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Olney Medal Address

Certain Aspects of Cellulose Crosslinking

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ABSTRACT

In the 1980's a new challenge for the textile chemist is to develop permanent press textiles made from cellulosic fibers alone and from blends with high cellulose content without undue strength losses and without impairing the soiling and comfort characteristics of the natural fibers. The permanent press finishing should be carried out by using energy saving, low moisture pickup and single-stage, rapid cure application techniques without the drawbacks (chlorine retention and increased formaldehyde release) of incomplete curing.

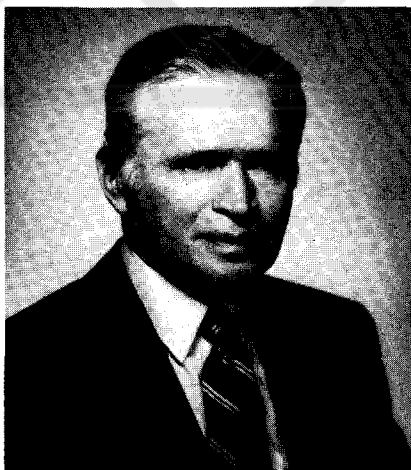
Within the framework of these investigations, we studied the effect of multiple launderings in the presence and absence of oxidative bleaches on cellulose crosslinked with cyclic alkyleneurea-formaldehyde resin. The analysis of the data obtained indicates that the absence of scorching damage due to retained chlorine does not guarantee the resistance of the finish towards launderings in the presence of active chlorine. The single-end reacted sites are primarily responsible for chlorine retention and formaldehyde release. However, in launderings in the presence of chlorine bleach, the cleavage of the carbon-oxygen bonds and simultaneous chloramide formation and formaldehyde release should also be considered. The results of these studies lead to a better understanding of the mechanism underlying the degradation caused by active chlorine and its correlation with formaldehyde release.

KEY TERMS

Cellulose
Chlorine Retention
Crosslinking
Durable Press
Formaldehyde Release

In the last four decades many investigations have been carried out with the objective to get a better understanding of the mechanism underlying textile chemical procedures and many empirical approaches have been replaced with methods developed by systematic experimental studies. Thus new textile chemicals and new textile finishing treatments have been introduced to impart specific functional properties.

Whereas in the late 1950's and in the 1960's the emphasis was placed on the development of new chemical finishes imparting novel or improved properties such as easy care (permanent press, soil release, etc.) characteristics, flame resistance, static control, oil and water repellency, and comfort stretch, in the 1970's most of the efforts have been concentrated on the protection of the worker, the environment and the consumer. Efforts have been made to reduce formaldehyde release, decrease cotton dust and replace



STEPHEN B. SELLO: Thirty-ninth recipient of the Olney Medal for achievement in textile chemistry. The medal was established in 1944 in honor of Dr. Louis Atwell Olney, founder and first president of AATCC. The medal was presented to Sello at AATCC's national technical conference last month in Atlantic City, N. J.

hazardous and polluting chemicals in accordance with the requirements of government (OSHA, EPA, CPSC) regulations. In addition, the emphasis has shifted from product to process development encompassing such methods as radiation processing, solvent finishing, low-moisture application techniques. While the first two of these have not gained any commercial acceptance, the low moisture application methods (foam finishing, kiss roll, vacuum slot, etc.) were widely accepted when energy savings became mandatory. Generally, the introduction of low moisture application methods resulted in an increased productivity.

In the late 1970's the natural fibers became the elite fibers in the developed countries. As a result, one new challenge for the textile chemist in the 1980's is to impart permanent press properties to natural fibers, primarily cotton or blends with high cellulosic content, without undue strength losses and without impairing their soiling and comfort characteristics. In addition, the permanent press finishing should be achieved by using energy saving low moisture pickup and single-stage rapid cure application techniques without increasing formaldehyde release during manufacture and use of the textile.

The objective of our recent investigations has been of achieving no-iron performance on 100% cellulosic substrate by a rapid single-stage curing process without the drawbacks of incomplete curing (1). Within the framework of these investigations, we studied systematically the effect of multiple launderings in the presence and absence of oxidative bleaches on cellulose crosslinked with the methylolated derivative of fully substituted cyclic alkyleneurea in an attempt to gain a better understanding of the mechanism underlying the degradation caused by active chlorine and its correlation with formaldehyde release (2).

