

A CRITICAL REVIEW OF METHODS FOR DIMENSIONALLY  
STABILIZING WOOD BY CROSSLINKING

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## INTRODUCTION

One of the major disadvantages of wood is that it swells and shrinks when water is adsorbed or desorbed below the fiber saturation point. This property causes numerous problems when wood is used as a structural material. Consequently, a considerable amount of research has been conducted on this problem, but has resulted in only a limited degree of success to date. There are several approaches to this problem (1) but this paper will be limited to a discussion of crosslinking by chemical methods. The discussion will include cotton as well as wood, because a great deal of research has been conducted on crosslinking cotton. This information will be of great value in future work on wood. A major emphasis will be placed on reaction mechanisms for the various compounds.

FUNDAMENTALS OF CROSSLINKINGThe Existence of Crosslinks

The existence of crosslinks in wood and cotton treated with polyfunctional chemicals has never been unequivocally established. However, there are a number of experiments which indicate that crosslinks do exist and are responsible for the ensuing dimensional stability. First, it has been shown that a small amount of reactant will produce a high degree of dimensional stability in wood (2) and cotton (3). Secondly, the reaction reduces the amount of swelling rather than the amount of shrinkage in wood (2). Thirdly, it has been shown for formaldehyde treated wood, that the dimensional stability is retained when treated with alkali but completely lost when treated with acid, (2). Since formaldehyde probably involves an ether linkage, which is cleaved by acid but not bases (4), this observation suggests a crosslink. Finally, observations of the swelling of treated cotton in cellulose solvents provides information on crosslinking. This technique involves treating the cotton with a crosslinking reagent followed by a 30 minute treatment with 0.5M cupraethylenediamine. The sample is then observed with an optical or electron microscope to determine the amount of swelling. In some cases, (3, 5), treatment with the crosslinking reagent completely inhibits swelling in cupraethylenediamine in contrast to the complete dissolution of untreated material. Different types and length of treatments produces material that swells to different degrees in cupraethylenediamine, presumably indicating different degrees of crosslinking.

### Site of Reaction

Since it appears that crosslinking does occur when cellulosic materials are treated with polyfunctional chemicals, an examination of the possible location of crosslinks is desirable.

Hydroxyl groups would be the most reactive groups in cellulosic materials and are generally considered to be the reaction site. This contention is verified by Steele (6) when he was able to show that the intensity of the infrared hydroxyl peak decreased upon treatment with formaldehyde. There are both primary and secondary hydroxyl groups in cellulose and the relative reactivity of these groups is dependent on the type of treatment (7). Hence, generalization about which hydroxyl reacts is not possible.

In terms of structure, there are three types of crosslinks that could theoretically exist: (a) links between individual cellulose chains, (b) links between microfibrils, and (c) links between groups of microfibrils. It appears that crosslinks at all three of these sites are present in cotton, and possibly in wood. There are several reasons for this conclusion. First, it has been established that the retention of small quantities of crosslinking reagents will drastically change the properties of wood (1) and cotton (8, 12). This relationship would not exist if crosslinking between individual chains were the only reaction. Secondly, the insolubility of crosslinked cellulose in cupraethylenediamine can be explained on the basis of a combination of links between individual chains on the surface of microfibrils and links between microfibrils. The combination of these two links should effectively hold the system together under conditions which would normally cause disassociation. Finally, it has been shown (9) that certain reactions

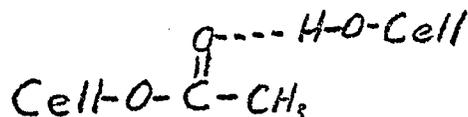
with cellulose are concentrated between the lamella of cotton. Hence, one would expect crosslinking reactions to occur between the lamella. However, crosslinking must also occur between the microfibrils within the lamella or dissolution would occur during the cupraethylenediamine treatment. Moreover, the cell walls of wood have also been shown to have a lamella structure (10) so the same phenomena probably exists in wood.

#### Effect of Crosslinking Reaction on Strength Properties

The major difficulty encountered in crosslinking cellulose is strength loss. In wood, crosslinking with formaldehyde reduced the toughness to 1/10 that of untreated wood, and greatly reduced the abrasion resistance (11). This extreme strength loss is the reason formaldehyde crosslinked wood is not commercialized. Cotton has been crosslinked by a number of reagents, and the strength loss varies considerably from one reagent to another. However, strength loss in cotton has been minimized sufficiently in most cases to permit commercial application (12). One of the major causes of strength loss in crosslinking treatments is degradation by the catalyst. Most crosslinking reagents require catalysts which are either Lewis acids or bases. In reactions which use acid catalysts, the degradation is caused by hydrolysis of cellulose which can cause appreciable strength loss in both cotton and wood. On the other hand, in base catalyzed reactions the catalyst has no appreciable influence on the strength of cotton (3). Although basic catalysts have not been used for crosslinking wood, one would anticipate strength losses because of the reaction with lignin. However, the degree of strength loss may not be as great as with acid catalysts and research in this area would be desirable.

