CHAPTER V

FABRIC TREATMENT
INTRODUCTION

A few years ago, cotton fabrics were finished almost exclusively with curable methylol and alkoxyethyl compounds of urea and melamine. These resin finishes are nowadays being displaced more and more by reactant crosslinking agents. A large number of other similar simple products have received attention at different times and some of them are of more than passing interest. Among these products, methylol compounds of acyclic and cyclic ureas, carbamates and acid amides are the most important groups of resin finishing agents for textile materials.

Formamide and acetamide each combine with about 1.5 moles of formaldehyde to form partially dimethylolated derivatives which impart crease resistance and shrink resistance when applied to cotton fabric. A process described by Vail et al involves treatment of the cellulosic textile with an aqueous solution containing the methylol derivatives of bisamides having the following structure:

\[
\begin{align*}
\text{HC} - \text{N} - (\text{CH}_2)_n - \text{N} - \text{CH} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]

where \( n \) is integer of 1 to 4.
A process for creaseproofing of cotton textiles described by Moran and Vail\textsuperscript{367} involves the impregnation of cellulosic fabric with an aqueous solution containing an acid amide-type compound having the following structure:

\[
\text{R-} \begin{array}{c}
\text{H} \\
\text{N-CH-CH-N-CR'} \\
\text{O} \quad \text{OH} \quad \text{OH} \quad \text{O}
\end{array}
\]

Where R and R' are the same or different alkyl groups containing from 1 to 4 carbon atoms.

A unique acid amide that has fairly recently achieved a level of commercial importance is methylolacrylamide. N-methylolacrylamide is monofunctional only with respect to its "formaldehyde hook". In spite of the fact that it is a primary amide, acrylamide resists all efforts to react it with more than one mole of formaldehyde. Reaction with cellulose can be effected, however, by invoking the very reactive double bond in the molecule, and to this end irradiation is employed in a variety of fashions. Secondly, crosslinking can be effected, with the N-methylol group reacting with cellulose under acid conditions and in a separate alkali-catalyzed step,\textsuperscript{368} the double bond of the acrylamidomethyl cellulose reacting further with cellulose to form crosslinks. Similar reaction can be made to occur in a single step with acid free-radical catalysts,\textsuperscript{369} and these conditions have been used in quantitative studies of the crosslinking of cotton.\textsuperscript{370,371}
Dimethylol derivative of the condensation product of two moles of acrylamide with one mole of ethylene glycol has been used as crosslinking agent for cotton. A very favourable balance of crease recovery and tensile strength in addition to flame retardancy has been achieved by a two stage process involving the treatment of cotton fabric treated with partially methylolated acrylamide, THPC and zinc acetate followed by curing and washing. In the second step, the fabric is padded with ceric ammonium nitrate catalyst, cured and washed.

In the early 1960's the Southern Regional Research Laboratory of the U.S. Department of Agriculture characterized a crosslinking reactant derived from ammonia, acrylamide, formaldehyde. The resultant methylolnitrilotrispropionamide is trifunctional

\[
\begin{align*}
\text{N} & : \text{CH}_2\text{CH}_2\text{CONHCH}_2\text{OH} \\
\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{OH} & \quad \text{CH}_2\text{CH}_2\text{CONHCH}_2\text{OH}
\end{align*}
\]

and imparts high levels of crease recovery to cotton fabric, but treated fabrics have a tendency to absorb chlorine from hypochlorite solutions. A similar compound based on the reaction of 4-6 moles of formaldehyde is also claimed.

Rainer has described the preparation and use of N-methylol acetamido amine compounds to improve crease resistance in the case of cotton fabrics and wet strength in the case
of paper. These compounds can be represented by the following general formula:

\[
\text{R}'' - \text{N} - \text{CH}_2 - \text{C} - \text{N} - \text{CH}_2\text{OH}
\]

Where \( R = \text{H, CH}_2\text{OH} \) or alkyl; \( R' = \text{H, Acyl, alkyl, aryl} \);
\( R'' = \text{alkyl, aryl} \).

Chance et al obtained crease resistance, flame resistance and rot resistance\(^{102}\) by treating cotton fabric with methylol dibromocyanoacetamide. Rot proofing of cellulosic fabric has been achieved by its treatment with an aqueous solution of a haloacetamide or a methylolhaloacetamide and an acid catalyst e.g. oxalic acid at \( 110-160^\circ \).\(^{376}\) Allied Chemical Corporation\(^{179,180}\) has disclosed the use of fluorinated amides in imparting durable oil and water repellent finishes to cellulosic fabrics.

A process described by Needleman\(^{377}\) is conducted by first preparing a polar solvent solution or bath which contains a saturated fatty acid amide and formaldehyde in specific molar ratios. Several saturated fatty acid amides as well as a few unsaturated fatty acid amides have been evaluated for wash and wear finishes.

Attempts to improve the abrasion resistance of cotton by using pairs of monofunctional and difunctional swelling reactants have been made; compounds tried include acetamide
and methylolated acetamide. It has been the consensus that fabrics containing lactamide and resin have a better hand than those containing resin alone. Lactamide contains an \( \alpha \)-hydroxyl group which undoubtedly accounts for this observation. Lactamide derivative acts in four ways: (1) by swelling cellulose, (2) by acting as a plasticizer for the resin, (3) by reacting with the cellulose, and (4) by reacting through its \( \alpha \)-OH group.

A wide range of phosphorus-containing carboxylic acid amides have been patented as flame resistant finishing agents for cotton fabrics.

**Fabric Treatment:**

The fabric treatment bath generally contains three main components:

(i) Finishing agent
(ii) Catalyst
(iii) Additive or additives, such as wetting agents, softeners or special compounds for some specific purpose.

The fabric is generally impregnated by the usual through and mangle arrangement. The highest possible expression should be achieved, and every attempt should be made to ensure that the fabric is evenly impregnated across its width. It is obviously best, however, to impregnate at a high pressure for not only does this save on drying costs but it minimizes
the dangers of resin migration as the product inside the fibre is less mobile. The drying of the impregnated fabric must be so conducted as to avoid the formation of interstitial and superficial resin; further, the drying must be effected in such a manner that the distribution of the reagents within the fibre is not disturbed. Usually drying of impregnated fabrics is carried out at 70° to 110°C. The final condensation of the crosslinking agent with cotton cellulose is an important stage in the finishing process for self-smoothing fabrics. In general, the temperature of curing is determined by the type of catalyst employed; organic acids, such as tartaric acid, require about 2 to 3 min. at 170°C, but the mineral acids, in the form of their ammonium salts, bring about the condensation at 120 to 130°C within the same time. The cured fabric should be washed as soon as possible so as to neutralize the catalyst and to obviate any acid hydrolysis of the condensate. Moreover, many organic reactions do not proceed to completion and it is therefore necessary to wash the fabric so as to remove any uncombined reagents which may give rise to unwelcome effects later. The solution used is generally soap and sodium carbonate or a synthetic detergent and sodium carbonate, (0.2 - 0.5 per cent of each product) are employed for the purpose.

Reactivities of Creaseproofing Agents:
It has been well-established that a creaseproofing agent penetrates into the interior of the fibres and alters the amorphous regions, but the mode of action has not been entirely
clear. One of the more controversial aspects of crease recovery centers around the question of crosslinking versus resin (polymer) formation. Consider, for example, the various reactivities of a single creaseproofing agent, such as dimethylol urea, applied to cellulose.

$$\text{H} \quad \text{H}$$

$$\text{HOCH}_2-\text{N}-\text{CO}-\text{N}-\text{CH}_2\text{OH}$$

Dimethylol urea

Dimethylol urea contains two types of reactive groups, N-methylol i.e., $\text{N}-\text{CH}_2\text{OH}$, and imido i.e., $\text{N-}$, having the following reactivitiess:

$$\text{N}-\text{CH}_2\text{OH} + \text{HOCH}_2\text{N} \rightarrow \text{N}_2\text{CH}_2\text{OCH}_2\text{N} + \text{H}_2\text{O}$$

$$\rightarrow \text{NCH}_2\text{N} + \text{CH}_2\text{O}$$

$$\text{N}_2\text{CH}_2\text{OH} + \text{NH} \rightarrow \text{N}_2\text{CH}_2\text{N} + \text{H}_2\text{O}$$

$$\text{Cell-OH} + \text{HOCH}_2\text{N} \rightarrow \text{Cell-O-CH}_2\text{N}$$

Based on these reactions, one may postulate at least nine modes of reaction, resulting in elimination of either one or more moles of water or formaldehyde when dimethylol urea is cured within cellulose fibres. For convenience dimethylol urea molecule is designated by the symbol $\text{M-}$

(1) Cyclic dimer $\text{M-}$

(2) Linear polymer $\text{M-M-M-M}$
(3) Thermoset Polymer

\[
\text{Cell} \quad M - M - M - M \quad M - M - M - M - M
\]

(4) Simple Crosslink

\[
\text{Cell} - M - M
\]

(5) Linear Polymer crosslinked to cellulose

\[
\text{Cell} - M - M - M - M - M - M
\]

(6) Thermoset polymer, crosslinked to cellulose

\[
\text{Cell} - M - M - M - M - M - M - M - M - M
\]

(7) Monomer linked to only one cellulose chain

\[
\text{Cell} - M
\]

(8) Linear polymer, linked to only one cellulose chain

\[
\text{Cellulose} - M - M - M - M
\]

(9) Thermoset Polymer, linked to only one cellulose chain

\[
\text{Cell} - M - M - M - M - M - M - M - M - M - M
\]

In the case of polymer linked to cellulose, there may be several links along the polymer chain. There is a further possibility, in any case, of obtaining a few simple methylene crosslinks from formaldehyde broken free during the cure.

N-methylol compounds can impart excellent smooth-drying properties to cotton fabrics and are used extensively. However, most of them are removed easily by acid hydrolysis and, to a
lesser extent, by basic hydrolysis. This weakness is not severe in home type laundering, but it results in substantial loss of cross-links when treated cotton goods are laundered by commercial procedures especially during the final acid rinse which is generally employed. In some cases, the pH has been observed to be as low as 3.5. Unfortunately, this low pH hydrolyzes most of the reaction products of the methylol compounds with cotton cellulose. Ease of acid hydrolysis is one of the greatest weakness of these N-methylol wash-wear finishing agents. When methylol compounds of the general structure \( R-C-N-\text{CH}_2\text{OH} \) (\( \gamma = \text{CH}_2\text{OH} \) or \( \text{H} \)) react with cellulose through acid catalysis (or \( \text{H} \)) the reaction is generally considered to have proceeded through the reverse reaction as shown below:

\[
\begin{align*}
\text{R-} & \quad \gamma \quad \text{C-} \quad \text{N-} \quad \text{CH}_2\text{OH} + \text{HO-Cell} & \rightarrow & \text{R-} \quad \gamma \quad \text{C-} \quad \text{N-} \quad \text{CH}_2\text{O-Cell}
\end{align*}
\]

The products which have been isolated after acid hydrolysis are either the original amide or derivatives with the amide group intact. Therefore, the hydrolysis route leading to the formation of an amide is more likely. Hydrolysis of the reaction product of amido-methylol compounds with cellulose, involves initial attack at the carbonyl oxygen, as shown below because many of the reactions of carbonyl-containing compounds are initiated by electrophilic attack on the carbonyl oxygen.
Hydrolysis route leading to the formation of an amide is more likely.

Wilson et al. favoured the hydrolysis mechanism (shown below) in which initial electrophilic attack is at the ethereal oxygen:

\[
\begin{align*}
R-C-N-CH_2-O-\text{Cell} & \xrightleftharpoons{H^+} R-C-N-CH_2-O-\text{Cell} \\
R-C-N-CH_2-O-\text{Cell} & \xrightleftharpoons{H^+} R-C-N-CH_2 + HO-\text{Cell} \\
R-C-N-CH_2 + HOH & \xrightleftharpoons{H^+} R-C-N-CH_2OH_2 \\
R-C-N-CH_2OH_2 & \xrightleftharpoons{H^+} R-C-N-CH_2OH + H
\end{align*}
\]
They proved by various substituted model compounds that hydrolysis was facilitated by electron-releasing groups attached to either the carbonyl carbon or the amido nitrogen. The rate-determining step in this mechanism is the formation of a carbonium ion. Formation of the carbonium ion is facilitated by increased electron density about the protonated ethereal oxygen and retarded by a decrease in electron density. Changes in the electron density in this region are dependent upon the electron-releasing properties of nearby groups and the ability of intervening bonds to transmit the effect. Transmission of electronic effects through the bond structure

\[
R - C - N - CH_2 - O
\]

would be expected because of the multiple bond and unshared electrons in it. In case of strongly electron withdrawing R and Y groups, it is difficult to hydrolyze ether linkages. At this time, electron withdrawing groups assist hydrolysis initiated at the carbonyl oxygen and hydrolysis follows the proposed mechanism.