Cellulose Crosslinking

Permanent press cellulosic or cellulose-

Cellulose Crosslinking

containing fabrics are produced by setting the fabric in the desired configuration via a crosslinking reaction between hydroxyl groups on adjacent cellulose chains. Such crosslinking imposes restraints on the movement of the chains and thus imparts to the fabric a tendency to recover from any subsequent deformation and to return to the state in which the crosslinks were introduced (3). The crosslinking reaction is generally attained via the acid catalyzed reaction of polyfunctional amide-formaldehyde crosslinkers with the cellulosic substrate. One undesirable side effect of the use of such agents can be the retention of chlorine by the nitrogenous compounds during exposure of the finished fabrics to hypochlorite bleach solutions and the subsequent fiber damage caused

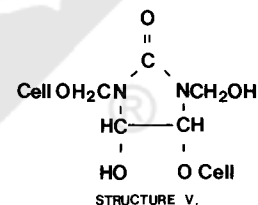
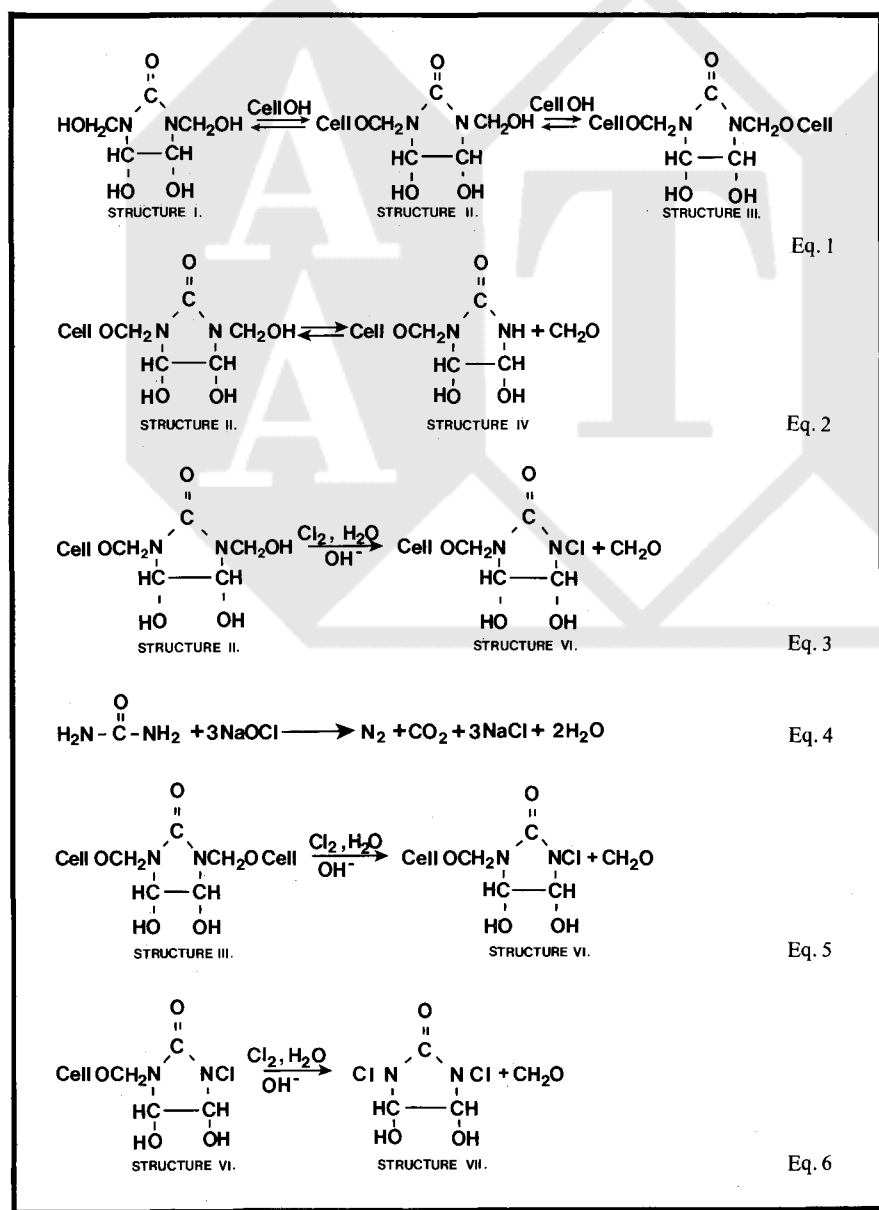
by active chlorine. The chemical structure of the nitrogen-containing cellulose finishing agent plays an important role in the extent of chlorine retention (4, 5). Fabrics treated with melamine-formaldehyde finishing agents turn yellow, while those crosslinked with urea-formaldehyde resins exhibit significant fiber damage on chlorination followed by scorching (6). The structure of the methylolated cyclic alkyleneureas suggests that they should not pick up chlorine from the hypochlorite solution because the nitrogen is fully substituted, although in practice some are known to do so. Such a fully substituted cyclic ethyleneurea, *N,N'*-bis(hydroxymethyl)-4,5-dihydroxyethyleneurea (DMDHEU), was used in our studies. This crosslinking agent was selected because it is the most widely used for cellulosic substrates, having low reactivity and high stability towards acid hydrolysis.

