CHAPTER 7

DURABLE PRESS FINISHES

Durable press finishes can be defined as those chemicals used to improve the properties and performance of washable fabrics. Apparel fabrics, from a historically perspective were made from natural fibers, namely wool, silk and cotton. Of these, cotton was the one best suited for washable fabrics because wool and silk would not stand up to the rigors of washing. Before 1960, 100% cotton yarns dominated the washable fabric market. Garments made from 100% cotton fibers are comfortable because they absorb perspiration. Even today cotton garments are preferred by many consumers because of the comfort factor. Unfortunately, garments made from cotton become badly wrinkled during wear, they don't retain the nice smooth "just ironed" look. After they have been washed and dried, they must be ironed otherwise they will look very rumpled. Garments also shrink in the washer. Most of these shortcomings can be improved by properly applying durable press finishes.

I. WHY FABRICS WRINKLE

Why do some fabrics wrinkle and others don't? Close examination of this question reveals a relationship between moisture absorption and wrinkling. Wool and cotton fabrics wrinkle, both fibers absorb water. Polyester and nylon fabrics are more resistive to wrinkling, they absorb much less than the other two.

To understand wrinkling of cellulose fibers, consider the stress and strain forces within a smooth rod as it bent - see figure 43. The stretching stresses at the outer reaches of the bend provide lateral forces to adjacent polymer chains which can cause them to move. The inner polymer chains are under compressive stresses - also providing lateral forces. A large diameter rod, because the radius of curvature is bigger, will exhibit greater strains than a thinner rod.

Under stress, the hydrogen bonds between adjacent cellulose chains can break allowing the chains to slip past each other. New H-bonds can form as the hydroxyl groups re-associate with different partners. Having done so, there are no forces to pull the neighboring chains back to their former position. The stressed shape of the fiber is just as stable now as was the original shape.

Figure 43. Bending Stresses in Fibers

## Bending Forces in a Thin Rod

Bending forces in a Thick Rod

Water will facilitate the disruption of these bonds by forming H-bonds between the water molecule and the cellulose hydroxyls. Now the hydrated polymer chains can slide past each other more easily so the strain level to deform the fiber is even lower than before. Water acts as a lubricant allowing the chains to slide past one another easily. Illustrative of this point is ironing wrinkles out of a cotton garment. It is impossible to iron out wrinkles from a dry garment. However, when the garment is dampened first or if a steam-iron is used, the wrinkles will iron out and the fabric becomes flat and smooth.

Figure 15. Lateral Forces Between Cellulose Chains

Before Stress

After Stress
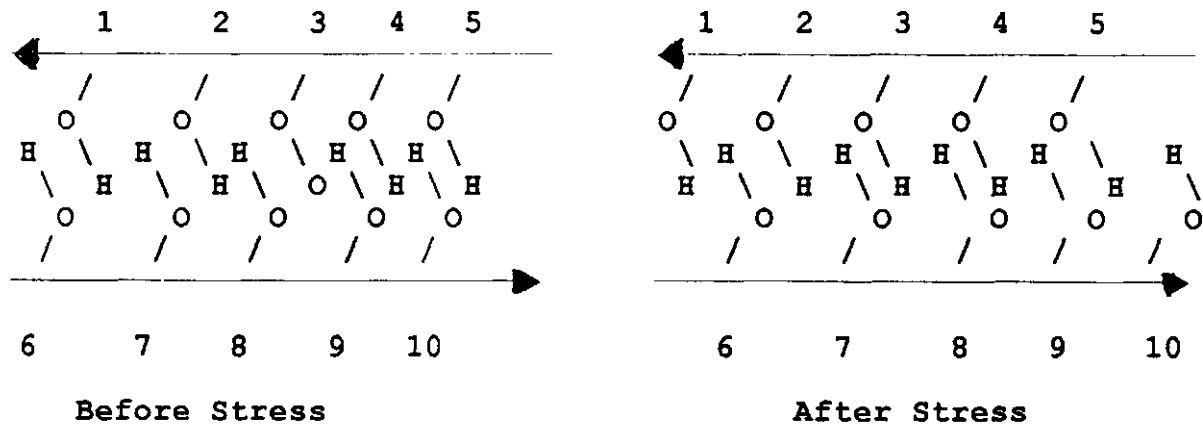
A. Factors Affecting Wrinkling

For wrinkles to set in, the forces distorting the fabric must be transmitted to the individual fibers. The forces must then place a strain on the individual fibers and distort them. Some of the physical factors that come into to play are summarized below.

1. Fiber Factors

Fabrics made from fine cotton fibers do not wrinkle as badly as fabrics from course fibers. The explanation for this observation is that the bending radius of curvature is greater for a thick fiber than for a thin one. The greater the radius, the greater is the stress on the polymer chains. Fabrics made from fine Egyptian cotton wrinkle less than those made 'from course fibers

2. Yarn Factors

Fabrics made from high twist yarns wrinkle worse than those made from low twist yarns. For low twist yarns, the distortion stresses are dissipated by the physical rearrangement that takes place as adjacent fibers slip by each other. The stress is dissipated before it can affect the individual fibers.

3. Fabric Factors

Tightly woven fabrics wrinkle worse than loosely constructed fabrics. In a loosely constructed fabric, the yarns can move as they respond to the wrinkling

forces. The individual fiber is spared. Woven fabrics wrinkle worse than knits. The knit loops allow an even greater freedom of yarn movement again sparing the individual fiber.

II. THEORY OF CREASE RECOVERY

In polymer chemistry, it is well known that certain types of polymers must be cross-linked before they develop elastic properties. Elastomers are materials that readily recover from deformation stresses. Since the case has been made that chain slippage under moist conditions is responsible for wrinkling, it is logical to reason that cross-linking adjacent cellulose chains should be a way of improving crease recovery. Time has shown that this theory does indeed work so the mechanism for improving cotton's resilience is to cross-link cellulose chains with appropriate reactants.

A. Crosslinking Cellulose

The hydroxyl groups on the anhydroglucose units of the cellulose polymer backbone are functional groups that can undergo typical reactions involving alcohols. Organic acids, isocyanates, epoxy and aldehydes all react with hydroxyl groups to form their corresponding reaction products. Over the years nearly all known reactions involving alcohols have been investigated as possible cellulose crosslinkers. Formaldehyde and formaldehyde derivatives were among the earliest ones discovered and have stood the test of time in terms of effectiveness and cost. They are still the mainstay of today's chemistry.

B. History of Crease Recovery

In the mid 1920's, the managing director of Tootal, Broadhurst and Lee challenged his research chemists to make cotton fabric as wrinkle resistant as silk. It was know that formaldehyde would react with cellulose, however formaldehyde is not a pleasant material to work with as it irritates mucus membranes, causes runny noses and watery eyes. The chemists discovered that phenol/formaldehyde condensates would also cross link cotton and at the same time reduce the formaldehyde risks. Unfortunately the phenol/formaldehyde resins caused the cotton fabrics to become severely discolored and excessively boardy. Soon thereafter, they discovered that urea/formaldehyde resins also improved crease recovery and did so without discoloring the fabric. While not completely free of formaldehyde odor, these resins could be handled on commercial equipment. From the 1930's until 1961, cotton fabrics were crosslinked with a number of N-methylol compounds to give fabrics that were classified as *Wash & Wear* or *Easy Care* fabrics. Several other names were associated with these fabrics e.g. *Crease Resistant, No Iron, CRF* etc. The performance of these fabrics were pretty good. As will be made more clear in ensuing discussions, the best balance of improved ease of care properties to fabric strength

loss was struck. All of the fabrics were treated at the mill in the flat state.

In 1961, The Koret Company marketed garments with permanent creases. This was revolutionary at that time because the activation of the cross-links was delayed until after the garment was made and the creases pressed in. What Koret did was to impregnate the fabric with the chemicals, carefully dry without activating the cross-links, make, press and then hang the garments in an oven to activate the cross-links. The consumer's reaction to these garments was double edged. They complained about the fact that the cuffs fell off and holes appeared in the sharp creased areas when the garments were worn and laundered, yet turned around and wanted more. The consumer had been freed from the tedious task of ironing their garments. signalling the birth of the *Permanent Press* era. From the chemist's point of view, the lack of abrasion resistance and weakened fabric was expected since the original garments were made from 100 % cotton. It was well understood at that time that creases set into the fabric prior to curing would be permanent and that excessive chemicals, curing times and temperatures would severely weaken the fabric and drastically reduce abrasion resistance. Nonetheless the industry, sensing a new marketable product, immediately launched into development programs to overcome the deficiencies and still maintain the permanent press qualities. The solution came about quickly. Serviceable garments were made from nylon blended with cotton. Soon thereafter, polyester blended with cotton also provided serviceable garments. At that point in history, polyester was relatively new, expensive and not a truly commercial item. Yarn spinners found that polyester was easier to blend with cotton than nylon, so it became the preferred fiber for permanent press fabrics. The original blend was 35 % polyester, 65 cotton. This amount of polyester provided the strength without interfering with cotton's contribution to shape retention.

It can be said that the commercial success of Permanent Press (Durable Press) is largely ,responsible for today's position enjoyed by polyester manufacturers. It provided the initial need for volume production which lead to the polymer's more competitive pricing structures, opening up more and more markets.

C. Definitions

- **Muss Resistance (Wrinkle Resistance).** The fabric must not wrinkle when a garment is worn. Wrinkling performance can be expressed in *Crease Recovery* terms. *Crease Recovery Angle (CRA)* are used to measure crease resistance or crease recovery.

- **So-Iron (DP Rating).** Fabric must have a smooth appearance after it is laundered dried (line dried or tumble dried). Fabric smoothness is referred to as *Durable Press Rating (DP Rating)* and is judged on a 1 to 5 scale. A 5 DP rating is the highest (most smooth) and a 1 is the most wrinkled. A 3.5 rating is considered commercially acceptable.

■ **Low Residual Shrinkage.** Fabric must shrink less than 2 % when laundered.

■ **Permanent Press.** Garment shape is maintained during wearing and washing. Creases must be sharp, flat areas must be smooth. Creases are rated on a 1 to 5 scale. A 5 rating is perfect.

■ **Delay Cure.** A process where the curing step is delayed until the garment has been made and pressed.

■ **Precure.** A process where the curing is done at the finishing plant in the flat state.

■ **CRA.** Crease recovery angles. AATCC Test Method 66-1984

■ **CRF.** Crease resistant finish.
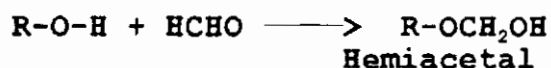

III. CELLULOSE CROSSLINKERS

Cellulose crosslinkers can be divided into two categories, those that predominately crosslink cellulose, also known as cellulose reactants, and those that self-polymerize as well as crosslink cellulose (aminoplasts). Both types involve the reaction chemistry of formaldehyde so a review of pertinent formaldehyde chemistry will help in understanding how these auxiliaries work.
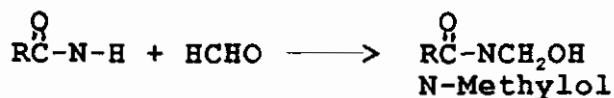
A. Reactions of Formaldehyde

Formaldehyde is capable of reacting with many active hydrogen compounds, e.g -OH, -NH and activated -CH.