Another well-known weakness of N-methylol finishing agents is chlorine retention causing either yellowing or loss of strength on subsequently heating to ironing temperatures. Nuessle reviewed hydrolysis of dimethylolethyleneurea finish primarily in relation to its being the cause for increased chlorine retention. When fabrics creaseproofed with compounds containing hydrogen bearing nitrogen atoms e.g. dimethyloleura and monomethylol carboxylic acid amides are bleached with hypochlorites, chloramine or chloramide compounds
can form by substitution of chlorine on the nitrogen. These compounds are thermally unstable. On application of heat, as in ironing, they decompose and hydrochloric acid is formed in the fabric, possibly through a free-radical mechanism. The damage is due to acid hydrolysis and possibly to oxidation of cotton cellulose. The extent of damage is modified by the buffering power of the cross-linking agents, augmented, if such metal salts as magnesium chloride or zinc nitrate have been used as catalysts, by the buffering power of the basic metal residue left in the fabric.

The cross-linking agent may be capable of neutralizing acids if it contains an amine group or a basic tertiary N atom, but the presence of primary or secondary amine is undesirable because of the possibility of chloramide formation. A tertiary nitrogen, such as that present in triazines and triazones, protects fabrics from hydrolysis.

EXPERIMENTAL

Methylol derivatives of acid amides were prepared by reacting one mole of acid amide with three moles of formaldehyde at pH 10 and at 55°C. After methylolation, pH of the solution was adjusted to about 6.5 by the addition of dilute hydrochloric acid.

(A) For crease-proof treatment of cotton fabric, magnesium chloride hexahydrate and then citric acid were added to the above-mentioned methylolated acid amide solutions in quantities
such that the concentration in the pad bath of magnesium chloride was 0.07 mole and pH was 3. Concentration of methylolated acid amide in pad bath was 0.5 mole. These solutions were used to pad fabric with 100% wet pick up. The fabric was then dried on a pin frame in a forced draft oven at 60°C for 7 minutes and cured at 125°C for 10 minutes.

(B) In case of methylolated halo acid amides 0.05 mole of magnesium chloride hexahydrate and necessary amount of citric acid to adjust the pH of pad bath to 4 were added. Concentration of methylolated halo acid amides in pad bath was 0.15 mole. These solutions were used to pad cotton fabric with 100% wet pick up after which the fabric was dried on a pin frame in a forced-draft oven at 60°C for 7 minutes and cured at 125°C for 5 minutes.

RESULTS AND DISCUSSION

The action of formaldehyde on cellulosic fibres was described by Eschalier. Studies made subsequently showed that the most likely mechanism was the formation of methylene bridges between cellulose molecular chains. Kress has found that polyformals of formaldehyde and ethylene glycol act as effective modifying agents for cellulosic textiles. The formals apparently act as formaldehyde donors and crosslink the cellulose molecular chain by methylene bridges. Dimethylol formamide and dimethylol acetamide are reported to have been marketed as formaldehyde
The finishing agents prepared are listed in Table No. 14.

**TABLE NO. 14**

**LIST OF FINISHING AGENTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Finishing Agent</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methylol formamide</td>
<td>MF</td>
</tr>
<tr>
<td>2.</td>
<td>Methylol acetamide</td>
<td>MA</td>
</tr>
<tr>
<td>3.</td>
<td>Methylol propionamide</td>
<td>MP</td>
</tr>
<tr>
<td>4.</td>
<td>Methylol butyramide</td>
<td>MB</td>
</tr>
<tr>
<td>5.</td>
<td>Methylol iso-butyramide</td>
<td>MIB</td>
</tr>
<tr>
<td>6.</td>
<td>Methylol trimethylacetamide</td>
<td>MTTMA</td>
</tr>
<tr>
<td>7.</td>
<td>Methylol dimethylaminoacetamide</td>
<td>MDMAA</td>
</tr>
<tr>
<td>8.</td>
<td>Methylol glycolamide</td>
<td>MG</td>
</tr>
<tr>
<td>9.</td>
<td>Methylol lactamide</td>
<td>ML</td>
</tr>
<tr>
<td>10.</td>
<td>Methylol β-chloropropionamide</td>
<td>MCP</td>
</tr>
<tr>
<td>11.</td>
<td>Methylol chloroacetamide</td>
<td>MCA</td>
</tr>
<tr>
<td>12.</td>
<td>Methylol mandelamide</td>
<td>MM</td>
</tr>
<tr>
<td>13.</td>
<td>Methylol α,β-dibromocinnamide</td>
<td>MDBC</td>
</tr>
<tr>
<td>14.</td>
<td>Methylol α,β-dibromopropionamide</td>
<td>MDBP</td>
</tr>
<tr>
<td>15.</td>
<td>Methylol 2,4,5-trichlorophenoxy acetamide</td>
<td>MTCPA</td>
</tr>
<tr>
<td>16.</td>
<td>Methylol 2,4,6-tribromophenoxy acetamide</td>
<td>MTBPA</td>
</tr>
<tr>
<td>17.</td>
<td>Dimethylol ethyleneurea</td>
<td>DMEU</td>
</tr>
<tr>
<td>18.</td>
<td>Dimethylol dihydroxy ethyleneurea</td>
<td>DMDHEU</td>
</tr>
</tbody>
</table>
Since one of the objectives of the present study was to evaluate methylolated acid amides as textile crosslinking agents, it was most desirable that the number of such methylene crosslinks was kept to the minimum. To achieve this, drying temperature of fabrics treated with methylolated acid amide and some free formaldehyde present in the pad bath, was kept as low as 60°C. To confirm whether formaldehyde reacts in the form of methylene glycol with cotton cellulose in the presence of highly active catalyst mixture consisting of magnesium chloride hexahydrate (0.07 mole) and sufficient quantity of citric acid to obtain the pH value of 3, at temperature as low as 60°C, cotton fabric was treated with 1.5 molar solution of formaldehyde under the above cited condition to simulate the reaction between the contents of pad bath (methylolated acid amide and some free formaldehyde) and cotton cellulose. For the above treatment 1.5 molar solution of formaldehyde was taken because even in case of best formaldehyde donor (i.e., methylolated acid amide which decomposes completely into formaldehyde and parent acid amide), the total formaldehyde available to the fabric (either present as free formaldehyde and donated by methylolated acid amide) for chemical reaction will not exceed 1.5 moles as this is the quantity of formaldehyde used for methylolation of 0.5 mole of acid amide. The findings of the above study are very interesting in the sense that for 100% wet pick-up donors to impart antishrink effect on cotton textiles.
only 0.09% (0.03 mole) of formaldehyde was found to be reacted with cotton cellulose. From the above observation, it may be concluded that free formaldehyde present in the pad bath and/or that donated by methylolated acid amide, in case the latter decomposes into formaldehyde and parent acid-amide under the said experimental conditions does not react appreciably with cotton cellulose and most of it is simply lost by evaporation. In this context, some calculations regarding the ability of acid amides to add formaldehyde and stability of their methylol derivatives were made and are recorded in Table No.15. It appears from the data that acid amides react with formaldehyde to yield their methylol derivatives, the conversion ranging from 61 to 87 percent as against 98 and 96 percent in the case of ethylene urea (EU) and dihydroxyethylene urea (DHEU) respectively. Another observation made while studying the extent of methylolation of bromoacetamide, trichloroacetamide and cyanoacetamide was their tendency to precipitate from the reaction mixture. This was extensive in case of trichloroacetamide and cyanoacetamide. In case of cyanoacetamide, formaldehyde was suspected to have reacted with its methylene hydrogens to give

\[ \text{CH}_2-(NC-\text{CH-CO-NH}_2)_2 \]

and hence are not included in Table No.14 and 15. The data under the column, "percent conversion of acid amide into its methylol derivative" and molar ratio HCHO/Acid Amide in pad bath indicate the ability of acid amides to add formaldehyde,
<table>
<thead>
<tr>
<th>No.</th>
<th>Finishing Agent</th>
<th>Percent Conversion of Acid Amides to their Methylol Derivatives</th>
<th>Molar Ratio HCHO/ Acid Amide in pad bath (a)</th>
<th>Molar Ratio HCHO/ Acid Amide on fabric (b)</th>
<th>Mole of HCHO Given off during Finishing Treatment (a) - (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MF</td>
<td>26 74</td>
<td>1.74</td>
<td>0.83</td>
<td>+ 0.91</td>
</tr>
<tr>
<td>2.</td>
<td>MA</td>
<td>27 73</td>
<td>1.73</td>
<td>1.67</td>
<td>+ 0.06</td>
</tr>
<tr>
<td>3.</td>
<td>MP</td>
<td>42 58</td>
<td>1.58</td>
<td>1.48</td>
<td>+ 0.10</td>
</tr>
<tr>
<td>4.</td>
<td>MB</td>
<td>54 46</td>
<td>1.46</td>
<td>1.36</td>
<td>+ 0.10</td>
</tr>
<tr>
<td>5.</td>
<td>MIB</td>
<td>53 47</td>
<td>1.47</td>
<td>1.14</td>
<td>+ 0.33</td>
</tr>
<tr>
<td>6.</td>
<td>MTMA</td>
<td>58 42</td>
<td>1.42</td>
<td>0.97</td>
<td>+ 0.45</td>
</tr>
<tr>
<td>7.</td>
<td>MCA</td>
<td>28 72</td>
<td>1.72</td>
<td>0.70</td>
<td>+ 1.02</td>
</tr>
<tr>
<td>8.</td>
<td>MCP</td>
<td>51 49</td>
<td>1.49</td>
<td>1.38</td>
<td>+ 0.11</td>
</tr>
<tr>
<td>9.</td>
<td>MG</td>
<td>78 22</td>
<td>1.22</td>
<td>1.36</td>
<td>- 0.14</td>
</tr>
<tr>
<td>10.</td>
<td>ML</td>
<td>78 22</td>
<td>1.22</td>
<td>1.54</td>
<td>- 0.32</td>
</tr>
<tr>
<td>11.</td>
<td>MDMA</td>
<td>55 45</td>
<td>1.45</td>
<td>2.55</td>
<td>- 1.10</td>
</tr>
<tr>
<td>12.</td>
<td>DMEU</td>
<td>4 96</td>
<td>0.98</td>
<td>1.07</td>
<td>- 0.09</td>
</tr>
<tr>
<td>13.</td>
<td>DMDHEU</td>
<td>8 92</td>
<td>0.96</td>
<td>0.98</td>
<td>- 0.02</td>
</tr>
</tbody>
</table>
whereas the last two columns of Table No.15 give the stability of their methylol derivatives under drying and curing conditions. Considering these data a correlation can be established between electron displacement and ease of decomposition of methylol acid amide. It has already been established that the substituent groups in acid amide molecule play an important role in the electron displacement and that electron releasing groups attached to either the amido nitrogen or the carbonyl carbon facilitate acid hydrolysis, whereas electron attracting groups hinder the acid hydrolysis.\footnote{379} Also the agents which yield finishes resistant to acid hydrolysis give better results than those which are easily hydrolyzed in moist-mild cure cross-linking technique in which strongly acidic catalysis and low curing temperature (as low as 105°C) are employed.\footnote{390}

The data on stability of various methylol acid amides under drying and curing conditions and the ease with which they decompose to give rise to formaldehyde can be explained in view of the fact that conditions employed for crosslinking reactions are comparable to those generally employed in mild cure process and that electron releasing groups in the crosslinker makes it more susceptible to acid hydrolysis. The ease of decomposition of methylolated acid amide \((R-CO-NH-CH_{2}OH\) or \(R-CO-N(CH_{2}OH)_{2}\) increases in the order \(R = \text{-CH}_3, \text{-C}_2\text{H}_5\) and \(\text{-C}_3\text{H}_7, \text{-CH(CH}_3\text{)}_2, \text{-C(CH}_3\text{)}_3\) as this is the order in which positive inductive effects of the alkyl group changes. Whereas in case of methylolated
acid amides with electron withdrawing substituent the order of their decomposition increases in the order

$\text{CH}_2\text{-CH}_2\text{-Cl} \prec \text{-CH}_2\text{OH} \prec \text{-CHOH} \prec \text{-CH}_2\text{-Cl}$

In the above discussion methylolated acid amides with electron releasing groups and those with electron withdrawing substituent are treated separately because they are found to differ markedly in their decomposition behaviour, for example methylolated acid amides with electron releasing groups and some other methylol acid amide with electron attracting group decompose during drying stage of the cross-linking treatment. These are grouped as those methylol acid amide which donate formaldehyde during drying stage i.e. at low temperature. The rest are grouped as those methylol acid amides which donate formaldehyde during curing stage, i.e. at higher temperature. Since the drying temperature employed in this study is as low as 60°C, the formaldehyde given off by methylolated acid amide due to their decomposition, does not react with fabric, and just evaporates. As a result, formaldehyde/acid amide molar ratio on fabric is found to be less than that in the pad bath. Acetamide could be considered as the best cross-linker in this series as the difference between the formaldehyde/acid amide molar ratio on fabric and that in the pad bath is least, indicating minimum decomposition of its methylol derivative.