It is well documented that the reactivity of the formaldehyde reagents towards cellulose correlates well with their ease of hydrolysis (7). The higher the reactivity, the lower is the hydrolytic stability and the greater is the formaldehyde release. The resistance to acidic hydrolysis of the nitrogenous finishes is determined primarily by chemical rather than physical properties (8).

It is generally accepted that all four hydroxyl groups of DMDHEU are capable of reacting with cellulose but the 1,3-hydroxymethyl groups are more reactive. The kinetic studies of the reaction of DMDHEU with cellulose indicate that the reaction rates are pseudo first order, and the infrared spectral data suggest that the methylol groups react preferentially with the primary hydroxyl sites whereas the ring hydroxyl groups react preferentially with the secondary hydroxyl groups (9,10). The reaction equilibria involved in the stepwise finishing reactions between the *N*-methylol moieties of DMDHEU and cellulose are shown in Eq. 1.

The single-end reacted product (II) is bound to the cellulose but bears a yet unreacted *N*-methylol group on the dihydroxyethyleneurea ring. It is the pendent methylol groups that are the primary source of formaldehyde release, and thus we should consider the formation of structure IV through the loss of formaldehyde (Eq. 2) from the single-end reacted product (II).

The amido group present in structure IV which is not fully substituted is responsible primarily for the retention of chlorine. It is also possible that the ring hydroxyls become involved in the reaction with cellulose (11). A product formed by



such a reaction is shown by the structure V. It should be also considered that 4,5-dihydroxyethyleneureas might undergo conversion to hydantoin (12,13).

In order to obtain optimum crosslinking with minimum number of single-end reacted sites, the appropriate catalysts should be selected. In the case of metallic salt catalysts, the crosslinking process is governed primarily by the proton concentration and not by the ionic strength. Coordination complexes between the metal ion (Mg or Zn) of the catalyst and the methylol oxygen of the formaldehyde reactant, and also between the metal and polyhydroxy compounds, have been reported earlier (14-17). In the case of MgCl_2 or $\text{MgCl}_2/\text{citric acid}$ and of

Zn(NO₃)₂ catalysts, the increased hydroxonium ion concentration in the curing step explains the greatly increased catalytic effect. When the fabric reaches the bone-dry state, the metal complex is formed and crosslinking takes place (1).

Materials and Methods

Reagents used were *N,N'*-bis(hydroxymethyl)-4,5-dihydroxyethyleneurea as the 45% aqueous solution (buffered and unbuffered), free formaldehyde content,

1.0%. Catalysts were Zn(NO₃)₂ · 6H₂O and MgCl₂ · 6H₂O

Nitrogen was determined by Kjeldahl digestion followed by titration of distilled ammonia. Total formaldehyde was determined by the method of Roff (18), and

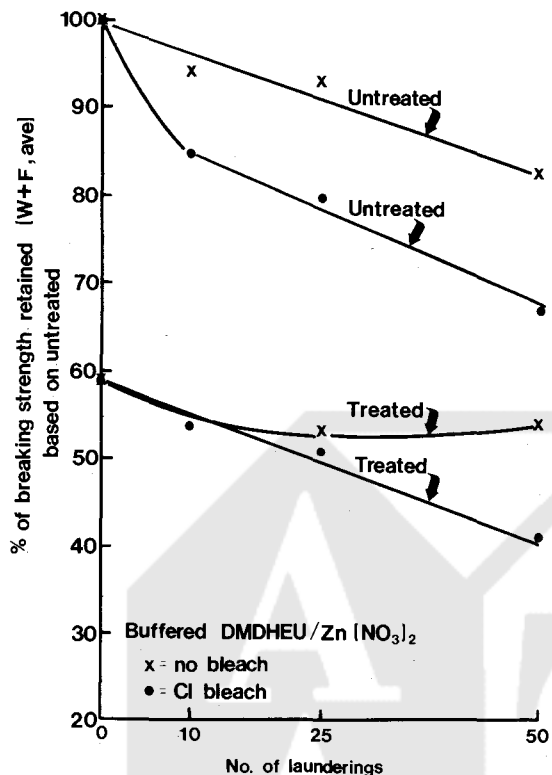


Fig. 1. Effect of laundering on breaking strength.

