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Crosslinking Cotton with Formaldehyde in Phosphoric Acid*

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Synopsis

Cotton print cloth was treated with a solution of formaldehyde in concentrated orthophosphoric acid (a strong cellulose swelling agent). The treatment produces a crosslinked cotton with extremely high wet wrinkle recovery and moisture absorptivity, and very low dry wrinkle recovery. The variations in physical properties are explained in terms of crosslink distribution throughout the fiber and specifically by differences in interlamellar and intralamellar crosslinking. Data on the chemical and physical properties of the fabric as well as electron micrographs of fiber cross-sections are presented and compared or contrasted with data from similar treatments employing other solvents such as water (a moderate swelling agent), acetic acid (a weak swelling agent), and sulfuric acid (a solvent which restricts crosslinking to the periphery of the fiber). Although the treatment causes extensive fiber swelling, it produces very little change in crystallinity and no change in crystal lattice type. Also discussed are the effects of combining this wet crosslinking and conventional dry-cure crosslinking with methylol amides in a two-stage process, in which the wet crosslinking is used either as a pretreatment or as an aftertreatment.

Introduction

In previous investigations at this laboratory it has been shown that when cotton is crosslinked at room temperature with formaldehyde in acidic solutions, the crosslink distribution within the fiber can be markedly affected by the particular solvent used.[1,2] For example, when acetic acid is used, as in the Form D treatment reported by Chance et al.,[3] the resultant crosslink distribution is essentially uniform throughout the fiber cross-section. Frick et al.[2] have shown that when most of this acetic acid is replaced by sulfuric acid, the crosslinking takes place preferentially in the peripheral regions of the fiber. Similarly, when crosslinking is carried out in an aqueous solution, as in the Form W process, still another type of distribution is observed. Each different distribution gives rise to a different set of physical properties in the treated fabric.

The present work extends previous investigations to wet crosslinking

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treatments with solutions of formaldehyde in concentrated orthophosphoric acid (H_3PO_4).

Phosphoric acid was chosen because its ability to swell cotton cellulose is considerably greater than that of previous solvents used. Phosphoric acid is a strong swelling agent, while water is a moderate swelling agent, and acetic acid is relatively weak.[4] The effects of these treatments on the chemical and physical properties of the treated fabrics will be discussed and correlations between the physical properties and the crosslink distribution will be made. The combination of wet formaldehyde crosslinking with conventional pad-dry-cure finishing with common methylol amide finishing agents will also be discussed.

Experimental

The fabric used was an 80 × 80 cotton print cloth weighing approximately 3.2 oz./yd.^{2}. The fabric had been desized, caustic-boiled, and bleached prior to treatment. The reactant solutions consisted of formaldehyde from commercial formalin (stabilized with methanol), distilled water, and reagent-grade acids. Fabric was treated by soaking it in the solution at room temperature for a given length of time, removing and rinsing in running tap water for several minutes followed by a thorough alkaline wash with detergent in a home-type washing machine. Bound formaldehyde on the treated fabric was determined by a method described earlier.[5] Wrinkle recovery angles were measured on the dry or conditioned fabric by using the Monsanto tester and the A.S.T.M. method.[6] Wet wrinkle recovery angles were measured by a similar procedure except that prior to testing, the samples were soaked in warm water containing a wetting agent for 5 min., and the excess water blotted off prior to insertion of the sample into the tester. Nitrogen contents were determined by the Kjeldahl method. Moisture regain was determined by first heating the sample for 5 min. at 105°C. then equilibrating at 70°F. and 65% R.H. for 72 hr. The equilibrated samples were weighed and then dried for 4 hr. at 105°C., and again weighed. The moisture regain was calculated from the change in weight due to moisture and the dry fabric weight. Breaking strength was determined on an Instron tensile tester on ravelled strips of fabric 1 in. wide with a gage length of 5 in. Cellulose crystallinity was estimated by two methods: by the infrared method of Nelson and O'Connor and by the x-ray diffraction method of Segal et al.[7,8]

