Absorption Phenomena in the Treatment of Cotton with Formaldehyde and Cyclic Oxymethylenes

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Synopsis

Monomeric formaldehyde and the cyclic oxymethylenes tetraoxane and pentaoxane were retained by cotton to similar extents at the high temperatures used in textile finishing, but the mechanisms of absorption appeared to differ. Trioxane, however, was not retained by cotton. The absorption of cyclic oxymethylenes did not seem to involve bonding to cellulose by primary valence bonds. The presence of other substances had a greater effect on the absorption of monomeric formaldehyde than of cyclic oxymethylenes, but changes in extent of absorption were not large enough to influence textile properties of treated fabric.

INTRODUCTION

In the finishing of cotton or other cellulosic fabric by the widely employed pad-dry-cure procedure, the finishing agent is dried on the fabric at an elevated temperature before the intended reaction between cellulose and the agent occurs. With a highly volatile agent such as formaldehyde, there must be some attraction to the fiber or a preliminary reaction to form a nonvolatile intermediate that holds the agent on the fabric until the finishing reaction occurs. The intended reaction during finishing with formaldehyde is the formation of formal crosslinks between the cellulose molecules. Although these crosslinks are formal linkages, they are quite durable to laundering. Before curing, the applied formaldehyde can be readily removed from the fabric by laundering, but it is retained tenaciously by the cotton in the absence of moisture.[1] During drying, a portion of the applied formaldehyde is lost as water evaporates, and a portion is retained for reaction with cellulose on curing. The most widely held explanation of the retention and water sensitivity of formaldehyde is the formation of cellulose hemiformals.

Tetraoxane, 1,3,5,7-tetroxocane, the cyclic tetramer of formaldehyde, has been used as a finishing agent for cotton.[2] The modification of fabric properties on finishing with tetraoxane is very similar to that produced by monomeric formaldehyde. The final reaction product of tetraoxane with

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cellulose appears to be the same as that from monomeric formaldehyde and cellulose. Yet, before the final reaction, the behavior of the two compounds on the fabric should differ. Tetraoxane is less volatile (bp 175–180°C versus −19°C for formaldehyde) and is unable to form hemiformals without opening the ring structure.

The intent of the present work was to explore and define these differences in the behavior on cotton of formaldehyde and cyclic oxymethylenes derived from formaldehyde. In the process, some additional light was cast upon the interactions that occur between cellulose and finishing agents of this type.

EXPERIMENTAL

The "monomeric" formaldehyde was from reagent-grade, 37% formalin that was stabilized with methanol. A few experiments were repeated with methanol-free formaldehyde, freshly prepared from paraformaldehyde, and essentially identical results were obtained. Tetraoxane and pentaoxane were obtained from Mitsui Toatsu Chemicals, Inc. Tetraoxane was commercial-grade, and pentaoxane was a reagent-grade chemical. Other agents were reagent-grade chemicals.

The cotton fabric was an 80 × 80 printcloth that had been desized, scoured, and bleached. This fabric was treated with the solutions described in the text by padding samples to a wet add-on that ranged between 68% and 84%, placing the samples on pin frames, drying in a mechanical convection oven for 7 min at 60°C, curing in a similar oven for 3 min at 160°C in most instances, and then washing in a home-type washing machine. A portion of the sample could be removed for analysis after any of these steps to determine the effect of the procedure through that point.

Formaldehyde content of fabric samples was determined by distilling the formaldehyde from the fabric specimens in boiling sodium sulfate-sulfuric acid solution[3] and analyzing the distillate by the method of Roff.[4] The method gives formaldehyde contents that also include the oxymethylene groups in linear and cyclic polymers. Results are reported as percent of the weight of dry fabric sample.

RESULTS AND DISCUSSION

Absorption on Cellulose

To determine whether formaldehyde and cyclic oxymethylenes were rendered nonvolatile on cotton by binding with cellulose or by associating with themselves to form nonvolatile aggregations, the agents were applied to cotton and to glass fabric as an inert substrate. Most of the experiments involved formaldehyde and tetraoxane because of their greater reactivity and availability. These two agents were applied with and without a catalyst, aluminum chlorhydroxide[5] or magnesium chloride in these examples. Changes in formaldehyde content of the fabric as the finishing proceeded are shown in Table I.