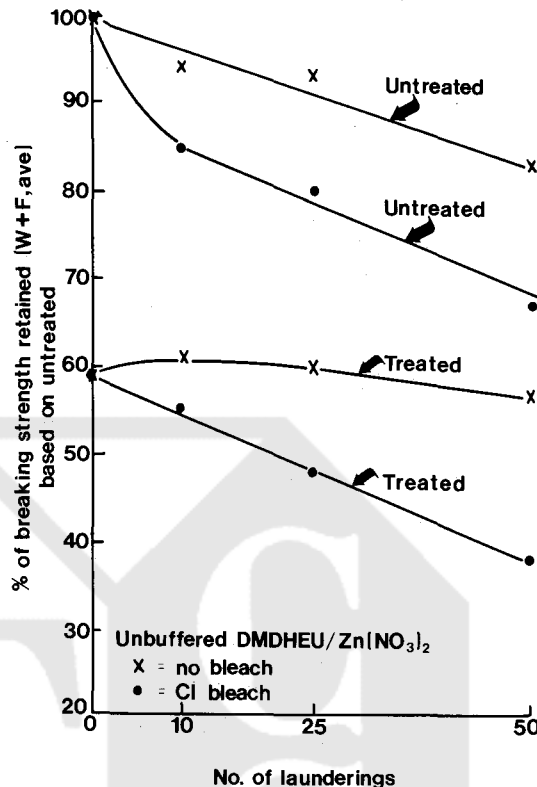


Fig. 2. Effect of laundering on breaking strength.

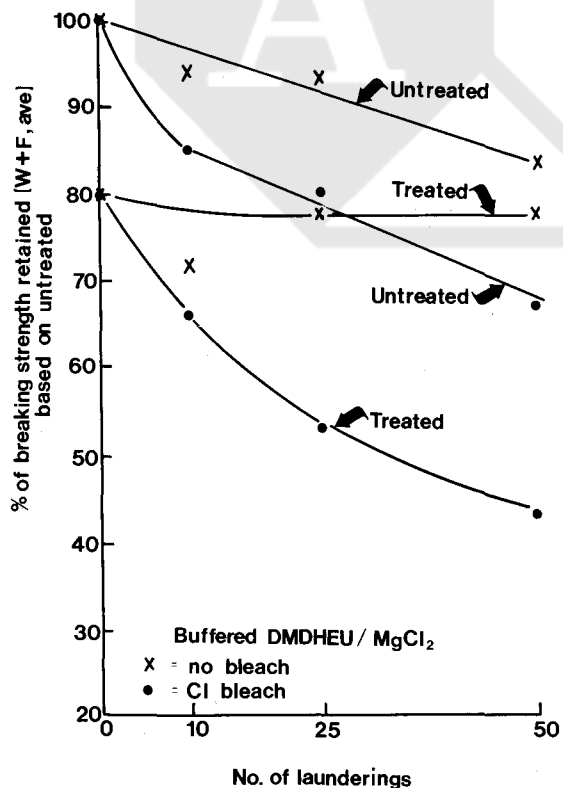


Fig. 3. Effect of laundering on breaking strength.

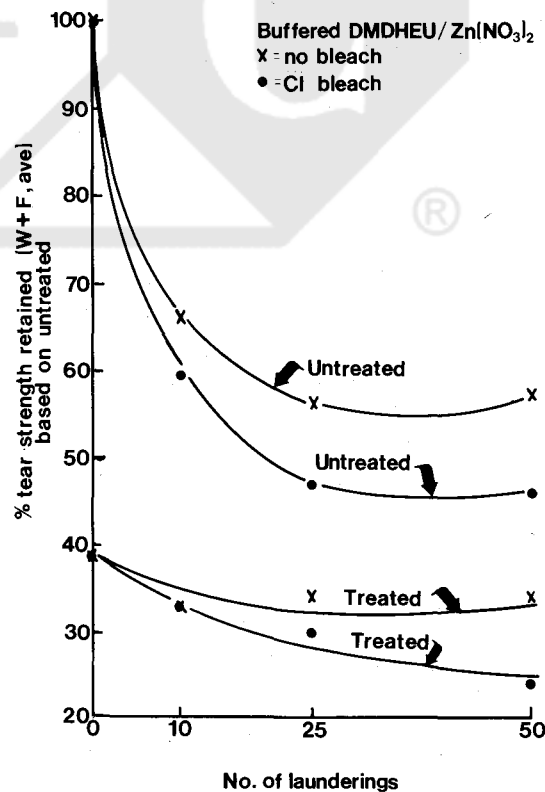


Fig. 4. Effect of laundering on tear strength.

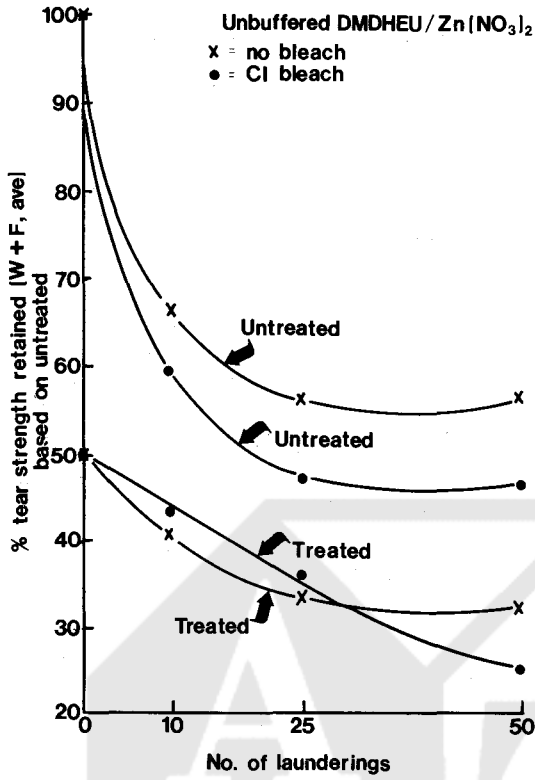


Fig. 5. Effect of laundering on tear strength.