Results and Discussion

A series of print cloth samples was treated with a solution containing 3.6% formaldehyde, 3.7% hydrogen chloride, 17.7% water, and 75% phosphoric acid for various time intervals. This treatment will be referred to as Form P. The chemical and physical properties of the treated fabrics are shown in Table I. For comparison, the properties of fabrics treated with formaldehyde in other solvents are also shown in Table I. In the

TABLE I
Treatment of Cotton Print Cloth with Various Formaldehyde Solutions

Treatment	Treatment time, min.	Bound formaldehyde, %	Moisture regain, %	Wrinkle recovery angle (W + F), deg.		Crystallinity index	
				Wet	Dry	Infrared	X-ray
Form P[a]	1	0.56	8.44	246	105	0.719	85.5
"	5	1.22	9.55	312	109	0.680	85.1
"	10	1.57	10.19	327	119	0.673	82.8
"	30	2.22	9.46	358	154	—	—
"	60	2.45	10.25	360	161	—	—
Form D[b]	10	0.42	—	215	219	—	—
"	120	1.24	—	267	269	—	—
Form W[c]	30	0.52	7.84	250	216	—	—
"	180	0.75	8.44	280	212	—	—
Form S[d]	5	0.99	7.27	199	217	—	—
"	30	1.87	7.84	230	258	—	—
Untreated control		—	6.68	161	175	0.795	88.2

[a] Treating bath contained 3.6% HCHO, 3.7% HCl, 17.7% water, and 75.0% phosphoric acid.

[b] Treating bath contained 3.6% HCHO, 3.7% HCl, 17.7% water, and 75.0% acetic acid.

[c] Treating bath contained 7.5% HCHO, 17.5% HCl, and 75.0% water.

[d] Treating bath contained 7.5% HCHO, 47.0% H_2SO_4, 17.7% water, and 27.8% acetic acid.

Form W treatment the formaldehyde and hydrochloric acid concentrations in the treating bath had to be increased in order to obtain fabrics with comparable levels of bound formaldehyde. The high water concentration in the Form W treating bath tends to shift the equilibrium of the crosslinking reaction to lower bound formaldehyde levels. The Form P treatment for short periods of time greatly enhanced the wet wrinkle recovery angle and at the same time markedly reduced the dry wrinkle recovery angle as compared to the untreated control fabric. Treatment for longer periods brought the wet wrinkle recovery to an almost maximum level, but dry recovery was still less than that of the untreated control.

The moisture regain of the Form P-treated samples, in general, increased with increasing degree of crosslinkage. In fact, the regains of the samples treated for the longer times approach that of rayon. The high moisture regains and the very high wet wrinkle recovery angles are indicative of extensive fiber swelling at the time of crosslinking. The low dry recovery angles indicate that the crosslinking is intralamellar rather than interlamellar. This latter conclusion is based on the results of work by Reeves et al.,[9] who demonstrated that crosslinking between fiber elements referred to as lamellae was present in fabrics with improved dry recovery, while fabrics without interlamellar bonding did not show dry recovery improvement. A somewhat similar set of circumstances exists in the Form

W-treated fabric. The dry wrinkle recovery angles are only slightly improved. The wet wrinkle recovery angles and the moisture regains are considerably improved, but not to the same degree as those in the Form P samples. In the Form D-treated samples, as the degree of crosslinking increases, both wet and dry wrinkle recovery are improved to approximately the same extent. In the Form S treatment, the rate of penetration of the reactants is much slower than the rate of reaction with cellulose. As a