Reduction in the number of hydrogen bonds is another possible factor in strength loss (13). This effect depends on the relative number of intramolecular and intermolecular reactions, with the former decreasing and the latter increasing the strength. A decrease in strength would occur only if excessive intramolecular reactions occurred. Furthermore, the effect depends on the hydrogen bonding ability of the reactant which has been demonstrated by monofunctional reactants. For example, acetylated wood has about the same strength properties as untreated wood (1).

This is in agreement with the above hypothesis because a carbonyl group is present for each hydroxyl group reacted, which can participate in a hydrogen bond as follows:



Hence, one would not expect any strength loss from this reaction.

Another example is the cyanoethylation of cotton. This treatment actually increases the strength of cotton which, according to O'Brien (13), is due to the tendency of nitrile groups to form electron-transfer bonds.

There is the possibility that the crosslinks themselves will lower the strength properties of cellulose by making the network more rigid, which gives rise to localized areas of high stress concentration. However, the existence of this factor depends on the material in question. For example, cellulose is stronger in the swollen wet condition than when dry (3). The reason for this is that dry cellulose is hydrogen bonded to such a degree that the strength is reduced below the maximum

by the reduced flexibility (3). When cellulose is swollen in water, the hydroxyl-to-hydroxyl hydrogen bonds are replaced by hydroxyl-to-water-to hydroxyl hydrogen bonds, which are more flexible and the strength increases. On the other hand, wood is different because the strength is lower in the swollen wet condition than in the dry condition. This would lead one to postulate that wood is not hydrogen-bonded to the same extent as cellulose. Hence, by drying wood more hydrogen bonds are formed and the strength increases. Comparison of these two materials indicates that the strength passes through a maximum as the crosslink density increases. In the dry condition cellulose is beyond the maximum and wood below the maximum. Therefore, one would expect that additional crosslinking by chemicals would decrease the strength of cellulose and could possibly increase the strength of wood. This hypothesis has been fairly well established for cotton cellulose (3), by using the base catalyzed epoxide reaction where the decrease in strength was due to crosslinks. In addition, research with N-methylol compounds (14), indicated that approximately 25 percent of the strength loss was due to crosslinks. On the contrary, there is insufficient evidence to reach any definite conclusions about wood.

One possible method of reducing strength loss during crosslinking is to use softening agents. For example, Arceneaux (20) found that both strength properties and crease recovery were enhanced if the cotton was pretreated with emulsified polyethylene prior to treatment with gaseous formaldehyde. Likewise, other researchers have shown that small quantities of silicones (15) and a number of organic compounds (16) can be applied

during the treatment to improve strength properties, with greatest improvement in abrasion resistance. Finally, Chipalkatti et al. (17) attempted to develop a crosslinking reagent with a built-in softener. This was accomplished by using 1, 3-dichloro-2-propanol as the backbone with esters of various length substituted at the hydroxyl group. The results were only partially successful, and more work is being done. In general, these methods of reducing strength loss show promise and should be evaluated for wood.

It should be pointed out that the above discussion of strength loss is concerned mainly with reactions within the cell walls. This is sufficient for cotton, but not for wood because wood is composed of numerous tracheids which are bound together by the middle lamella. Consequently the middle lamella is a potential point of weakness and may very well be the weak link in the system during chemical treatments such as crosslinking. Any future research on causes of strength loss during crosslinking certainly should include this factor.

#### Relationship Between Crosslinked Cotton and Wood

Although this paper is concerned mainly with crosslinking wood, an examination of the literature indicates that a great deal more work has been done with cotton. This large reservoir of information should aid future research on crosslinking wood. However, the properties required for cotton are different than those for wood. The basic reason for crosslinking wood is to reduce shrinking and swelling while the objective for cotton is to impart wet and dry crease recovery. Retention of strength is desirable for both materials.

In order to utilize the cotton research data, a relationship between crease recovery and dimensional stability is required. Fortunately, such a relationship appears to exist between dry crease recovery and dimensional stability. There are four factors which support this contention. First, it was shown previously in this paper that crosslinking is the basic requirement for improving dimensional stability. Research indicates that improvement of dry crease recovery is also related to crosslinking (12). Secondly, improvement of dry crease recovery in cotton and dimensional stability in wood both result in a decrease in moisture regain of the materials under a given relative humidity (5, 8, 18, 19). Thirdly, the amount of swelling of crosslinked cotton in cupraethylenediamine is related to the degree of dry crease recovery (5). Finally, both the amount of dimensional stability in wood and the extent of dry crease recovery in cotton imparted by crosslinking depend on the degree of swelling of the material at the time of treatment (12).