Methylolated acid amides with electron withdrawing substituents
are found to be reasonably stable during the drying stage of the crosslinking reaction but they undergo decomposition during curing stage of the crosslinking reaction. Since curing is carried out at comparatively high temperature (125°C) for ten minutes, the formaldehyde given off by methylolated acid amides due to their decomposition, does react with fabric. As a result, formaldehyde to acid amide ratio on fabric is found to be higher than that in the pad bath.

Methylol chloroacetamide was found to be highly sensitive to heat. Fabric finished with methylol chloroacetamide showed considerable discolouration under the curing conditions mentioned above. As reported earlier acid amides with electron withdrawing substituents have reasonably good to excellent resistance to acid hydrolysis. This implies that methylolated chloroacetamide should have fairly good stability towards acid hydrolysis. Higher molar ratio of formaldehyde/acid amide in pad bath compared to that on the finished fabric can only be explained on the assumption that MCA being highly sensitive compound to heat starts decomposing during drying stage of crosslinking treatment and hence the formaldehyde set free does not get reacted with cotton cellulose at drying temperature of 60°C. MCP also appears to behave like acid amides with electron releasing substituents. This could be due to the fact that chlorine atom in MCP is at such position that it fails to exert its expected influence. Another noteworthy point is that the mole of formaldehyde given
off during drying is only 0.11 in case of MCP compared to 1.02 observed in case of MCA. This could be explained as follows: The extent of methylolation in case of chloroacetamide is 86 percent compared to 74 percent in case of MCP. Considering methylolated acid amides as formaldehyde donor, it can be argued that higher is the extent of methylolation of acid amide more is the possibility for its decomposition into formaldehyde and parent acid amide.

In case of these methylol acid amides which donate formaldehyde at relatively higher temperature, the following order of decomposition during curing stage is found

\[
\text{DMDEU} < \text{DMEU} < \text{MG} < \text{ML} < \text{MDMAA}
\]

Though extent of methylolation in case of MG and ML is the same, the stability of ML during curing stage is less than MG, possibly due to the presence of -CH\(_3\) group in the former. This is in conformity with the statement made earlier that those methylol acid amides which contain an electron releasing substituent decompose at comparatively lower temperatures. In case of MDMAA molar ratios of formaldehyde/acid amide on fabric and that in pad bath are found to be 2.55 and 1.45 respectively. Results indicate considerable decomposition of MDMAA during curing process. Excessive decomposition of MDMAA is possibly due to the excessive acidity produced by the decomposition of quaternary salt.
produced while the reaction mixture is being neutralized with hydrochloric acid after methylolation.

**Methylolel Acid Amides as Cellulose Reactants:**
Methylolel acid amides, as they exist in pad bath, are very likely a mixture of monomethylolel and dimethylolel acid amides. The monomethylolel acid amide may undergo acid catalyzed condensation reaction with cotton cellulose, leaving \( \text{R-C-N} \) unit as a pendant group. The same may also undergo complete decomposition into volatile formaldehyde and acid amide. The former being highly volatile will either evaporate or react with cotton cellulose depending upon the reaction temperature, whereas the latter being highly soluble in water will be washed out, during process wash of the treated fabric after resin finishing. The dimethylolel acid amide may undergo either acid-catalyzed crosslinking reaction with cotton cellulose or processes like dimerization, trimerization or polymerization with the evolution of volatile formaldehyde. The dimer, trimer or polymer may get linked to cotton cellulose by acid-catalyzed reaction through their methylol group/s located at the end/s of the chain. The dimethylolelated acid amide may undergo either partial decomposition into volatile formaldehyde and monomethylolelated acid amide which may in turn
give all the reactions of monomethylolated acid amide as discussed above. Vail et al. have stated that N-methylol cross-linking agents, in general, react with cellulose without being appreciably modified under the reaction conditions in a conventional pad-dry-cure treatment; no matter what is the nature of the reaction of methylolated acid amide with cellulose. This implies that moles of $R-C-N$ units on fabric should not change if the same molar concentration of different fully methylolated acid amides are reacted with cotton cellulose having the same affinity for the substrate and the same reaction efficiency. In practice, it is impossible to keep all the above cited variables constant because different amides have different affinity for formaldehyde. As a result, they get methylolated to different extent; also the factors such as structural characteristic and molecular size of the cellulose reactant affect the fibre penetration of the resin molecule greatly and thereby the efficiency of the crosslinking reaction.

Therefore, the data in Table No. 16 under the column, "Moles of amide reacted with 100 gm. fabrics", give the overall but accurate picture of reactivities of various methylolated acid amides.

In the same Table, percent addon of various reactants on the fabrics treated with them are given which are calculated by addition of percent $R-C-N$ unit and percent formaldehyde content of the treated fabric. In this context, one may expect
increase in percent addition with increase in molecular weight of the reactant. In the Table, therefore, acid amides are arranged in ascending order of their molecular weights. Based on these data, an attempt has been made to rate methylolated acid amides as cellulose reactants.

(A) Methylol Acid Amides as Formaldehyde Donor

Methylolated acid amides are formaldehyde donors, i.e. they undergo partial or complete decomposition under the influence of heat into formaldehyde and monomethylolated acid amide or acid amide. In view of the unstable nature of methylolated acid amides at higher temperature, a combination of highly active catalyst mixture and as low drying and curing temperatures as possible have been employed for crosslinking treatments.

(B) Minimization of the Reaction Between Formaldehyde/Donated Formaldehyde and Cotton Cellulose

The linear relationship between concentration of formaldehyde in treating bath and the amount of formaldehyde fixed on the fabric in the presence of highly active catalyst system is known. Since one of the objectives of the present study was to evaluate methylolated acid amides -- formaldehyde donors -- as textile crosslinking agents it was considered important to keep the reaction between formaldehyde and cotton cellulose to the minimum. To achieve this, drying temperature in the above reaction was kept at 60°C. It is observed that this
temperature is not sufficiently high to bring about any appreciable reaction between formaldehyde and cotton cellulose. It is also observed that at this temperature, most of the free formaldehyde present in the pad bath or that donated by methylolated acid amides escapes without getting reacted with cellulose.

(C) Decomposition of some Methylolated Acid Amides into Formaldehyde and Amide during the Drying Process

If the mono or dimethylol acid amide under examination is too unstable to exist under drying condition which is as low as 60°C, it will decompose into formaldehyde and parent acid amide. The former will leave the fabric as discussed above while the latter being water soluble, will be washed off during process wash after resin curing. In such events resin addon obtained on the fabric, and hence percent formaldehyde and percent \( R-\text{CO-N}^- \) unit fixed on the fabric will be less than the expected.

(D) Partial Decomposition of Dimethylol Acid Amide during the Drying Process

In the event of partial decomposition of dimethylol acid amide into formaldehyde and monomethylol acid amide, the former being highly volatile will leave the fabric as discussed above, while the latter will get reacted with cotton cellulose during the curing stage. This will no doubt lead to less addon than the expected but the extent to which addon is reduced will be much less than the above case. One interesting after effect
of such event may be that the percent $R_8^G - N < \text{unit fixed}$ on the fabric may remain very close to the expected value.

(E) Decomposition of Methylol Acid Amides into Formaldehyde and Amide during the Curing Process

If the mono or dimethylol acid amide under examination is too unstable to exist under curing condition employed (which is definitely milder than conventional one, in pad-dry-cure process), it will decompose into formaldehyde and parent acid amide. The former will react with cotton cellulose since curing temperature, which is $125^\circ C$, is sufficiently high to bring about the reaction between them, while the latter being water soluble will be washed off during process wash after resin curing. In such event, resin addon obtained on the fabric will be no doubt less than the expected one, but also the analysis of fabric treated with such compound is likely to show higher percentage of bound formaldehyde compared to percent $R_8^G - N < \text{units fixed on the fabric}$. One interesting point about the fabric treated with such compounds would be that it might be lacking in true crosslinks formed by dimethylol acid amide. No doubt methylene crosslinks formed by formaldehyde are present which will give high levels of crease recovery angle but at the cost of fabric strength. It is known that methylene crosslinks give rise to higher strength loss than crosslinks formed by dimethylol nitrogenuous compound.
Partial Decomposition of Dimethylol Acid Amide during Curing Process

In the event of partial decomposition of dimethylol acid amide into formaldehyde and monomethylol acid amide, both the components set free will get reacted with cotton cellulose as conditions (sufficiently low pH and sufficiently high temperature) are favourable for the reaction to occur. Explanation regarding fewer true crosslinks formed by dimethylol acid amide, larger number of methylene crosslinks formed by formaldehyde, higher level of crease recovery and higher strength losses is the same as above.

Based on case studies, i.e. on the basis of percent $\text{R-C-N}^\text{O}$ units and percent addon of resin on the fabric, the individual methylol acid amide among the series of methylol acid amides which are listed in Table No. 16 is evaluated as textile crosslinking agent and is placed in one of the following arbitrary categories:

1. Below Average (BA)
2. Average (A)
3. Above Average (AA)

This evaluation may not give a very correct and absolute picture of reagent's ability but is likely to give comparative picture of a particular reagent in the given series of reagents. For instance a reagent evaluated as 'AA' may not be ideal but its rating as 'AA' could be due to the inferior performance of rest of the reagents.
As explained earlier, one may expect gradual increase in addon of the resin and percentage of R-CO-N^< units fixed on the fabric as one passes from Mf to MCP in the above series of methylolated acid amides, as this is the order in which molecular weight of acid amide increases. In Table No. 16 under the column, "finishing agents", "percent R-CO-N < unit" and "percent addon" certain figures are given within brackets. These figures indicate the position of methylolated acid amides in the given series of methylol acid amides if arranged in ascending order of their molecular weights, percent R-CO-N < unit and percent addon respectively. If, for example, a methylol acid amide occupies position four in the ascending series of methylolated acid amides on the basis of its molecular weight, it is expected that it will also occupy position four if these acid amides are arranged in ascending order on the basis of percent R-CO-N < unit and percent addon fixed on the fabric. If this is so, this particular methylol acid amide can be placed under the category "Average." If it occupies a position which is higher than four or lower than four in the series of methylolated acid amide if arranged in ascending order on the basis of "percent RCON < unit" and "percent addon" fixed on fabric; this particular methylolated acid amide can be placed under the category "Above Average", and "Below Average" respectively.

The calculations regarding reaction efficiency are based on moles of amide reacted with 100 gms of fabric. As indicated in Table No. 16, cotton fabrics have been heated with 0.05 mole
of methylol acid amide per 100 cc. solution using 100% wet pick up. This indicates that the maximum resin that can be fixed on fabric or the maximum number of RCON< per 100 gm. of fabric can be 0.05.

