1

3,357,784
EXPOSURE TO INTENSE ULTRAVIOLET LIGHT TO IMPROVE CHARACTERISTICS OF CELLULOSIC FABRICS IN DIVINYL SULFONE AND GLYOXAL CROSS-LINKING PROCESSES

Andrew A. Kasper, Watertown, Mass., assignor to The Kendall Company, Boston, Mass., a corporation of Massachusetts
No Drawing. Filed Sept. 30, 1964, Ser. No. 400,548
10 Claims. (Cl. 8—116.4)

This invention relates to improvements in the art of rendering cellulosic fabrics, or cellulosic blends, wrinkle-resistant and shrinkage-resistant. More particularly, it relates to an advance in the art of treating cellulosic materials with certain unsaturated non-resin forming reactants, whereby enhanced and unexpected stabilization is attained without excessive strength loss.

It has long been common in the textile industry to treat cellulosic fabrics such as those composed of cotton or rayon with certain reagents which increase the resilience of the fabrics, making them less prone to creasing or wrinkling, and simultaneously minimizing the progressive shrinkage which occurs in laundering, particularly in the case of rayon fabrics. Such reagents as urea-formaldehyde, melamine-formaldehyde and the triazone resins are widely used: epichlorhydrin, formaldehyde, and divinyl sulfone are reagents of the "reactant" type, sometimes distinguished from reagents of the resinous type. The reagents of the resinous type, applied to cellulosic fabrics, tend to develop unpleasant and persistent odors in the fabric: their degree of fixation on the fabric is not secure, the resin content gradually decreasing by wash down as the fabric is repeatedly laundered: many of them are sensitive to a chlorine bleach: and they unduly stiffen and embrittle the fabric.

Reagents of the reactant type are primarily not resin precursors, but are smaller mobile molecules with active groups which tend to react with the hydroxyl groups of the cellulose molecule, thereby crosslinking various elements of the cellulose chain to stabilize the fibers and hence the fabrics. The application of some reactants is expensive and hazardous. Formaldehyde is relatively inexpensive, but does not crosslink or react with cellulose in a permanent fashion until a critically low pH of about 3.0 is reached. This results in appreciable tensile loss in fabrics thus treated, which together with the irritating and toxic nature of formaldehyde vapors, mitigates against more widespread use of this reagent.

Many attempts have been made to utilize glyoxal, $(CHO)_2$, to react with cellulose. One of the earliest mentions is in the 1,857,263 U.S. patent of May 10, 1932, to Sponsel, who dried dilute solutions of glyoxal on rayon fabrics and found an increase in strength. He makes no mention of having obtained any creaseproofing or non-shrinking effect. Groves, in British Patent 439,294, of Dec. 4, 1935, indicates a "good resistance to creasing" developed in a cotton fabric by soaking the fabric in a 15% solution of glyoxal and calendering it at 110° C. (230° F.). U.S. Patent 2,412,832, of Dec. 17, 1946, to Pfeffer et al., also discloses the use of glyoxal to stabilize cellulosic fabrics.

However, it has hitherto been difficult if not impossible to utilize glyoxal in a convenient commercial process

2

for imparting wrinkle-resistance and shrinkage-resistance to cellulosic fabrics without excessive embrittlement and tensile strength loss accompanying the reaction. The disclosed art has suggested various pH ranges of operation, various drying-curing temperatures, various catalysts such as metallic salts, and various adjuncts and additives to moderate the reaction. None of these suggestions has provided a solution to the problem of tensile strength loss. As is pointed out by Hurwitz and Condon (Textile Research Journal 28, 257–266, 1958), all heat-promoted dialdehyde reactions with cellulose approach the performance of formaldehyde: that is, crease-recovery as measured by Monsanto angle of 250° or higher, but with an unsatisfactory tensile strength loss of 60% or more. For satisfactory commercial fabrics this tensile strength loss should be cut in half, since it is normal expectation in the trade that a product such as a resin-treated shirting broadcloth is commercially acceptable with a tensile strength loss of 30% to 40%. Losses of 50% and over, however, lead to premature wearing-out of garments, and are not acceptable.