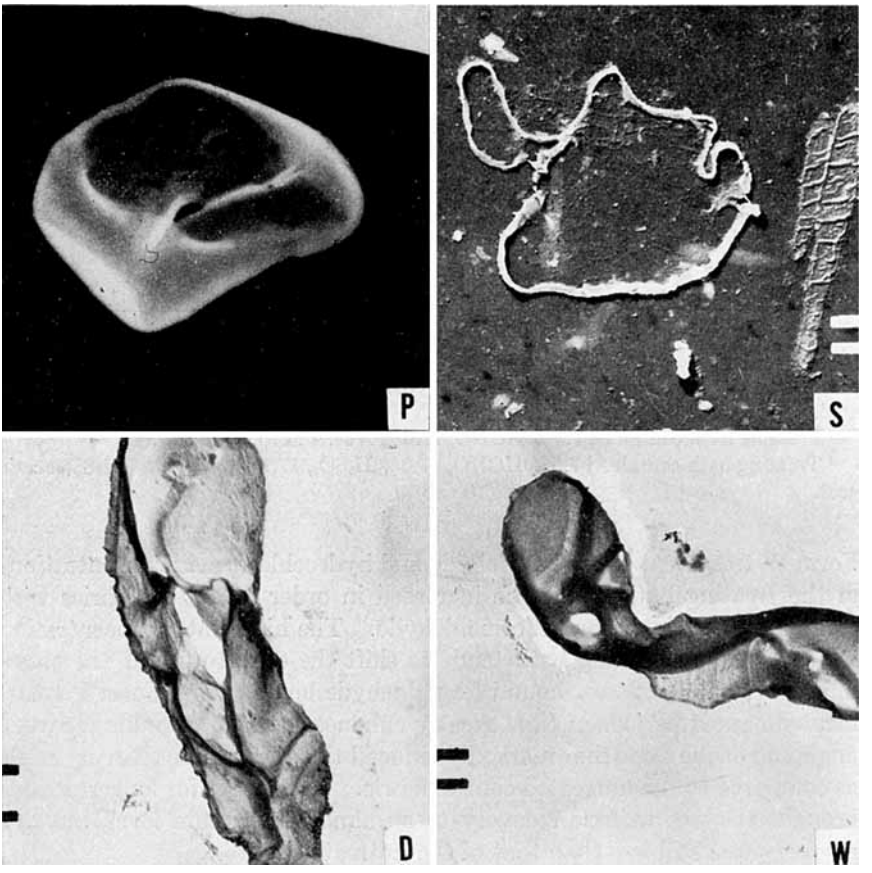

Fig. 1. Electron photomicrographs of fiber cross-sections after treatment with 0.5*M* cupriethylenediamine: (*a*) Form P; (*b*) Form S; (*c*) Form D; (*d*) Form W.

result, short-time reactions result in peripheral crosslinking. In this case, the majority of the fiber cross-section is not crosslinked, and neither wet nor dry wrinkle recovery is greatly improved. As reaction time is extended, the reactants eventually penetrate the entire fiber. Since dry wrinkle recovery is improved by these longer treatments, it is concluded that interlamellar crosslinking is taking place. The moisture regains of Form S cottons indicate that only moderate fiber swelling takes place in this treatment.