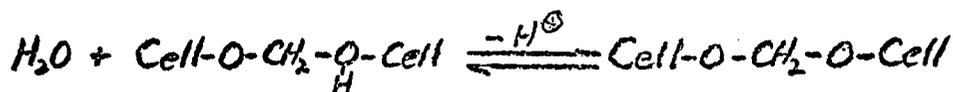
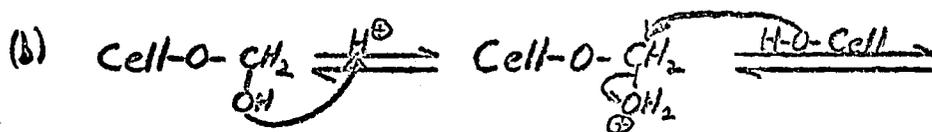
The remainder of this paper will cover a review of the various reagents which have been used to crosslink cotton and wood. Emphasis will be placed on reaction mechanisms which have been treated only lightly in the majority of the literature. This neglect is understandable since in most cases insufficient experimental data is available to support proposed mechanisms. However, the author feels that it is desirable to introduce reaction mechanisms because they are required if one is to fully understand the reactions. Furthermore, they suggest areas for future research.

FORMALDEHYDE

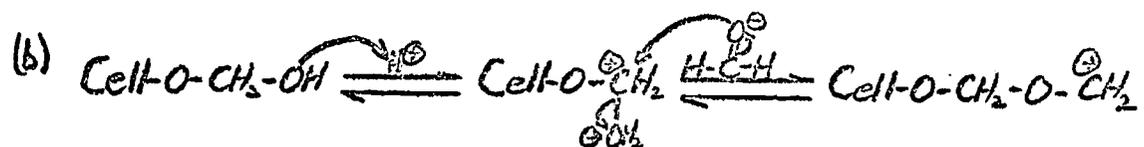
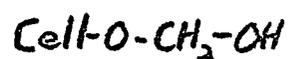
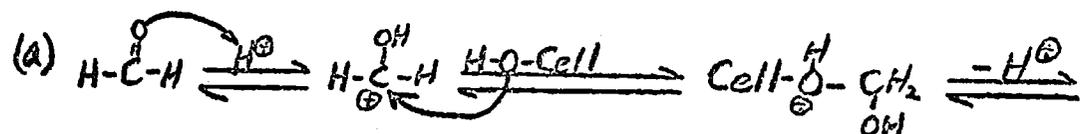
The reaction of formaldehyde with cellulose has been extensively studied for many years (8). The main reason for this extensive work is that formaldehyde is inexpensive, efficient, and durable (8). However, it does have weaknesses which include excessive strength loss and lack of reproducibility. Nevertheless, it appears that these problems have been overcome, which will permit its use in the finishing of cotton (8). The initial research with wood indicates that extensive strength losses must be overcome before it can be used for dimensional stabilization of this material (2, 11).

From the research conducted, it appears that formaldehyde crosslinks both cotton (6) and wood (2). In terms of crosslinking, there are two possible products (6): (a) methylene ether --- Cell-O-CH<sub>2</sub>-O-Cell, and (b) polyoxymethylene ether -- Cell-(OCH<sub>2</sub>)<sub>n</sub>-O-Cell. Proposed mechanisms for these acid catalyzed reactions are as follows:

Methylene ether :



Polyoxymethylene ether :



From the work by Arceneaux (20) it appears that the cellulose formaldehyde reaction is reversible. The rate of the reverse reaction is dependent on temperature and is accelerated between the range of approximately 40 to 65°C. Consequently, the rate of crease recovery angle and combined formaldehyde content increases with increasing temperature up to a maximum at about 40°C., then decreases to a minimum at about 65°C., after which they increase again. It also appears that the catalyst concentration has an influence on the crease recovery angle and combined formaldehyde over this temperature range. It is not possible to determine whether or not these same temperature effects hold for wood. The only similar experiments conducted with wood (21) were limited to the temperature range from 65° to 115°C. Therefore, it would seem that future work should include this lower temperature range where reduction in strength properties should be smaller.

There appear to be only two kinetic studies concerned with this reaction, and these produced conflicting results. Datye (22) studied the rate of combination of formaldehyde with cellulose using hydrochloric acid as a catalyst, and concluded that the reaction was first order with respect to formaldehyde concentration, and more or less independent of the catalyst concentration. On the other hand, Klein (23) studied the kinetics using magnesium chloride as a catalyst, and concluded that reaction was pseudo-first order with respect to formaldehyde concentration, and dependent on catalyst concentration similar to surface catalysis. Because of these conflicting results and lack of other information, it is impossible to determine whether the reaction

proceeds by an Sn1 or Sn2 mechanism; hence, the mechanism proposed above does not necessarily imply either of these mechanisms.