It is an object of this invention to provide a process whereby glyoxal may be reacted with cellulose to give a fabric which meets acceptable commercial standards of wrinkle-recovery and shrinkage-resistance while displaying only a loss in strength associated with most wash-wear resin finishes, said loss being recognized and considered acceptable by the trade.

All prior attempts of which I am aware to promote a true crosslinking reaction between glyoxal and cellulose have been based on a low pH of reactant, and a rather intensive heating step, together with the use of a catalyst. I have made the discovery that by irradiating a glyoxal-impregnated fabric with a strong source of ultraviolet light, the desired degree of reaction between cellulose and glyoxal can be obtained with a fabric strength loss that is acceptable. The reaction may be carried out using organic solutions of glyoxal, but for obvious commercial reasons, aqueous solutions are preferred. Catalysts, wetting agents, and other reaction accelerators or modifiers may be employed in the conventional manner.

In addition to glyoxal, I have found that the reaction between cellulose and divinyl sulfone is promoted by ultraviolet light, in a manner set forth below.

GENERAL STATEMENT OF THE GLYOXAL REACTION

An essentially dry cellulosic fabric is impregnated with an aqueous solution of 2% to 8% glyoxal, containing about 0.5% zinc chloride, 1% to 2% formic acid, and 0.06% parabromoacetophenone. The role of these reaction additives will be discussed below. After impregnation the sample is squeezed to the desired calculated pickup, and is baked to dryness over the course of 1½ to 2 minutes in a circulating hot air oven adjusted to about 150° C.

The dry sample is then irradiated with a stream of photons of wave length 2,800 to 4,000 Angstrom units, with the 2,800 to 3,200 Angstrom units range being particularly effective due to the heightened sensitivity of glyoxal and parabromoacetophenone in this region. The stream of photons is conveniently derived from a bank of sun lamps of the type which provide an average photon density of 10^{14} to 10^{15} photons per second per square centimeter. Irradiation is continued for from 4 to 9 min-

utes, after which the sample is washed and tested for crease recovery by the well-known Monsanto angle recovery test, explained below. In general dry Monsanto angles (combined warp and filling) of 280°–290° are realized, wet Monsanto angles of 250° or more, and a tensile strength loss of 35% or less.

TEST METHODS

Fabrics treated in accordance with the process of this invention were tested for crease recovery by the so-called Monsanto Tester, accepted by and described in Federal Specification CCC–T–191B (M5212), and in A.S.T.M. D1295–53T. Samples of fabric 1.5 by 4.0 centimeters are cut from the fabric in both warp and filling directions, conditioned at 70° F. and 65% R.H. for at least 4 hours for the dry Monsanto angle, or immersed in water containing a few drops of detergent solution for at least 30 minutes for the wet angle test.

The sample is creased at 180° and compressed under controlled conditions of time and load. After five minutes recovery, the recovery angle is measured. The reported Monsanto angle is the sum of warp plus filling tests, 360° representing complete restoration in warp and filling.

Tensile strength determinations were made on the Instron machine.

VARIABLES IN THE PROCESS

As base fabrics suitable for treatment by the process of this invention there may be mentioned conventional cotton fabrics such as broadcloths, poplins, sheetings, and print cloths: rayon fabrics such as rayon challis or sateen: fabrics containing blends of cotton and rayon, either fiber-to-fiber blends or yarn blends: and blends of cellulosic with non-celluolsic fibers provided that in the blend there is a sufficiently substantial percentage of reactive cellulosic fibers to be effective, generally 35% or more. The fabrics should be sufficiently purified from the grey loom state to allow the fibers to absorb the glyoxal solution. Mercerization before conducting the process of this operation has the beneficial effect of increasing the Monsanto angles by about 10%, and reducing the tensile loss by about 10% presumably by fiber swelling and the opening-up of new reaction sites inaccessible in native cellulose.

Glyoxal is available as a 40% aqueous solution commercially, in which solution it is generally regarded to be hydrated to a cyclic structure known as tetrahydroxy naphthodioxane. The heating and dehydrating stage of the present process regenerates glyoxal.