Evaluation of Individual Methylol Acid Amide as Crosslinking Agents:

**MF:** As reported earlier MF has the lowest molecular weight in the series of acid amides under examination hence its position in this series is "one" (Table 16; column I). Looking to the ascending order of percent RCON< unit and percent addon fixed on the fabric (Table 16; column IV and VI), it appears that MF has retained its position one in the series. On this basis, it can be rated as "Average" (Column V and VII). The last column of the Table No. 16 shows that 0.037 mole of HCON< has reacted with 100 gm. of cotton cellulose which indicates 74% reaction efficiency. On the basis of formaldehyde content, H-CO-N< Unit and percent addon, this reagent can be said to belong to 'C' category i.e. some part of the reagent undergoes complete decomposition during drying process.

**MA:** As shown in the column of the Table, MA occupies position "two" in the series of methylolated acid amides if arranged in ascending order of molecular weight. Looking to the ascending order of percent RCON< unit fixed on the fabric (Column IV), it seems that MA has retained its position two in the series. On this basis, it can be rated
as "A". Looking to the ascending order of percent addon on the fabric (Column VI), it appears that the position of MA has risen to 8. This surprising rise in its position could be due to inferior or below average performance of other methylolated acid amide during finishing operation especially during the drying stage of it. However, MA can be rated as "AA" since it has risen from position 2 to 8. The last column of Table No.16 indicates that 0.049 mole of $\text{CH}_3\text{-CO-N}<$ has reacted with 100 gm. of cotton cellulose which indicates 98% reaction efficiency. This is indicative of the fact that decomposition of dimethylolated acid amide does not exceed beyond monomethylol acid amide stage.

On the basis of formaldehyde content, $\text{CH}_3\text{-CO-N}<$ unit and percent addon, this reagent can be said to belong to 'F' category i.e. some part of the reagent undergoes partial decomposition during curing operation.

**MP:** As shown in the column I of the Table, MP occupies position three in the series of methylolated acid amide if arranged in ascending order of molecular weight. Taking into consideration the fourth position which it occupies in the ascending series of percent RCON<unit fixed on the fabric, it seems that MP has an edge over the other methylol acid amides in the series and hence it is rated as "AA". The same explanation holds good if MP is rated on the basis of percent addon on the fabric. The last column indicates 86% reaction efficiency since, 0.043 mole of MP has reacted per 100 gm. of fabric.
on the basis of formaldehyde content, $C_2H_5\cdot CO\cdot NH_2$ unit and percent addon, this reagent can be said to belong to 'D' category i.e. some part of the reagent undergoes partial decomposition of dimethylol acid amide during the drying process.

MG: This is an interesting case representing those hydroxyl acid amide which show poor affinity for formaldehyde in the methylation reaction, poor stability at curing stage of resin finishing and still showing high reaction efficiency in the reaction with cotton cellulose. As reported earlier, extent of methylation in case of glycolamide is of the order of 61 percent i.e. 1.22 moles of formaldehyde get reacted per mole of glycolamide. It has already been reported earlier in Table No. 15 that methylol glycolamide undergoes decomposition during curing operation and 0.14 mole of formaldehyde is given off. This implies that after decomposition some 1.08 moles of formaldehyde are attached to glycolamide molecule. The 92% reaction efficiency which it shows in its reaction with cotton cellulose can partly be attributed to the presence of primary hydroxyl function attached to carbon atom in the glycolamide molecule which helps in fixing it to cotton cellulose. The rest of the contribution for its fixation to cotton cellulose comes from $-NH\cdot CH_2\cdot OH$ group present in MG. To prove that hydroxyl function attached to carbon atom of MG and other amides contributes to their fixation to cotton cellulose, experiments were carried out wherein cotton cellulose was treated
with 100 ml. solution containing 0.05 mole of 4,5-dihydroxy-ethylene urea, glycolamide, lactamide and formamide under standard conditions i.e. using 0.07 mole of MgCl₂, 6H₂O and sufficient quantity of citric acid to obtain 3 pH of the pad bath. Drying was carried out at 60°C for 7 minutes and curing was done at 125°C for 10 minutes. A process was given after the curing operation. The results of these experiments are given in the following Table:

TABLE No. 17
REACTION EFFICIENCY OF C-HYDROXYL FUNCTION

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Nitrogen Content of fabric</th>
<th>Reaction Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>DHEU</td>
<td>0.49</td>
<td>35</td>
</tr>
<tr>
<td>2.</td>
<td>Glycolamide</td>
<td>0.08</td>
<td>12</td>
</tr>
<tr>
<td>3.</td>
<td>Lactamide</td>
<td>0.06</td>
<td>9</td>
</tr>
<tr>
<td>4.</td>
<td>Formamide</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen in the above Table C-hydroxyl compounds do react with cotton cellulose regardless of the nature of hydroxyl function. However, the extent of reaction with cellulose is higher in the case of primary C-hydroxyl compound (glycolamide) compared to secondary C-hydroxyl compound (lactamide). DHEU with two secondary C-hydroxyl functions has shown to have the highest reaction efficiency, while formamide which is lacking in C-hydroxyl functions has failed to react with cotton cellulose.
So far as the rating of M3 in the given series of methylolated acid amide is concerned, it can be rated as "AA" since it has occupied higher position in the ascending series of percent RCON unit on the fabric and percent addon than what it should have been on the basis of its molecular weight in this series of methylol acid amides if arranged in ascending order of their molecular weight.

On the basis of formaldehyde content, OHCH\textsubscript{2}-CO-N unit and percent addon this reagent can be said to belong to 'F' category i.e. some part of the reagent undergoes partial decomposition during curing operation.

**MB:** This can be rated as "AA". The explanation regarding this remains the same as above. This reagent has shown 86% reaction efficiency.

On the basis of formaldehyde content, C\textsubscript{3}H\textsubscript{7}-CO-N unit and percent addon, this reagent can be said to belong to 'D' category i.e. some part of the reagent undergoes partial decomposition of dimethylol acid amide during the drying process.

**MIB:** This can be rated as "AA". The explanation being the same as above. This reagent has shown 97% reaction efficiency indicating the fact that decomposition of this reagent does not go beyond monomethylol stage.

On the basis of formaldehyde content, C\textsubscript{3}H\textsubscript{7}-CO-N unit and
percent addon, this reagent can be said to belong to 'D' category i.e. some part of the reagent undergoes partial decomposition of dimethylol acid amide during the drying process.

**ML:** As reported earlier, extent of methylolation in case of lactamide is of the order of 61% i.e. 1.22 moles of formaldehyde get reacted per mole of lactamide. It has already been reported earlier in Table No. 15 that methylolated lactamide undergoes decomposition during curing operation and 0.32 mole of formaldehyde is given off. This implies that after decomposition some 0.9 mole of formaldehyde is attached to lactamide molecule. In other words, decomposition of ML proceeds beyond monomethylol stage. This is probably why reaction efficiency of this reagent is only 77%. Its rating as 'BA' indicates its lower position in the ascending series of percent addon on the fabric than what it should have occupied on the basis of its molecular weight in the ascending series of methylolated acid amide. This reagent can be rated as 'A'. However, on the basis of percent RCON<CH3 unit on the fabric, this improvement in rating can be attributed to C-hydroxyl function present in ML molecule which helps its fixation to cotton cellulose.

On the basis of formaldehyde content, \( \text{CH}_3 \text{CHO} \text{CO-N}< \) unit and percent addon, this reagent can be said to have belonged to 'E' category i.e. some part of the reagent undergoes complete decomposition of some methyol acid amide during the curing operation.
MCA: This is again an interesting case representing those haloacid amide which partially get converted into hydroxy acid amide (about 34%) during methylolation reaction under alkaline condition. This partial substitution of halogen atom in haloacid amide molecule by hydroxyl function not only helps in increasing its extent of methylolation (chloroacetamide gets methylolated to the extent of 86%) but also helps in its fixation to cotton cellulose. This is probably why MCA has shown 86% reaction efficiency in its reaction with cotton cellulose inspite of the fact that it undergoes considerable decomposition under drying operation to almost monomethylol stage. Since decomposition does not proceed beyond monomethylol stage and since MCA molecule has about 34% of its halogen replaced by hydroxyl, it has been possible for this reagent to occupy a higher position in the ascending series of percent RCON unit on the fabric than what it occupies in the ascending series of methylolated acid amide on the basis of molecular weight. So far, its rating on the basis of percent RCON unit on fabric is concerned it is 'AA', whereas it can be rated as 'BA' on the basis of percent addon on the fabric. The lower addon is largely due to the unstable nature of MCA under drying condition.

One of the basis of formaldehyde content, Cl.CH\_2CON\_< unit and percent addon, this reagent can be said to have belonged to 'D' category i.e. some part of the reagent undergoes partial decomposition of dimethylol acid amide during the drying process.
**MTMA:** This reagent can be rated as "BA" from different aspects. Its rating as "BA on the basis of percent RCON unit on the fabric is indicative of the fact that decomposition of this reagent proceeds beyond monomethylol stage. This also explains poor reaction efficiency (66%) of this reagent in its reaction with cotton cellulose. Finally, poor reaction efficiency explains the occurrence of less addon of resin on the fabric than expected.

On the basis of formaldehyde content -\((\text{CH}_3)_3\text{-C-CON-N}\) unit and percent addon, this reagent can be said to belong to 'C' category i.e. some part of the reagent undergoes complete decomposition during the drying process.

**NDMAA:** This reagent can also be rated as "BA" from different aspects. The explanation regarding this will remain the same as above.

On the basis of formaldehyde content, \((\text{CH}_3)_2\text{-N-CH}_2\text{-CON}\) unit and percent addon, this reagent can be said to belong to 'E' category, i.e. some part of the reagent undergoes complete decomposition of some methylol acid amide during the curing operation.

**MCP:** This reagent is rated as "A" since it has been able to maintain the same position in ascending series of methylolated acid amide on the basis of their molecular weight; in ascending series of percent RCON unit on the fabric and ascending series of percent addon on the fabric. This
reagent has also shown 80% reaction efficiency in its reaction with cotton cellulose.

On the basis of formaldehyde content, C1-C2H4-CO-N unit and percent addon, this reagent can be said to belong to 'D' category i.e. some part of the reagent undergoes partial decomposition of dimethylol acid amide during the drying process.

DMEU and DMDHEU: These standard reagents have been included in this Table not with a view to comparing methylol acid amide with them but with the object of keeping a check on calculations made regarding percent RCON unit on the fabric, percent addon on fabric and percent reaction efficiency.

CONCLUSIONS

(1) Although most of the acid amides under study have shown fairly good extent of methylolation, the stability of methylolated acid amide especially under drying or curing operation was found to be extremely poor. One interesting point that deserves mention is that in most of the cases decomposition of these reagents has not proceeded beyond monomethylol stage and hence the major component of the reagent which reacts with cotton cellulose is the monomethylol acid amide. Since this is not a crosslinking reaction, R-CO-N units reacted through their methylol groups with cotton cellulose will remain as pendant groups and will not contribute to any improvement in crease recovery angle.