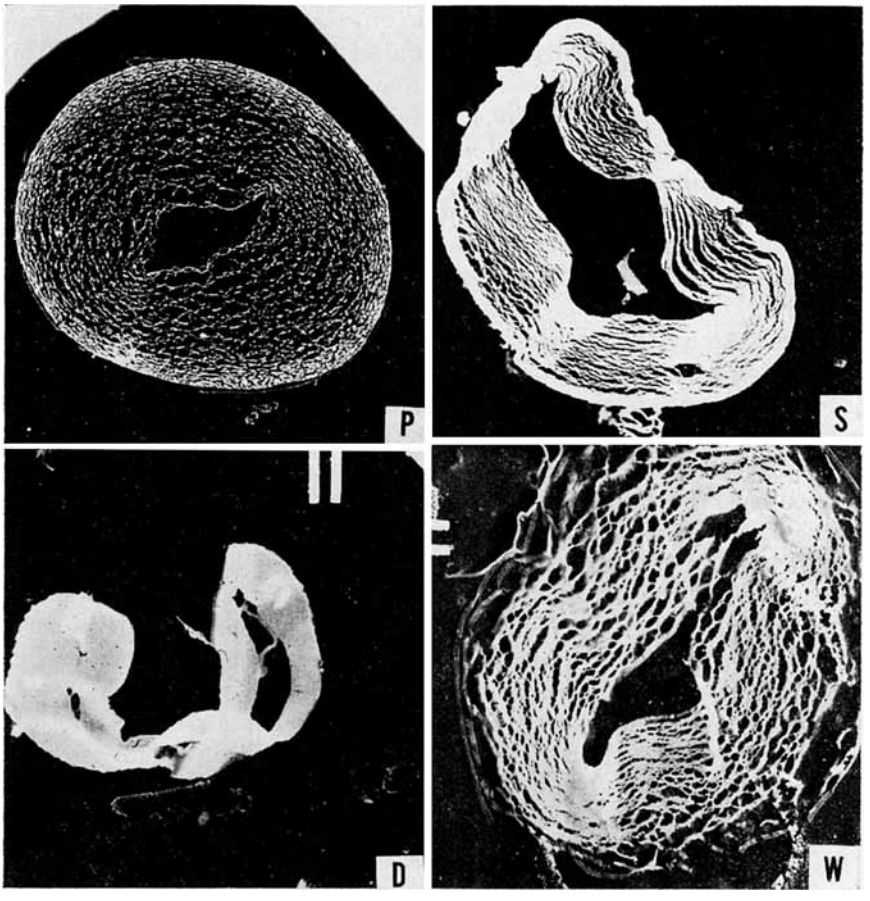

Fig. 2. Electron photomicrographs of fiber cross-sections after treatment with methyl methacrylate: (*a*) Form P; (*b*) Form S; (*c*) Form D; (*d*) Form W.

It will be noted from the data in Table I that the dry wrinkle recovery angle improvement per unit of bound formaldehyde is reduced in going from Form D to Form W treatment. This reduction has been attributed in previous investigations to a less favorable distribution of the crosslinks caused by the increased formaldehyde and hydrochloric acid concentration in the Form W treating bath.[10] A further reduction occurs in going from Form W to Form P treatment. This reduction is probably caused by the increased acidity from the phosphoric acid acting in conjunction with the hydrochloric acid. Alternatively, since phosphoric acid swelling is much more extensive than the water swelling associated with Form W treatments, this swelling, *per se*, might have some influence on crosslink distribution and thereby affect the wrinkle recovery to bound formaldehyde relationship.

Further evidence for the type of crosslink distribution in Form P treated samples is presented in the electron micrographs shown in Figures 1 and 2.

The first set of pictures shows ultrathin cross-sections of fibers after treatment with cupriethylenediamine by the method of Tripp et al.[11] This procedure distinguishes crosslinked from noncrosslinked cellulose, since noncrosslinked cellulose is soluble in 0.5*M* cupriethylenediamine. Again for comparison, cross-sections of fibers treated with formaldehyde in other solvents are also presented. It will be noted that the Form P, the Form D, and the Form W samples exhibit uniformly crosslinked structures, while the Form S sample exhibits crosslinkage in the peripheral portions of the fiber and no crosslinkage in the center. The second set of pictures shows ultrathin cross-sections of fibers after swelling with water and methyl methacrylate by the method of Rollins and Tripp.[12] This test has been used by previous investigators to distinguish between interlamellar and intralamellar crosslinking. Interlamellar crosslinking restricts movement of certain fiber elements and, thereby prevents layer separation by the expanding methacrylate. The photomicrographs in Figure 2 show extensive layer separation throughout the Form P and Form W samples, and in the central portion of the Form S sample. This behavior is in agreement with the low dry wrinkle recovery associated with these treatments. In contrast, the Form D sample and the periphery of the Form S sample do not exhibit layering. The Form S treatment does impart a high degree of dry wrinkle resistance (as does the Form D treatment) provided enough time is allowed for uniform penetration.

