to cross-link the cellulose molecules with the formation of two hemiacetal groups. The reaction is represented by the equation

\[
ROH + OHO-R'-CHO + HOR \rightarrow OH\;\;\; OH
\]

where ROH is a cellulose molecule and OHC—R’—CHO the dialdehyde.

Hemiacetal groups are easily hydrolysable under the conditions obtaining in domestic laundering, and this, we think, is the explanation of the impermanence of the modifications resulting from the simple reaction of dialdehydes and cellulose.

The stability of the cross-links can be significantly improved by converting the hemiacetal groups to acetal and this can be achieved by reacting alcohols or aldehydes with the primary reaction product of a dialdehyde and cellulose.

This reaction is formulated in any of the equations

\[
R-O-\;CH-\;CH-\;CH-O-R + 2R''(OH) \rightarrow R''-\;R'' + 2H\;\;\;O
\]

where R is alkyl, R''(OH) is therefore a monohydric alcohol.

\[
R-O-\;CH-\;R-\;OH-\;R + R"'(OH)\rightarrow R''\;R'' + 2H\;\;\;O
\]

where R'' is an alkylene group and R'''(OH)₂ is a glycol.

\[
R-O-\;CH-\;CH-\;O\;\;R + 2H\;\;\;O
\]

where R''' is alkyl or hydrogen and R' is methyl or hydrogen. The compound R'''COR' is therefore an aliphatic ketone or aldehyde.

Whilst it is a feature of this invention that the dialdehyde and the compound capable of forming an acetal may be reacted simultaneously with the cellulose, we prefer the process in which the dialdehyde and cellulose are reacted and the product dried before it is impregnated with the acetal-forming compound, particularly where the latter compound is reactive to cellulose.

The reaction of the dialdehyde and cellulose does not require catalysis. The dialdehyde is preferably applied as an aqueous dispersion and the physical conditions of the application and any step of removing the excess dispersion from the cellulose should be governed so that the fibres retain from 4 percent to 10 percent, based on the weight of the dried fibres, of the dialdehyde. The aqueous dispersion should have a pH in the range 3 to 8, preferably 5 to 6, to avoid fully the disadvantages of degradation or discolouration of the cellulose due to the dispersion being too acid or too alkaline.

The reaction of the acetal forming compound with the hemiacetal-containing cellulose requires catalysis and the compound should be applied to the cellulose as an aqueous dispersion, subject to the same preferred pH limitations imposed on the dialdehyde/cellulose reaction. A suitable catalyst is a metal salt which is soluble to the extent of at least 0.3 gram per litre in water at 20° C. at pH 5 and is zinc sulphate or a salt of a Group II metal with a monobasic acid which should be ionised to the extent of at least 50 percent if in normal aqueous solution at 18° C.

The salts may be salts of magnesium, the alkaline earth metals (i.e. calcium, barium and strontium), cadmium or zinc with the monobasic inorganic acids indicated. Salts of magnesium and, in somewhat less measure, salts of calcium are preferred.

The monobasic acid is preferably an inorganic acid and may be hydrochloric, hydrobromic, hydroiodic, nitric, perchloric or thiocyanic acid.
Specific salts which may be employed as catalysts for the purpose of the present invention include the following:

- Magnesium chloride, bromide or iodide
- Magnesium nitrate or perchlorate
- Calcium chloride, bromide, iodide, nitrate or perchlorate
- Strontium chloride
- Barium chloride
- Cadmium chloride
- Zinc chloride, nitrate or sulphate
- Magnesium benzenesulphonate

The preferred conditions of retained reactant, pH range and catalyst imposed on the first and second stages of the two stage process should be simultaneously imposed in the one stage process.

The process may be applied to textile fabrics containing cellulose fibres; they may be woven or knitted fabrics or the so-called non-woven fabrics. The fabrics may consist wholly of cellulose fibres or in part of those fibres and in part of other fibres, but in the latter case it is preferred that the cellulose fibre content should not be less than 35 percent by weight.