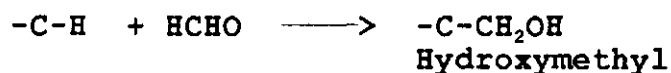### 1. Formation of Hydroxymethyl Derivatives

a. With Alcohols

$$R-O-H + HCHO \longrightarrow R-OCH_2OH$$
$$\text{Hemiacetal}$$

b. With Amides

$$\underset{\text{O}}{RC}-N-H + HCHO \longrightarrow \underset{\text{O}}{RC}-NCH_2OH$$
$$\text{N-Methylol}$$

c. Activated C-H
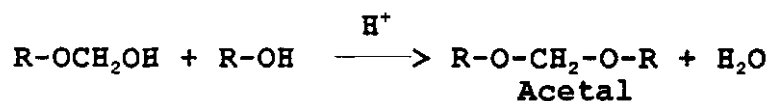
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-C-H  + HCHO  ———>  -C-CH₂OH
                      Hydroxymethyl
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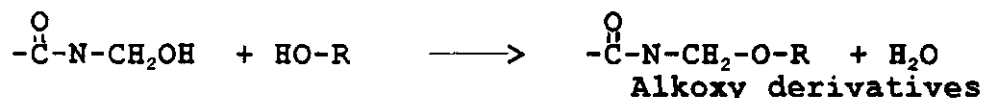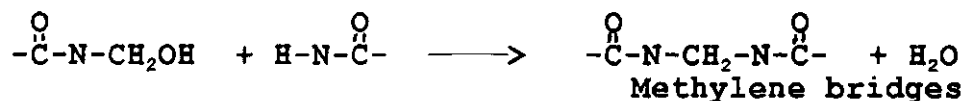
The hydroxymethyl group formed in the first reaction is also capable of undergoing a second reaction. The second reactions also involve activated hydrogens described above and result in the formation of a methylene link (-CH₂-) between the reacting species. Usually this reaction requires an acid catalyst and heat.

2. Reactions of Hydroxymethyl

a. With Alcohols

$$R\text{-}OCH_2OH + R\text{-}OH \xrightarrow{H^+} R\text{-}O\text{-}CH_2\text{-}O\text{-}R + H_2O$$
$$\text{Acetal}$$

