CHAPTER IV
PRACTICAL ASPECTS AND ADVANTAGES
OF THE PRESENT CATALYTIC SYSTEM.

Introduction

The different methods of application of cross-linking agents to cellulosic materials as practised today, can be classified mainly into three groups as given below.

(1) The pad-dry-cure process in which the reaction between cellulose and cross-linking agent is brought about at high temperatures used in the curing stage under conditions in which the cellulosic fibres are in a collapsed and deswollen state.

(2) The wet-cure process which takes place at room temperature on wet or swollen fibres. An example of this is the "Form W" process (1). However, the wet-cure process is very rarely employed nowadays, except in conjunction with dry recovery processes: as in Teb-X-Cel process (2); even this combination is seldom practised.

(3) The "moist cure" process also operates at room temperature but the fabric only contains a prescribed amount of residual moisture. Under these conditions the fibres are very slightly swollen. The "mild cure" process which is more common in the U.S.A is similar to the moist cure process which is practised in Europe.
In the conventional pad-dry-cure process, there is a combination of molecular entanglements and hydrogen bonds at the high temperatures used in curing (150° and above) under which conditions, strictly speaking, the fabric is "over-heated and over-dried with the result that it is set in an unnatural and deformed state" (3). Consequently the energy to rupture is reduced which is reflected by the excessive strength losses.

The wet cure processes on the other hand, are operated at room temperature; the fabric is therefore neither over-heated or over-dried. The cellulose structure under these conditions is somewhat distended and somewhat disrupted. The fibre is set in an unnatural and deformed state although in a quite different manner from that produced by the pad-dry-cure process. The process therefore, brings about loss in strength properties of the fabric, in spite of the fact that the reaction takes place at room temperature.

The moist cure process has been studied extensively by Liljemark et al (4) who have cross-linked cellulose at 5% moisture regain using acid catalysts. They claim better wash and wear and strength properties by this technique than those obtained using conventional pad-dry-cure method. The mild cure process which is a modification of the moist cure process has been developed by the Southern Regional
Research Laboratory of U.S.A and it is claimed that the properties of cotton fabrics finished by this process are essentially the same as those treated by the conventional pad-dry-cure technique except that a higher level of wet crease recovery is produced (5).

Marsh (6) has reviewed the literature on moist cure methods. He has pointed out that the superior smooth appearance of fabrics cross-linked in a slightly swollen or damp condition is caused by the uniform distribution of chemical bonds. If bond distribution is not uniform the fibre will swell in certain critical uncross-linked areas and during the drying period wrinkles may be set by formation of hydrogen bonds. Also, the better strength properties claimed by this process may be the result of a more uniform product as distinct from one with excessive bonding in certain areas which can unduly weaken the whole structure. With the moist cure process, "the amount of swelling is small indeed and it seems probable that the benefits are associated with hydrogen bond break-down before the onset of swelling to any appreciable extent. Thus hydrogen bonds are replaced by chemical bonds and the cellulose is reinforced at its most susceptible point but under conditions which produce a better distribution of cross-links resulting in a more uniform product" (6).
The catalytic system described in the previous chapters has the following characteristics: (i) The cross-linking reaction is promoted at less severe conditions of temperature (ii) Considerable extent of the cross-linking reaction is achieved at the drying stage of the fabric when the fabric attains its natural moisture content (6 – 8%) resulting in the development of wet crease recovery predominantly.

These properties of the present catalytic system have been investigated in more detail, and the various advantages accrued have been assessed and compared to those of conventional pad-dry-cure method using inorganic metal salts as catalysts.

Experimental

Materials: Desized, scoured, bleached and mercerised cotton fabrics were used for the experiments. These were: (i) Cotton poplin 33/38 yarn count with 128/78 end/picks per inch (ii) cotton coating 20/14 yarn count with 84/48 ends/picks per inch.

Fabric properties: The crease recovery angles and tensile strength properties were measured as described in Chapter II.

Flex abrasion: This was measured on a Stoll Quarter-master Universal Abrasion Tester using recommended head and bar weights (7).
Storage stability: The storage stability of the dried (sensitised) fabric samples in terms of their crease recovery properties was assessed by storing them for various intervals of time in airtight desiccators containing saturated solutions of appropriate salts to maintain the required humidity (25, 50 or 75%) at two different temperatures viz. 25° and 50°.