TABLE I
Retention of Formaldehyde by Cotton and by Glass Fabrics

Solution applied[a]	Formaldehyde content of fabric, % of dry weight			
	After padding	After drying	After curing	After curing and washing
Cotton Fabric				
4% Formaldehyde				
without catalyst	3.11	1.82	1.46	0.02
with catalyst[b]	2.81	1.24	1.18	0.77
4% Trioxane				
without catalyst	0.77	0.02	—	—
4% Tetraoxane				
without catalyst	3.02	1.77	1.87	0.02
with catalyst[b]	3.16	1.73	1.56	1.19
4% Pentaoxane				
without catalyst	3.18	2.74	—	—
Glass Fabric				
4% Formaldehyde				
without catalyst	0.34	0.002	0.002	—
with catalyst[b]	0.31	0.006	0.004	—
4% Tetraoxane				
without catalyst	0.37	0.013	—	—
with catalyst[b]	0.40	0.005	—	—
4% Pentaoxane				
without catalyst	0.61	0.01	—	—

[a] Approximately 80% wet add-on.

[b] Catalyst is 2% $Al_2(OH)_5Cl$, on weight of solution, for formaldehyde and 2.5% $MgCl_2 \cdot 6H_2O$ for tetraoxane.

When formaldehyde was applied to cotton, there was a large loss of applied agent on drying and only a small additional loss after curing at 160°C promptly after drying. Under these curing conditions, only in the presence of catalyst were more than trace amounts of formaldehyde bound securely enough to resist removal by washing. For tetraoxane on cotton, results were similar, but less formaldehyde-containing material was lost on curing without catalyst than when monomeric formaldehyde was used. This characteristic showed up more strikingly under stronger curing conditions. Curing for 10 min at 180°C in the absence of catalyst resulted in retention of 0.48% formaldehyde from application of monomer and 1.53% from application of tetraoxane. However, in the presence of the catalyst, a greater retention of applied agent did not occur with tetraoxane. The catalyst broke the cyclic compound to monomeric formaldehyde or to linear oxymethylenes that behave like residues from the applied monomer.

In the case of application of monomeric formaldehyde or tetraoxane to glass fabric, practically no formaldehyde remained after drying. More than 44% of the applied materials remained on cotton, whereas 3.5%, at most, remained on glass. No effect attributable to the lower volatility of tetraoxane was evident.

Reaction to form a nonvolatile hemiformal of cellulose seems an unlikely explanation for the retention of tetraoxane by heated cotton. Cleavage of the ring structure would be required at a temperature of 60°C in the absence of any catalyst unless it be cellulose itself. The stability of the tetraoxane ring favors an explanation involving absorption of the intact ring by physical attraction or secondary valence bonding.

Trioxane was not retained on cotton as was tetraoxane but was lost with the water on drying. If the intact trioxane ring and tetraoxane are similarly bonded to cellulose, the bonding of the former to water is stronger. Such bonding to water is evidenced by the existence of a trioxane–water azeotrope (70% trioxane, boiling point 91°C). No evidence was found for existence of a tetraoxane–water azeotrope.

The low levels of trioxane applied at the usual wet add-on were a repeated phenomenon. The difference between the retention of trioxane on the wet fabric after padding (24%) and that of the other agents (94–99%) appeared unreasonable. The presence of cotton had no effect on the analysis of trioxane solutions. However, trioxane was lost rapidly upon evaporation of solution from the fabric. For example, the first 10% of solution lost by evaporation contained approximately 25% trioxane. The loss of solution from impregnated fabric at room temperature was determined. In 6 min of exposure in open air, about 12% of the wet add-on was lost. This loss would reduce the trioxane to approximately 1% or less. The low figure for trioxane content of wet fabric shown in Table I is apparently due to evaporation during treatment of the fabric, and it is evident that use of trioxane for crosslinking cotton is not practical.

On the basis of limited experimentation, pentaoxane (1,3,5,7,9-pentoxecane) seemed to be retained to a greater extent after drying than formaldehyde or tetraoxane. A bonding similar to that of tetraoxane should occur and is possibly aided by the lower vapor pressure of pentaoxane (bp 226°C). However, results from the application to glass fabric gave no indication of any retention due to the higher boiling point.

Because the presence of water affects the retention of formaldehyde on cotton, substitution of other solvents for water as a medium for application could make a difference in the amount of formaldehyde retained through finishing. A comparison of the formaldehyde retained on application of formaldehyde and tetraoxane from water, methanol, a mixture of the two, and dimethylformamide is shown in Table II. Although trends were not distinct, retention of monomeric formaldehyde through finishing seemed to decrease as methanol was substituted for water. The methanol may compete with the cellulose for association with formaldehyde, and the complex formed from methanol and formaldehyde is volatile enough to leave the fabric. When formaldehyde was applied from dimethylformamide, the reduction in amount of retained formaldehyde was more pronounced. The low reactivity on application from dimethylformamide, as indicated by the small fraction of bound formaldehyde present after curing, was apparently due to deactivation of the catalyst by the solvent.