b. With N-Methylol

```
 O                  O                     O            O
 ‖                  ‖                     ‖            ‖
-C-N-CH₂OH  + H-N-C-   ———>    -C-N-CH₂-N-C-   + H₂O
                                      Methylene bridges
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```
 O                                  O
 ‖                                  ‖
-C-N-CH₂OH  + HO-R    ———>    -C-N-CH₂-O-R  + H₂O
                                    Alkoxy derivatives
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B. Resin Formers (Aminoplasts)

There are two major types of formaldehyde condensates that fall into the resin former category, urea/formaldehyde and melamine/formaldehyde. These condensates are capable of self-crosslinking to form resinous, three-dimensional polymers as well as crosslinking cellulose. They find non-textile applications as plastics, adhesives and are also used to modify other polymeric systems. Because of the tendency to self-condense, the two mentioned above are often called *Aminoplasts.* The tendency to self-crosslink adds stiffness to fabrics. While stiffness may be undesirable on some fabrics it can be an asset as for example when *Handbuilders* are needed to enhance fabric properties.

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1. Urea/Formaldehyde (U/F)

The reaction of an amide -N-H with HCHO to form a -NCH$_2$OH is often termed *Methylolation* because the reaction product is called an N-methylol group. Accordingly urea can be metholylated with up to 4 moles of formaldehyde and the reaction products used as crease resistant finishes. When 2 moles of HCHO is reacted with one mole of urea, dimethylol urea is formed. Being difunctional, it is capable of serving as a crosslinking agent.

a. Synthesis of Dimethylol Urea

$$NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + 2\ CH_2O \longrightarrow HOCH_2NH-\overset{O}{\overset{\|}{C}}-NHCH_2OH$$
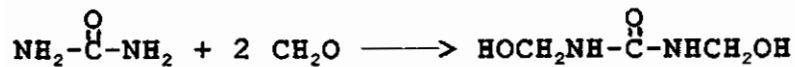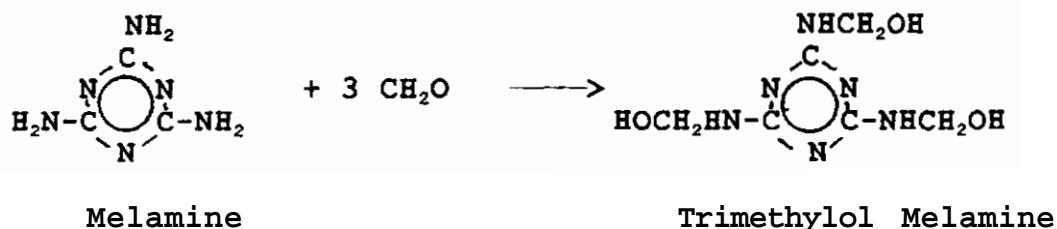
b. Important Features

1. The condensate has an extremely short shelf life. It must be used within a few days after its been made. When formulated with catalyst, the finish bath must be used within a few hours. The solution has high free formaldehyde and will readily liberate formaldehyde into the work place. 2. It is easy to cure on fabrics and imparts outstanding crease recovery. Fabric hand becomes stiffer which is usually undesirable for many cotton fabrics. Most rayon fabrics are very limp compared to cotton so the added firmness is desirable. 3. Finished fabrics have poor durability to repeated laundry. Crease recovery is lost because the crosslinks have poor stability to hydrolysis. 4. The finish adversely affect the light fastness of direct and fiber reactive dyes. 5. The finish reacts with hypochlorite bleaches to form a reaction product which decomposes with heat to form HCl. Acid degradation of the cellulose scorches the fabric and causes it to become very much weaker (tender). 6. Finished fabric is prone to liberate formaldehyde odor. Released formaldehyde is high. Overcured fabrics also develop an unpleasant fish odor.

2. Melamine/Formaldehyde

Melamine can react with up to 6 moles of formaldehyde to form a variety of products. Commercially, trimethylol and hexamethylol melamine are the more important condensates. In storage, the hydroxymethyl (N-methylol) groups tend to polymerize and liberate formaldehyde. By converting them to the methoxymethyl derivative, the shelf life is much improved. Most of the commercial products are methylated.

a. Synthesis of Trimethylol Melamine

Melamine   Trimethylol Melamine

b. Synthesis of Trimethoxy Melamine

Trimethoxymethyl Melamine
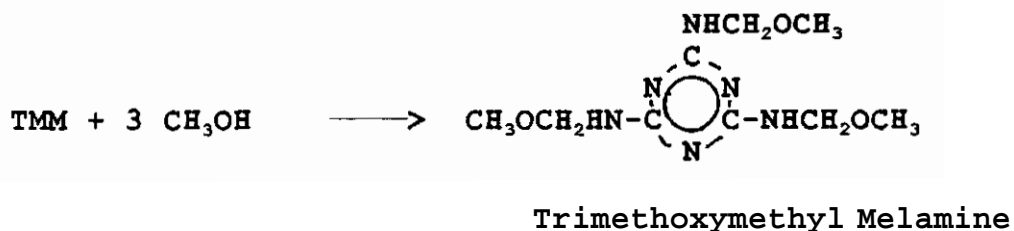
c. Synthesis of Hexamethoxymethyl Melamine

The corresponding hexamethylol- and hexamethoxymethyl condensates are made by increasing the formaldehyde/melamine mole ratio to 6:1.

d. Important Features

1. The tri- products produce firmer hands than the hexa derivatives and are extensively used as hand builders for fabrics other than cotton (Acrylic, nylon, polyester). 2. Durability to repeated laundering is much better than U/F. This feature is a plus for permanent hand builders. 3. Chlorine bleaches cause the fabrics to yellow; however, the reaction product does not decompose with heat to liberate HCl and tender the fabric. 4. They are used in combination with phosphorus flame retardants as a source of nitrogen. Nitrogen synergism enhances phosphorus flame retardants and melamine is an excellent source of nitrogen. 5. They are used as finishes for reducing wool shrinkage.

C. Reactants

Reactant N-methylol compounds differ from aminoplasts in that reactants do not form three-dimensional polymers by self-condensation. When applied to cellulose, they mainly crosslink adjacent polymer molecules. The commercially important ones are derived from ethylene urea, 4,5-dihydroxy- ethylene urea and hydroxyethyl carbamate. There is a wealth of literature published about these and related compounds - the reader is urged to consult these reference for greater depth.

1. Dimethylolethylene Urea (DMEU)

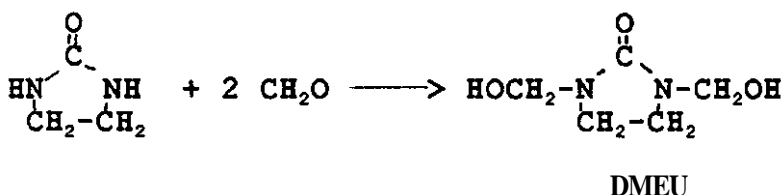The starting material for making dimethylolethylene urea (DMEU) is ethylene urea. a 5 membered heterocyclic, nitrogen compound (imidazolidone-2). It is made by reacting ethylene diamine with urea. Ethylene urea contains 2 N-H groups capable of reacting with formaldehyde and forms a difunctional product. Since there are no other active hydrogen sites, the N-methylolated product cannot self-condense.

a. Synthesis & Monomer

$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \;+\; H_2CH_2CH_2NH_2 \;\longrightarrow\; \underset{\underset{\displaystyle CH_2-CH_2}{|\quad\quad|}}{HN\overset{\overset{\displaystyle O}{\|}}{\underset{C}{\diagup\;\diagdown}}NH} \;+\; 2\; NH_3$$

Ethylene urea
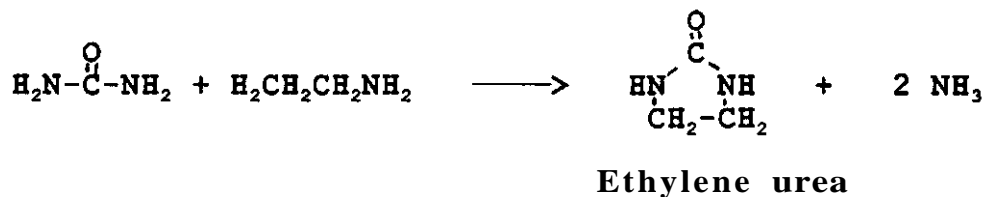
b. Methylolation Reaction

$$\underset{\underset{\displaystyle CH_2-CH_2}{|\quad\quad|}}{HN\overset{\overset{\displaystyle O}{\|}}{\underset{C}{\diagup\;\diagdown}}NH} \;+\; 2\; CH_2O \;\longrightarrow\; \underset{\underset{\displaystyle CH_2-CH_2}{|\quad\quad\quad\quad|}}{HOCH_2-N\overset{\overset{\displaystyle O}{\|}}{\underset{C}{\diagup\;\diagdown}}N-CH_2OH}$$
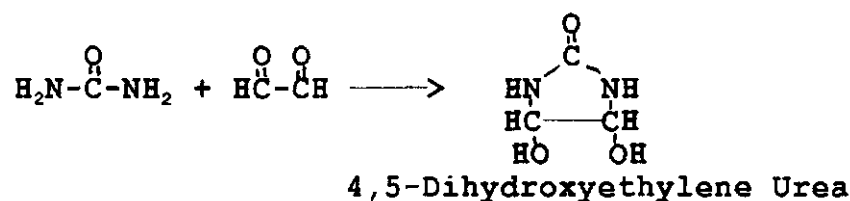
DMEU

c. Important Features

1. It was widely used prior to 1961 as a wash and wear finish. 2. The product has moderately good shelf life, much better than the aminoplasts. Even with catalyst mixed in, the bath life is more than adequate for most commercial applications. 3. DMEU is easily cured. It will begin to cure at 90 to 100^0 C. 4. It is highly efficient and gives good wrinkle recovery with nominal losses in fabric strength. 5. The product does affect lightfastness of certain direct and fiber reactive dyes. 6. Chlorine resistance is poor even though there are no remaining N-H groups. 7. Hydrolysis resistance is poor. Crosslinks are not durable to laundering, especially industrial laundering conditions.

2. Dimethylol-4,5-Dihydroxyethylene Urea (DMDHEU)

DMDHEU is the workhorse durable press finish. It and some of its modified versions account for over 85% of all crease resistant chemicals consumed today. DMDHEU achieved this prominent role in 1961 when delay cure processing came into being. In the trade, DMDHEU is often referred to as the *Glyoxal* resin. This jargon came as a way to distinguish it from DMEU, in that glyoxal was used to make the starting monomer. The starting heterocycle is made by reacting stoichiometric

amounts of urea and glyoxal. The reaction is straightforward and can be carried out in regular laboratory glassware. The methylolation step is also straightforward. While the synthesis is shown in two steps, commercially **DMDHEU** is made directly in one step. Urea, formaldehyde and glyoxal are all combined together and heated. The extent of reaction is followed by monitoring the free formaldehyde content. The product is sold as a 46% solution.

a. Synthesis of 4,5 - Dihydroxyethylene Urea

$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \ + \ \overset{\overset{\displaystyle O}{\|}}{H}C-\overset{\overset{\displaystyle O}{\|}}{C}H \ \longrightarrow \ \begin{array}{c} \overset{\overset{\displaystyle O}{\|}}{C} \\ HN \diagup \quad \diagdown NH \\ HC{-}{-}CH \\ HO \quad \ OH \end{array}$$

4,5-Dihydroxyethylene Urea

b. Methylolation

$$\begin{array}{c} \overset{\overset{\displaystyle O}{\|}}{C} \\ HN \diagup \quad \diagdown NH \\ HC{-}{-}CH \\ HO \quad \ OH \end{array} \ + \ 2 \ CH_2O \ \longrightarrow \ \begin{array}{c} \overset{\overset{\displaystyle O}{\|}}{C} \\ HOCH_2{-}N \diagup \quad \diagdown N{-}CH_2OH \\ HC{-}{-}CH \\ HO \quad \ OH \end{array}$$
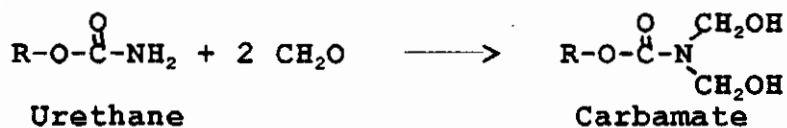
DMDHEU
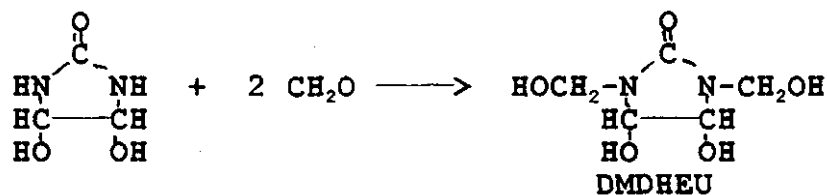
c. Important Features

The commercial product has low free formaldehyde which makes it easy to handle in a finishing plant. It does not liberate formaldehyde from the reverse reaction as rapidly as do other reagents. The product has extremely good shelf life and even finish baths with catalyst present are stable for prolong periods of time. Fabric temperatures exceeding 130^0 C are needed before the cross-linking reaction takes place. This feature is responsible for why it has become the dominate DP finish. The reactant does not crosslink on storage so fabrics can be left in a sensitized state (uncured) for over six months before post curing. Hydrolysis resistance of the cellulose crosslinks are much better than DMEU so durability to laundering is very acceptable. Resistance to chlorine bleach is also acceptable. While this finish reduces the light fastness of direct and fiber reactive dyes, it is better than DMEU.

3. Carbamates

Carbamates are a family of related compounds that also react with formaldehyde to form N-methylol derivatives. A general structure of the starting compound is shown in the box below. This structure is also called a urethane so carbamates are simple urethanes. The alkyl group (R-) can be methyl, ethyl, propyl