Phosphoric acid acts as a strong swelling agent for cotton in these treatments, as is evidenced by the high moisture regain values shown in Table I. However, this swelling action seems to be restricted to the

TABLE II
Form P Treatment Followed by Conventional Crosslinking with Dimethylol Ethyleneurea

Treatment[a]	Bound formaldehyde, %	Bound nitrogen, %	Moisture regain, %	Wrinkle recovery angle (W + F), deg. Wet	Wrinkle recovery angle (W + F), deg. Dry	Breaking strength (warp), lb.
Form P (1 min.)	0.69	—	8.75	244	85	57.8
Form P (1 min.) + DMEU	3.10	1.50	6.84	296	230	30.7
Form P (5 min.)	1.84	—	10.20	347	104	29.0
Form P (5 min.) + DMEU	4.93	1.69	7.82	323	236	17.9
Form P (10 min.)	1.48	—	9.56	330	104	35.5
Form P (10 min.) + DMEU	4.42	1.70	7.49	311	229	22.4
DMEU control	2.58	1.73	4.60	274	290	33.4
Untreated control	—	—	6.64	154	195	52.6

[a] Conventional crosslinking entailed impregnating the fabric with an aqueous solution containing 8% DMEU and 0.5% $Zn(NO_3)_2 \cdot 6H_2O$, drying for 7 min. at 60°C. followed by curing for 3 min. at 160°C.

amorphous regions of the fiber, since only a very slight decrease in crystallinity takes place. The x-ray diffraction data also indicate that the cellulose I crystal structure is maintained. Frick et al.[13] have used phosphoric acid swelling as a pretreatment to improve the wash-wear properties of crosslinked cotton. The Form P treatment was applied as both a pretreatment and a post-treatment to dry-cure crosslinking with nitrogenous finishing agents. The results are summarized in Tables II and III.

TABLE III
Conventional Crosslinking with Dimethylol Methyl Carbamate Followed by Form P

Treatment[a]	Bound formaldehyde, %	Bound nitrogen, %	Moisture regain, %	Wrinkle recovery angle (W + F), deg.		Breaking strength (warp), lb.
				Wet	Dry	
DMMC control	2.68	0.83	4.62	275	281	30.2
DMMC + Form P (1 min.)	2.58	0.67	5.81	273	246	30.0
DMMC + Form P (5 min.)	2.98	0.45	8.89	340	148	27.6
DMMC + Form P (10 min.)	2.95	0.54	7.66	308	189	29.0
Untreated control	—	—	6.64	154	195	52.6

[a] Conventional crosslinking entailed impregnating the fabric with an aqueous solution containing 8% DMMC and 0.5% $Zn(NO_3)_2 \cdot 6H_2O$, drying for 7 min. at 60°C., followed by curing for 3 min. at 160°C.

Table II presents data on print cloth which was given a Form P pretreatment for 1, 5, or 10 min., washed, dried, and then given a dry-cure treatment with 8% dimethylol ethyleneurea (DMEU) and 0.5% zinc nitrate hexahydrate as catalyst. Table III presents data on print cloth which was given a dry-cure treatment with 8% dimethylol methyl carbamate (DMMC) and 0.5% zinc nitrate hexahydrate as catalyst, and then after-treated by the Form P process for 1, 5, or 10 min. Dimethylol methyl carbamate was chosen for this experiment since it possesses greater stability to acid hydrolysis than does dimethylol ethyleneurea. Dry-cure crosslinking of Form P samples produced fabric with wet wrinkle recovery higher than that produced by dry-cure crosslinking alone and with moisture regain even higher than the untreated control. However, dry wrinkle recovery and breaking strength were considerably reduced, compared to dry-cure crosslinking alone. In addition, the Form P pretreated samples had a slightly stiffer hand than the dimethylol ethyleneurea control. When Form P was used as an aftertreatment, wet wrinkle recovery and moisture regain were increased, dry wrinkle recovery was drastically reduced, and the breaking strength remained essentially the same. The Form P aftertreated samples had a stiffer hand than the pretreated, crosslinked samples.