Depending on the degree of crease recovery desired, balanced against the tensile strength loss that can be tolerated, glyoxal add-ons of from 1% to 10% based on fabric weight are of interest in the practice of this invention, with a preferred range of 3% to 8%. In general, as the glyoxal add-on is increased from 3% to 8%, the wet Monsanto angle increases and the tensile strength loss decreases. In the vicinity of around 8% or 10%, a plateau is reached in crease resistance, and increasing the glyoxal content of the fabric above this point does not bring about a corresponding improvement in the fabric.

The zinc chloride in the impregnating bath seems to serve one particular purpose, which is to increase the permanence of the wet Monsanto angle. Irradiated products where zinc chloride has been omitted have high dry Monsanto angles, and high wet Monsanto angles after brief immersion of up to 30 minutes in water. However, the bond between the glyoxal and cellulose formed in the absence of zinc chloride shows an apparent hydrolysis of up to 80% over 60 to 80 hours, as indicated by a steadily decreasing wet Monsanto angle, even though sufficiently high dry Monsanto angles are attained. Since there are fabrics such as draperies and the like which are meant to be dry-cleaned and not laundered, there are obviously cases wherein only the dry Monsanto angle is of concern. Therefore I regard the use of zinc chloride as optional,

depending on the nature and end-use of the fabric, and do not wish to be restricted to its use. As an example of the effect of zinc chloride, the general procedure above was duplicated with 5% glyoxal, .06% parabromoacetophenone, 2¼ minutes drying at 150° C., 7 minutes irradiation, and with a similar solution containing 0.75% zinc chloride and 1.25% formic acid. The dry Monsanto angles were about the same, 300°. The "immediate" wet Monsanto angle—that is, the angle measured after 30 minutes immersion, was 250° in each case. However, on longer soaking of 64 hours, the wet Monsanto angle was 240° in the case of the sample run with zinc chloride, whereas it decayed to 200° in the case of the sample run without zinc chloride. By periodic measurements, the rate of decay of the wet Monsanto angle was determined to be about 5% of the initial value per hour of immersion for samples not treated with zinc chloride.

Other acidic salts which may replace the zinc chloride include the other zinc halides (except the fluoride), zinc sulfate, zinc nitrate, magnesium chloride, and magnesium nitrate. In general, the effective range of concentration of the zinc chloride is from 0.25% to 2 or 3%. At the higher range, the tensile strength loss is liable to be excessive, so a range of 0.5% to 0.8% zinc chloride is preferred as resulting in adequate stabilization of the wet Monsanto angle combined with minimum tensile loss.

The exact mechanism by which zinc chloride stabilizes the cellulose-glyoxal bond is not known to me. It may be of significance that approximately equal stability may be attained by including the zinc chloride in the initial impregnating bath, curing, and irradiating, or by impregnating without zinc chloride, curing, irradiating, saturating with dilute zinc chloride solution, and recuring. The effect therefore is probably an independent effect on the nature of the bond, rather than a modification of the initial cellulose-glyoxal reaction.

The use of formic acid in the impregnating bath is advantageous principally when zinc chloride is used. Zinc chloride alone in the reaction has been found to hydrolyze to a certain extent to basic zinc chloride, which precipitates onto the fabric and which has been reported to be more acidic than zinc chloride itself. In the drying operation this acidity causes additional tensile strength loss. The presence of formic acid or similar material apparently prevents the formation of basic zinc salts, and helps preserve tensile strength.

The parabromoacetophenone, present in trace quantities, is desirable as a sensitizer to promote the photon-induced reaction between cellulose and glyoxal. Photosensitizers in general have the property of absorbing spectral energy at some given wave length, being thereby lifted from their normal or ground states to excited states. In the excited state, a photosensitizer is postulated to enter into an energy change with a second substance, in this instance glyoxal, thereby raising the reactant to an activated or excited stage and facilitating the reaction between the reactant and the cellulose molecule.