or hydroxyethyl. The methyl and ethyl carbamates are carcinogenic and no longer used. The propyl and hydroxyethyl are safe and are used today. Carbamates react with formaldehyde to form N-methylol derivatives. They can react with up to two moles as shown below. The reaction is difficult to drive to completion and the equilibrium is such that the best that can be done is 1.7 to 1.8/1. This leads to products that have high free formaldehyde.

a. Synthesis

$$R-O-\underset{\underset{\text{Urethane}}{}}{\overset{\overset{O}{\|}}{C}}-NH_2 + 2\ CH_2O \longrightarrow R-O-\underset{\underset{\text{Carbamate}}{}}{\overset{\overset{O}{\|}}{C}}-N\overset{CH_2OH}{\underset{CH_2OH}{}}$$

b. Important Features

Carbamate finished fabrics have good DP properties. These products are harder to cure and require stronger catalyst and/or higher curing conditions. This leads to greater losses in strength and abrasion resistance. The crosslinks are extremely stable to alkaline hydrolysis and stand up well to the rigors of commercial laundries. Fabrics treated with carbamates are well suited for industrial laundry applications such as rental uniforms and hospital linens. Chlorine resistance is good. The commercial products have high free formaldehyde leading to fabric with high formaldehyde release.

IV. CONTROLLING FORMALDEHYDE EXPOSURE

A. Atmospheric Formaldehyde

Strict exposure limits to formaldehyde vapor in the work place have been imposed on all industries using formaldehyde products. OSHA has lowered worker exposure to airborne formaldehyde to 0.75 ppm over an 8 hour time weighted period. Worker training, medical surveillance, removal of those sensitive to its exposure are other requirements of the new regulations. Worker exposures in the dyeing and finishing plant and in garment sewing plants are the issues. Better ventilation in those areas where formaldehyde is prone to be present has been particularly effective in meeting the limits. Another area of concern is the formaldehyde emanating from DP finished fabrics. If the amount coming from a roll of fabric is high, it would soon fill the air space around it and exceed the control limits. This is a particularly bad problem in cut-and-sew industries which manufacture consumer products. Newer reactants containing lower free formaldehyde have been developed to combat this problem. Towards this end, a lot of effort has been spent to reduce the formaldehyde released from a DP finished fabric and still maintain the desirable DP performance. The discussions that follow describe efforts in modifying reagents to reduce the

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formaldehyde release.

B. Formaldehyde in Fabrics

1. Free Formaldehyde

Free formaldehyde is defined as the uncombined monomeric formaldehyde that exist in finish solutions. Usually, its sources are stoichiometric excesses that may have been included in the resin manufacturing step to drive the reaction and/or the amount arising from the equilibrium established by the particular reactants. Free formaldehyde is determined by suitable analytical titration procedures.

2. Formaldehyde Release

Formaldehyde release, not to be confused with free formaldehyde, is the amount of formaldehyde that escapes from a fabric into the atmosphere. It is determined by the mason jar method, AATCC Test Method 112. The method calls for suspending 1 gram of fabric in a sealed quart mason jar containing distilled water in the bottom. The jar is incubated for 20 hours at 49⁰ C. The formaldehyde that collects in the water is analyzed and the results are reported in ppm or µg/g fabric. There are other fabric test methods used for determining formaldehyde in fabric. For example the Japanese method calls for titrating the free formaldehyde in the fabric by a cold procedure. The box below shows a comparison of the results obtained on the same piece of fabric tested by the different analytical procedures. The results obtained by the mason jar method are much higher than the Japanese method so the reader is cautioned to be sure of the details of what is being reported before jumping to conclusions.
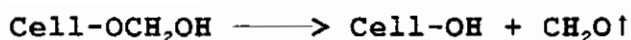
TABLE 11

HCHO TEST METHOD COMPARISON

Method	HCHO (ppm)
Cold Sodium Sulfite	57
MITI	250
Japanese Law	454
AATCC 112-1983	818

The analytical procedures for the jar test usually call for the use of a colorimetric method using Nash Reagent. This procedure is not very reproducible for low levels of HCHO without extreme care. Methods using chromotropic acid to develop the color are more accurate. Recently, even more accurate methods utilizing HPLC techniques have been introduced.
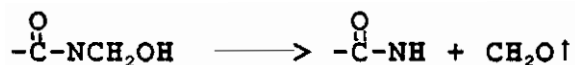
3. Linkages Responsible for HCHO Release

There are three major types of formaldehyde linkages that are responsible for released formaldehyde. The most labile linkage is cellulose hemiformal. Cellulose readily picks up formaldehyde from the atmosphere and give a positive reading by the jar test. Free formaldehyde in solutions and formaldehyde made available from the N-methylol equilibrium are also sources. A second linkage that can be a source of gaseous formaldehyde is uncured resin or pendant N-methylol groups. These linkages are rather labile and easily revert back to their starting materials. It is difficult to cure 100% of the resin that is applied and make sure there are no pendant N-methylol groups left. Therefore, all fabrics will have some, and the amount will depend on how well the fabric was cured. The third source of released formaldehyde is the crosslink itself. The finish will decompose under the jar test conditions and liberate CH_2O.
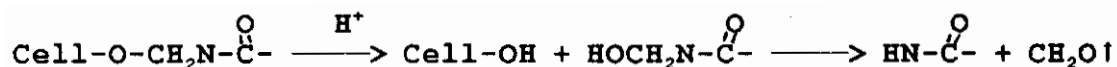
a. Cellulose Hemiacetal

$$Cell-OCH_2OH \longrightarrow Cell-OH + CH_2O\uparrow$$

b. Pendent N-Methylols

$$-\overset{O}{\overset{\|}{C}}-NCH_2OH \longrightarrow -\overset{O}{\overset{\|}{C}}-NH + CH_2O\uparrow$$

c. -Cellulose Crosslinks

$$Cell-O-CH_2N-\overset{O}{\overset{\|}{C}}- \overset{H^+}{\longrightarrow} Cell-OH + HOCH_2N-\overset{O}{\overset{\|}{C}}- \longrightarrow HN-\overset{O}{\overset{\|}{C}}- + CH_2O\uparrow$$

## 4. Fabric pH and Formaldehyde Release

Fabric pH has a great influence on the mason jar test results. As seen in figure 20, a pH of 7 will result in the lowest release values. However if the pH is alkaline or acidic, all else being equal, the test will show much higher values. If the same swatch is resubjected to the jar test? additional formaldehyde will be released and test values will be in the same ballpark as the first run. The swatch will continue to give positive release values until all the crosslinks have been broken. The shape of this curve can be explained by an understanding of the three linkages that are responsible for HCHO release.

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Figure 45. Effect of pH on CH₂O Release.
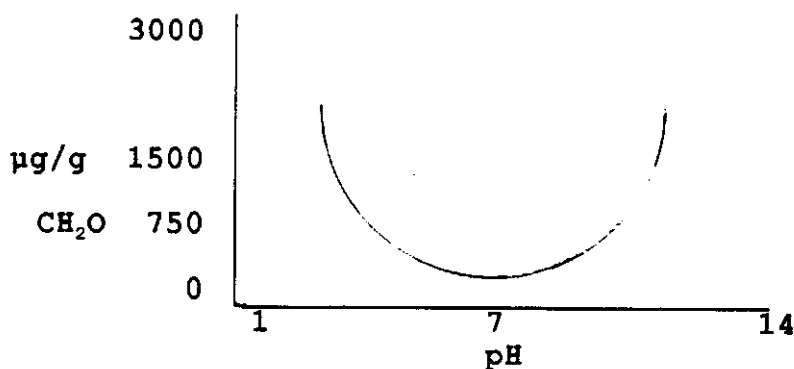
The cellulose hemiacetals are the ones that most easily revert back to HCHO monomer. They are the ones that are released at neutral pH. The pendent N-methylols are unstable at alkaline pH. Fabric tested under alkaline pH would liberate both the hemiacetals and the pendent N-methylols. Under acidic conditions, cross links are broken so all three linkages would contribute to the total amount emitted.

V. METHODS OF REDUCING FORMALDEHYDE RELEASE

A number of approaches have been tried to reduce HCHO release. These approaches range from afterwashing the cured fabric to developing non-formaldehyde reactants. The section that follows will review some of the more important developments.

A. Scavengers

Scavengers are defined as materials capable of reacting with monomeric formaldehyde and tying it up. Scavengers are added to the finish formulation and can be grouped into two categories, nitrogenous compounds and alcohols. The two groups control HCHO by different mechanisms. The nitrogenous additives not only react with HCHO to form N-methylols, but also react with the pendent N-methylols to form methylene bridges. Essentially they compete with the cellulose and when enough additive is present to lower HCHO release, cellulose cross links are reduced resulting in lower DP performance. Additional N-H groups are in the fabric further affecting chlorine damage and reduced lightfastness. Effective nitrogenous scavengers are urea, ethylene urea and carbohydrazide.
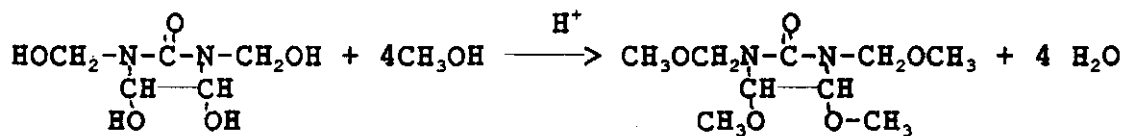
High boiling alcohols also act as scavengers and lower HCHO release. Their mechanism involves capping pendent N-methylol groups. The capped end-groups are more stable than the hydroxymethyl so the equilibrium of the reverse reactions is shifted. These additives also compete with crosslinking so DP ratings are somewhat diminished. Not having N-H groups, however, mitigates against chlorine resistance and lightfastness problems. Effective alcohol scavengers are nitroalcohols, ethylene glycol, diethylene glycol and sorbitol.

B. Modified DMDHEU

Modifying DMDHEU has been the most successful approach for reducing HCHO release. Among the first modified versions were those made from purer starting materials and rigidly controlling the stoichiometry. Later versions led to alkylated DMDHEU and two types have become commercially important products, methylated and glycolated DMDHEU.
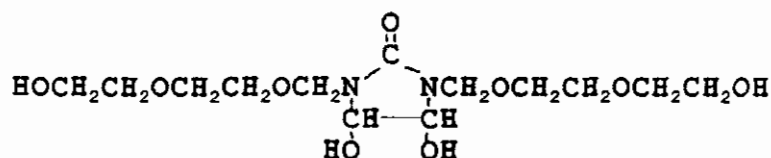
1. Methylated DMDHEU

DMDHEU has 4 reactive hydroxyls. The 4,5-ring hydroxyls are as reactive to alkylation as are the pendent N-methylols. Alkylating with methanol can replace anywhere from 1 to 4 -OH groups with -OCH$_3$. Partially methylated DMDHEU refers to products where an average of two methoxy groups are attached. Fully methylated refers to products where all four have been reacted. To accomplish the latter, the reaction must be driven to completion by removing water of reaction. This involves a distillation step making the fully methylated product more expensive.

$$HOCH_2-N-\overset{\overset{O}{\|}}{C}-N-CH_2OH + 4CH_3OH \xrightarrow{H^+} CH_3OCH_2N-\overset{\overset{O}{\|}}{C}-N-CH_2OCH_3 + 4\ H_2O$$

$$\underset{HO\quad\ OH}{CH-CH} \qquad\qquad \underset{CH_3O\quad O-CH_3}{CH-CH}$$