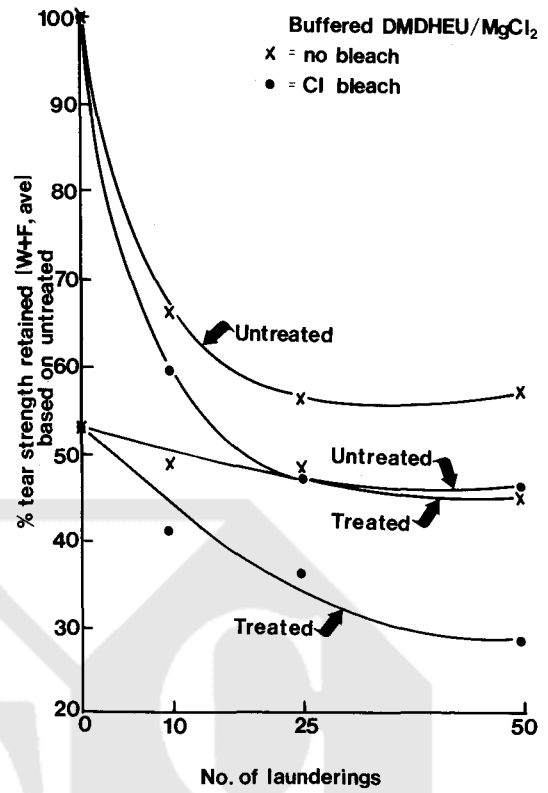


Fig. 6. Effect of laundering on tear strength.

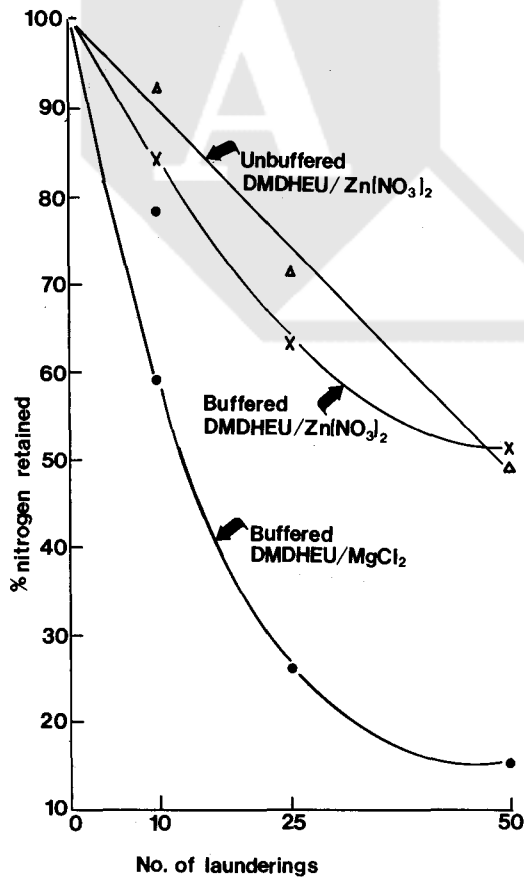


Fig. 7. Effect of Cl launderings on nitrogen content.

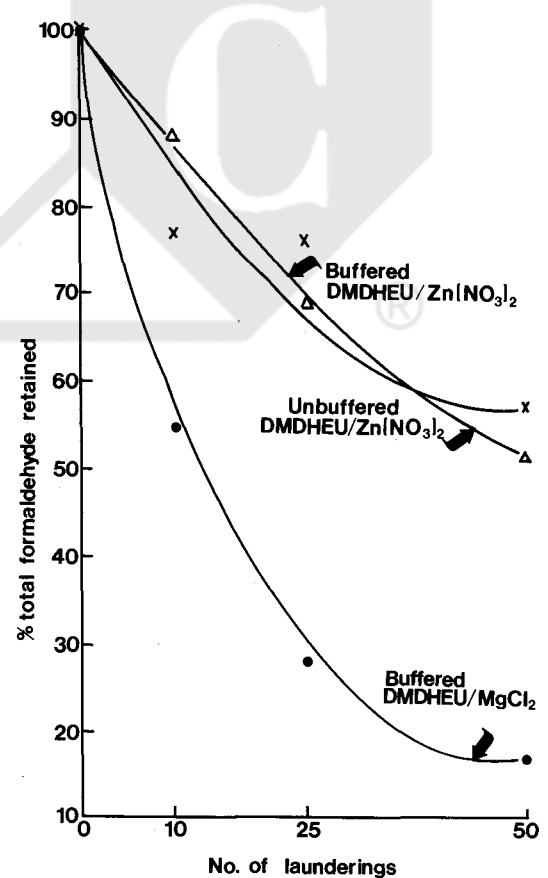


Fig. 8. Effect of Cl launderings on HCHO content.