In addition to parabromoacetophenone, sensitizers such as benzophenone, acetophenone, and chloranil may be employed. They should be regarded as facilitating the reaction, rather than as being essential to it. Where dry Monsanto angles of around 280°, wet angles of around 240°, and tensile strength losses of 40% or so are allowable, the sensitizer may be omitted. Its use does, however, promote the realization of wrinkle-resistant fabrics of high commercial acceptability.

I have found that the drying-baking step of the impregnated material, prior to irradiation, is an essential and critical step. The exact chemical nature of simple aldehydes in aqueous solution has not been explicitly determined. As set forth above, some authorities believe that in the presence of water, two molecules of glyoxal hydrate with two molecules of water to form tetrahydroxy naphthodioxane. Others have postulated a simpler reaction wherein two molecules of water hydrate a single molecule

5

of glyoxal to form tetrahydroxy ethylene. Regardless of the particular hydrated aldehyde species present on the saturated fabric, it must be dehydrated to the simpler dialdehyde form before reaction with the cellulose. A mere air-drying to normal moisture regain is not sufficient to promote a desirable cellulose-glyoxal reaction, which is why I have referred to this step as a "dry-bake" process, rather than drying. It has been my experience that the moisture content of the dried fabric must be reduced to at least 2.5% and preferably to below 1.5%, for optimum results. This moisture content is below the normal regain of a fabric that has been simply air dried after impregnation with a glyoxal solution. It may be that in a fabric with normal regain, the most available potential reactive sites are associated with loosely-bound or adsorbed water molecules, and that this type of hydration competes with the desired glyoxal-cellulose reaction. Whatever the reason, it appears that removing a substantial part of the normal regain moisture facilitates a more extensive and a more durable wrinkle-resistant effect when cellulose is reacted with glyoxal which has been applied from an aqueous solution. This is borne out by the following Table 1, showing the effect of various pre-irradiation conditions on the crease-resistance of a standard fabric.

TABLE 1

Drying Condition	Irradiation	Percent Add-on	Tensile Loss, percent	Monsanto Dry, deg.	Angle Wet, deg.
None	Wet	7.2	10	241	220
Room temperature	Dry	6.9	24	262	240
Warm Air	Dry	7.0	33	277	259
Circulating, 100° C. air	Dry	7.5	33	285	271

When glyoxal has been applied from an acetone solution, there is apparently a semi-dehydrating action on the cellulose, due presumably to the mutual solubility of acetone and water, and a cellulosic fabric saturated with a glyoxal-acetone solution may be irradiated wet without the need for a preheating step.

For the irradiation step, ultraviolet light in the region of from 2,800 Angstrom units to 4,000 Angstrom units has been found effective. Presumably, the glyoxal is activated by the ultraviolet light. The wave length of the excitation reaction:

$$(CHO)_2 + hv = (CHO)_2^*$$
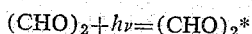
has been reported to be 3,130 Angstrom units (Calvert et al., "Journal of the American Chemical Society," 75, 856–9, 1953). The activated glyoxal molecule in part reacts with cellulose, and in part is subject to photolytic decomposition according to the following reactions:

$$(CHO)_2^* = H_2 + CO$$
$$(CHO)_2^* = HCHO + CO$$
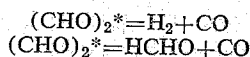
the latter reaction being more probable. In the latter case, the formaldehyde formed by photolysis can itself react with the cellulose molecule to give cross-linking. The system therefore is very efficient in light-energy utilization, and the photo-induced reaction glyoxal and cellulose effects a combination of maximum glyoxal add-on with minimum tensile strength loss which cannot be realized by any other process with which I am familiar.

The activating influence of ultraviolet radiation in this reaction is quite different from the influence of the infrared irradiation previously used in glyoxal-cellulose reactions in which the driving force is purely thermal, as in conventional curing or baking reactions. The following example will illustrate the difference between irradiation plus curing and purely thermal curing.