Fabric treatments: The various cross-linking agents used for fabric treatments were the following reagents having a purity of 98-99% based on their nitrogen and formaldehyde analyses.

- Dimethylol Ethylene Urea (DMEU)
- Dimethylol Dihydroxy Ethylene Urea (DMDHEU)
- Dimethylol Methyl Carbamate (DMMC)
- Dimethylol Urea (DMU)

The methods of treatment were the same as given in Chapter II unless otherwise specified.

Results and Discussion

With the present catalytic system the cross-linking reaction can be promoted at much lower temperatures. Therefore a comparatively lower curing temperature (e.g. 125°) can be employed without sacrificing the efficiency of resin curing. This is illustrated in Fig. 14 where the improvement of dry crease recovery angles at four different curing temperatures, viz. 125°, 135°, 150° and 180° are shown when (a) magnesium
Fig. 14. Effect of time at different curing temperatures using (a) MgCl₂·6H₂O and (b) MgCl₂·6H₂O in combination with Na-Mg-citrate as catalysts.
chloride alone and (b) magnesium chloride in combination with sodium-magnesium-citrate are used as catalysts. It is seen that at all the curing temperatures studied, the efficiency of the curing in terms of improvement in dry crease recovery is higher for the combined catalyst than that of magnesium chloride alone.

With the use of the combined catalysts, the cross-linking reaction can be initiated at the drying stage of the fabric when the fabric attains its natural moisture content of 6 - 8%. Consequently, wet crease recovery can be developed at the drying stage effectively (Fig. 15). While complete salts like sodium-magnesium-citrate can be employed to control wet and dry crease recovery development at drying and curing stages respectively, the more acidic partial salts like magnesium-mono-hydrogen-citrate can be utilised as faster catalysts to achieve both wet and dry crease recovery properties at the drying stage itself. In other words, crease recovery levels equivalent to what is achieved by the fabric at the curing stage can be obtained at the drying stage itself, by using suitable concentrations of the partial salt of organic acids in combination with magnesium chloride.

The crease recovery - tensile strength relationship of fabrics treated with various cross-linking agents using magnesium chloride and the combined catalysts has been
Fig. 15. Effect of drying temperature (for 1 min.) on WCR and DCR.

Fabric: cotton poplin.
extensively investigated. The results are illustrated in Fig. 16. It is seen that for the same crease recovery level, the retained tensile strengths of the fabric are higher when the combined catalyst using a low temperature of cure (125°/10 min.) is employed than in the case of magnesium chloride using a higher temperature of curing (150 - 170°/5 - 3 min.).

The abrasion resistance of fabric samples cross-linked with dimethylol ethylene urea and dimethylol dihydroxy ethylene urea using magnesium chloride alone and the combined catalyst (MgCl₂ + Na-Mg-Cit) has been examined. The results are illustrated in Fig. 17. It is seen that there is a marginal benefit in abrasion resistance in the case of samples cured at lower temperature employing the mixed catalyst. However, the extent of losses in abrasion are considerably high (> 60%) and the marginal advantage observed in abrasion resistance at low crease recovery levels tends to diminish further at higher levels of crease recovery.

The detrimental effect of over-curing on strength properties of the fabric is minimised with the combined catalysts employing a lower temperature of cure (125°) as compared to that using magnesium chloride alone at a comparatively higher temperature of cure (170°). The results are shown in Fig. 18. This advantage is particularly helpful in curing of garments where the risk of over-curing is substantial at the high curing temperatures and longer
Fig. 16. Effect of low temperature curing on percent retained tensile strength.

Fabric: cotton coating.
Fig. 17. DCR vs. percent retained abrasion (Stoll) cycles.

Fabric: cotton coating.
Effect of time of curing on tensile strength.