Table I. Effect of Laundering on Durability of Finish

	Buffered DMDHEU		Unbuffered DMDHEU,
	Zn(NO ₃) ₂	MgCl ₂	Zn(NO ₃) ₂
Original			
% N	0.79	0.74	0.85
% Total HCHO	1.14	1.23	1.38
50 Launderings, No Bleach			
% N	0.69	0.58	0.77
% Total HCHO	0.87	0.79	1.18
50 Launderings, Perborate Bleach			
% N	0.66	0.55	0.74
% Total HCHO	0.84	0.78	1.10
50 Launderings, Cl Bleach			
% N	0.40	0.11	0.42
% Total HCHO	0.67	0.21	0.70

strength (Grab Method), ASTM D1628-64; tear strength (Elmendorf Method), ASTM D1424-63; and damage caused by retained chlorine, AATCC test method T114-1980.

The fabric was 100% cotton sheeting, weight = 146 g/m², plain weave, desized, bleached (not mercerized).

Laundering was with an automatic home type agitator washing machine at 60C for a full cycle, using an anionic, phosphate-built detergent (AATCC standard detergent) and a 2.3 kg load. When sodium hypochlorite bleach was used, the available chlorine content of the wash liquor was 0.02% and the pH was 9.1. When perborate bleach was used, the available oxygen content of the wash liquor was 0.03%. The samples were tumble dried after each laundering at a medium setting.

Fabric samples were impregnated on a laboratory padder with an 8.1% active aqueous solution of the unbuffered resin in the presence of 0.9% Zn(NO₃)₂ · 6H₂O catalyst OWB and with a 7.3% active aqueous solution of the buffered resin in the presence of 1.2% Zn(NO₃)₂ · 6H₂O or MgCl₂ · 6H₂O catalyst OWB. The pressure of the squeeze rolls was adjusted to obtain 80% wet pickup. The samples were framed to original dimensions, dried at 60C, and cured at 180C for one minute in a laboratory Benz oven. They were washed in a nonionic detergent solution, rinsed and dried.

Results And Discussion

The cotton fabric samples treated with the DMDHEU resins exhibited nitrogen contents ranging from 0.74 to 0.85% and total formaldehyde contents ranging from 1.14 to 1.38%. Curing of both the buffered and unbuffered resins was complete when Zn(NO₃)₂ catalyst was employed, as indicated by high dry crease recovery values and no or negligible damage due to retained chlorine. When MgCl₂ was used as the catalyst, low dry crease recovery angles and high levels (approximately 60%) of chlorine retention damage in scorching indicated incomplete curing, even though the nitrogen contents were comparable to those of samples cured with Zn(NO₃)₂ catalyst (Tables I and II).

By exposing the crosslinked samples to multiple launderings in the absence of bleach, minimal losses were observed in strength and crease recovery properties (Figs. 1-6 and Table II). The decreases in strength based on the original values were significantly less for the crosslinked samples than for the untreated control. The greater strength retention of the crosslinked samples in multiple launderings may be attributed to their reduced swelling in the wash liquor. The behavior of the samples was comparable in launderings in the absence of bleach and in the presence of perborate bleach.

The nitrogen losses, and corresponding the total formaldehyde losses, were

Table II. Effect of Laundering on Crease Recovery

	Dry Crease Recovery Angle (W + F)		
	Buffered DMDHEU,	DMDHEU	Unbuffered DMDHEU,
	Zn(NO ₃) ₂	MgCl ₂	Zn(NO ₃) ₂
Original	263	221	265
50 Launderings, No Bleach	240	192	239
50 Launderings, Perborate Bleach	251	191	239
50 Launderings, Cl Bleach	233	164	229

greater for the crosslinked samples when laundered in the presence of chlorine bleach (Table I). These data indicate that even the finishes which did not exhibit any chlorine damage in the AATCC chlorine retention test had only limited durability in multiple launderings in the presence of chlorine (Figs. 7 and 8).

In chlorine-free home launderings, the durability of the finishes was excellent, and the amount of releasable formaldehyde decreased substantially as the number of launderings increased (Table III). In launderings in the presence of chlorine, the releasable formaldehyde did not decrease significantly, although the nitrogen losses were substantial. Thus the ratio of releasable formaldehyde to resin retained by the fabric increased (Fig. 9).