```
When CH₃-  = 4,  Product is Fully Methylated
When CH₃-  = 2,  Product is Partially Methylated
```

2. Diethyleneglycolated DMDHEU (ULF)

Glycolated DMDHEU is made by reacting 2 moles of diethylene glycol, (DEG), with 1 mole of DMDHEU. It is often referred to as a *ULF* (ultra low formaldehyde) reactant. This product evolved from the successful experiences noted when DEG was added to the finish formulation. Precapping before it is applied insures that there are no pendent N-methylol groups so the HCHO release is even lower. The DEG still functions as a leaving group during cure so crosslinking with cellulose is not severely impaired.

$$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{N} \overset{\displaystyle \overset{O}{\overset{\|}{C}}}{\diagup \diagdown} \text{NCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$$
$$\underset{\underset{\text{HO}}{|}}{\text{CH}}\!-\!\!\underset{\underset{\text{OH}}{|}}{\text{CH}}$$

C. Important Features of Alkylated DMDHEU

Both fully and partially methylated DMDHEUs are harder to cure than their un-methylated counterpart. Stronger catalyst are needed to cure these products. DP properties of the methylated varieties are not quite as good as their un-methylated counterpart. Lowering of formaldehyde release is accomplished at the expense of DP performance. The ULFs produce fabrics with the lowest formaldehyde release of all. Surprisingly, the DP performance of the ULFs is still as good as the un-alkylated products. Unmodified DMDHEU when properly applied to fabrics will give values in the 750-1000 µg/g range. If the fabric is undercured or if the fabric has an acidic pH (catalyst dependent), the values will be higher. Methylated DMDHEU are better, with the partially methylated ones being 300 to 500 range and the fully methylated at 300 µg/g. DMDHEU modified with diethylene glycol will give fabrics at 50 or below.

Table 12

Formaldehyde Release

Comparison of Modified DMDHEU

	HCHO Release µg/g	DP Ratings
Unmodified DMDHEU	750 - 1000	4
Partially Methylated	300 - 500	3.0
Fully Methylated	< 300	3.0
Glycolated (ULF)	< 50	3.25

▮ NOTE: DP performance is somewhat lower for the low release types: Where 3.5 or higher ratings were once marketplace requirements, acceptable standards have been lowered to 3 in order to meet low formaldehyde release.
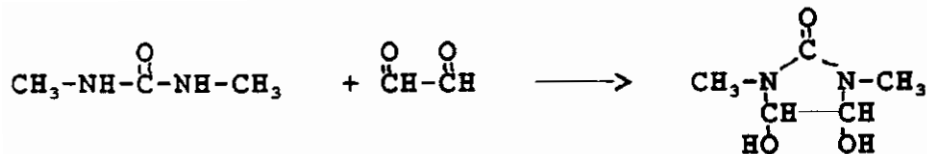
VI. NON-FORMALDEHYDE DP FINISHES

Impending OSHA regulations and several state regulations require that products manufactured with formaldehyde containing components be labeled with a warning label. Even though the use of formaldehyde will not be completely banned, compliance with the safety aspect requires a lot of effort and expense, e.g. work place monitoring and worker medical surveillance. Industry management would prefer to manufacture their products without HCHO rather than put up with the hassle of dealing with the regulations.. Several countries such as Japan and Germany have even more stringent HCHO requirements than the USA. Because of this, there has been and continues to be interest in non-formaldehyde DP finishes. The section that follows describes two products that fit the description "non-formaldehyde" finishes.

A. Dimethyl-4,5, Dihydroxyethylene UREA (DMeDHEU)

DMeEU is the reaction product of dimethyl urea and glyoxal. The -4,5- ring hydroxyls are reactive with cellulose and form the same ether links as do the N-methylol groups. Even though the electronic configuration around the ring hydroxyls are the same as the pendant N-methylol groups, the reaction is much more sluggish because of steric hindrance and therefor require harder cures and more and stronger catalyst. Even with all this, the DP results are not near as good as the more conventional reactants. The product is more expensive; however, the fabric can truthfully be labeled as formaldehyde-free.

1. Synthesis

2. Important Features

This product can be absolutely classified as a non-formaldehyde finish. It is much harder to cure and the DP properties are poor. It is more expensive than DMDHEU.

B. Butanetetracarboxylic Acid (BTCA)

BTCA reacts with cellulose hydroxyls to form ester cross-links. The reactions of carboxylic acids with cellulose is rather old knowledge and has been practiced commercially for many years to make a variety of fibers and plastics from wood pulp. Using dibasic acids to cross-link cotton is also old technology. Problems with this in

the past were excessive strength loss, poorer DP performance and poor durability to laundering. Recently, workers at USDA's Southern Regional laboratories reported some unexpected and useful DP properties obtained with several specific polycarboxylic acids, BTCA being one of the better ones. They also reported that certain phosphorous based salts were effective catalyst for the reaction. Because this too is classified as non-formaldehyde, there was a great deal of interest in this approach. The exact mechanism of the reaction is not know, nor is it known why the crosslinked product are so much more resistant to hydrolysis than are other cellulose esters. The following rational has been suggested as a possible mechanism.

1.   BTCA   ⟶   BTCA Anhydride

CELL-OH   +   DIANHYDRIDE   ⟶   CELL-O-C-CH$_2$-CH-CH-CH$_2$-C-O-CELL
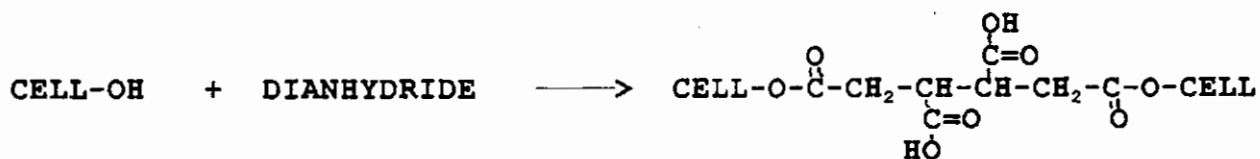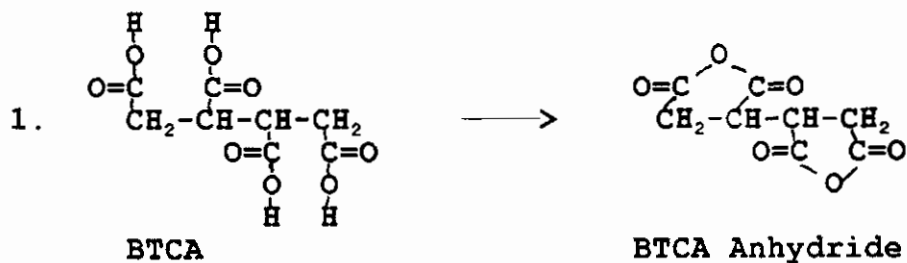
1. Catalyst

a. Sodium Hypophosphite

The most effective catalyst for promoting Durable Press properties. DP rating and shrinkage control equivalent to DMDHEU have been obtained. Catalyst is expensive higher than normal amounts are needed. The hypophosphite is a reducing agent. This is beneficial for maintaining white fabrics, however, it discolors certain dyes especially sulfurs.

b. Sodium Phosphate

Not as effective in promoting DP ratings. Requires higher temperature cure. Much less expensive than hypophosphite. Discolors whites at higher temperatures. Does not affect dye shade.

C. Reactive Silicones

Elastomeric, amino functional and epoxy functional silicones will give a modest boost to DP performance. The elastomeric silicones add resiliency to the fabric improving wrinkle recovery. The amino and epoxy functional improve fiber and yarn slippage, reducing the transmission of the wrinkling force to the fiber. Also wrinkles will fall out easier. These products are often included with conventional resins to boost performance.

D. Liquid Ammonia

Ammonia (NH_3) is a liquid at - 18^0 C. It will cause cellulosic fibers to swell and bring about some of the changes associated with Mercerizing. As a fabric treatment, it will remove stresses and strains and stabilize the fabric. When done properly, cotton fabrics will have somewhat improved DP ratings and improved residual shrinkage. Although the performance does not rival conventional resin treatment, a process using anhydrous liquid ammonia (Sanforset) has been commercialized for stabilizing Denim fabrics. Smooth drying ratings and reduced residual shrinkage were improved without losses in strength and abrasion resistance. The improvement was not to the level one would expect of durable press but enough to warrant the expense. A variation of this process has also seen commercial usage. Cotton shirting fabric was passed through the liquid ammonia process and then topped with a low level of DMDHEU. The DP performance was higher than if the resin had been used alone. The losses in strength and abrasion were minimized by the low level resin treatment.

The liquid ammonia process involves passing the cotton fabric containing a controlled, low level of moisture into a pad bath of liquid ammonia. The ammoniated fabric is put through a Palmer unit and removing the ammonia while the fabric is pressed flat against the drum. A Palmer unit is a large heated cylinder with an endless rubber belt pressing against it.

VII. DURABLE PRESS CATALYST

The reaction of $N\text{-}CH_2OH$ with cellulose is acid catalyzed. The stronger the acid. the faster the reaction. Selecting the proper catalyst becomes important because acids also damage cellulose fibers. Here too the stronger the acid, the greater the damage. Since some reactants are less reactive than others, there are times when stronger catalysts are needed to achieve proper curing. Maximizing crosslinking while keeping acid hydrolysis to a minimum is tricky. It requires a good understanding of acid/base chemistry and of buffers. With this in mind, a quick review of acids is appropriate. There are three types of compounds that create acidity. 1. Compounds that ionize to liberate protons (hydrogen ions). These are further divides into strong

and weak acids, depending on their ionization constant and are called Bronsted acids. 2. Neutral salts of strong acids and weak bases that decompose under certain conditions to liberate protons (latent acids). 3. Metal ion with vacant orbitals capable of accepting a pair of electrons. These are called Lewis acids.

A. Bronsted Acids

Compounds that ionize in water to form protons (H$^+$) are called Bronsted acids. Strong acids are those that completely ionize, e.g. hydrochloric, sulfuric, and formic, Weak acids are those that partially ionize in water, e.g. acetic, boric and citric acids. The ionization constant of acids can be expressed by the equilibrium shown in the box below. The equilibrium established between the ionized and un-ionized species is a steady source of controlled amounts of hydrogen ions. Strong acids provide an immediate source of protons. The number of protons depend solely on the initial concentration of acid. For weak acids, the hydrogen ion concentration depends not only on the initial concentration of acid, but also on its ionization constant.

a. Ionization Constant

The ionization constant is determined by the expression:

$$HA \longrightarrow H^+ + A^-$$

$$Ki = \frac{[H^+][A^-]}{[HA]}$$
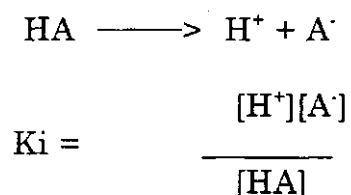
b. Hydrogen Ion Concentration

The hydrogen ion concentration is a function of the ionization constant and 'can be calculated by rearranging the above expression.

$$[H^+] = Ki \frac{[HA]}{[A^-]}$$

Another factor to considered when selecting an acid as a catalyst is its volatility. For example, acetic acid does not function as a catalyst. Citric acid, on the other hand does. The major reason for this is that acetic acid is volatile and will be driven off the fabric before curing temperatures are reached. Citric acid is non-volatile at curing temperatures therefore it stays where it is needed to function as a crosslinking catalyst. Acetic acid's volatility is an asset when it come to adjusting fabric and bath pH, the acid is gone before temperature becomes high enough to
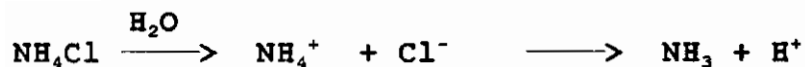
damage cellulose fibers.

1. Latent Acids