Fig. 13. Effect of time of curing on tensile strength.
A comparison of wet crease recovery and dry crease recovery levels of fabrics treated with dimethylol ethylene urea using magnesium chloride alone and a higher curing temperature and the combined catalysts employing a lower temperature of curing shows that the combined catalysts impart equivalent extent of these properties (WCR and DCR) at all resin add-ons. This is illustrated in Fig. 19 where the dry crease recovery and wet crease recovery angles are plotted as a function of each other, at various resin add-ons. The important point to be noted is the improved levels of wet crease recovery attained when the combined catalyst is employed under low curing temperature conditions. This is similar to the properties obtained in the mild cure process reported by the Southern Regional Research Laboratory (8). This improved method of wet crease recovery property produces considerable increase in the smooth drying performance after drip-drying as compared to fabric finished with conventionally cured techniques.

The present catalytic system can also be applied to carbamates which are normally more difficult to cure and require stronger acid catalysts. One such example is dimethylol methyl carbamate which is reported to be more difficult to cure than most of the other methylolated alkyl carbamates (9). Table XIII shows that the present system of
Fig. 19. Effect of curing temperature on DCR/WCR.
## TABLE XIII

**EFFECT OF COMBINED CATALYSTS ON DRYING AND CURING OF DIMETHYLOL METHYL CARBAMATE ON COTTON FABRIC.**

Fabric: Cotton Poplin 38\(^{a}/38^{b}\); 128/72

Concentration of DMMC in pad bath = 12\% (w/v);
% Wet pick up = 75 - 80.

<table>
<thead>
<tr>
<th>Catalyst and % conc.(w/v) in pad bath.</th>
<th>pH of pad bath.</th>
<th>Temp.of drying (1 min.)</th>
<th>CR on drying</th>
<th>Temp.of curing (4 min.)</th>
<th>CR on curing</th>
<th>Tensile st. of cured sample (kg).</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl(_2)·6H(_2)O 2% + Na-Mg-Cit 2.5%</td>
<td>4.4</td>
<td>140\°C</td>
<td>222</td>
<td>198</td>
<td>140\°C</td>
<td>250 258 16.0 8.0</td>
</tr>
<tr>
<td>MgCl(_2)·6H(_2)O 2% + Mg-H-Cit 2.5%</td>
<td>3.5</td>
<td>120\°C</td>
<td>248</td>
<td>220</td>
<td>140\°C</td>
<td>298 300 14.5 5.4</td>
</tr>
<tr>
<td>MgCl(_2)·6H(_2)O 2% + Na-H(_2)-Cit 2.5%</td>
<td>2.8</td>
<td>120\°C</td>
<td>264</td>
<td>232</td>
<td>140\°C</td>
<td>290 297 11.9 4.2</td>
</tr>
<tr>
<td>MgCl(_2)·6H(_2)O 2.5% only</td>
<td>6.6</td>
<td>140\°C</td>
<td>193</td>
<td>183</td>
<td>140\°C</td>
<td>215 218 18.0 10.8</td>
</tr>
<tr>
<td>ZnCl(_2) 1.5% only</td>
<td>6.1</td>
<td>140\°C</td>
<td>197</td>
<td>181</td>
<td>140\°C</td>
<td>235 215 18.0 10.0</td>
</tr>
<tr>
<td>Untreated fabric</td>
<td>-</td>
<td>160°</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>25.0 12.0</td>
</tr>
</tbody>
</table>
catalysts is efficient in bringing about the reaction even at the drying stage as shown by the substantial development of crease recoveries at drying.

The present catalytic system has also been found to give better wash-fastness when employed as a catalyst for urea formaldehyde resins. Table XIV shows the comparative results of magnesium chloride and the mixed catalyst in terms of the wash fastness obtained with urea formaldehyde resins. The improved wash-fastness of dimethylol urea resins can be attributed in this case to the greater degree of polymerisation, more complex structure and considerable cross-linking within the resin polymer as obtained with strongly acid catalysts (10).

Application of the catalysts in permanent-press: The most advantageous application of this catalytic system (11) has been made in permanent-press finishing of polyester-cotton blends in which during sensitisation of the fabric, bulk of the wet crease recovery is developed and during curing of the garments, bulk of the dry crease recovery is developed (Fig. 20). The storage stability of the sensitised fabric is excellent in terms of crease recovery properties as shown in Table XV, where the crease recovery of sensitised fabrics stored under different temperatures and relative humidities are shown.
TABLE XIV

EFFECT OF COMBINED CATALYSTS ON THE WASH FASTNESS OF DIMETHYLOL UREA RESIN

Fabric: Cotton Poplin 38/38; 128/72

Dried at 120°/1 min. and cured at 150°/4 min.