It should be noted that it is extremely difficult to study the kinetics of crosslinking because a good method for determining the extent of reaction is lacking. The above studies used retained formaldehyde as a measure of the extent of reaction and this only implies a reaction between cellulose and formaldehyde which can occur without crosslinking.

The work by Steele (6) indicates that the methylene ether crosslink is the most likely reaction. In this study, infrared spectroscopy was used to detect loss of hydroxyl groups during the formaldehyde reaction with deacetylated cellulose acetate. Comparison of the formaldehyde retention with the loss in hydroxyl groups indicated that approximately two hydroxyl groups were lost for each molecule of formaldehyde retained. This observation is compatible with the methylene ether linkage but not with the polyoxymethylene ether linkage. In another study, Gruntfest (24) used a direct gravimetric technique to measure formaldehyde retention with cotton and rayon, and concluded that methylene ether linkage is predominate in reactions with low formaldehyde concentration and the polyoxymethylene linkage is predominate in reactions with high formaldehyde concentration. Therefore, it appears that the type of linkage depends on the reaction conditions and suggests that a certain amount of control is possible. This is important because the type of linkage could influence both the treatment costs and physical properties of the product.

### Types of Treatment

The reaction of cellulose with formaldehyde can be carried out either in the gas or aqueous phases. Both of these techniques have been studied and will be reviewed at this time.

Gas Phase Treatment. Both wood (2, 11, 18, 19, 20, 25, 26, 27, 28, 29) and cotton (20, 30) have been successfully crosslinked with gaseous formaldehyde and comparison of the results of these studies are of interest. First of all, it appears that both cotton and wood strength properties are reduced by the formaldehyde treatment. For cotton it has been shown that strength loss is influenced by reaction temperature and catalyst concentration (20). Higher strength properties can be gained by using lower temperatures, but at the expense of reaction rate and crease recovery angle. It appears that in order to obtain high crease recovery angles approximately a 50 percent decrease in breaking strength results (20). The resulting strength properties for wood have been studied only at higher temperatures (2, 11), where strength losses have been extremely high. However, Goto (25) observed that the use of anhydrous hydrogen chloride instead of hydrochloric acid as a catalyst resulted in less coloration of the wood. This would seem to indicate a reduction in the amount of degradation. More work in this area may prove fruitful in the future. With respect to both cotton (20) and wood (2, 11) it has been observed that an increase in wrinkle recovery, or increase in dimensional stability is gained only with a resulting loss in strength properties. Therefore, it would appear that the best one could expect would be to minimize strength loss by using optimum reaction conditions.

Another point of interest is that a study of the cotton-formaldehyde reaction (20) and wood-formaldehyde reaction (21) indicates that considerably more formaldehyde is combined with wood than with cotton under similar reaction conditions. For cotton the combined formaldehyde rarely goes above one percent (based on the weight of the material) and for wood the combined formaldehyde is in the range of 5 to 7 percent. This clearly illustrates basic differences in the structure of the two materials which can best be explained on the basis of internal contact area (1).

Aqueous Phase Treatment. The treatment of cotton with formalin solution has been extensively studied (31, 32, 33, 34). This research indicates that good dry-wrinkle recovery can be obtained only when crosslinking occurs at low degrees of swelling. Hence, with aqueous systems some means of controlling swelling must be employed, and this can be accomplished by the addition of calcium chloride (33) or acetic acid (31). By adding these materials, the extent of swelling is reduced and dry-wrinkle recovery properties are improved.

The use of formalin to crosslink wood was used in one instance (2) but it was not successful. This is not surprising since wood swells rapidly in water, and any crosslinks formed in the swollen state would not be expected to stabilize the wood. However, it seems logical that by using a formalin - hydrochloric acid - calcium chloride treating system, effective crosslinking could be obtained. In order to test this hypothesis, the author and Mike Hittmeier performed a few simple experiments with this system. The initial experiments were conducted with the sample placed in a formalin - hydrochloric acid - calcium

chloride solution with the calcium chloride concentrate varying from 30 to 50 percent. This system was then heated at different temperatures for varying periods of time according to the method outlined by Chance (33), which was successful for cotton. This method was found to be unsuccessful for wood. It was felt that excessive swelling was the cause of failure, so swelling rates were measured in the solution with varying concentrations of calcium chloride. The rates decreased with increasing calcium chloride concentration, but were too fast to allow time for crosslinking to occur before excessive swelling occurred. However, the rate was quite slow in solutions saturated with calcium chloride so a new method was devised.