TABLE II
Effect of Solvent on Formaldehyde Retention

Solution applied	Wet add-on, %	Formaldehyde content of fabric, %		
		After drying	After curing	After curing and washing
4% Formaldehyde without catalyst in:				
water	71	1.82	1.46	0.02
50% water–50% methanol	75	1.32	1.30	0.07
methanol	63	1.43	0.96	0.06
dimethylformamide[a]	73	0.77	0.04	—
4% Formaldehyde with catalyst[b] in:				
water	71	2.01	1.69	1.07
50% water–50% methanol	79	0.89	0.78	0.71
methanol	73	1.26	1.11	0.81
dimethylformamide[a]	80	1.08	0.04	0.05
4% Tetraoxane without catalyst in:				
water	—	1.77	1.87	0.02
50% water–50% methanol	77	2.19	2.10	—
methanol	63	1.56	1.54	—
dimethylformamide	76	0.84	0.95	—
4% Tetraoxane with catalyst[b] in:				
water	—	1.73	1.56	1.19
50% water–50% methanol	78	2.07	1.85	1.14
methanol	65	1.55	1.20	0.87
dimethylformamide	77	1.02	0.81	0.19

[a] Formaldehyde solutions in dimethylformamide contain 4% methanol.
[b] Catalyst is 2.5% $MgCl_2 \cdot 6H_2O$ on weight of solution.

Application of tetraoxane from water and from methanol gave even less clear trends. Formaldehyde contents after application from methanol seemed lower than those after application from water, but exceptionally high formaldehyde contents were obtained after application from the water–methanol mixture.

Application of trioxane from methanol gave 1.87% formaldehyde after padding and 0.18% after drying. These retentions, although still low, are higher than from aqueous application. This, again, is believed to be a reflection of the stronger bonding between trioxane and water.

Extraction of Retained Agent

A further comparison between the states of retained formaldehyde and retained tetraoxane on cotton was made by testing the resistance of absorbed agents to extraction by various solvents. Formaldehyde and tetraoxane were applied without catalyst from 4% aqueous solution, and the fabric was dried. Fabric samples were soaked in solvent for 24 hr, rinsed in the solvent, and analyzed for residual formaldehyde. Results are given in Table III. Water, as expected, removed essentially all of both agents.

TABLE III
Removal of Retained Agent by Solvent

Solvent for extraction	Residual formaldehyde, %[a]	
	From formaldehyde	From tetraoxane
None (no extraction)	1.73	1.45
Water	0.03	0.02
Methanol	0.49	0.01
Isopropanol	0.84	0.03
Dioxane	0.39	0.03

[a] After application from 4% solution without catalyst, drying, and extraction.

However, the other solvents removed tetraoxane almost completely but left appreciable residue from formaldehyde. A different bonding mechanism or different site of bonding in the fiber for each agent seems evident. It is interesting to note that dioxane, a solvent with low polarity and no reactive groups, removes formaldehyde more effectively than do the alcohols.

Efficiency of Treatments

In Table IV, the efficiencies of treatments with formaldehyde and cyclic oxymethylenes in binding formaldehyde to cotton are compared. Efficiency is the percentage of applied agent that is bound. Also in the table is reactivity, the bound agent as percentage of total agent present after curing.

Comparisons were made at two catalyst concentrations and two temperatures of cure. One value of each was less vigorous than usual to emphasize differences. Because of its rapid removal from the fabric, trioxane gives essentially no bound formaldehyde and hence was not compared.

The data suggest that both cyclic derivatives are less reactive than formaldehyde to cellulose, probably because ring opening must occur before reaction. Tetraoxane was decidedly less efficient than formaldehyde until reaching the strongest curing conditions where the lower reactivity of tetraoxane was offset by a higher retention. Pentaoxane was more efficient than tetraoxane because of greater retention by cotton on drying. At the strongest curing conditions, it was also more efficient than formaldehyde because of this greater absorption.

Influence of Inorganic Compounds on Absorption

The presence of inorganic compounds, whether catalysts for reaction with cellulose or not, influences the total amount of formaldehyde retained through drying and curing.[6] This effect can be observed in the present data in Table V, where several catalysts for finishing with monomeric formaldehyde are compared. Most catalysts increased absorption. Aluminum chlorhydroxide, however, had a negative effect on absorption; it decreased the total amount of formaldehyde retained through drying and curing.