Neutral salts of weak bases (amines) and strong acids will dissociate under certain conditions to become sources of protons.   The ease with which these compounds dissociate is related to the ionization constant (K_b) of the base. The weaker the base, the easier it is to liberate the conjugate acid. Amine hydrochlorides are particularly useful neutral salts that function as latent catalyst in DP finishing. They will dissociate to liberate hydrochloric acid under curing conditions. Ammonium salts also function as latent catalyst. Ammonium chloride, ammonium sulfate, ammonium phosphate are sources of ammonium ions in water. Under certain conditions, the ammonium ion will dissociate into ammonia and a proton. Under curing condition, some of the ammonia is lost into the atmosphere and the system become acidic. Another mechanism involved with ammonium salts becoming acidic is their ability to react with formaldehyde to form trimethyl amine hydrochloride and formic acid.   The reaction intermediate in this transition is methyleneimine hydrochloride. Both the methyleneimine and trimethylamine are weak bases so the dissociation of their respective hydrochlorides occurs easily.   The reaction with formaldehyde can be followed with a pH meter. Solutions of ammonium chloride are neutral and remain so even after boiling for several hours. However if formaldehyde is present, the pH will begin to drop. With time the solution becomes highly acidic. The reactions schemes are shown in the box below.

a. Dissociation & Amine Hydrochlorides

$$R-NH_3^+Cl^- \longrightarrow R-NH_2 + HCl$$
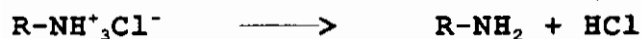
b.   Dissociation of Ammonium Chloride

$$NH_4Cl \xrightarrow{H_2O} NH_4^+ + Cl^- \longrightarrow NH_3 + H^+$$

c. Reaction of Ammonia with Formaldehyde

$$NH_4Cl + CH_2O \longrightarrow HOCH_2NH_2 \cdot HCl \longrightarrow HOCH_2NH_2 + HCl$$

$$HOCH_2NH_2 \cdot HCl + CH_2O \longrightarrow CH_3NH_2 \cdot HCl + HCOOH$$
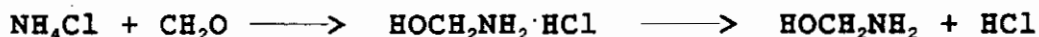
B. Lewis Acids

Metal ions that have unfilled orbitals capable of accepting a pair of electrons function as Lewis acids. Mg^{++}, Zn^{++}, Al^{+++} and Fe^{+++} are examples of metal ions that can function as Lewis acids. True Lewis acid maintain a neutral pH when in

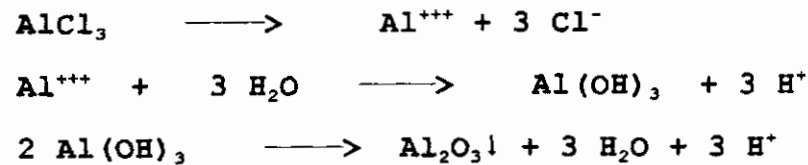solution, however, some metal ions form soluble hydrates with water. When these hydrates polymerize to form an insoluble oxide, they leave protons behind (Bronsted acid). For example, when aluminum chloride is dissolved in water, the solution will develop a measurable acidity on standing. This comes about because aluminum ions form partial covalent bonds with water to form aluminum hydroxide. At this point all of the ionic species are in equilibrium so the solution's pH is neutral. Aluminum hydroxide, in time, will precipitate as aluminum oxide. When this happens, the neutral balance of all the ionic species is disrupted because the hydroxyl ions supplied by the water molecules have been consumed, leaving behind their corresponding protons.

1. True Lewis Acids

$$M^{++} \quad + \quad \overset{..}{:}O{-}H \quad \longrightarrow \quad M\overset{+}{:}O{-}H$$
$$\qquad\qquad\qquad R \qquad\qquad\qquad\qquad\qquad R$$

2. Metal Hydrates

$$AlCl_3 \quad \longrightarrow \quad Al^{+++} + 3\ Cl^-$$

$$Al^{+++} \quad + \quad 3\ H_2O \quad \longrightarrow \quad Al(OH)_3 \ + \ 3\ H^+$$

$$2\ Al(OH)_3 \quad \longrightarrow \quad Al_2O_3\downarrow + 3\ H_2O + 3\ H^+$$

3. Important Considerations

Solutions of magnesium chloride do not develop measurable acidity on standing. Magnesium chloride therefore acts like a classical Lewis acid. The reason for this is that magnesium does not form partial covalent bonds with hydroxyl ions unless the pH is very high. Aluminum, ferric and chromic salts are the most acidic. They are much stronger catalyst and are prone to degrade cellulose as well. Zinc salts are in between aluminum and magnesium. Zinc salts are good curing catalyst. Unfortunately the discharge of Zn in waste water is frowned upon. Magnesium is considered the mildest of the effective Lewis acids.

C. Specific Catalyst and their Use

1. Free Acids

Mineral acids, citric, tartaric are used when faster cures are wanted. They are also effective on hard to cure reactants or when curing at lower temperature. Disadvantages are reduced bath stability, damage to the fiber and increased formaldehyde release.

2. Latent Acids

Ammonium chloride, amine hydrochloride are used to cure U / F and M/F resins when fast, low temperature curing is wanted. Disadvantages are fabric pH is acidic. Ammonium salts give rise to trimethyl amine, fish odor.

3. Metal Salts

Magnesium chloride is a mild catalyst that can be used at high temperatures. It is non-corrosive and presents the fewest side reaction problems, e.g. shade change, fiber damage etc. Zinc nitrate and zinc chloride are more reactive than magnesium chloride. Zinc presents effluent disposal problems. Zinc nitrate cause dye shade changes.

4. Hot Catalyst

Usually a mixture of magnesium chloride and a source of proton such as citric acid, aluminum chloride, aluminum sulfate or ammonium chloride. These are used when stronger catalyst are needed.

D. Buffers and Alkalinity

1. Buffers

Buffers are salts of weak acids or bases that maintains a solution's pH at a constant level. Spurious amounts of H^+ or OH^- ions are neutralized, and a constant level of each is maintained by the equilibrium established by ionization constants of the buffering agents. The net effect is that buffers will neutralize equivalent amounts of catalyst. Some commercial DMDHEU solutions will have buffers added to them. This is done to overcome certain problems that may exist on specific fabrics i.e. shade changes, poor lightfastness, yellowing etc. When buffered resins are used in place of unbuffered resins, the catalyst ratio must be increased to compensate for the amount that will be consumed by the buffer.

2. Alkalinity

Alkalinity is defined as salts that consume acids. They are the salts formed when a strong base is neutralized by a weak acid e.g sodium acetate. Fabric preparation is a source of problems associated with alkalinity. Mercerized, causticized and caustic scoured fabrics are neutralized with acetic acid to control the final fabric pH. If the amount of NaOH left on the cloth varies when it reaches the acetic acid bath, the amount of sodium acetate formed by the neutralization reaction will also vary even though the fabric pH appears to be consistant. Alkalinity and buffers consume acid catalyst, therefore both must be consistently controlled to give

consistently performing finished fabric. Fabric alkalinity can be determined analytically. If this value is inconsistent throughout the fabric, one can expect inconsistent performance of the finish.


VIII. CHEMICAL MECHANISMS

The chemistry associated with durable press finishing can be broken into three separate steps. 1. Reaction of amido compounds with HCHO to form N-methylol compounds. 2. Alkylation of N-methylol compounds. 3. Stability of the alkylated linkage. One can considers the cellulose crosslink to be identical in nature to the lower alcohol alkylates. The performance of the various products that make up this family of finishes can be summarized and explained by examining the underlying reaction mechanisms. This section is devoted to understanding the mechanisms.
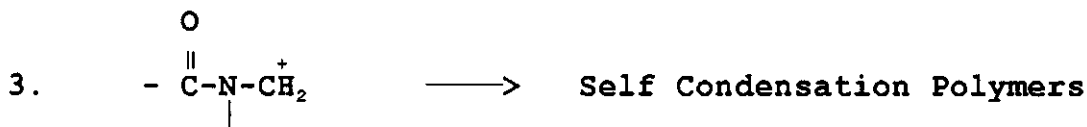
A. Methylolation

The reaction of amido compounds with HCHO can be catalyzed with acids or base. When base is used, the reaction terminates at the N-CH_2OH, however, with acids the reaction can continue and form crosslinked polymers reducing the usefulness of the reactant.

1. Base Catalyzed Methylolation
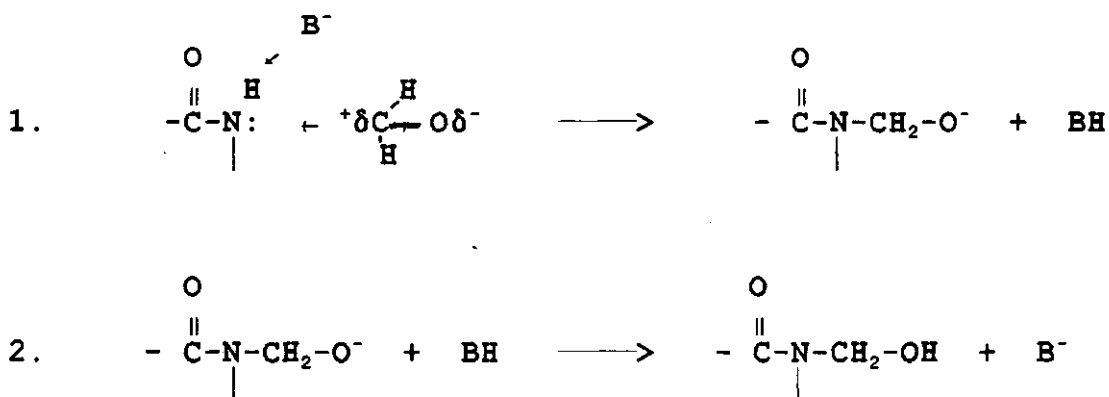
Equation 1 shows the base catalyst attacking the N-H group as the carbonyl group in HCHO approaches the unshared electrons on the nitrogen atom. In equation 2, the transition state abstracts a hydrogen from the BH group regenerating the base ion. In so doing, the formation of the N-methylol is completed. The only other reactions going on are the equilibriums involved in each phase.

2. Acid Catalyzed Methylolation

1.
$$-\overset{O}{\overset{\|}{C}}-\overset{}{\underset{|}{N}}: \quad +\; \overset{H^+}{\overset{\nearrow}{\underset{\underset{H}{\overset{}{\swarrow}}}{^+\delta C}}} \overset{H^+}{\longleftarrow} O\delta^- \quad \longrightarrow \quad -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-OH$$

2.
$$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2 \rightarrow \overset{H^+}{\overset{\swarrow}{OH}} \quad \longrightarrow \quad -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 \;+\; HOH \quad \longleftrightarrow \quad -\overset{O}{\overset{\|}{C}}-\overset{+}{\underset{|}{N}}=CH_2$$

3.
$$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 \quad \longrightarrow \quad \textbf{Self Condensation Polymers}$$
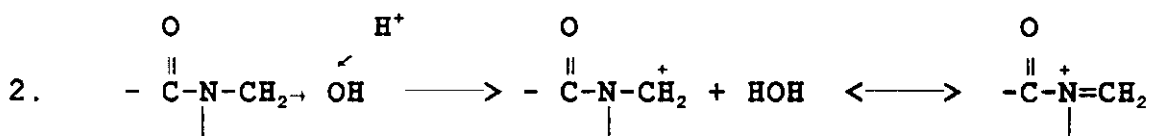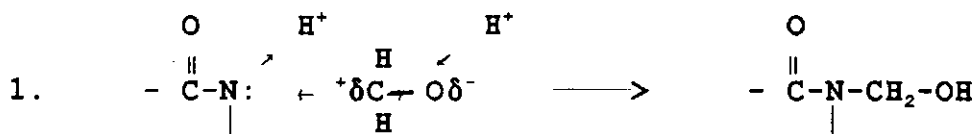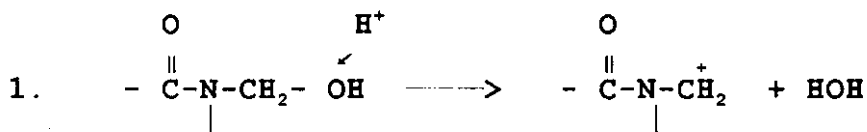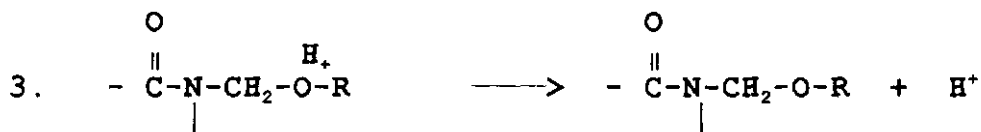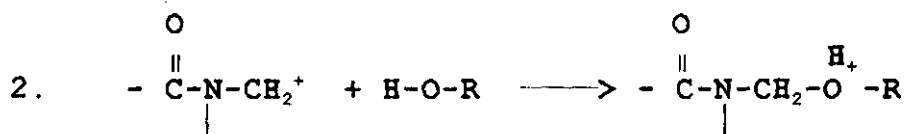
Equation 1 shows the catalyst protonating the carbonyl oxygen in HCHO. As the protonated molecule approaches nitrogen's unshared electrons, the N-H bond breaks, regenerating a proton. This completes the formation of the N-methylol group. Equation 2 shows that protons can initiate a second reaction. A molecule of water is split off creating a carbo-cation which is stabilized by resonance structures shown in the transition equilibrium. Equation 3 indicates that the carbo-cation is capable of undergoing self condensation and creates polymers linked by methylene bridges.

B. Alkylation of N-Methylol Compounds

The alkylation reactions of N-methylol compounds are continuations of the reactions described in the acid catalyzed methylolation mechanism. The carbo-cation is capable of reacting with alcohols as well as self-condensing with N-H groups. When the alcohols are lower alcohols such as methanol or diethylene glycol, alkoxylated modified reactants are created. If the alcohol is a cellulose hydroxyl, cross links are formed. Both protons and Lewis acids promote the reaction.

1. Proton Activated Alkylation

1.
$$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-CH_2-\overset{H^+}{\overset{\swarrow}{OH}} \quad -\!-\!-\!\longrightarrow \quad -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{+}{C}H_2 \;+\; HOH$$

$$2. \quad -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2^+ \;+\; H\text{-}O\text{-}R \;\longrightarrow\; -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-\overset{H_+}{O}\text{-}R$$

$$3. \quad -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-\overset{H_+}{O}\text{-}R \;\longrightarrow\; -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-O\text{-}R \;+\; H^+$$
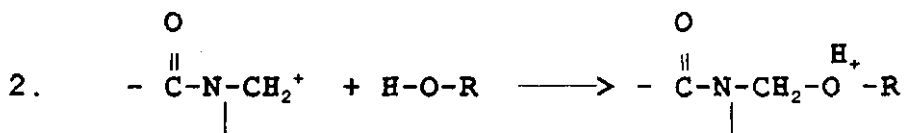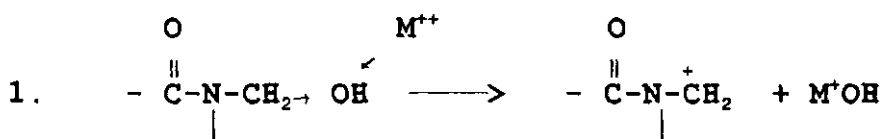