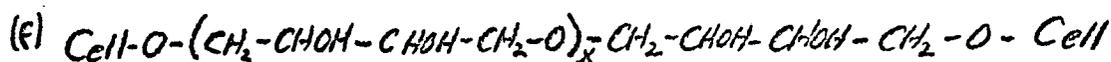
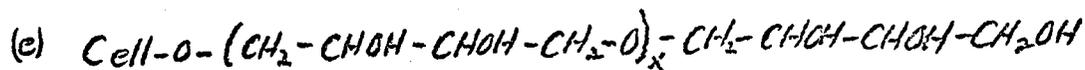
It was found that a high degree of stabilization could be obtained by starting with an oven-dry sample, 2 x 2 x 1/8 inches in the radial, tangential and longitudinal directions, respectively. This sample was soaked for 5 minutes in a solution which contained 20ml formalin, 0.75ml hydrochloric acid and excess calcium chloride. Next, the samples were removed from this solution and placed in an oven at 105° C. for one hour, then washed in running water overnight. Measuring before and after this treatment indicated that a high degree of dimensional stability was obtained. Another sample was treated by the same procedure except that it was heated overnight at 40° C. and approximately the same degree of dimensional stability was obtained. No strength measurements were made in these samples, but it did appear that they were degraded to some degree. More research will be required to fully evaluate this method of treatment.

### Conclusions

Formaldehyde has many properties which make it an interesting crosslinking reagent. There is no doubt that this is an effective crosslinking compound for wood. However, the treatment conditions employed always result in excessive strength loss which makes treatment by this method impractical. It would appear that future research should be directed toward this problem of strength loss. Specifically, it would be desirable to know whether the area of rupture is within the cell wall or in the middle lamella.



There are also several other possibilities in this reaction since water and epoxide would compete with cellulose for reactions (b) and (c). These respective products would be:



It appears that in the base catalyzed reaction compounds (d), (e) and (f) are the major products. This conclusion is based on several facts (3). First of all, the major gain is in wet crease resistance with very little improvement in dry crease resistance. Secondly, an increase in crease resistance requires a considerable amount of epoxy add-on. Finally, microscopic examination of samples swollen in cupriethylenediamine (cuene) indicated appreciable crosslinking occurred only with high epoxy add-on.

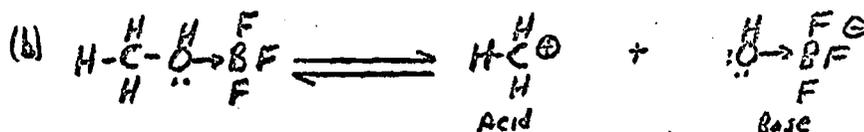
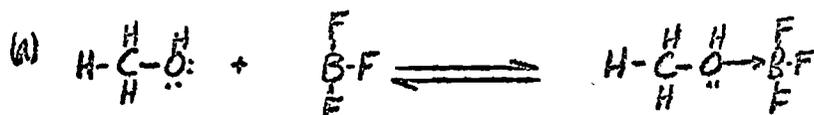
An examination of the proposed mechanism indicates that the experimental results are logical. In the reaction of epoxy with cellulose, the cellulose hydroxyl group acts as a leaving group. Since hydroxyl groups are not particularly good leaving groups (4), the frequency of the cellulose-epoxy reaction would be reduced, especially since this reaction is in competition with the water-epoxy and epoxy-epoxy reactions. Consequently, a considerable amount of epoxy is required to produce appreciable crosslinking because of the non-crosslinking products

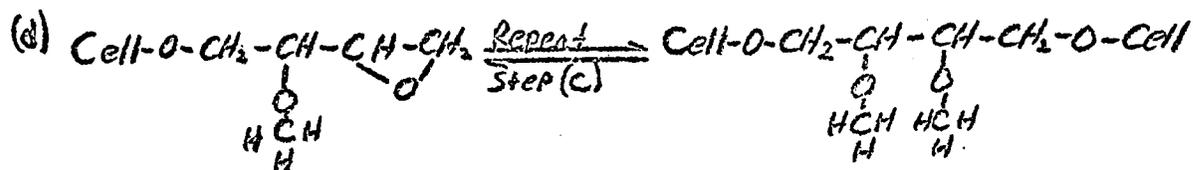
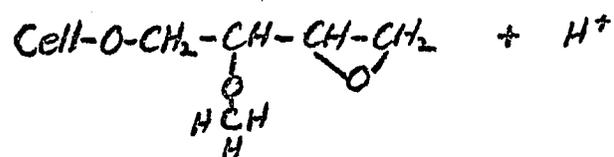
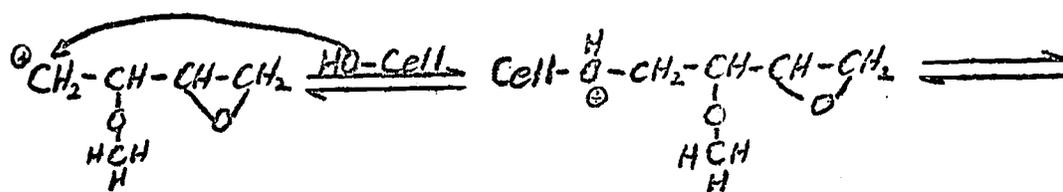
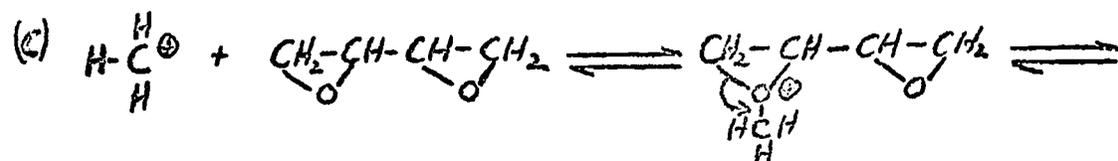
produced and the longer crosslinks introduced. These results would seem to indicate that base catalyzed epoxy reactions are of little interest as cellulose crosslinkers.