(2) Out of some eleven methylolated acid amides which have been studied (Table No.16), methylolated acetamide appears to be the best.
Stability of Methylol Acid Amide towards Acid Hydrolysis:

The detailed discussion given earlier is only a part of the total effort made to evaluate methylolated acid amides as crosslinking agents on the basis of their extent of methylation, their reaction efficiency and the closeness of percent $R$-$CO$-$N$ units and percent formaldehyde fixed on the fabric with theory. The percent $R$-$CON$ units on the fabric for a particular acid amide is a measure of the reaction efficiency of its methylol derivative with cotton cellulose. If percent $R$-$CON$ for a particular acid amide is close to theory it may indicate that its dimethylol derivative has more or less fully reacted with cotton cellulose or if it has undergone decomposition during drying and/or curing operation the same has not proceeded beyond monomethylol stage, the latter having reacted more or less fully with cotton cellulose. If percent $R$-$CON$ units on the fabric for a particular acid amide is way below the theoretical value, one may conclude that its methylol derivative is highly unstable during drying and/or curing operations resulting in decomposition beyond monomethylol stage and the hydrolyzed amide getting washed out during process wash. In other words, the information regarding percent $R$-$CON$ units on the fabric for particular acid amide gives some idea regarding the stability of methylolated acid amide during drying and/or curing operations and its reaction efficiency with cotton cellulose. The information regarding formaldehyde
content of the fabric for a particular acid amide is less informative than that regarding percent R-CO-N units on the fabric. No doubt, if methylolated acid amide undergoes decomposition during drying operation, the formaldehyde which is set free fails to react or does not react to any appreciable extent with cotton cellulose under the drying conditions employed (temperature and pH) as confirmed earlier. This is definitely reflected in formaldehyde content of the treated fabric which is less than the theoretical value and is clearly indicative of poor stability of methylolated acid amide under drying conditions. However, if formaldehyde content of the fabric for a particular acid amide is very close to theory it may indicate either high reaction efficiency of its dimethylol derivative with cotton cellulose or some decomposition of dimethylol derivative into monomethylol derivative and free formaldehyde, and both of them getting more or less fully reacted with cotton cellulose under the curing conditions employed. This high reaction efficiency indicated by the formaldehyde content of the treated fabric, however, fails to indicate as to whether this is really due to dimethylol compound getting reacted with cotton cellulose or monomethylol compound and formaldehyde (produced by the decomposition of the dimethylol compound) getting reacted with cotton cellulose separately under the curing conditions employed. To understand this aspect of the reaction, a study of the acid hydrolysis of the treated fabric was undertaken. The treated fabrics were treated with 0.1N HCl at 66°C for
40 minutes. This was considered as one acid hydrolysis treatment. Five such treatments were given to fabrics treated with various methylol acid amides and their nitrogen content, formaldehyde content and molar ratio of formaldehyde nitrogen after 1st, 3rd, 5th hydrolysis were determined. Findings of these experiments are given in Table No. 18. Over and above this, certain other physical properties such as dry crease recovery angle and percent solubility of the fabric in cuprammonium hydroxide after 1st, 3rd and 5th hydrolysis were also determined and are given in Table No. 19. Based on these findings, an attempt is made to evaluate methylolated acid amides as crosslinking agents. This evaluation is based on findings made by Cooke, Dusenbury, Kienle and Lineken which indicate that true crosslinks formed by the reaction between dimethylol compound and cotton cellulose, chemical bond resulting from condensation between monomethylol compound and cotton cellulose and polymeric crosslinks can be hydrolysed or can be broken gradually employing acid hydrolysis under the conditions stated above. On the other hand, methylene crosslinks formed by the reaction between formaldehyde and cotton cellulose remain unaffected even on repeated hydrolysis.

The data on molar ratio of CH₂O/Amide on the fabric in Table No. 18 for various methylolated acid amides before hydrolysis and after 1st, 3rd and 5th hydrolysis show a gradual increase which is indicative of the fact that methylene
<table>
<thead>
<tr>
<th>Finishing Agents</th>
<th>MF</th>
<th>MA</th>
<th>MP</th>
<th>MB</th>
<th>MIB</th>
<th>MTMA</th>
<th>MCA</th>
<th>MG</th>
<th>ML</th>
<th>MCP</th>
<th>MDMA</th>
<th>AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen content</td>
<td>0.52</td>
<td>0.69</td>
<td>0.60</td>
<td>0.60</td>
<td>0.68</td>
<td>0.46</td>
<td>0.60</td>
<td>0.64</td>
<td>0.54</td>
<td>0.57</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde content</td>
<td>0.92</td>
<td>2.50</td>
<td>1.91</td>
<td>1.75</td>
<td>1.66</td>
<td>0.95</td>
<td>0.90</td>
<td>1.86</td>
<td>1.77</td>
<td>1.69</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>Molar ratio HCHO/Acid amide</td>
<td>0.83</td>
<td>1.67</td>
<td>1.48</td>
<td>1.36</td>
<td>1.14</td>
<td>0.97</td>
<td>0.70</td>
<td>1.36</td>
<td>1.54</td>
<td>1.38</td>
<td>2.55</td>
<td></td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>0.224</td>
<td>0.304</td>
<td>0.144</td>
<td>0.096</td>
<td>0.10</td>
<td>0.03</td>
<td>0.29</td>
<td>0.168</td>
<td>0.14</td>
<td>0.087</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde content</td>
<td>0.375</td>
<td>1.40</td>
<td>0.50</td>
<td>0.59</td>
<td>0.71</td>
<td>0.30</td>
<td>0.34</td>
<td>0.82</td>
<td>0.83</td>
<td>0.37</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>Molar ratio HCHO/Acid amide</td>
<td>0.78</td>
<td>2.15</td>
<td>1.61</td>
<td>2.89</td>
<td>3.31</td>
<td>4.66</td>
<td>0.73</td>
<td>2.28</td>
<td>2.73</td>
<td>1.98</td>
<td>2.55</td>
<td></td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>0.19</td>
<td>0.12</td>
<td>0.086</td>
<td>0.073</td>
<td>0.04</td>
<td>0.018</td>
<td>0.08</td>
<td>0.079</td>
<td>0.042</td>
<td>0.063</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde content</td>
<td>0.32</td>
<td>0.563</td>
<td>0.313</td>
<td>0.48</td>
<td>0.35</td>
<td>0.190</td>
<td>0.16</td>
<td>0.53</td>
<td>0.486</td>
<td>0.27</td>
<td>2.18</td>
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</tr>
<tr>
<td>Molar ratio HCHO/Acid amide</td>
<td>0.79</td>
<td>2.20</td>
<td>1.70</td>
<td>3.07</td>
<td>4.1</td>
<td>4.92</td>
<td>0.93</td>
<td>3.12</td>
<td>5.39</td>
<td>2.00</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>0.067</td>
<td>0.11</td>
<td>0.025</td>
<td>0.017</td>
<td>Nil</td>
<td>Nil</td>
<td>0.063</td>
<td>0.039</td>
<td>0.027</td>
<td>0.011</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde content</td>
<td>0.114</td>
<td>0.55</td>
<td>0.12</td>
<td>0.13</td>
<td>0.125</td>
<td>0.025</td>
<td>0.13</td>
<td>0.53</td>
<td>0.48</td>
<td>0.19</td>
<td>2.18</td>
<td></td>
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<tr>
<td>Molar ratio HCHO/Acid amide</td>
<td>0.79</td>
<td>2.30</td>
<td>2.24</td>
<td>3.57</td>
<td>∞</td>
<td>∞</td>
<td>0.96</td>
<td>6.25</td>
<td>8.30</td>
<td>8.10</td>
<td>2.84</td>
<td></td>
</tr>
</tbody>
</table>
crosslinks formed by the reaction between formaldehyde donated by methylolated acid amides and cotton cellulose are present in all cases excepting MF. The conclusion drawn earlier on the basis of the data in Table No.15 is that all methylolated acid amides excepting MG, ML and MDMAA undergo decomposition mainly under drying operation. The acid hydrolysis study suggests, in addition, that some decomposition also takes place during curing operation. In case of MDMAA nitrogen content of the fabric and formaldehyde content of the fabric remain practically unaffected by acid hydrolysis indicating that this finish is very stable to acid hydrolysis. This exceptionally good stability towards acid hydrolysis could be due to the fact that MDMAA has a strongly basic dimethylamino group. This is substantiated by reports in the literature that finishes which passes a basic nitrogen are stable to acid hydrolysis, e.g. fabric treated with hydroxy methylated -2,substituted, 4,6-diamino-s-triazine has excellent stability towards acid hydrolysis. The stability of MDMAA to acid hydrolysis substantiates the findings of Cooke et al. that methylene crosslinks formed by the reaction between formaldehyde and cotton cellulose cannot be cleaved by acid hydrolysis under the acid conditions.

This study also supports the hypothesis given earlier that of the methylol acid amides studied, MG and ML undergo decomposition under curing conditions whereas the remaining decompose under drying conditions (Table No.15). Those compounds which undergo decomposition during curing produce methylene
crosslinks from liberated formaldehyde. These crosslinks, as stated earlier, remain unaffected during acid hydrolysis. The higher percentage of methylene crosslinks in the fabric, which will remain unaltered on acid hydrolysis, and the gradual removal of the amide finish by acid hydrolysis will bring about a fast increase in the molar ratio of formaldehyde to acid amide. This is actually the case with MG and ML. These two finishes give a very high formaldehyde content on the fabric after 5th hydrolysis compared to nitrogen content indicating high percentage of methylene crosslinks in the fabric. In order to ascertain the extent of decomposition during curing operation of those methylolated acid amides which decompose mainly under drying operation, data on molar ratio of formaldehyde to acid amide after acid hydrolysis of the finished fabric are given in Table No. 18. Molar ratio of formaldehyde upon acid amide after three hydrolysis has been selected because, it has been observed in case of MIB and MTMA that the finish gets completely removed after five hydrolytic treatments. Based on the molar ratio of formaldehyde to acid amide before hydrolysis, the percent increase in $CH_2O/Amide$ after three hydrolyses for various methylolated acid amides has been calculated and is included in the last column of the following Table:

It is evident from the data in this Table that the percent increase in $CH_2O/Amide$ after three hydrolyses gradually increases as one passes from MA to MTMA. This could be due
TABLE NO. 19
EXTENT OF DECOMPOSITION DURING CURING OPERATION OF METHYLOL ACID; AMIDES WHICH DECOMPOSE MAINLY UNDER DRYING OPERATION

<table>
<thead>
<tr>
<th>Finishing Agent</th>
<th>Molar ratio HCHO/Acid Amide</th>
<th>Molar ratio after three hydrolysis HCHO/Acid Amide</th>
<th>Percent increase in molar ratio after three hydrolysis HCHO/Acid Amide</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>1.67</td>
<td>2.20</td>
<td>32</td>
</tr>
<tr>
<td>MP</td>
<td>1.48</td>
<td>1.70</td>
<td>45</td>
</tr>
<tr>
<td>MB</td>
<td>1.36</td>
<td>3.07</td>
<td>126</td>
</tr>
<tr>
<td>MIB</td>
<td>1.14</td>
<td>4.10</td>
<td>259</td>
</tr>
<tr>
<td>MT</td>
<td>0.97</td>
<td>4.92</td>
<td>407</td>
</tr>
<tr>
<td>DMEU</td>
<td>1.07</td>
<td>4.30</td>
<td>402</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>0.98</td>
<td>6.95</td>
<td>709</td>
</tr>
<tr>
<td>MCA</td>
<td>0.70</td>
<td>0.93</td>
<td>33</td>
</tr>
<tr>
<td>MCP</td>
<td>1.38</td>
<td>2.00</td>
<td>45</td>
</tr>
</tbody>
</table>

to following reasons:

(1) As reported earlier in Chapter IV, the extent of methylolation of substituted acid amide \( R-\text{CO-NH}_2 \) decreases as \( R- \) passes from \(-\text{CH}_3\) to \(-\text{C(CH}_3)_3\). Since the same amount of formaldehyde (three moles of formaldehyde per mole of acid amide), has been used for methylolation of all acid amides under study, it is implied that as one passes from acetamide to trimethylacetamide, the concentration of free formaldehyde in the pad bath increases. From this would
follow that formaldehyde content of fabrics in terms of methylene crosslinks with these finishing agents will also increase as one passes from acetamide to trimethylacetamide. Since initial formaldehyde content in terms of methylene crosslinks gradually increases in the above series, the gradual removal of these finishes by acid hydrolysis will bring about gradual increase in the value of CH₂O/Amide.

The increase in molar ratio (after acid hydrolysis) of CH₂O/Imino compound in case of fabrics treated with DMEU and DMDHEU indicates the presence of methylene crosslinks, in the finished fabrics. Table No. 18 shows the same formaldehyde content of fabric (0.17%) treated with DMEU and DMDHEU since both of them have the same amount of free formaldehyde in the pad bath. The higher nitrogen content of fabric treated with DMDHEU as compared to that treated with DMEU is indicative of the fact that the fixation of DMDHEU compared is much better. This is largely due to the presence of two secondary hydroxyl functions per mole of DMDHEU (in addition to N-methylol functions).

(2) It is known that acid hydrolysis of fabrics treated with N-methylol compounds results in gradual removal of finishing agents. N-methylol compounds in the present study could be either dimethylol acid amide or monomethylol acid amide or a mixture of both. Regardless of the nature of N-methylol compound, the acid hydrolysis will bring about their gradual removal from fabrics treated with them. It can
safely be assumed that the gradual removal of finish by acid hydrolysis will result in gradual decrease in nitrogen content and formaldehyde content of fabrics treated with them. However, the formaldehyde content of fabrics in terms of methylene crosslinks will remain unaltered. Since acid hydrolysis brings about the removal of both the methylol groups (not methylene crosslinks but the formaldehyde attached to 'N' of acid amide) and acid amide. The increase in molar ratio of \( CH_2O/amide \) could only be due to gradual formation of methylene crosslinks in fabric from liberated formaldehyde. This in turn may indicate gradual increase in decomposition during curing operation.