In equation 1, the -OH group on the N-methylol is protonated to form the transition state which splits water to become a carbo-cation. Equation 2 shows the carbo-cation attacking a R-OH group to form a transition state In equation 3, a proton is ejected and the alkylated reaction product is formed. The original amount of acid is still present at the end of the reaction. This acidity is responsible for side reactions, e.g. tendering the fiber and promoting hydrolysis of the cross-link.

Lewis acids can also promote alkylation, however, higher temperatures needed to drive the reaction. For this reason, these catalyst are only used for crosslinking cellulose. There is one other difference that should be noted. The Lewis acids are neutral to start with and leave the fabric neutral after the reaction is completed. This minimized side reactions such as fiber tendering and hydrolysis of the crosslink, making them the preferred catalyst for DP finishes.

2. Cellulose Crosslinking with Lewis Acids

$$1. \quad -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2 \!\rightarrow\! \overset{M^{++}}{OH} \;\longrightarrow\; -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-\overset{+}{C}H_2 \;+\; M^+OH$$

$$2. \quad -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2^+ \;+\; H\text{-}O\text{-}R \;\longrightarrow\; -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-\overset{H_+}{O}\text{-}R$$

$$3. \quad -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-O\text{-}R \;\longrightarrow\; -\overset{\overset{\textstyle O}{\|}}{\underset{|}{C}}-N-CH_2-O\text{-}R \;+\; H^+$$

$$4. \quad M^+OH \;+\; H^+ \;\longrightarrow\; M^{++} \;+\; H_2O$$

Equation 1 shows formation of a transition state metal complex where the metal ion attaches to the pair of electrons on the oxygen atom of the -OH group splitting out metal hydroxide and forming the carbo-cation. In equations 2 and 3, the reaction follows the same path as was postulated for proton catalysis. Equation 3 shows a proton being liberated from the crosslinking reaction. This proton is now available to function as an active catalyst in a manner identical to the mechanism depicted for proton catalysis. Both Lewis acid and protons are available to catalyze crosslinking. The activity of the proton is moderated (buffered) by neutralization with the metal hydroxide that was formed in equation 1. The stoichiometry is such that one equivalent of base is formed for each proton so the fabric should remain neutral after curing. Since it takes elevated temperatures to activate Lewis acid catalysis, nothing really happens until curing conditions are reached. When the fabric cools down, the remaining protons are neutralized and the fabric pH remains neutral, minimizing any side reactions.
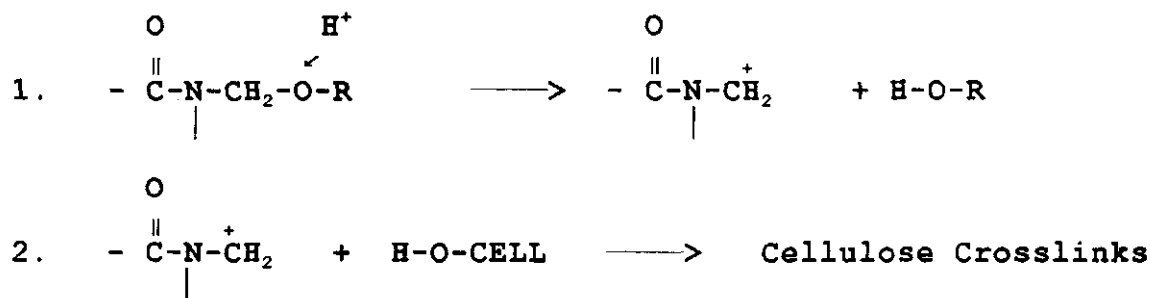
From the mechanisms shown, it is readily apparent why most finishers prefer to use Lewis acid catalysts. Magnesium chloride has become the preferred catalyst for the following reasons: 1. Alone, magnesium chloride is the least damaging to cotton. It does not affect fabric strength as much as other catalysts. 2. It does not affect dye shade or lightfastness of direct and fiber reactive dyes. 3. It is not a particularly active catalyst and may have to be supplemented with additional time or temperature of cure. 4. It can be made more active by blending in a small amount of a "hot catalyst". Citric acid, ammonium chloride and aluminum salts are added to magnesium chloride to make a class called *"Hot Mug Chloride"*.

C. Reaction of Alkoxylated Products

Alkoxylated derivatives of N-methylol compounds can be viewed either as those derived from the lower alcohols or the cellulose crosslink itself. Both alkoxylates are capable of undergoing acid catalyzed reactions. For the lower alcohols, the reactions are similar to the N-methylol and lead to the same cellulose crosslinks. The value of using the lower alcohol alkoxylates is textile fabrics with lower HCHO release. For the crosslink, the reactions lead to de-crosslinking and loss of DP properties. The latter is responsible for laundry durability and is referred to as hydrolysis stability. The crosslinks eventually revert back to the original starting materials.

Not all alkoxy groups have the same rate of reaction. For example isopropyl groups are good leaving groups so the rate of reaction of isopropoxy N-methylol are very close to that of the hydroxymethyl. On the other hand, methyl and diethylene glycol are poor leaving groups meaning that they are more stable. Because of this, they require more stringent curing conditions, e.g. stronger catalyst /higher temperature cures. Also because they are more stable, the pendent groups remaining after cure are less prone to decompose back and contribute to HCHO release.

1. Crosslinking with Alkoxykated N-Methylol Compounds

$$1. \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-CH_2-O-R \quad \xrightarrow{\;H^+\;} \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-\overset{+}{C}H_2 \quad + \quad H-O-R$$

$$2. \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-\overset{+}{C}H_2 \quad + \quad H-O-CELL \quad \longrightarrow \quad \text{Cellulose Crosslinks}$$
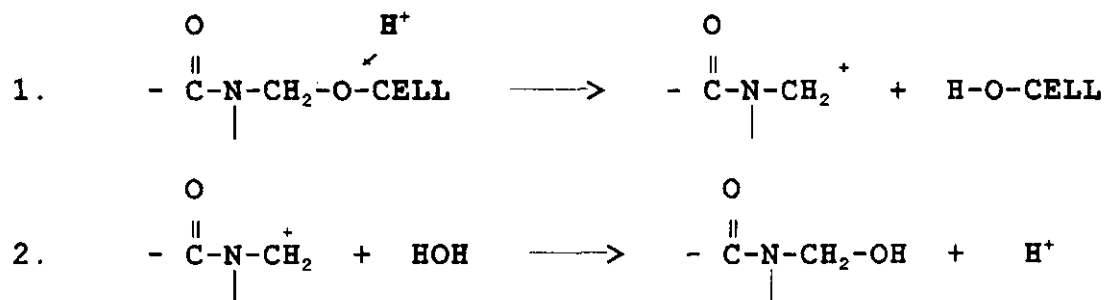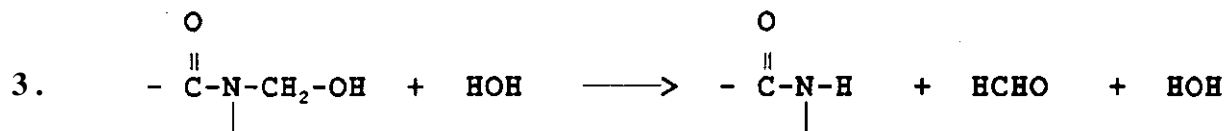
Equation 1 shows catalyst complexing with the oxygen atom, splitting off alcohol to form a carbo-cation. Since this is done under the influence of temperature, the lower alcohol is volatilized favoring the formation of the carbo-cation. In equation 2, the carbo-cation partakes of the reactions leading to cellulose linkages. The rate of reaction is influenced by the alcohol leaving group. Methyl and diethylene glycol are poor leaving groups requiring stronger catalyst and curing conditions. Because of this, pendant groups that have not entered into a cellulose crosslink are more stable and therefore less prone to contribute to HCHO release.

D. Stability of Crosslink to Laundering

The stability of the crosslinks to repeated laundering can also be considered a manifestation of alkoxy reactivity. In this case the alkoxy linkage is hydrolyzed with water. the hydrolysis reaction proceeds much faster under acidic conditions and at higher laundry temperatures. These conditions are met when goods are laundered under commercial laundry procedures. Another factor to consider is the chemical nature of the reactant. Carbamates and DMDHEU crosslinks are much more durable than DMEU and U/F crosslinks. The ability/inability of the structure to delocalize the electrons on the amido nitrogen influences this relationship. As is seen below, after the cellulose linkage is broken, the reaction can continue in the reverse direction eventually reverting back to starting materials.

1. Hydrolysis of Cellulose Crosslinks

$$1. \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-CH_2-O-CELL \quad \xrightarrow{\;H^+\;} \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-CH_2^+ \quad + \quad H-O-CELL$$

$$2. \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-\overset{+}{C}H_2 \quad + \quad HOH \quad \longrightarrow \quad -\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{|}{\underset{|}{N}}-CH_2-OH \quad + \quad H^+$$

$$3. \quad -\overset{\overset{\textstyle O}{\|}}{C}-\underset{|}{N}-CH_2-OH \quad + \quad HOH \quad \longrightarrow \quad -\overset{\overset{\textstyle O}{\|}}{C}-\underset{|}{N}-H \quad + \quad HCHO \quad + \quad HOH$$

IX. FABRIC PROPERTIES

Changes in fabric properties are related to the number of crosslinks imparted to the fiber. Improvements in wrinkle recovery and DP ratings, and reduction in residual shrinkage are proportional to the number of crosslinks. Losses in strength and abrasion resistance are also related to the number of crosslinks and to the degree of cellulose damage by the acid catalyst. The number of cross-links is influenced by the add-on, (the amount of reagent deposited on the fabric) and the degree of curing (percentage of the amount applied that become actual cross-links). The degree of curing is influenced by the chemical structure of the reagent, the type of catalyst, the ratio of catalyst to resin, the presence of buffers and the time and temperature of cure.

A. Durable Press Performance versus Add-on

The most obvious way to increase DP performance is to add more finish to the fabric. The relationships between fabric performance and add-on of DMDHEU can be seen in figures 46. Figure 46 shows that both wet and dry wrinkle recovery improve with increasing concentration of reagent in the bath. Also shown is the relationship between DP rating (fabric smoothness) and add-on.

1. Important Points

There is a sharp increase in wrinkle recovery with increasing resin level. As bath concentration approaches 7 % DMDHEU (15-20 % commercial product in bath), wrinkle recovery and DP Rating begin to levels-off. Above this level, the rate of improvement is less rapid and only modest gains are obtained with massive amounts of resin.

Figure 15. Relationship of DP Performance versus DMDHEU Add-on

Wet and Dry   CRA   DP Ratings

% Commercial DMDHEU in Bath
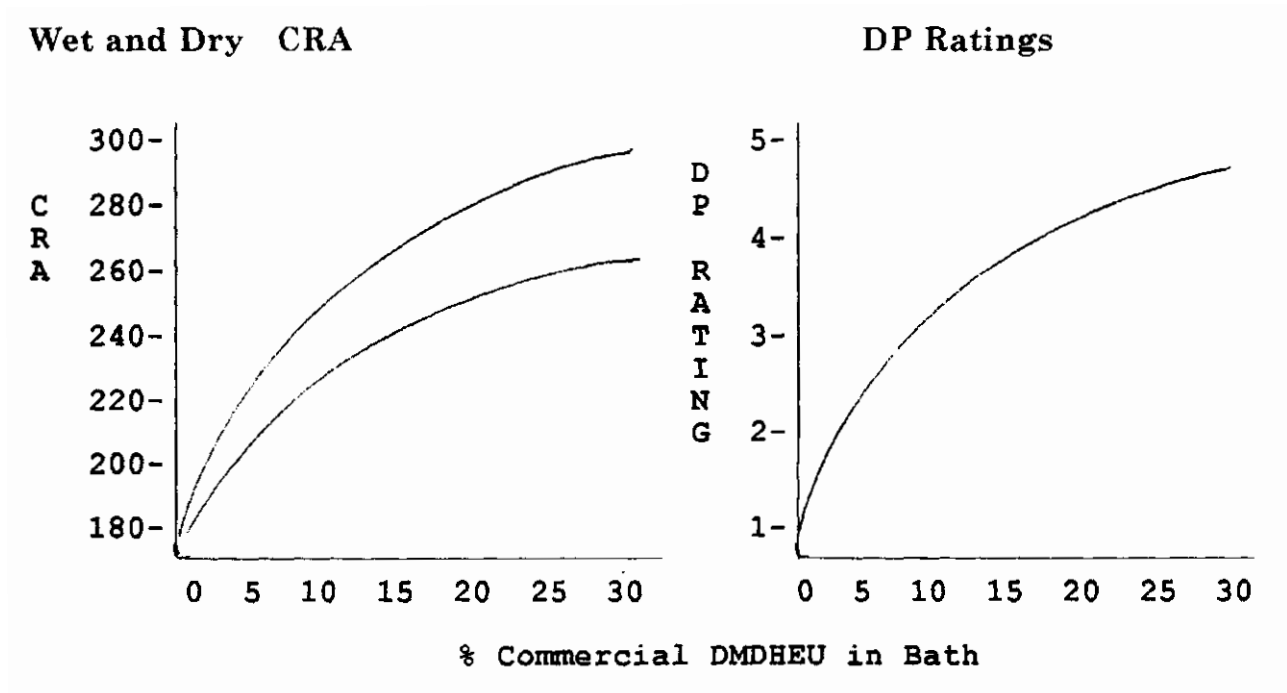
B. Effectiveness of Different Crosslinkers

How many cross-links does it take to obtain optimum performance? Are some cross-linkers more effective than others? The answer to these questions can be seen in figure 47. Figure 47 is a composite chart where wrinkle recovery is plotted against the concentration (expressed as millimoles of reagent per 100 grams of fabric) of a number of different reagents. It is interesting to note that one curve fits all the data points. Wrinkle recover levels-off at 2 to 2.5 millimoles of reagent. While DMDHEU was not included in figure 16, 6 to 7% weight add-on calculates to be 2 to 2.5 millimoles per 100 grams of fabric and so it too follows the same general trends.

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Figure 16. Crease Recovery versus Resin Concentration
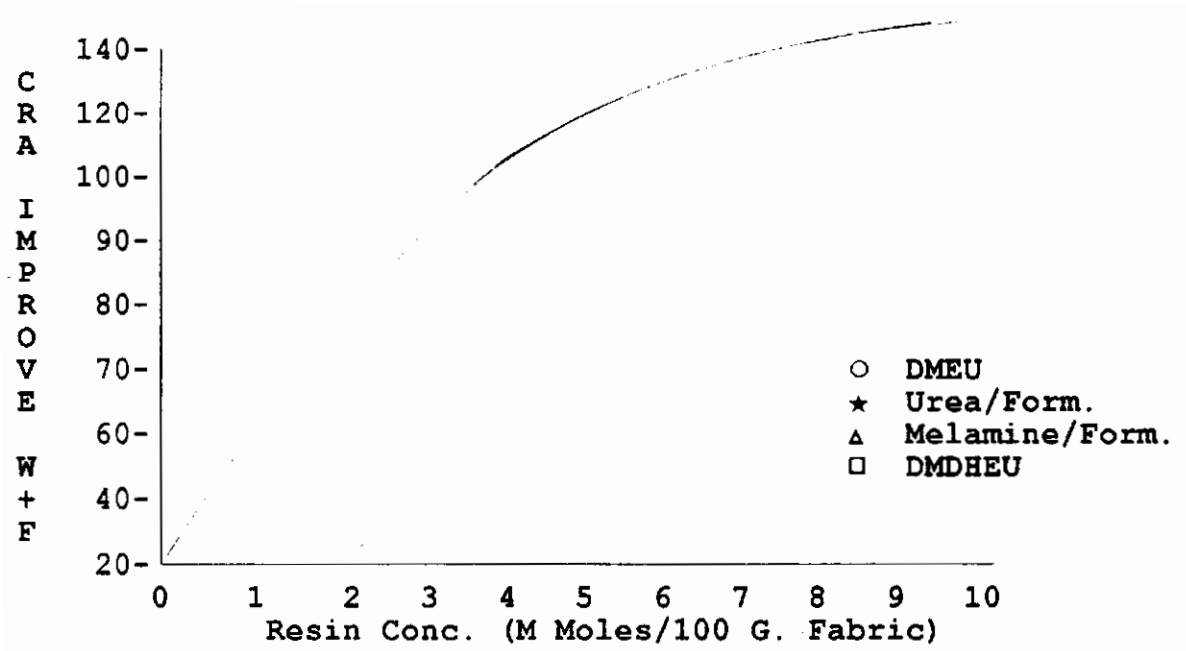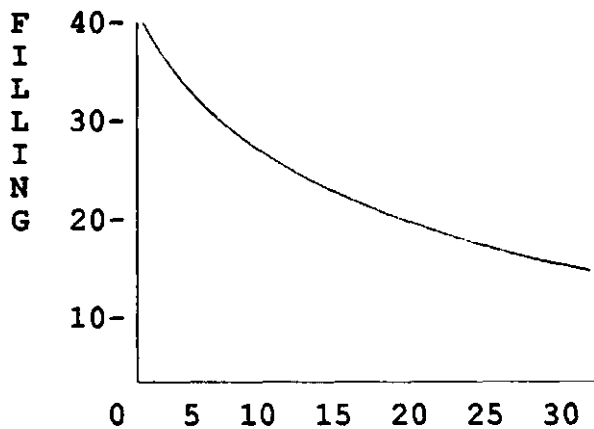

C Tensile, Tear and Abrasion Resistance

Losses in tensile, tear and abrasion resistance in 100% cotton are directly related to the number of cross-links, The relationship between abrasion resistance, tensile and tear strength versus resin add-on is seen in figure 48. The trends established in these curves mirror those seen in figures 46 and 47, except these are going the opposite direction. The steep part of each curve appears to level off at 15 % commercial DMDHEU (7 % bath solids) in the bath. Improved DP properties also tend to level off at this concentration. Strength and abrasion resistance losses will amount to between 30 to 60 % of the original fabric values.
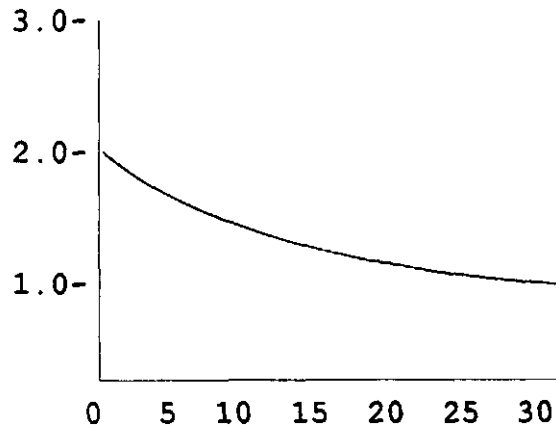
Figure 17. Physical Properties versus Add-On
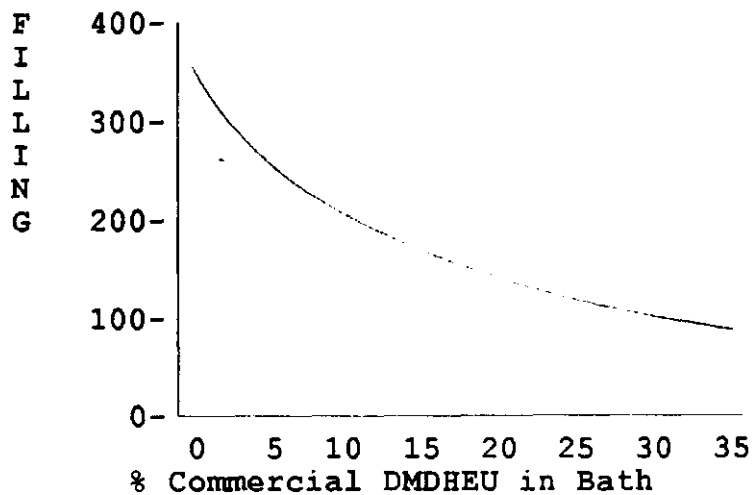
Fabric Strength

<u>Tensile</u> (Lbs)

<u>Tear</u> (Lbs)