TABLE IV

Efficiency of Formaldehyde Treatments

Agent (2.5% applied with 80% wet add-on)	Formaldehyde content, %			Efficiency (bound formaldehyde, % of 2%)	Reactivity (bound formaldehyde, % of content after cure)
	After drying	After curing	After curing and washing		
Cured at 140°C with 1.0% $MgCl_2 \cdot 6H_2O$					
Formaldehyde	1.40	1.04	0.30	15	29
Tetraoxane	1.00	0.96	0.06	3	6
Pentaoxane	1.51	1.60	0.13	7	8
Cured at 140°C with 2.5% $MgCl_2 \cdot 6H_2O$					
Formaldehyde	1.14	1.11	0.52	26	47
Tetraoxane	0.94	0.92	0.21	11	23
Pentaoxane	1.69	1.63	0.49	25	30
Cured at 160°C with 1.0% $MgCl_2 \cdot 6H_2O$					
Formaldehyde	1.40	0.95	0.56	28	59
Tetraoxane	1.00	0.91	0.29	15	32
Pentaoxane	1.51	1.35	0.41	21	30
Cured at 160°C with 2.5% $MgCl_2 \cdot 6H_2O$					
Formaldehyde	1.14	0.84	0.74	37	88
Tetraoxane	0.94	0.95	0.64	32	67
Pentaoxane	1.69	1.39	1.04	52	75

TABLE V

Effect of Catalyst on Formaldehyde Retention

Formaldehyde solution applied, %	Catalyst	Wet add-on, %	Formaldehyde content of fabric, %		
			After drying	After curing	After curing and washing
2		78	0.90	0.72	0.02
4	none	75	1.79	1.31	0.03
8		76	3.45	2.19	0.05
2		74	0.95	1.03	0.59
4	2.5% $MgCl_2 \cdot 6H_2O$	78	2.04	1.70	1.16
8		81	3.88	3.37	2.35
4	3.0% $MgCl_2 \cdot 6H_2O$	76	1.98	1.83	1.16
4	4.0% $MgCl_2 \cdot 6H_2O$	76	1.90	1.73	1.26
4	0.6% $Zn(NO_3)_2 \cdot 6H_2O$	68	1.90	1.64	0.87
4	2.0% $Al_2(OH)_5Cl$	70	1.24	1.18	0.77
4	1.4% $Zn(BF_4)_2 \cdot 6H_2O$	72	1.84	1.54	1.17

TABLE VI
Retention of Formaldehyde from Tetraoxane on Cotton

Tetra-oxane applied, %	Catalyst	Formaldehyde content of fabric, % of dry wt			
		After padding	After drying	After curing	After curing and washing
4	None	3.02	1.77	1.87	0.02
4	2.5% $MgCl_2 \cdot 6H_2O$	3.16	1.73	1.56	1.19
4	2.0% $Al_2(OH)_5Cl$	2.75	1.85	1.36	1.16
4	1.4% $Zn(BF_4)_2 \cdot 6H_2O$	3.14	2.06	1.58	1.48

The effect that a different absorption from changing catalyst had on bound formaldehyde (that retained after washing) seemed small. In fact, the differences in catalytic activity overshadowed any differences in absorption. This is the reason that attempts to exploit the effect from addition of neutral salts failed.[6]

Increasing the amount of catalyst beyond an optimum increased neither the total amount of formaldehyde retained through drying and curing nor the fraction of the total formaldehyde that was bound. Increasing the amount of applied formaldehyde, at least up to 6.5% of cotton weight (from 8% solution) with the lowest concentration of magnesium chloride employed, increased the total formaldehyde retained and the bound formaldehyde in proportion.

Retention of tetraoxane with various catalysts is shown in Table VI. The inorganic compounds had little influence on retention through drying and curing. This may be another result of a different mechanism for absorption than is operative with monomeric formaldehyde. Under these conditions, the reactivity of tetraoxane was high with aluminum chlorhydroxide and zinc fluoborate catalysts.

SUMMARY

Tetraoxane and pentaoxane, like monomeric formaldehyde, were absorbed on cotton, but differences in the properties of the absorbed materials indicated that different mechanisms might operate with these cyclic oxymethylenes and with monomeric formaldehyde. Absorption of tetraoxane and pentaoxane occurred under such mild conditions that ring opening for chemical reaction is unlikely. Bonding by physical or secondary valence forces seems a more likely reason for absorption. Trioxane, although also a cyclic oxymethylene, was not retained by cotton on application from water. Existence of a water–trioxane azeotrope indicates the presence of bonds between water and trioxane that probably are stronger than those between trioxane and cellulose. Cotton retained less monomeric formaldehyde when it was applied from methanol or dimethylformamide instead of water. Here also, formaldehyde was probably lost by association with the evaporating solvent.

Although other components of the pad bath in these pad-dry-cure treatments of cotton affected retention of formaldehyde from the monomer to some extent, the change in retention was too small to exert any appreciable effect on the properties of the treated cotton.   Retention of tetraoxane seemed unaffected by other components of the pad bath.

The efficiency of the reaction of cyclic oxymethylenes with cotton was similar to that of monomeric formaldehyde, except under reaction conditions that were more vigorous than usual.   Monomeric formaldehyde was more reactive with cellulose because a preceding reaction to open an oxymethylene ring was not required.

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