To summarise, it can be said that as one passes from acetamide to trimethylacetamide in the given series of acid amides, the tendency of their methylol compounds to decompose during curing operation also (as reported earlier they decompose mainly under drying operation) increases.

(3) It has been reported by Reeves et al\(^{379}\) that substituent groups in the amido- methylol compounds play an important role in the electron displacement. Electron releasing groups attached to either the amido- nitrogen or the carbonyl carbon facilitate acid hydrolysis. The mechanism of acid hydrolysis with initial attack at the ethereal oxygen has been discussed at great length in the introduction part of this Chapter. As per theory given by Reeves et al\(^{379}\) the extent of acid hydrolysis of the reaction product of
N-methylol acid amide with cotton cellulose should increase as the substituent group \( R \) in the substituted acid amide molecule, \( R-\text{CO-NH}_2 \), passes from \(-\text{CH}_3\) to \(-\text{C-(CH}_3)_3\) in the given series of acid amides. This is also the order in which +I effects or electron releasing capacity of the alkyl group increases. In other words, the extent of removal of these finishes by acid hydrolysis from the fabrics treated with them will also increase as one passes from methylol acetamide to methylol trimethylacetamide in the given series of alkyl acid amide. Since the initial percentage of formaldehyde on the fabric in terms of methylene crosslinks remains unaltered on acid hydrolysis, the gradual increase in the extent of removal of finishes by acid hydrolysis brings about gradual increase in the molar ratio of CH\(_2\)O/Amide.

(4) Data on percent increase in molar ratio of CH\(_2\)O/Amide after three acid hydrolysis in case of MGA and MCP seem to support the finding made by Reeves et al that electron attracting groups attached to either amido nitrogen or carbonyl carbon hinder the removal of the finish by acid hydrolysis. Since the extent of removal of finishes in case of MCA and MCP is less than (due to the presence of electron attracting chlorine atom) that observed in case of finishes with electron releasing groups, the percent increase in molar ratio of CH\(_2\)O/Amide is also comparatively less. In the case of MCA, chlorine atom is comparatively closer to amido nitrogen than that in case of MCP which make the removal
of the finish more difficult in the case of MCA. This is also reflected in less increase in molar ratio of \( \text{CH}_2\text{O}/\text{Amide} \) after acid hydrolysis of MCA-finished fabric. The data given in Table No. 20 also seem to support the inferences drawn earlier regarding the presence of methylene crosslinks on fabrics finished with finishes under study. Thus, the finished fabrics show high insolubility in cuprammonium hydroxide solution and the solubility is not increased appreciably even after the 5th hydrolysis with acid. These results would indicate that the insolubility is due to methylene cross-links which are resistant to the hydrolytic treatment given to the fabric. The fact that DMEU and DMDHEU also show high insolubility in cuprammonium solution after acid hydrolysis indicates that some methylene cross-links are also produced by these reagents.

The data on percent nitrogen retained by fabrics finished with methylolated acid amides after five hydrolyses seem to support the results obtained by Reeves et al on electronic effects of substituent groups on the acid hydrolysis of amido methylol finished cotton. In the given series of methylolated acid amide the percent nitrogen retained by fabrics finished with them after five hydrolyses gradually reduces as one passes from MA to MB and then it becomes nil in case of MIB and MITMA indicating their gradually reducing resistance to acid hydrolysis. Methylolated acid amides with electron attracting substituent also seem to follow the theory given by Reeves et al.
The data in Table No. 20 indicate the following increasing order for resistance to acid hydrolysis of fabrics finished with methylol acid amides with electron attracting substituents

\[ MOP \ll ML \ll MG \ll MCA \]

This is in accordance with the following increasing electron attracting capacity of substituent attached to the acid amide molecule

\[
\begin{align*}
&\text{Cl} &\text{H}_2\text{C}-\text{CH}_2-\text{O} \\ &\text{CH}_3 &\text{H}_2\text{C}-\text{CH}_3\text{O} \\ &\text{CH}_2 &\text{H}_2\text{C}-\text{CH}_2\text{O} \\ &\text{H} &\text{H}_2\text{C}-\text{CH}_2\text{O}
\end{align*}
\]

The fabrics finished with MDMA need a special mention. These fabrics on progressive hydrolysis with acid lose very little of the finishing agent as shown by retained nitrogen and therefore maintain a high crease recovery level even after the 5th hydrolysis.

**Chlorine Damage**

The discussion given on the results obtained so far has indicated the following facts:

(1) The extent of methylolation of substituted acid amides \(\text{RCONH}_2\) containing electron releasing groups decreases as \(\text{R}^-\) passes from \(-\text{CH}_3\) to \(-\text{CH}(_3)_3\) whereas in the case of amides containing electron withdrawing groups the extent of methylolation decreases in the order

\[
\text{R} = \text{ClCH}_2 \rightarrow \text{Cl.CH}_2\text{CH}_2 \rightarrow \text{HOCH}_2
\]
The reasons for this behaviour have been discussed in Chapter IV. This implies that as one passes from acetamide to trimethylacetamide and from chloroacetamide to \( \alpha \)-hydroxy acid amide the amount of monomethylolated substituted acid amide increases in the pad bath, which in turn may give gradually increasing ratio of \(-CONH/-CON^-\) on the fabrics finished with them.

(2) The picture regarding gradually increasing ratio of \(-CONH/-CON^-\) on fabrics finished with substituted methylolated acid amides with electron releasing groups magnifies when coupled with data on stability of these finishing agents under drying and/or curing operations of the finishing treatment. The data given in Table No.15 of this Chapter clearly indicate that as one passes from MA to MTMA, their extent of decomposition increases. This implies that the ratio of \(-CONH/-CON^-\) on fabrics finished with these reagents increases as one passes along the above-mentioned series of methylol acid amides. In case of methylol acid amides with electron attracting substituents, the extent of methylolation is found to be very low except in case of chloroacetamide. Nevertheless all have undergone decomposition during drying and/or curing operations of the finishing treatment, the decomposition being highest in case of MCA. Combining the results obtained from methylolation study and calculation made on the extent of decomposition, it can be said that all methylol acid amides with electron attracting substituents have reacted with cotton cellulose as monomethylol
compounds and hence ratio of $-\text{CONH}$/$-\text{CON}$ on fabrics is very high.

In order to determine the effect in terms of a higher ratio of $-\text{CONH}$/$-\text{CON}$ on fabrics finished with methylol acid amides as compared to fabrics finished with conventional cross-linking agent, such as DMEU and DMDHEU, a study on chlorine retention damage was undertaken. In discussing chlorine damage of fabrics, it may be helpful to define certain terms normally used in describing this phenomenon.

(a) Chlorine retention may be defined as the phenomenon of chloramide formation by the action of hypochlorite solution on fabrics containing fixed nitrogeneous materials.

(b) Chlorine damage may be defined as the loss of fabric strength which occurs when a fabric containing chloramides is subjected to elevated temperatures and is normally measured by the AATCC tentative test method.

(c) A chlorine damage depressant may be defined as any material, which when added to a finish normally showing high chlorine damage of the finished fabric, will reduce chlorine damage.

With the above-mentioned definitions in mind, the chemical reactions involved in the phenomenon of chlorine retention and chlorine damage may be schematically represented as follows:

\[ \text{OCI}^- + \text{H}^+ \xrightarrow{\text{HOCI}} \]

\[ \text{C} \rightarrow \text{NH} + \text{HOCI} \xrightarrow{\text{HOCI}} \text{C} \rightarrow \text{N} \rightarrow \text{Cl} + \text{H}_2\text{O} \]

\[ \text{(A)} \]

\[ \text{(B)} \]
Reaction A and B are involved in chlorine retention. It can be seen from the equations that the amount of chlorine retained by a fabric will be determined by the following parameters: (i) The concentration of hypochlorite ion in the chlorination bath, (ii) the number of -C-NH groups present in the resin on the fabric, (iii) the equilibrium constant of reaction B for the particular resin temperature (provided that the fabric is in the chlorination bath long enough for equilibrium to be established), (iv) the temperature of the reaction, and (v) the rate or equilibrium constant of the reverse of reaction B which will depend on the method of rinsing, if rinsing after chlorination is involved. In addition, the rate of decomposition of the chloramide at room temperature must be taken into account if chlorine retention is to be measured a considerable length of time after chlorination takes place. In chlorine damage where reactions A through E are involved, the degree of damage will be determined by the degree of chlorine retention, the rate of reaction 'C' at the temperature of scorching, the strength of the fabric bases or the acidities of their hydrochlorides, the rate of reaction E at the scorching
temperature, and the time of scorching. In the AATCC test for chlorine damage, where many of the variables listed above are kept constant, the determining factors become the number of $-\text{C}-\text{NH}_2$ groups present in the resin, the equilibrium constant by reaction B, the rate of reverse reaction B, the rate of reactions C and E, and the strength of the fabric bases. The details of test method for determining the percent damage in tensile strength due to retained chlorine are given in Chapter II. The results on chlorine damage are given in the Table 21 below:

**TABLE No. 21**

**CHLORINE DAMAGE**

<table>
<thead>
<tr>
<th>No.</th>
<th>Finishing Agent</th>
<th>% Loss in T.S. due to Chlorine damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MF</td>
<td>..</td>
</tr>
<tr>
<td>2.</td>
<td>MA</td>
<td>..</td>
</tr>
<tr>
<td>3.</td>
<td>MP</td>
<td>..</td>
</tr>
<tr>
<td>4.</td>
<td>MB</td>
<td>..</td>
</tr>
<tr>
<td>5.</td>
<td>MIB</td>
<td>..</td>
</tr>
<tr>
<td>6.</td>
<td>MTMA</td>
<td>..</td>
</tr>
<tr>
<td>7.</td>
<td>MCA</td>
<td>..</td>
</tr>
<tr>
<td>8.</td>
<td>MG</td>
<td>..</td>
</tr>
<tr>
<td>9.</td>
<td>MCP</td>
<td>..</td>
</tr>
<tr>
<td>10.</td>
<td>ML</td>
<td>..</td>
</tr>
<tr>
<td>11.</td>
<td>MDMAH</td>
<td>..</td>
</tr>
<tr>
<td>12.</td>
<td>DMEU</td>
<td>..</td>
</tr>
<tr>
<td>13.</td>
<td>DMDHEU</td>
<td>..</td>
</tr>
</tbody>
</table>
It is observed from the data that as one passes from fabrics finished with MA to MTMA in the series of methylolated acid amides containing electron releasing groups, the percent loss in tensile strength due to retained chlorine gradually reduced. This is contrary to the expected order based on the ratio of $-\text{CONH}/-\text{CON}'$ on the fabrics. This ratio gradually increases as one passes from fabrics finished with MA to MTMA. This could possibly be explained as follows:

(a) It is well-known that in organic compounds belonging to the same homologous series, the melting point increases with the increase in the molecular weight of the homologue. It can be argued that chlorine retention by fabrics finished with the above-mentioned methylol acid amides may gradually increase as one passes from MA to MTMA on the basis of gradually increasing ratio of $-\text{CONH}/-\text{CON}'$ on fabrics finished with them, but the rate and extent of decomposition of chloramides formed on the fabrics may gradually reduce on the basis of their gradually increasing molecular weights. This will give gradually decreasing order of percent damage in tensile strength due to retained chlorine on fabrics finished with the said methylol acid amides as one passes from MA to MTMA.