Summary

When cotton print cloth is treated with solutions of formaldehyde in concentrated phosphoric acid, a crosslinked fabric is produced which possesses extremely high wet wrinkle recovery and moisture absorptivity, and very low dry wrinkle recovery. The crosslinks which are introduced are predominantly intralamellar and are distributed uniformly throughout the fiber cross section. This treatment produces less increase in dry wrinkle recovery per unit of bound formaldehyde than most wet treatments. This reduction could be due to the increased acidity of the treating bath, or to the extensive swelling produced by the concentrated phosphoric acid, or a combination of both. The treatment produces little change in crystallinity and no change in crystal lattice type. Combining this wet crosslinking with conventional dry-cure crosslinking with methylol amides increases the wet wrinkle recovery and moisture regain but markedly reduces dry wrinkle recovery, compared to dry-cure crosslinking alone.

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Throughout this paper the mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

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Résumé

Du tissu de coton imprimé a été traité avec une solution de formaldéhyde dans l'acide ortho-phosphorique concentré (agent gonflant énergique de la cellulose). La traitement produit un coton ponté ayant une récupération au froissement extrêment élevée à l'état humide de même qu'une grande capacité d'absorption d'humidité, mais un recouvrement

au froissement très faible à l'état sec. Les variations des propriétés physiques sont expliquées sur la base de la distribution des ponts à travers la fibre et spécifiquement par la différence dans les pontages interlamellaire et intralamellaire. Des résultats concernant les propriétés chimiques et physiques du tissu ainsi que des micrographies électroniques de sections transversales de la fibre sont présentées et comparées ou mises en contraste avec les résultats provenant de traitements similaires, faisant usage d'autres solvants tels que l'eau (un agent gonflant modéré), l'acide acétique (un agent gonflant faible), et l'acide sulfurique (un solvant qui limite le pontage à la périphérie de la fibre). Bien que le triatement cause un gonflement très élevé de la fibre, il produit peu de modification dans la cristallinité et aucun changement dans le réseau cristallin. On discute également les effets de la combinaison en un processus à deux étapes de ce pontage humide et du pontage conventionnel par traitement à sec avec les amides méthyloliques; dans ce processus le pontage humide est utilisé soit comme prétraitement, soit comme post-traitement.

Zusammenfassung

Baumwoll-Druckstoff wurde mit einer Lösung von Formaldehyd in konzentrierter Orthophosphorsäure (einem starken Baumwollquellungsmittel) behandelt. Die Behandlung führt zu vernetzter Baumwolle mit extrem hoher Nassknitterfestigkeit und Feuchtigkeitsabsorption sowie sehr niedriger Trockenknitterfestigkeit. Die Änderungen der physikalischen Eigenschaften werden mit der Vernetzungsverteilung in der Faser und zwar spezifisch mit Unterschieden in der interlamellaren und intralamellaren Vernetzung erklärt. Daten über die chemischen und physikalischen Eigenschaften des Gewebes sowie elektronenmikroskopische Aufnahmen von Faserquerschnitten werden vorgelegt und den Daten für ähnliche Behandlung mit anderen Lösungmitteln wie Wasser (einem mässigen Quellungsmittel), Essigsäure (einem schwachen Quellungsmittel) und Schwefelsäure (einem Lösungsmittel, welches die Vernetzung auf die Peripherie der Faser beschränkt) gegenübergestellt. Obgleich die Behandlung eine starke Faserquellung verursacht, führt sie nur zu einer sehr geringen Kristallinitätsänderung und zu keiner Änderung des Kristallgittertyps. Weiters werden die Effekte einer Kombination dieser Nassvernetzung mit der konventionellen Trockenvernetzung mit Methylolamiden in einem Zweistufenprozess diskutiert, bei welcher die Nassvernetzung entweder als Vorbehandlung oder Nachbehandlung verwendet wird.

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