```
F   40-
I
L
L   30-
I
N
G   20-

    10-


     0   5   10  15  20  25  30
```
```
3.0-



2.0-




1.0-


     0   5   10  15  20  25  30
```

% Commercial DMDHEU in Bath

Abrasion Resistance

<u>Stoll Flex,   Cycles</u>

```
F   400-
I
L
L   300-
I
N
G   200-


    100-



      0-
         0   5   10  15  20  25  30  35
```

% Commercial DMDHEU in Bath

1. Points to Consider

1. Losses in physical properties due to rigidification of the fiber are unavoidable. Losses in strength due to cross-links can be recovered by a mild acid strip. Boiling for one hour in 1% phosphoric acid buffered with urea will remove almost all cross-links and restore about 70% of the lost strength. 2. Catalyst damage also lead to losses in physical properties. That portion of the loss not recovered by the acid strip was the damage of the cellulose backbone by the catalyst. Ways to minimize this damage is to avoid overly strong catalyst and to avoid over curing. 3. Tensile strength is directly proportional to fiber damage. Tearing strength, however, is affected by fiber damage and fabric stiffness. Stiff fabrics tear more easily than softer ones even if the fiber strength is not lowered. 4. From a practical point of view, the exact formulation and application conditions are determined by trial and error, first at a laboratory scale and finally under production conditions. 5. Commercially functional 100% cotton fabrics with improved DP performance can be produced by carefully balancing all of the variables. 6. In those cases where the finished fabric is too weak to function in its intended end-use, serviceable fabrics can still be made by re-engineering the greige fabric with the loss in physical properties in mind. This might include over-constructing the 100% cotton fabric or to blend in yarn strengthening fibers such as polyester or nylon.

D. Crease Recovery versus Curing Temperature

The relationship between crease recovery and temperature of cure is shown in figure 49. The temperature required to obtain cross-linking is very much a function of the reactant structure. The reactant structures included in figure 18 fall into two groups, easy to cure and hard to cure. U/F and DMEU fall into the easy to cure category. Curing starts as soon as the fabric is dry. These reagents would not be suitable for delay cure where one needs the resin to remain unreacted until after the garment is made and pressed. DMDHEU and carbamates fall in the hard to cure category where curing temperatures must exceed 130° C. DMDHEU has been successfully used in delay cure applications. The fabric can be handled on commercial ranges where nearly all of the resin is still uncured after drying.

Figure 18. Crease Recovery versus Temperature of Cure and Resin Type
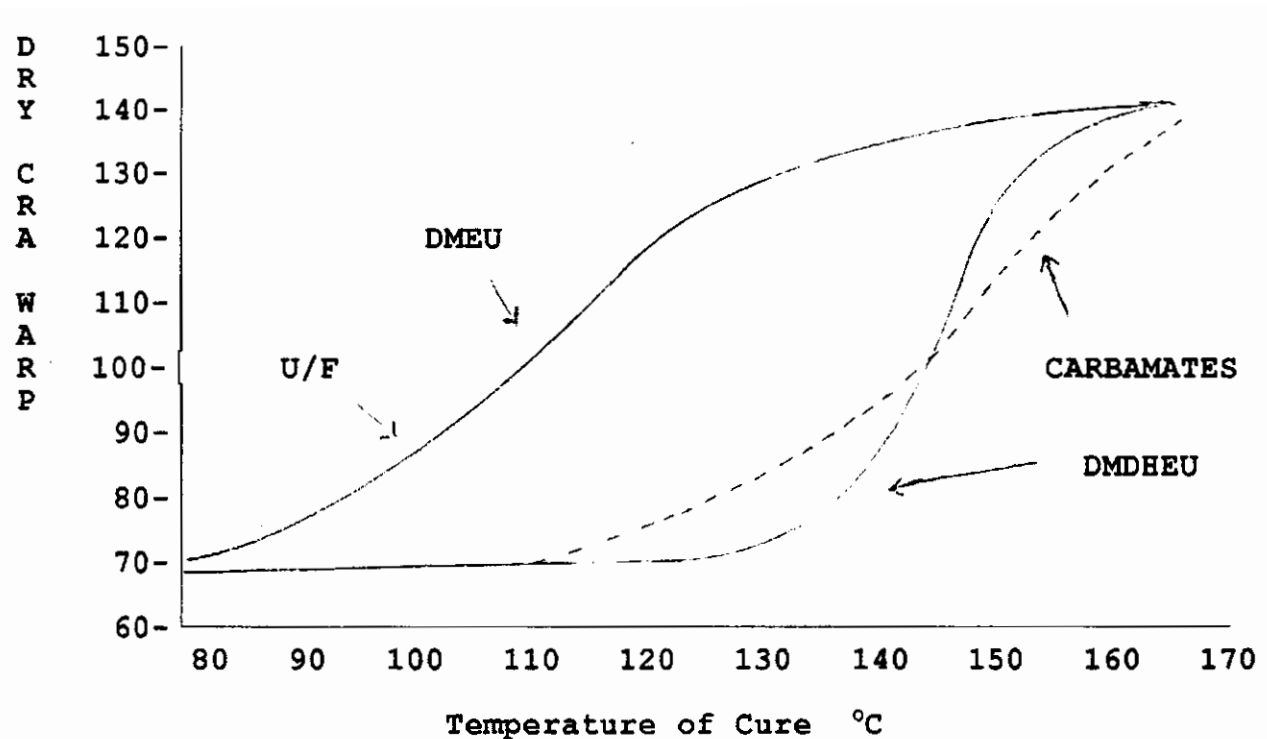
1. Points to Consider

1. DMEU and U/F will begin curing as soon as the fabric is dry. Longer exposure time to lower curing temperatures will eventually increase the total amount of crosslinks. 2. DHEU and Carbamates, however, require fabric temperatures to reach 13 to 150° C. before crosslinking takes place. Longer times below this threshold temperature will not induce crosslinking. 3. Some commercial processes are run at what might appear to be unrealistically high curing temperatures, about 420° F. These processes are run at very high linear speeds. Since drying and curing are accomplished at the same temperature setting, the actual fabric temperature does not reach the air temperature until all the water is gone. It is unlikely that the fabric temperature ever reaches the oven setting because of the short residence time. This technique is called *Flash Curing*. There is danger of overcuring should the range slow down or stop for any reason.

E. Other Fabric Properties

1. Shrinkage

Much of a fabric's residual shrinkage is the result of tensions applied to the fabric during wet processing. Some woven fabrics will shrink both in width and length during preparation and dyeing. These must be pulled out to maintain width and yardage yields. These stresses add to residual shrinkage. Knit goods are inherently wrinkle resistant; however, some are pulled out to a width wider than the fabric's knitted gauge and this too adds to residual shrinkage. Much of the stress induced shrinkage can be eliminated by mechanically compacting the fabric. Compacting will result in reduced yardage yields. Crosslinking also reduces fabric shrinkage. For this reason, chemical stabilization of cellulosic fabric has real economic value. Without resin finishes, the fabrics described here will have excessively high residual shrinkage. Fortunately, a good resin finish will stabilize the fabric and reduce the residual shrinkage to less than 2%. The degree of stabilization required by chemical finishes will depend on the fabric's previous history. In some cases, much more finish is applied than one would reasonably consider simply to keep residual shrinkage within the required tolerances. In these cases, reduced shrinkage is the real reason for DP finishes rather than wrinkle resistance or no-iron features.
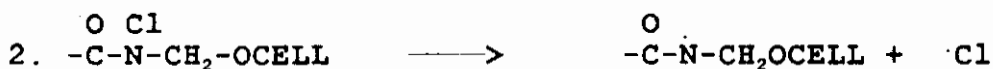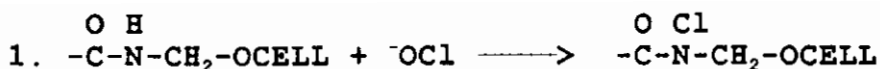
2. Yellowing

Yellowing of DP finished fabrics can be caused by a number of conditions. For example, excessive curing temperatures and /or excessive catalyst will scorch cellulosic fabrics. Some reactants have color bodies that cause yellowing. Usually nitrogenous compounds discolor with heat. Buffers are often added to commercial finishes to combat yellowing problems.

3. Chlorine Resistance

The term chlorine resistance encompasses two problems, yellowing of fabric by the bleach and tendering (strength loss). Nitrogenous finishes will react with hypochlorite bleaches to form a reaction product (chloramides) that decomposes with heat. These chloramides liberate hydrochloric acid which degrade cellulose. Fabric develops the characteristic scorched look and the fibers become very weak. Residual -NH groups are responsible for the formation of chloramides. Resins and reactants with residual -NH groups and cross-links that hydrolyze in laundering are especially prone to pick-up chlorine from a bleach bath. Both tendering and scorching are caused by the breakdown of the chloramide with heat to form hydrochloric acid. The reactions can be written as follows:

a. Mechanism of Chlorine Damage

```
         O  H                               O  Cl
1. -C-N-CH₂-OCELL + ⁻OCl  ─────>   -C-N-CH₂-OCELL


        O  Cl                              O
2. -C-N-CH₂-OCELL        ─────>     -C-N-CH₂OCELL +   ·Cl


3.  ·Cl  +  CELLULOSE  ─────>   HCl  +  degraded cellulose
```

4. Fabric Odor

Finished fabrics are beset by two types of odors, fish odor and formaldehyde odors. Some overcured fabrics develop an unpleasant burnt or fish odor. Fish odor is trimethyl amine which is produced by the reaction of free formaldehyde with ammonia. Overcuring causes urea based chemicals to break down into ammonia and carbon dioxide so this is one source of ammonia. NH_4Cl is a popular catalyst and is also a source of ammonia. The reactions that take place are believed to be:

$$NH_3 + 6\ CH_2O \longrightarrow (CH_3)_3N + 3\ HCOOH$$
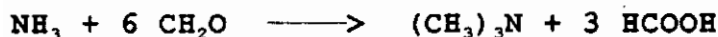
While trimethyl amine is a volatile gas, its formate salt is not. It will be trapped in the fabric and dissociate very slowly with time and humidity. Oftentimes, consumer products (drapes, comforters etc.) are shipped in sealed plastic bags. When these are first opened, a mal-odor emanates from the cloth. With time, in the open, the odor will disappear. The mal-odor is a combination of trimethyl amine and formaldehyde. Formaldehyde causes eyes to water and nasal irritation.

A simple way of checking for fish odor is to place several drops of a sodium carbonate solution on the fabric, wad it up in your hands and rub it vigorously. Any amine odor will easily be detected by smell. Scouring the fabric with alkali will permanently remove this type of odor.

X. REFERENCES