(b) In Chapter IV, an attempt was made to explain the rates of methylolation of various acid amides which were found to be contrary to the expected one on the basis of inductive effect, by taking into consideration the relationship between conformation of acid amide and its reactivity. In Table No.10
of Chapter IV staggered conformation of various acid amides were shown. Taking into consideration those staggered conformations of acid amides on the fabrics treated with their methylol derivatives, it can be argued that as one passes from acetamide to highly substituted trimethylacetamide or as the bulk of the alkyl group increases in the series, the space around -CONH (which is responsible for chlorine retention) also decreases. As a result, the approach of the other reactant which is HOCl in the present study will be sterically more and more hindered. This may result in gradually decreasing chlorine retention by the finish. It appears from the data recorded in Table that percent damage in tensile strength due to retained chlorine decreases in the order

\[
-\text{CH}_3 \succ -\text{CH}_2\text{CH}_3 \succ -\text{CH}_2\text{CH}_2\text{CH}_3 \succ -\text{CH}(_3)_2 \succ -\text{C}(_3)_3
\]

i.e. as the substituent passes from a positive inductive (+I) to a more positive inductive (+I), the percent damage in tensile strength due to retained chlorine decreases. This could be explained by saying that as substituent groups in acid amide molecules fixed on fabrics through their methylol groups, pass from -\text{CH}_3 to -\text{C}(_3)_3, their electron donating tendency to amide nitrogen increases which ultimately results in the gradual strengthening of the N-H bond (responsible for chlorine retention) as one passes along the said series. In other words, N-H bond attached to -\text{CH}_3 group is weakest in the series, whereas that attached to
-C(CH₃)₃ group is the strongest one and hence the ease of substitution of H attached to N by chlorine is greatest acetamide and will be poorest in the case of trimethylacetamide. The same explanation holds good for fabrics finished with methylol acid amide with electron attracting substituent. The percent damage in tensile strength due to retained chlorine decreases in the order

\[-\text{CH}_2\text{Cl} = -\text{CH}_2\text{OH} \quad \text{CH}_3\text{Cl} = -\text{CHOH}\]

i.e. as the substituent passes from a negative inductive (-I) to less negative inductive (-I) substituent, the percent damage in tensile strength due to retained chlorine decreases. This could be explained by saying that as substituent groups in acid amide molecules fixed on fabrics through their methylol groups, pass from -CHOH to -CH₂Cl electron attracting tendency increases from amido nitrogen which ultimately results in the gradual weakening of N-H bond as one passes along the said series. In other words N-H bond attached to -CHOH is weak whereas that attached to -CH₂Cl is the weakest in the series and hence the ease of substitution of H attached to N by chlorine is higher in case of chloroacetamide than that in case of lactamide. This explains the chlorine retention being highest and hence highest chlorine damage on the fabric treated with MCA and that being lowest on fabric treated with ML.
(c) One noteworthy point in this study is that the fabric treated with MDMAA has shown very low percent damage in tensile strength due to retained chlorine (comparable to DMEU and DMDHEU) inspite of the fact that dimethylaminoacetamide has shown comparatively low extent of methylolation and its methylol derivative underwent considerable decomposition mainly under curing condition resulting into large number of -CONH groups on the fabric treated with it. This low chlorine retention damage can be attributed to the presence of highly basic -N(CH$_3$)$_2$ group.

**IR Spectra of Cotton Cellulose Treated with Methyololated Acid Amides:**

The IR spectra of various acid amides have been discussed at some length in the Chapter III, Table No.5. The salient features of that discussion are as follows:

(1) The amide II band appears close to Amide I band on low frequency side in case of all alkyl acid amides, so much so that it is difficult to distinguish between amide I and amide II bands. This is attributed to the sensitivity of amide I band to substitution on the $\alpha$-carbon atom. In other words, the presence of electron releasing groups in alkyl acid amide brings amide I band so close to amide II band that they almost merge with each other, the band position of amide I and amide II remaining insensitive to chain length of the substituted 'R' in acid amide molecule RCONH$_2$. 
The sensitivity of amide I band to substitution on α-carbon atom is more clearly understood by studying the IR spectra of acid amides containing electron attracting substituents which bring about the separation between amide I and amide II bands thereby making them distinguishable.

The above-mentioned two points explain the effect of the nature of substituents attached to -CONH₂ group of acid amide molecule on the band position of amide I. To understand the effect of substituents on the amido nitrogen atom on the band position of amide II and to understand the nature of reaction product between methylolated acid amides and cotton cellulose, IR spectra of cotton cellulose treated with methylolated acid amides with electron releasing substituents were taken by the method given in Chapter II. These spectra (Nos. 1-10) are shown in this Chapter. The Spectral Analysis is given in Table 22.

The spectra indicate the following facts:

(1) The band position of amide II which is insensitive to chain length of the substituent 'R' in acid amide molecule RCONH₂ appears to be sensitive to substitution on amido nitrogen atom. Due to the presence of substituent attached to amido nitrogen (R-NH-CH₂-O-Cell) its position is influenced and has ultimately brought about the separation of amide I and amide II bands thereby making them distinguishable.
INFRA RED SPECTRAS OF CHEMICALLY MODIFIED COTTON FABRICS

TRANSMITTANCE (%)

WAVELENGTH (MICRONS)

1. Blank
2. Formaldehyde
3. MF
4. MA
5. MP

6. MB
7. MIB
8. MTMA
9. MDAA
10. MG
TABLE No. 22
IR SPECTRAL ANALYSIS OF FABRICS TREATED WITH METHYLOL ACID AMIDES

<table>
<thead>
<tr>
<th>Spectrum No.</th>
<th>Methylol acid amide</th>
<th>Amide I band</th>
<th>Amide II band</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Untreated fabric</td>
<td>1639 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Formaldehyde treated</td>
<td>1639 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>MF</td>
<td>1695 cm(^{-1})</td>
<td>1613 cm(^{-1})</td>
</tr>
<tr>
<td>4.</td>
<td>MA</td>
<td>1667 cm(^{-1})</td>
<td>1563 cm(^{-1})</td>
</tr>
<tr>
<td>5.</td>
<td>MP</td>
<td>1667 cm(^{-1})</td>
<td>1563 cm(^{-1})</td>
</tr>
<tr>
<td>6.</td>
<td>MB</td>
<td>1667 cm(^{-1})</td>
<td>1563 cm(^{-1})</td>
</tr>
<tr>
<td>7.</td>
<td>MIB</td>
<td>1667 cm(^{-1})</td>
<td>1550 cm(^{-1})</td>
</tr>
<tr>
<td>8.</td>
<td>MTMA</td>
<td>1667 cm(^{-1})</td>
<td>1563 cm(^{-1})</td>
</tr>
<tr>
<td>9.</td>
<td>MDMAA</td>
<td>1667 cm(^{-1})</td>
<td>1550 cm(^{-1})</td>
</tr>
<tr>
<td>10.</td>
<td>MG</td>
<td>1667 cm(^{-1})</td>
<td>1587 cm(^{-1})</td>
</tr>
</tbody>
</table>

(2) The amide II band is weaker than the amide I band.

(3) The band at 1639 cm\(^{-1}\) in IR spectra of untreated cellulose which can be attributed to adsorbed water, has disappeared after treatment with methylolated acid amides.

(4) The amide II band is generally observed in the range 1570 cm\(^{-1}\) to 1510 cm\(^{-1}\) in the solid state. The IR spectral analysis of fabrics treated with methylol acid amides which show amide II band in the above range in most of the cases confirms the presence of -NH- groups on the fabric, which in turn indicates that cotton cellulose has reacted with mono-methylol acid amides.
An indication that methylol acid amides have reacted with cotton cellulose is given by the presence of amide I band at 1667 cm\(^{-1}\) which is due to C = O stretching.

Physical Properties of Fabrics Treated with Methylolated Acid Amides:

As reported earlier three moles of formaldehyde per mole of acid amide were used for the methylolation of various substituted acid amides at 10 pH and 55°C. At the end of two hours when the extent of methylolation for all acid amides under study had reached its maximum, the reaction mixtures were brought to 7 pH. Necessary dilutions were made to adjust the resin concentration after the addition of required quantity of MgCl\(_2\).6H\(_2\)O and sufficient quantity of citric acid to adjust the pH of the pad bath to 3 and reacted with cotton poplin employing low temperature drying and curing technique. A process wash was given to the treated fabric and after conditioning under standard conditions for required time, fabric properties in terms of dry and wet crease recovery angles, percent retained tensile and tear strength were determined. These data are given in Table 23. It is evident from this Table that except for MCA and MCP, high levels of dry crease recovery angle (DCR) ranging from 290° to 305° are obtainable with methylol acid amides listed in the above table as against DCR angles of 318° and 315° in case of DIMEU and DMDHEU respectively. It is also evident from the data that except for MCA and MCP high level of wet crease recovery angles (WCR) ranging from
273° to 298° are obtainable with the said finishing agents as against WCR of 287° for DM3U and DMDHEU.

As reported earlier in Table No. 15 of this Chapter, all acid amides except formamide and acetamide have shown low extent of methylolation and the methylol derivatives thus formed have shown a tendency to decompose during drying and/or curing operations. This implies that most of the methylol acid amides have reacted with cotton cellulose in the monomethylol form. This will lead to lower percentage of true crosslinks on the fabrics finished with methylolated acid amides than that generally obtainable in case of such crosslinking agents as DMEU and DMDHEU. Thus, it appears surprising that the high level and also of almost same level of crease resistance is imparted to cotton cellulose by methylolated acid amides (MF, MA, MP, MB, MIB, MIMA) regardless of the extent of methylolation of parent acid amide and decomposition of their methylol derivatives. This is possible only if formaldehyde donated mainly under curing conditions by these finishing agents gets reacted with cotton cellulose giving thereby methylene crosslinks. This is substantiated by the data (Table 28) on properties of fabrics, treated with methylol acid amide, after acid hydrolysis. The data show gradual fall in DCR angle as acid hydrolysis treatment gradually removed resins fixed on the fabrics in the form of true crosslinks, polymeric crosslinks and as pendant groups. It appears from the data on DCR angle and percent nitrogen retained after one hydrolysis that as compared to nitrogen
(resin) lost during acid hydrolysis, the fall in DCR angle is less which is not the case with DMEU and DMDHEU. This indicates the presence of fewer crosslinks in case of former than latter. Examining the data on DCR angles and percent nitrogen retained after five acid hydrolysis, it appears that fabric treated with DMEU shows improvement in DCR angle over the control fabric (the untreated fabric has DCR angle of 134°) in spite of the fact that almost all DMEU which was crosslinked with cotton cellulose has been removed; this could only be due to the presence of methylene crosslinks. This has been proved by an experiment wherein cotton poplin was treated with 4.5 formaldehyde solution under the conditions comparable to those employed for finishing of cotton poplin with methylol acid amides. The results indicated the presence of 0.09% formaldehyde on the treated fabric which brought about an improvement in DCR angle by 60° (Table 23). In the case of DMDHEU, DCR angle of 184° with some 9% retained nitrogen indicates the presence of some DHEU attached to cotton cellulose through its secondary C-hydroxyl functions, with its methylol groups removed due to acid hydrolysis. The DCR angle of 184° is due to the presence of methylene crosslinks. In case of MIB and MTMA it appears that the finish has been completely removed and DCR angles of 197° and 186° respectively are due to the presence of methylene crosslinks. In case of MP and MB it appears that there is some finish left on the fabric which does not contribute to improvement in DCR angles.
<table>
<thead>
<tr>
<th>Finishing agents</th>
<th>Crease recovery angle $(W + F)^\circ$</th>
<th>Tear strength (percent tear strength retained)</th>
<th>Tensile strength (percent tensile strength retained)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>$W$</td>
</tr>
<tr>
<td>MF</td>
<td>305</td>
<td>273</td>
<td>560 $(48.6)$</td>
</tr>
<tr>
<td>MA</td>
<td>300</td>
<td>291</td>
<td>528 $(45.8)$</td>
</tr>
<tr>
<td>MP</td>
<td>295</td>
<td>289</td>
<td>604 $(52.4)$</td>
</tr>
<tr>
<td>MB</td>
<td>293</td>
<td>287</td>
<td>544 $(47.2)$</td>
</tr>
<tr>
<td>MIB</td>
<td>298</td>
<td>298</td>
<td>368 $(31.9)$</td>
</tr>
<tr>
<td>MTMA</td>
<td>290</td>
<td>292</td>
<td>320 $(27.8)$</td>
</tr>
<tr>
<td>MDMAA</td>
<td>314</td>
<td>306</td>
<td>360 $(31.2)$</td>
</tr>
<tr>
<td>ML</td>
<td>297</td>
<td>272</td>
<td>478 $(41.5)$</td>
</tr>
<tr>
<td>MG</td>
<td>295</td>
<td>268</td>
<td>456 $(39.6)$</td>
</tr>
<tr>
<td>MCP</td>
<td>255</td>
<td>248</td>
<td>558 $(48.5)$</td>
</tr>
<tr>
<td>MCA</td>
<td>198</td>
<td>198</td>
<td>1008 $(87.5)$</td>
</tr>
<tr>
<td>DMEU</td>
<td>318</td>
<td>287</td>
<td>368 $(31.9)$</td>
</tr>
<tr>
<td>DMIDHEU</td>
<td>315</td>
<td>287</td>
<td>337 $(29.2)$</td>
</tr>
<tr>
<td>4.5% formaldehyde treated fabric</td>
<td>194</td>
<td>218</td>
<td>192 $(16.7)$</td>
</tr>
<tr>
<td>Untreated fabric</td>
<td>134</td>
<td>157</td>
<td>1152 $^{1}$</td>
</tr>
</tbody>
</table>