The active chlorine present in the resin-treated fabrics was determined by titration. Even though in some cases the absolute value of the chlorine content decreased after multiple chlorine launderings (Table IV), its ratio to the amount of resin retained increased in each case (Fig. 10).

The losses in nitrogen and total formaldehyde and the decrease in crease recovery in multiple chlorine launderings suggest degradation of the finish. The losses in tensile and tear strength correlate also with the lack of durability of the finish in chlorine launderings; i.e., the rate of strength loss becomes similar to that of the noncrosslinked counterpart.

The presence of active chlorine in the crosslinked samples laundered in the presence of chlorine bleach indicates chlora-

Table III. Effect of Launderings on HCHO Release

	Releasable HCHO (%)		
	Buffered DMDHEU	DMDHEU	Unbuffered DMDHEU,
	Zn(NO ₃) ₂	MgCl ₂	Zn(NO ₃) ₂
Original	0.030	0.039	0.016
50 Launderings, No Bleach	0.005	0.005	0.005
50 Launderings, Perborate Bleach	0.006	0.007	0.005
50 Launderings, Cl Bleach	0.020	0.018	0.024

Table IV. Chlorine Retained in Chlorine Launderings

Catalyst	Active Chlorine (%)		
	10 Launderings	25 Launderings	50 Launderings
	Buffered DMDHEU/ Zn(NO ₃) ₂	0.044	0.070
Buffered DMDHEU/MgCl ₂	0.103	0.066	0.042
Unbuffered DMDHEU/ Zn(NO ₃) ₂	0.079	0.153	0.228

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amide formation (21). First the single-end reacted sites are attacked, formaldehyde is released and chloramide is formed (Eq.3).

In addition, it should be considered that a Hoffman degradation reaction is also possible between the active chlorine and the amides. This reaction is well known between the resin nuclei and hypochlorite; the reaction for urea is as shown in Eq.4.

Many research workers attribute the resin degradation in chlorine laundering solely to the hydrolysis of the resin during the laundering cycles or to the acid release by the chloramide during hot ironing (22). However, the simultaneous loss of nitrogen and formaldehyde as well as the presence of available chlorine after multiple chlorine laundings and tumble dryings would tend to indicate that removal of the resin is caused by cleavage of the carbon-oxygen bonds and simultaneous chloramide formation.

Since the *N*-alkoxymethyl compounds are generally stable to alkaline hydrolysis, the chloramide formation cannot occur as a result of prior hydrolysis. It is postulated that a direct exchange of the alkoxy-methyl group for chlorine takes place (Eqs. 5 and 6).

It is the electron density at the nitrogen

atom of the *N*-alkoxymethyl moieties that is responsible for the rate of this exchange reaction. Compounds with high electron density at the nitrogen atoms exchange the alkoxy-methyl group rapidly against active positively charged chlorine (5). This might explain our observation that even the absence of damage in scorching due to retained chlorine does not guarantee the resistance of the finish toward laundings in the presence of chlorine bleach.

The damage due to retained chlorine is attributed to the release of HCl from the chloramide in the scorching subsequent to the chlorination, when chloramide might decompose; if reactive hydrogen atoms are present, as in the cellulose substrate, the chlorine radicals abstract a hydrogen atom to form HCl (21). The stability of the chloramide depends on the structure of the resin (23), and thus a resin which retains chlorine in the form of a stable chloramide will not release HCl to a great extent in moderate scorching. Chloramides formed from cyclic ethyleneureas possess limited stability (4), and in our investigations the scorching temperature was higher than the temperature of the decomposition of the chloramide, as indicated by the substantial (>50%) loss of active chlorine in scorching. It is also indicated by the extensive scorching damage observed for under-cured samples which have a significant number of single-end reacted sites. Therefore, it is desirable to cure the resin-treated cotton complete-

ly to minimize the chlorine retention and formaldehyde release. The incomplete curing might be due to insufficient curing conditions (temperature or dwell time) or to the use of catalyst with low activity or insufficient catalyst concentration. It should be considered, however, that excessively high catalyst concentrations might lead to hydrolysis of the finish and thus to increased chlorine retention and formaldehyde release, especially at very high curing temperatures and/or extended curing time (24).

Summary And Conclusions

Crosslinking reduces the strength properties of cellulosic fabrics, but it should be considered that the crosslinked fabric retains a greater proportion of its strength in multiple laundings than does its untreated counterpart.