Example 1

Samples of 80-square cotton print cloth were impregnated with 100% to 110% of their weight in a solution of

6

5% glyoxal (aqueous) containing 0.06% parabromoacetophenone and 1% zinc chloride, air dried, and cured at 170° C. in a circulating air oven for 70 seconds. The wet Monsanto angles after 30 minutes immersion in water plus detergent were excellent, the sum of warp and filling angles being over 300°. The tensile strength loss, however, was unbearably excessive, being 69%, and the fabric was so brittle as to be friable and commercially worthless. A similar set of fabric samples was impregnated with an aqueous 5% solution of glyoxal plus 0.06% parabromoacetophenone, without zinc chloride, to 100–100% pickup, and air-dried. The samples were then irradiated by radiation from a bank of ultraviolet sun lamps for 7 minutes, after which they were dipped into 1% zinc chloride solution, squeezed to 100% pickup, air-dried, and heated in a circulating air oven for 60 seconds. The wet Monsanto angle, after 30 minutes immersion in water plus detergent, was 262°, an acceptable commercial level, and the strength loss was only 36%, also a commercially acceptable level, said acceptable commercially acceptable levels of wrinkle-resistance and maintenance of tensile strength being generally characteristic of the products made according to this invention.

THE DIVINYL SULFONE REACTION

Divinyl sulfone is known to react with cellulose, as set forth in U.S. Patent 3,106,439, of Oct. 8, 1963. However, as pointed out in that patent, the reaction must be carried out in an alkaline medium, at a pH of 8.5 or higher. Under such conditions, the reaction is accompanied by side reactions which cause more or less extensive discoloration of the fabric, which must be subjected to a thorough scouring after reaction to restore its color to an acceptable commercial level.

I have found that divinyl sulfone can be crosslinked with cellulose under acid conditions, and without the formation of colored by products, if a small amount of glyoxal is present as an activator or sensitizer, and provided that the impregnated sample is irradiated with ultraviolet light during the reaction. The preferred general procedure is to impregnate the fabric with a mixture of divinyl sulfone, glyoxal, and formic acid; then, in the wet condition and on a thermally controlled surface the fabric is irradiated for several minutes, washed, and dried.

Concentrations of formic acid as low as 0.5% are moderately effective, but my preferred range is 2% to 5%, such concentrations generally resulting in fabrics with Monsanto angles in excess of 240°. The exact role played by the glyoxal in this reaction is not known to me. I have found that in the concentrations preferred, 2% to 3%, and under comparable reaction conditions, glyoxal alone does not result in commercially acceptable Monsanto angle. Neither does the use of divinyl sulfone alone. A mixture of 3 to 5 parts of divinyl sulfone to 1 part of glyoxal, however, is effective, in acid medium, in imparting an acceptable crease-proofing property to cellulosic fabrics, as set forth below in Example 2.

Example 2

A sample of the 80-square print cloth of Example 1 was impregnated with an aqueous solution of 9.8% divinyl sulfone, 2% glyoxal, and 5% formic acid. The wet pickup was adjusted to 110%. While still wet, the sample was placed on a metal surface heated to 210° F. and irradiated

7

for 7 minutes under a bank of ultarviolet sum lamps. The dry product was then thoroughly washed in a dilute solution of sodium carbonate and detergent, rinsed to neutrality, and dried. The cloth had increased in weight by 5.4%; the tensile strength loss was 37%; dry Monsanto angle was 285°; and the wet Monsanto angle after soaking the fabric 86 hours in detergent solution was 240°. The fabric had no odor, was not discolored, and the finish was resistant to hydrolysis as evidenced by retention of high Monsanto angle after immersion for 84 hours in aqueous solutions varying in pH from 3.5 to 11.0.

In addition to formic acid, other acids may be used provided that a pH solution range of 1.5 to 3.5 can be thereby realized. Suitable acids include oxalic, malic, maleic, tartaric, fumaric, citric, and chloracetic.

Although the reaction of Example 2 was carried out without a sensitizer, parabromoacetophenone and sensitizers of analagous action may be utilized, in concentrations of 0.01% to 0.06%, to accelerate the reaction.

I am aware that it has been proposed to promote grafting reactions between cellulose and resin precursors by the use of high energy radiation. High energy electron beams, however, are in the class of ionizing radiation, and in general their use leads to ionization of at least one of the reactans, and to secondary chemical changes. The ultraviolet irradiation of this invention is substantially non-ionizing, the energy density is lower, and the net effect is the promotion of a cross-linking between cellulose and reactant, rather than the promotion of a surface grafting of a polymer onto cellulose.