<table>
<thead>
<tr>
<th>Resin and % add-on</th>
<th>Catalyst.</th>
<th>Crease Recovery</th>
<th>After mild wash ¹</th>
<th>After severe wash ²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMU 6%</td>
<td>MgCl₂ + Na-Mg-Cit</td>
<td>DCR 270 WCR 262</td>
<td>DCR 224 WCR 255</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot; + Mg-H-Cit</td>
<td>275 260</td>
<td>254 262</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>MgCl₂ only</td>
<td>248 236</td>
<td>198 220</td>
</tr>
<tr>
<td>DMU 4% + DMSU 2%</td>
<td>MgCl₂ + Na-Mg-Cit</td>
<td>269 259</td>
<td>230 260</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot; + &quot;</td>
<td>MgCl₂ + Mg-H-Cit</td>
<td>289 269</td>
<td>267 270</td>
</tr>
<tr>
<td></td>
<td>&quot; + &quot;</td>
<td>MgCl₂ only</td>
<td>256 236</td>
<td>198 224</td>
</tr>
<tr>
<td>*DMU 4% + DMSU 2%</td>
<td>MgCl₂ + Mg-H-Cit</td>
<td>290 270</td>
<td>278 270</td>
<td></td>
</tr>
<tr>
<td>* &quot; + &quot;</td>
<td>MgCl₂ only</td>
<td>256 240</td>
<td>200 228</td>
<td></td>
</tr>
<tr>
<td>Untreated fabric</td>
<td></td>
<td></td>
<td>150 162</td>
<td>150 164</td>
</tr>
</tbody>
</table>

¹ Mild wash at 40° for 30 min. with 5 gm/1 neutral soap + 2 gm/1 soda ash.
² Severe wash at 90° for 45 min. with 5 gm/1 neutral soap + 2 gm/1 soda ash.
* Cured at 160° / 4 min.
Fig. 20. Schematic representation of ATIRA process compared to post- and pre-cure methods.
### TABLE XV

**Storage Stability of Dried (Sensitised) Fabric Samples After Different Periods of Storage Under Varying Conditions of Temperature and Relative Humidity.**

Fabric used: Cotton Coating 20/5/14; 84/48, Dried at 120°/min.

Concentration of cross-linking agent = 12% (w/v);
% Wet pick up = 75 - 80.

<table>
<thead>
<tr>
<th>Cross-linking agent</th>
<th>Storage period (days)</th>
<th>Initial DCR of samples stored at Room temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>75%RH 50%RH 25%RH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50° 50° 50°</td>
</tr>
<tr>
<td>DMBU</td>
<td>30</td>
<td>255 255 256 264 270</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>255 256 260 270 275</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>30</td>
<td>235 236 237 239 240</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>235 238 240 244 250</td>
</tr>
<tr>
<td>DMPU</td>
<td>30</td>
<td>252 250 255 258 260</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>252 255 260 262 265</td>
</tr>
</tbody>
</table>
Since the temperature of cure can be much lower than those required with conventional catalysts, the conditions required for curing the garment are less severe. Thus for example, garments can be efficiently cured for permanent-press using ordinary garment presses (working at 80 - 120 psig) with temperature of cure ranging from 150 - 155°. Neither a hot-head press nor a baking oven is necessary. Simultaneously several problems associated with high temperature of garment curing at longer intervals of time can be eliminated or minimised. For instance, the risk of discolouration due to migration of dispersed dyes, harsh feel of the fabric etc. are substantially reduced. The process, therefore, offers considerable advantages to the garment manufacturer over conventional ones.

Summary and Conclusions

The present catalytic system has a number of advantages in resin finishing of cellulosic textiles: The most important is the low temperature curing made possible with this catalytic system. The low temperature cure also has been found to give better crease recovery-strength relationship and improved balance of WCR/DCR. The present catalytic system can also be used for low temperature curing of carbamates which generally require high curing temperatures. The system has been successfully applied for the production of permanent-press garments from polyester/cotton blends using far less severe conditions of garment curing than are normally used.