### Acid Catalyzed Reaction

- The acid catalyzed reaction appears to offer the best possibility for crosslinking cellulose with diepoxides (3). This conclusion is based on the fact that low add-on - 2 percent by weight - will provide high dry crease resistance and insolubility in cuene. Furthermore, tensile strength losses were in the range of 50 percent for cotton and McKelvey (3) has shown that this strength loss was mainly due to the crosslinking and not to degradation by the catalyst.

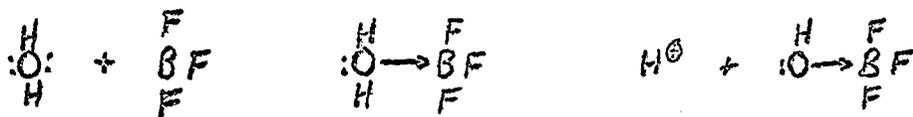
The crosslinking reaction appears to be most efficient when zinc fluoborate is used as a catalyst, and methanol is used as the solvent. The reaction is carried out by heating this mixture (75-125° C.) with the cotton present for the desired reaction time (3). With this treatment, a possible reaction mechanism would be:





In this reaction, zinc fluoborate acts as a latent catalyst. That is to say, boron trifluoride is the actual catalyst (35) and is generated by heating, *i.e.*,  $\text{Zn}(\text{BF}_4)_2 \rightleftharpoons \text{ZnF}_2 + 2\text{BF}_3$ . The  $\text{BF}_3$  then reacts with the methanol to form a coordinate compound (a) which in turn dissociates into an acid and base (b). This acid then reacts with the epoxide to open the ring so that the epoxide can react with cellulose.

There are two experimental facts which are of particular interest in this reaction. First, it has been established that strong proton catalysts, like sulfuric acid, give poor results in terms of crosslinking (3). Secondly, zinc fluoborate is an efficient catalyst for crosslinking when methanol is used as the solvent and not when water is used as a solvent (3). In reality, these two experimental facts compliment one another, and lend support to the proposed reaction mechanism. As shown above, when methanol is the solvent,  $\text{CH}_3^+$  is the species which opens the epoxide ring. On the other hand, when water is used as a solvent, it can be shown that  $\text{H}^+$  is the species that opens the epoxide ring, *i.e.*,



which would be essentially the same as a strong proton acid.

The fact that strong proton acids will not catalyze the crosslinking reaction suggests the possibility of a general acid catalysis mechanism (4). In general acid catalysis, strong acids will not work because in addition to opening the epoxide ring, they would also protonate the

cellulose hydroxyl  $\text{--- CELLON + H}^+ \xrightarrow{\hspace{2cm}} \text{Cell-O}_H^+ \text{H}$   $\text{---}$  which effectively prevents cellulose from reacting as a nucleophile as is required in the above mechanism. Such reactions are generally catalyzed by massive amounts of weak acids (4). McKelvey (35) found that when weak acids were used as catalysts, very little crosslinking occurred, but only low concentrations of the acids were used so a test of this hypothesis remains to be made. Additional research along this line would be desirable because verification of this mechanism would make it possible to crosslink cellulose in buffered acid solutions, which should reduce strength loss.

There is another possible explanation of the differences due to solvents. The explanation here would be that water is more strongly hydrogen bonded to the cellulose hydroxyl than is methanol. This could decrease the reactivity of the cellulose and reduce crosslinking because the cellulose hydroxyl must compete with the solvent for reaction with the epoxide. If excessive reaction occurs between the epoxide and the solvent, the efficiency of the treatment decreases.