The process may also be applied to loose fibres. The cellulose fibres may be natural fibres such as cotton, silk, flax, hemp, jute or ramie, or regenerated cellulose artificial fibres, for example those made by the viscose, cuprammonium, or nitrate process, or by the saponification of fibres of cellulose esters, for example cellulose acetate.

The regenerated cellulose fibres may be in the form of staple fibres or continuous filaments and these may be in the form of yarns or of tows i.e. relatively large substantially untwisted bundles of continuous filaments. Regenerated cellulose filaments may be such as have never been dried.

The dialdehyde is preferably glyoxal but glutaraldehyde, succinylaldehyde and hydroxy-8-dialdehyde are other examples of useful compounds. In the past we have found that technical grades of glyoxal solutions discoloured and weakened the cellulose fibres to which they were applied. We have found, more recently, that purer glyoxal solutions, i.e. solutions containing less than 5 percent of impurities, do not give rise to these colour-forming reactions to the same extent and their use is preferred in this process. It so happens that the technical grades contain oxidants and aldehydic impurities, but we are unable to attribute the colour-forming reaction to any specific impurity.

The acetal-forming compound is preferably an aldehyde, for example, formaldehyde, acetaldehyde or acrolein. Formaldehyde is particularly useful because of its cheapness, availability and efficient reactivity in this invention. The acetal-forming compound may be an alcohol or glycol, but these substances are less reactive than the aldehydes and, therefore, more severe and stringent process conditions may be necessary to obtain the same modification.

The acetal-forming compound is preferably an aldehyde to the dried fibres. Thus in the second stage of the two-stage process or in the single stage process, the impregnated fibres should be dried and heated above 100°C. The steps of drying and heating can be separated, for example by allowing the fibres to dry below 100°C and subsequently heating the fibres. Otherwise, the fibres may be dried and heated in a continuous process in which the steps are involved. Thus the fibres may be heated by contact with a heated fluid or solid surface, for a time long enough to dry the fibres and complete the reaction. Temperatures of from 140°C to 180°C are preferred for completing the reaction.

A major benefit of the use of the metal salt catalysts during the heat-treatment of the fibres, is that the tendency to discoloration of the fibres, resulting from the use of an impregnating solution having a pH at the upper end of the preferred range, say about 8, is reduced or eliminated completely. Magnesium chloride is very efficient in this respect.

We prefer that the fibres take up from 4 percent to 10 percent by weight (based on the weight of the dry fibres) of the dialdehydes. This can be controlled by the concentration of the dialdehyde in the applied dispersion and the amount of liquid which the impregnated fibres are allowed to retain. For example, to impregnate fibres with 4 percent of the dialdehyde, the fibres can be immersed for a short period in a solution containing 4 percent of dialdehyde and then mangled or centrifuged so that the fibres contain an equal weight of liquid. We have found that the dialdehydes are substantive to cellulose to such a degree that dilute solutions containing say 2 percent of dialdehyde and retained by the centrifuged fibres in a weight equal to that of the dry fibres, have caused a 4 percent pick up of dialdehyde. However, this result is only achieved by prolonging the contact of fibres and impregnating solution and is similar in this respect to certain dyeing processes in which dye-bath exhaustion is achieved slowly.

In theory, the greatest gain in wash-fastness will result when two equivalent proportions of the acetal-forming compound are reacted with every molar proportion of reacted dialdehyde. Significant gains are to be had even when less acetal-forming compound is reacted, but at least 1 equivalent proportion must be used if the gain is to be substantial. This minimum required take-up in grams/100 gm. of fibres of acetal-forming compound may be calculated from the equation:

\[
\text{Take-up} = (X)(Y)
\]

where X is the equivalent weight of the acetal-forming compound and Y is the number of gram-molecules of dialdehyde reacted with 100 gms. of fibres. However, it can happen, particularly when the acetal-forming compound is an aldehyde, that the take-up amount of that compound required to achieve the maximum stabilisation of the cellulose/dialdehyde product is greater than that theoretically required to convert the hemiacetal groups to acetics. This can arise from one of a number of causes. For example, when, instead of a single aldehyde molecule reacting with a pair of hemiacetal groups according to Equation C, the latter groups are reacted with and connected through a polymer of the aldehyde. Such polymeric aldehydes, or polyoxalkyllyenes, fulfill only the function of the monomeric aldehyde and can account for the larger than theoretical quantity of aldehyde sometimes required. Again, if the acetal-forming compound has a significant volatility under the conditions of the process, it may be necessary to allow for losses by impregnating the cellulose with more than the required amount of the compound.