Having thus described my invention, I claim:

1. A process of producing a crease-resistant finish on a cellulosic fabric which comprises impregnating said fabric with a reactant selected from the group consisting of glyoxal and divinyl sulfone containing a sensitizing amount of glyoxal and subjecting the impregnated fabric to ultraviolet irradiation of an intensity of at least 10^{14} photons per square centimeter per second for a period of from 4 to 9 minutes.

2. A process for producing a crease-resistant finish on a celulosic fabric which comprises impragnating said fabric with an aqueous solution of glyoxal, drying said fabric, and subjecting said fabric to ultraviolet irradiation of an intensity of at least 10^{14} photons per square centimeter per second for a period of from 4 to 9 minutes.

3. A process according to claim 2 wherein the impregnated sample is dried to a moisture content below its normal regain level prior to irradiation and is maintained at said lower moisture level during irradiation.

4. A process for producing a crease-resistant finish on a celulosic fabric which comprises
   impregnating said fabric with an aqueous solution comprising glyoxal,
   in an amount and at a concentration sufficient to equal between 1% and 10% of glyoxal, based on the weight of said fabric,
   said aqueous solution also comprising between 0.25% and 3.0% of an acidic salt catalyst,
   and between 1% and 2% of an organic acid;
   drying said impregnated fabric to a moisture content below 2.5%;

8

   and maintaining said fabric at or below said 2.5% moisture content
   while subjecting said fabric for a period of from 4 to 9 minutes
   to ultraviolet irradiation of an intensity of at least 10^{14} photons per square centimeter per second.

5. A process according to claim 4 in which the acid salt catalyst is zinc chloride and the organic acid is formic acid.

6. A process according to claim 4 in which the aqueous solution comprises, in addition to glyoxal, acid salt catalyst, and organic acid, a trace amount of a photosensitizing agent.

7. A process according to claim 6 in which the photosensitizing agent is chosen from the class consisting of benzophenone, acetophenone, chloranil, and parabromoacetophenone.

8. A process for producing a crease-resistant finish on a cellulosic fabric which comprises
   impregnating said fabric with an aqueous solution comprising divinyl sulfone, glyoxal, and an organic acid sufficient to reduce the pH to at least 3.5,
   and irradiating said impregnated fabric for a period of between 4 and 9 minutes at a temperature of at least 200° F.
   with ultraviolet radiation of an intensity of at least 10^{14} photons per square centimeter per second.

9. A process according to claim 8 wherein the impregnating solution contains between 3 and 5 parts of divinyl sulfone per part of glyoxal and the acid is formic acid.

10. A process for producing a crease-resistant finish on a cellulosic fabric which comprises
    impregnating said fabric with an aqueous solution of glyoxal,
    drying said impregnated fabric,
    reducing the moisture content of said fabric below 2.5% while simultaneously subjecting said fabric to intense ultraviolet irradiation of an intensity of at least 10^{14} photons per square centimeter per second for a period of from 4 to 9 minutes,
    immersing said fabric in an aqueous solution of an acidic salt catalyst,
    and drying and curing said fabric.

References Cited

UNITED STATES PATENTS

1,857,263	5/1932	Sponsel et al.	8—116.4
2,436,076	2/1948	Pfeffer et al.	8—116.4
2,484,545	10/1949	Beer	8—116.4
2,521,328	9/1950	Beer	8—116.4
2,530,175	11/1950	Pfeffer et al.	8—116.4

OTHER REFERENCES

Egerton: J.S.D.C., vol. 63, pp. 161–171 (1947).
Egerton: J. Textile Inst., vol. 39, pp. T293–T304 (1948).
Egerton: J.S.D.C., vol. 65, pp. 764–780 (1949).

J. TRAVIS BROWN, *Acting Primary Examiner.*

NORMAN G. TORCHIN, *Examiner.*

J. C. CANNON, *Assistant Examiner.*