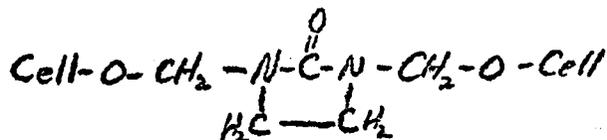
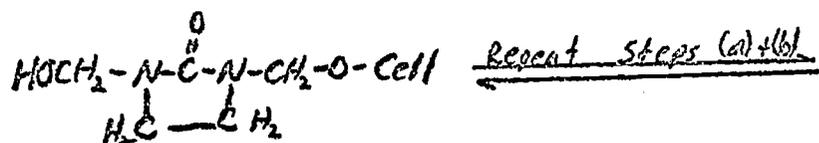
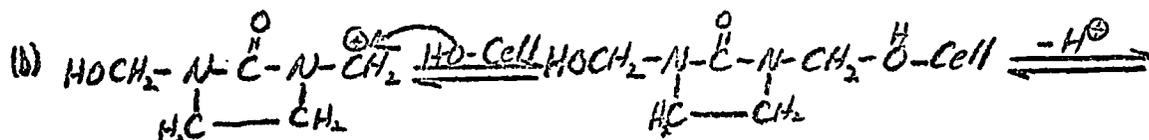
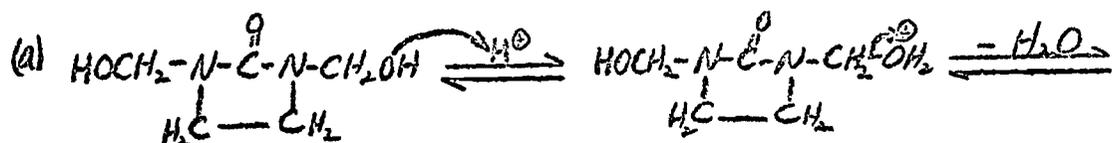
### Conclusions

A survey of the literature did not reveal any research on the use of diepoxides to crosslink wood. Although the costs and treatment condition are not ideal, it appears that this method of crosslinking should be investigated since it appears to be very efficient when used with cotton. With regard to wood, one possible application would be to use the epoxy as a combination finish and surface stabilizing agent. This should be a durable finish since it would be bonded directly to the surface.

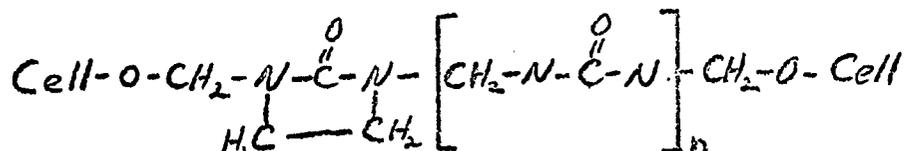
N-METHYLOL COMPOUNDS

N-methylol compounds are the major reagents used for crosslinking cotton at the present time (8). There are a large number of these compounds and a few examples are: dimethylolurea, trimethylolmelamine, dimethylol ethyleneurea and dimethylol ethyl triazone.

A proposed reaction mechanism for the reaction of dimethylol ethyleneurea with cellulose is as follows:



It should be noted that work with cotton (14) indicates that the end product does not contain a single ethylene urea residue as shown above but is:



where  $n$  is approximately 0.5.

It appears that this reaction may proceed by the  $S_N1$  mechanism, as shown above, and is reversible. The reverse of the forward cross-linking reaction is a hydrolysis reaction (12), and is an important factor. In this respect, Reeves (12) was able to show that the ease of hydrolysis is influenced by the substituents attached to the nitrogen atom and carbonyl group. Hydrolysis was accelerated when the substituents were electron release groups and retarded when they were electron withdrawal groups. These results would be anticipated if the  $S_N1$  reaction is operative because of the substituent effect on the stability of the carbonium ion formed in step (b). That is to say, electron release groups would stabilize the carbonium ion and electron withdrawal groups have the opposite effect. Likewise, these substituents would be expected to have the same effect on the forward reaction.

The reverse or hydrolysis reaction is important in crosslinked cotton because of the commercial laundering conditions which use acidic and basic solutions (12). In contrast to this, the hydrolysis reaction

would not be of importance for crosslinked wood. Consequently, the use of reagents with electron release groups attached to the nitrogen and carbonyl group would be desirable for wood because milder treating conditions could be used.