$^{1}$ Dry $^{2}$ Wet $^{3}$ Average
The DCR angle of 182° in this case is due to the presence of methylene crosslinks. In the case of MF and MA which appear to be more resistant to acid hydrolysis in the given series of methylolated alkyl acid amides, have 13 and 16% nitrogen retained respectively with DCR angles of 213° and 234° respectively. It may be said that these DCR angles are largely due to methylene crosslinks with some true crosslinks, contributing to DCR angles. The cases of MG and ML appear to resemble that of DMDHEU. DCR angles of 183° and 215° respectively are due to the presence of methylene crosslinks and the nitrogen retained by the fabric indicates the presence of glycolamide and lactamide fixed on the fabric through their C- hydroxyl functions and N-methylol functions which are likely to remain unhydrolyzed as per statement given earlier based on experimental facts that acid amides having electron attracting substituents attached to them have their methylol groups more resistant to acid hydrolysis than those attached to acid amides having electron releasing groups attached to them. The case of MCP seems to support the statement given above by retaining some finish attached to cotton cellulose through its N-methylol (mono) groups which does not contribute to DCR angle. The DCR angle of 180° is due to methylene crosslinks. In the case of MCA, since curing was not possible due to its sensitivity to heat the question regarding the existence of true crosslinks does not arise at all. Due to the presence of electron attracting substituent, it has retained some finish attach to cotton.
cellulose through its N-methylol groups. Lastly, since MDMMAA is very resistant to acid hydrolysis it has retained large percentage of proton fixed on cotton cellulose. Taking into consideration the data on extent of methylolation of dimethylaminoacetamide and the nature of decomposition of its methylol derivative it appears that high DCR angle before and after acid hydrolysis is largely due to the presence of methylene crosslinks.

WCR of Fabrics Treated with Methylol Acid Amides:
It is evident from data in Table 23, that except for MCA and MCP high levels of WCR angles ranging from 273° to 298° are obtainable with methylol acid amides listed in the above referred table. These could be due to the fact that temperatures during drying and curing were comparatively low. This implies that the reaction between methylol acid amides and cotton cellulose took place in a somewhat swollen state of the latter. It is a well-known fact that resin finishing of cotton cellulose in its swollen state brings about improvement in DCR angles and WCR angles of the treated fabrics over the control keeping a good balance between them.

Tear and Tensile Strength Losses of Fabrics Treated with Methylol Acid Amides:
It is evident from the data in Table 23 that high losses in strength ranging from
48% to 72% (warp tear strength),
59% to 84% (weft tear strength),
15% to 61% (warp tensile strength),
48% to 80% (weft tensile strength),

have resulted due to finishing treatment on cotton cellulose. This can be attributed to high percentage of methylene crosslinks on the treated fabrics. However, tear strength losses in case of DMEU and DMDHEU are more as compared to methylol acid amides.

**Mildewproofing and Rotproofing:**

Cotton, in common with the other natural cellulosic textile fibres, is inherently susceptible to utilization as a source of food by many microorganisms. These are, therefore, a source of great loss when they attack organic materials of economic value. These organisms produce chemical, physical and microbiological changes in the fibre involving loss of strength and usually marked discolouration. Indian cotton is least resistant to degradation by bacterial attack. The microorganisms are invariably present in greater or lesser numbers in the soil, in the air and upon the surfaces of textile materials and other substances. They become active whenever favourable situations for their growth occur. When drastic structural damage or actual disintegration of the textile occurs, the term "Rot" is customary, while "Mildew" is generally used when the destructive action is less severe. Many thousands of compounds have been screened for antimicrobial
potency in the past few years for textile preservation. Failures have been many and successes so few that some faint-hearted researches have fallen by the way side. Nevertheless, many factors indicate work of this sort must and will continue and will ultimately repay the efforts taken.

The subject of mildewproofing and rot resistant treatment was extensively reviewed in 1947\textsuperscript{393} and again in 1949.\textsuperscript{394} The general principles of rotproofing were outlined by Higgins\textsuperscript{395} in 1958. Rotproofing, which combines weather resistance with resistance to bacterial attack, was an ancillary advantage obtained with the Willesden waterproofing process\textsuperscript{396} used for tents and many other military and civilian applications.

Phenolic resins were claimed to have rotproofing properties,\textsuperscript{397} and better results were obtained more recently by using bromophenol-formaldehyde\textsuperscript{398} or chlorophenol formaldehyde\textsuperscript{399} resins for this purpose. The use of amino resins in conjunction with copper 8-hydroxyquinolinolate has also been suggested,\textsuperscript{400} and with melamine resins, which themselves have a rotproofing action, a synergistic effect is claimed.\textsuperscript{401} In the last few years zirconium salts have been proposed for use either alone or with copper or silver fungicides as rotproofing agents for cotton,\textsuperscript{402,403} and attention has been drawn\textsuperscript{404} to the bactericidal properties of finishes based on THPC. Vigo and Welch have reported\textsuperscript{405} that in chlorodeoxy celluloses
rot resistance is found proportional to the percent chlorine in the cellulose. Recently, Srivastava and co-workers have also shown that chlorodeoxy cellulose fabrics show very good rot resistance.

Although nonreactive rotproofing finishes for cellulosics are well known, the use of reactive compounds for this purpose has only been very recently published. The first attempt in this direction was the use of N-methylolchloroacetamide in the presence of an acid catalyst. The other attempt to improve rot resistance of cellulosic material involved the impregnation of cotton cellulose with an aqueous solution of haloacetamide or hydroxymethylacetamide, formaldehyde and an acid catalyst.

Thus, previous researches on halogen-containing compounds and hydroxy compounds suggest the hypothesis that compounds containing both methylol group and halogen and hydroxyl group would impart permanent rot resistance to cotton cellulose. With this hypothesis in mind, a few halogen-containing N-methylol acid amides and N-methylol hydroxy acid amides have been synthesized, reacted with cotton cellulose in presence of acid catalyst under drying and curing conditions given in the Table 24. The treated fabrics have been evaluated for their rot-resistant properties using the conventional soil burial test method. The results of these experiments are summarized in Table 24.
TABLE NO. 24

ROT RESISTANCE OF FABRICS TREATED WITH N-METHYLOL HALO AND HYDROXY ACID AMIDES

<table>
<thead>
<tr>
<th>No.</th>
<th>N-Methylol halo and hydroxy acid amides and (their designation)</th>
<th>Nitrogen content of fabric (%)</th>
<th>Halogen content of fabric (%)</th>
<th>Percent tensile strength retained (in soil burial test) After 7 days</th>
<th>After 14 days</th>
<th>After 21 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methylol lactamide (ML)</td>
<td>0.18</td>
<td>-</td>
<td>66</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Methylol mandelamide (MM)</td>
<td>0.14</td>
<td>-</td>
<td>61</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Methylol α,β-dibromopropionamide (MDBP)</td>
<td>0.18</td>
<td>2.0</td>
<td>94</td>
<td>87</td>
<td>85</td>
</tr>
<tr>
<td>4.</td>
<td>Methylol α,β-dibromocinnamide (MDBC)</td>
<td>0.13</td>
<td>0.8</td>
<td>88</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>Methylol 2,4,5-trichlorophenoxyacetamide (MTCPA)</td>
<td>0.08</td>
<td>0.6</td>
<td>97</td>
<td>52</td>
<td>35</td>
</tr>
<tr>
<td>6.</td>
<td>Methylol 2,4,6-tribromophenoxyacetamide (MTBPA)</td>
<td>0.04</td>
<td>0.7</td>
<td>69</td>
<td>41</td>
<td>32</td>
</tr>
</tbody>
</table>

Control fabric loses 90% of its original tensile strength after seven days of exposure. In cases of MM, MDBP, MDBC, MTCPA and MTBPA methylolation was carried out in dimethylformamide and for fabric treatment water was added to a point when N-methylol compound was about to precipitate. Water was used for methylolation and for fabric treatment in the case of methylol lactamide.
It is evident from the data in Table 24, that although fabrics have been finished with 0.15 mole of N-methylol haloacid amides and N-methylol hydroxy acid amides, their fixation on the fabric is different. Based on percent nitrogen on the treated fabrics, fixation of various N-methylol compound on fabric finished with them can be arranged in the following ascending order:

\[
\text{MTBPA} < \text{MTCPA} < \text{MDBC} < \text{MM} < \text{MDBP} = \text{ML}
\]

The result contained in the Table 24, seem to support the findings made by Vigo and Welch\textsuperscript{405} that halo compounds impart rot resistance to cotton cellulose and this resistance is proportional to the percent halogen on the fabric. MDBP, by virtue of its reasonably low molecular weight, high bromine content and highest fixation on the fabric in the given series of N-methylol compound has highest percent halogen on the fabric treated with it. This has resulted in maximum rot resistance to fabric amongst the compounds tested.

MTCPA, by virtue of its higher fixation than MTBPA on the fabric has imparted higher rot resistance to cotton fabric than MTBPA. In the case of MDBC, although its fixation and thereby percent halogen on cotton fabric is reasonably high in the given series of N-methylol compounds the rot resistance imparted to cotton fabric treated with it is quite low.

Among N-methylol hydroxy acid amides ML, by virtue of its higher fixation on cotton fabric has imparted higher rot resistance than MM.
Effect of Introduction of Basic Groups in Cellulose on its Dyeing Behaviour

In the case of literature survey it was found out that introduction of basic residues in cellulose result in the formation of a strong affinity for acid dyes\textsuperscript{409}. Little later, it was found out that this is not only true of acid dyes but also most cotton dyes are taken up more rapidly by aminised cellulose and show better light fastness and washfastness than acid dyes\textsuperscript{410}. The fact that even very low degree of substitution of basic residue on cotton (compared with other modifications of cellulose) can alter the properties of cotton made us explore the possibility of higher dye uptake by fabric treated with N-methylol dimethylaminoacetamide (MDMAA) compared to untreated fabric by the virtue of its basic nature due to the presence of highly basic dimethylamino group fixed on the fabric due to the said treatment.

To evaluate the dyeing performance of cotton fabric which has been rendered basic, dyeing of the said fabric and that of control fabric for comparison was carried out under identical conditions. The details of dyeing technique employed and test methods for the evaluation of dyed fabrics are given in the Chapter II.

It has been found that the fabrics which have been rendered basic have shown high affinity for the dye than that shown by the normal fabric.
So far as lightfastness and washfastness is concerned it can be said that they are comparable, but so far as staining on white is concerned, modified fabrics are inferior to unmodified fabric.

The higher affinity of the fabric which has been rendered basic, for reactive dyes and thereby higher dye uptake shown by the said fabric than that shown by the normal fabric can be explained as follows:

It is well-known that the reactivity of the triazine dye may further be increased by replacing the chloro group of the monochlorotriazine dye by a quarternary-ammonium radical. It is also known that such tertiary amine as trimethylamine can be used as a catalyst to increase the reactivity of monochloro reactive dyes. The tertiary amine reacts with chlorotriazine reactive dyes forming quarternary ammonium compound. When this dye, which is more reactive than the original dye, reacts with the fabric, the tertiary amine is reformed. This amine gets quarternised with further amount of dye, thereby activating it. This process continues till all the reactive dye has reacted either with fabric or water.

In the present case there is no tertiary amine catalyst added to the dye bath but tertiary amine catalyst built in cellulose, which is responsible for dye uptake.