The amount of acetal-forming compound taken up by the cellulose may be controlled by the same methods employed to regulate the take-up of the dialdehyde.

In the one stage process, in which the dialdehyde and acetal-forming compound are applied simultaneously to the cellulose, the ratio of reactants taken up by the cellulose is, in general, similar to the ratio existing in the impregnating solution.

The invention is illustrated by the following examples.

The mechanical features of all examples were identical and a single fabric quality was used throughout. The variables in the examples are the quantity and quality of the dialdehyde and quantity of the acetal-forming compound and the catalyst.

The fabric was an all-filament viscose rayon construction having the following properties:

- Weave: plain
- Warp: filament denier 100; number of filaments 51; reed 76
- Wet: filament denier 120; number of filaments 33; rate 80.
The processing conditions common to Examples 1 and 3 were that the cloth was padded with dialdehyde during 5.6 seconds in passing through a bath containing a 10 percent aqueous solution of the dialdehyde at 60° C. The solution was maintained at 20° C and controlled for pH. The impregnated fabric passed from the bath to a double immersion, double-nip, pad-mangle to reduce the quantity of retained liquor to 85 percent by weight based on the weight of the dry fabric. From the mangle, the fabric was led onto a pin-stenter and then dried to width in 15 minutes at 80° C. The recently dried fabric was then padded once again in a bath containing an aqueous solution of the acetal-forming compound and a catalyst, at the same rate as for the first padding. The padding bath was controlled at a temperature of 20° C and a pH characteristic of the example. Allowed to retain only 85 percent by weight of the second padding solution, the fabric was once more dried to width on a stenter before being cured at 160° C for 5 minutes. An interval of 10 minutes was allowed before the fabric was scoured with a 2 percent soap solution at 60° C, rinsed and dried to width at 80° C.

Examples 2, 4 and 5 to 8 employed a single padding bath, the fabrics being treated thereafter in the same way as the twice padded fabric of Example 1.

The fabrics of all examples were submitted to a number of tests both during the treatment and after. These tests were standard through the series and are, therefore, comparable. A Hoover washing machine was used in the tests to examine the extent to which the beneficial properties conferred on the fabric by this invention withstood ten washing cycles in a domestic washing machine. Each cycle comprised washing a 4 lb load for 15 minutes at 60° C with 2 gm./litre of soap, followed by a rinse, spin-dry and press. After the tenth cycle, samples were rinsed twice, spin-dried, pressed and conditioned at 65 percent R.H. Fabrics were also submitted to a cotton wash (55 minutes at 95° to 100° C.) as described in B.S. 118 and the properties measured once again. The results from all these tests are recorded in the accompanying table.

<table>
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<tr>
<th>No.</th>
<th>State of Fabric</th>
<th>Water imbibed, percent</th>
<th>Bound reagents, percent</th>
<th>Crease recovery, percent</th>
<th>Warp strength, (lb.)</th>
<th>Shrinkage, percent</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>unsoured</td>
<td>89</td>
<td>91</td>
<td>2.50</td>
<td>40.4</td>
<td>1.3</td>
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<td>2.97</td>
<td>40.0</td>
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<td>4.13</td>
<td>33.4</td>
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<td>100</td>
<td>1.43</td>
<td>28.1</td>
<td>(a)</td>
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<tr>
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<td>100</td>
<td>1.43</td>
<td>28.1</td>
<td>(a)</td>
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<tr>
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<td>100</td>
<td>1.43</td>
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<tr>
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<td>102</td>
<td>1.90</td>
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<tr>
<td>D</td>
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<td>100</td>
<td>101</td>
<td>2.01</td>
<td>30.7</td>
<td>(a)</td>
</tr>
</tbody>
</table>