An attempt was made to crosslink wood with dimethylol ethyleneurea but to no avail (36). One would expect this compound to work with wood as well as with cotton and a review of the experiment by Weaver *et al.* (36) suggests two possible reasons for this failure. In the first place, the treatment was carried out by impregnating the wafers with a 25 percent aqueous solution followed by a two hour cure at 130° C. With this treatment, the samples would be in a swollen condition during the cure. As shown previously for the aqueous formaldehyde treatment, reactions in the swollen condition do not produce crosslinking. However, one would expect a polymerization reaction that would bulk the wood without crosslinking. In the second place, Frick *et al.* (14) have shown for cotton that in order to maximize crosslinking a cure temperature in the range of 160° C. should be used. Lower temperatures produce more polymerization; hence this would be a factor since the experiment with wood was conducted at 130° C.

### Conclusions

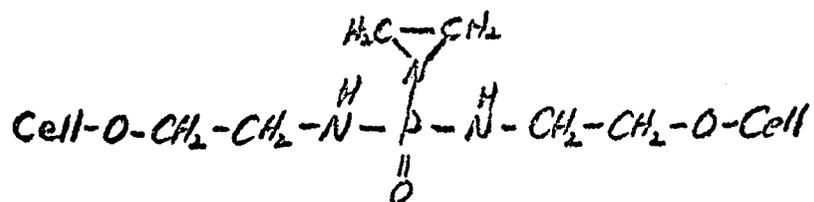
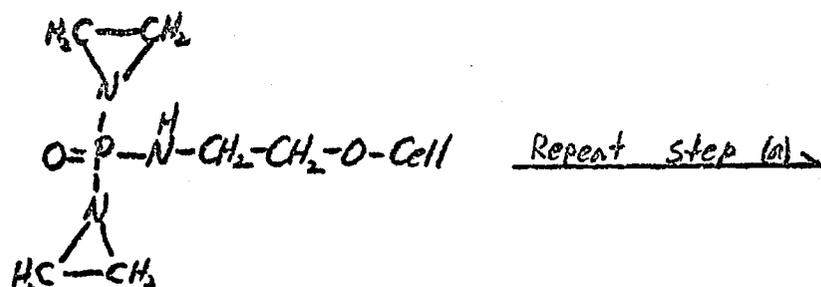
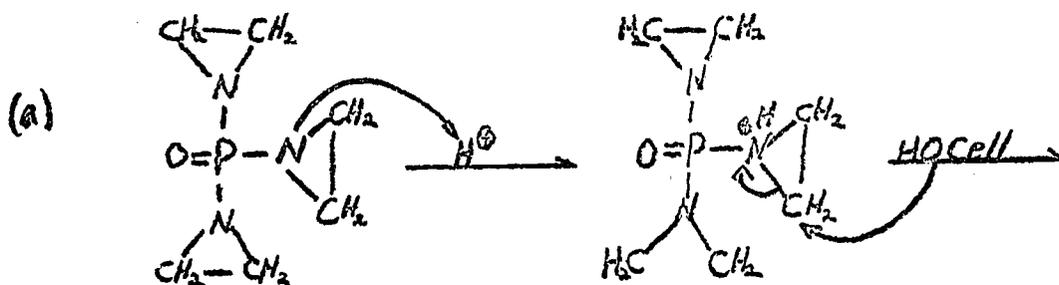
It appears that N-methylol type compounds may have some value as crosslinking agents for wood even though initial work was unsuccessful. However, success will depend on developing a treatment that can be applied while wood is in a relatively unswollen state. Perhaps the addition of calcium chloride will solve this problem.

It should be emphasized that high molecular weight compounds are not as desirable as low molecular weight compounds. The reason for this

is that the total weight of reagent required for a given degree of crosslinking increases with the molecular weight of the reagent. Hence the cost of treatment would increase.

APO

Another interesting compound which is being evaluated as a cross-linking agent for cotton is tris (1-aziridinyl) phosphine oxide, commonly called APO. This is a trifunctional compound and the proposed reaction mechanism with cellulose is as follows (37):



APO is an interesting compound because it acts as a fire retardant as well as a crosslinking agent for cotton (37). Although this compound is a fairly good fire retardant by itself, improvement is obtained by adding other compounds like tetrakis (hydroxymethyl) phosphine oxide (37).

The crosslinking results with cotton are encouraging. Drake (38) states that the tear and tensile strength properties of treated fabrics are better than those obtained with most crease resistant resins. Furthermore, very good dry crease recovery was obtained with an APO-Zn(BF<sub>4</sub>)<sub>2</sub> treatment, which indicates a high degree of crosslinking.

APO is a highly reactive compound and has been used to crosslink cotton without the aid of a catalyst (38), but the crosslinking efficiency can be improved with a catalyst. This high reactivity suggests the possibility of using this compound to determine the influence of crosslinking on strength properties of wood.

### Conclusions

APO is a high molecular weight compound which would be undesirable from the cost standpoint. However, the fact that this compound imparts fire resistance along with dimensional stability is an advantage. Furthermore, the high reactivity of this reagent suggests that strength loss can be minimized.

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