The chlorine damage of crosslinked cellulosic fabrics is associated with the amide-formaldehyde resin used for the durable press treatment. The absence of damage due to retained chlorine in scorching does not guarantee the resistance of the finish towards laundings in the presence of active chlorine. The cotton fabrics crosslinked with fully substituted methylolated cyclic alkyleneureas, if completely cured, do not exhibit any damage in the chlorine retention test, but the durability of such finishes is limited in multiple laundings in the presence of

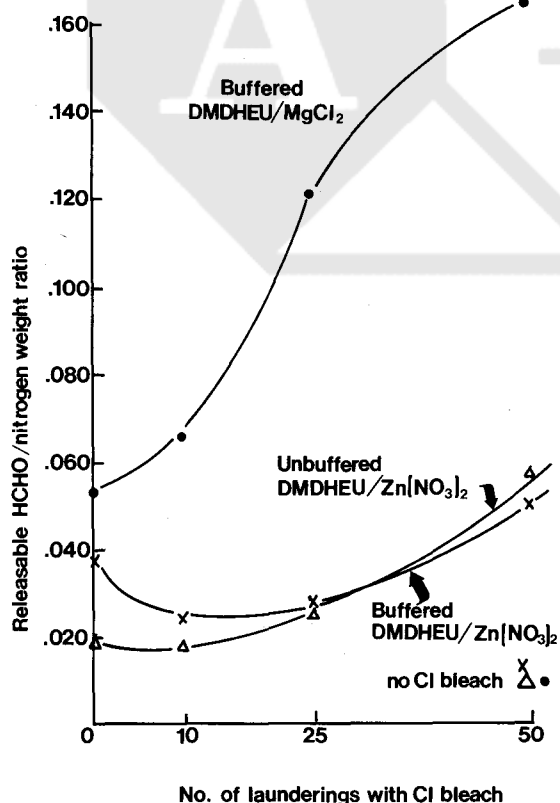


Fig. 9. Effect of Cl laundings on releasable HCHO/resin ratio.

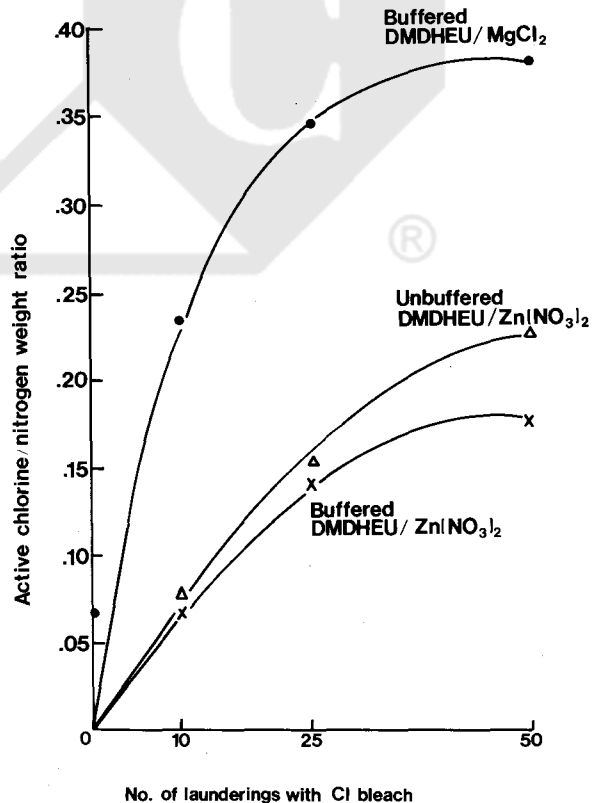


Fig. 10. Effect of Cl laundings on active chlorine/resin ratio.

chlorine bleach, as indicated from the losses in nitrogen, total formaldehyde and crease recovery. As the finish is removed, the cellulosic fabric loses strength in subsequent launderings at an increased rate similar to that observed for a noncross-linked fabric.

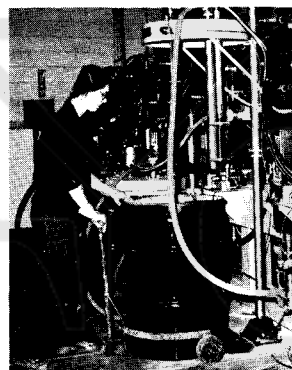
In launderings in the presence of active chlorine, primarily the single-end reacted sites are responsible for chlorine retention and formaldehyde release. However, the cleavage of the carbon-oxygen bonds with simultaneous chloramide formation and formaldehyde release, and even the possibility of the Hoffman degradation of the amides, should also be considered. In order to reduce the detrimental effect of the active chlorine, improve the durability of the finish and reduce the formaldehyde release, the number of the single-end reacted sites should be minimized by assuring the complete curing of the resin treated fabric. ∞∞

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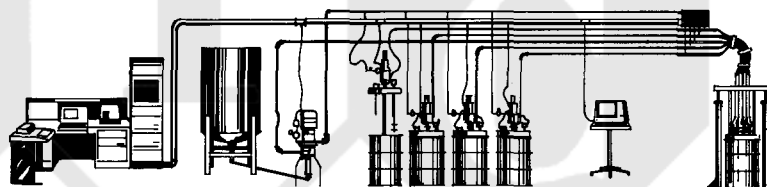
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