1 Sample tore during washing. No shrinkage figures available.
Examples 1 to 4 demonstrate the utility of the invention. Examples 5 to 7, none of which accord with the invention, are included to show the disadvantages of omitting the scell-forming compound from the process. Example 8 gives the properties of the fabric, which has been through the wet treatments and heat treatments of Example 1, but in the absence of reactants.

It will be seen from the accompanying table that the results from the fabric treated according to Example 1 are consistently the best in all tests and that the group, Examples 1 to 4, shows distinct advantages over the remaining examples. Attention is drawn to the good washing fastness of the excellent crease-recovery properties conferred by the process of this invention and the relatively small loss of tear strength and augmented tensile strength resulting from the process of Examples 1 and 2. The crease-recovery properties of the wet fabrics are also much improved. It is a feature of the treated fabrics of Examples 1 to 4 that they have a resilient nature. Not only do they recover well from creasing, but they do this very rapidly. A treated fabric sample, crushed in the hand, springs to a more open configuration when the hand is opened, quite unlike the sluggish response of the untreated fabric to this test. The poorer fabric strengths resulting from the processes of Examples 3 and 4 are directly attributable to the technical grade of glyoxal used in these processes. The low-water imbibitions of fabrics issuing from Examples 1 to 4 are noteworthy also as helping the easy-care characteristics of the fabrics.

Examples 3 and 4 were discoloured and the discolouration was permanent throughout the washing tests Examples 6 and 7 were discoloured before scouring, but the colour diminished during the scouring and the machine washing test and almost disappeared in the cotton wash samples.

What I claim is:

1. A process for the manufacture of cross-linked cellulose fibres comprising impregnating the cellulose fibres with an aqueous solution of glyoxal at a pH of from about 3 to about 8 and cross-linking the cellulose fibres by dry curing the impregnated fibres at a high temperature, and further impregnating said cross-linked fibres with an aqueous solution of formaldehyde at a pH of from about 3 to about 8 in the presence of a catalyst which is an inorganic metal salt soluble to the extent of at least about 0.3 gram mole per liter in water at about 20° C. at about pH 5 and is zinc sulphate or a salt of a Group II metal with a monobasic acid ionized to the extent of at least about 50 percent in normal aqueous solution at about 18° C., there being present on said cross-linked fibres a molar ratio of at least about 1 mole of formaldehyde to about 1 mole of reacted glyoxal, drying said fibres, and dry curing the dried product at a temperature above about 100° C.

2. A process as claimed in claim 1, in which the glyoxal contains less than 5 percent of the impurities which normally contaminate technical grades of glyoxal solutions.

3. A process as claimed in claim 1, in which the catalyst is magnesium chloride.

4. A process as claimed in claim 1 wherein both the aqueous impregnating solution of glyoxal and the aqueous formaldehyde solution have a pH of from about 5 to about 6.

5. A process as claimed in claim 1 wherein the aqueous impregnating solution of glyoxal has a pH of from about 3 to about 8, and the aqueous formaldehyde solution has a pH of from about 5 to about 6.

6. A process as claimed in claim 1 wherein the cellulose fibres cross-linked with glyoxal and impregnated with formaldehyde are heated at a temperature of from about 140° C. to about 180° C. during the dry curing step.

7. A process for the manufacture of cross-linked cellulose fibres comprising impregnating and reacting cellulose fibres with an aqueous solution containing glyoxal and formaldehyde in a molar ratio of at least 1 mole of formaldehyde to each mole of glyoxal, and magnesium chloride as a catalyst, the solution having a pH in the range of 3 to 8, drying the fibres, and dry curing the fibres at a temperature in the range from about 140° C. to about 180° C.

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