CHAPTER I

INTRODUCTION
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At the beginning of this century, man was still clothing himself almost exclusively in the materials which were in use in ancient Egypt and ancient China: cotton and wool and for rich also silk. This provided little variety in clothing material, and the clothes of the greater part of the population were drab and uninteresting; they also required considerable care and labour in washing and drying them. But, today there is a wide range of apparel fabrics which are attractive to look at, pleasing to handle, and are easy to wash and dry. A feature of modern life is the attention which is paid to dress to making it attractive, varied and smart; and the achievement of this has been made possible by the discoveries and development work in the field of fibres made by man. The fabrics made from polyester and polyamide fibres show the property of crease resistance in addition to having high tensile strength. While these properties are superior to those of cotton fibre and fabrics, the latter give maximum comfort during wear inasmuch as they are able to absorb the perspiration of the body and therefore give a cooling effect. In order to combine the good points of polyester and cotton fibers, they are blended with each other and the fabric prepared from such blends are quite satisfactory both in self-smoothing.
characteristics and in wear life. Although synthetics have made fairly deep inroads into the textile industry, cotton is still the major raw material for textiles, the world over. The following data on world production of cotton\(^1\) substantiate the above statement.

### TABLE I

<table>
<thead>
<tr>
<th>Year</th>
<th>World Cotton Production (million bales)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970-71</td>
<td>52.5</td>
</tr>
<tr>
<td>1971-72</td>
<td>57.0</td>
</tr>
<tr>
<td>1972-73</td>
<td>59.5</td>
</tr>
</tbody>
</table>

The other factor in its favour so far as India is concerned is its much lower cost as compared to synthetic fibres.

Compared to synthetic fibres, cotton fibre has a very low level of crease recovery with the result that garments made out of pure cotton have to be ironed after each wash to give a well-dressed appearance to the wearer. Even a well-ironed cotton garment after having been worn for a short time presents a messy appearance because the creases which are produced during wear are not smoothened out. Removal of this serious defect from cotton by cross-linking is perhaps one of the greatest achievements in the history of textile finishing and is an outstanding example of the application of chemistry to textile technology.
Current researches on cotton aim at producing crease-proof fabrics which equal man-made fibre-fabrics in easy-care performance with as little sacrifice as possible of other desirable qualities possessed by cotton.

Though it was known as early as 1906, that formaldehyde reacts with cellulose in the presence of strongly acidic catalysts forming methylene cross-links, which greatly reduce water imbibition and improve crease-recovery properties, the first commercially successful start in this field was made only in the year 1928. Messrs: Tootal Broadhurst and Lee Company Ltd. patented a finishing treatment of viscose fabrics with urea-formaldehyde and claimed antishrinking properties for the finished fabrics. Marsh, a pioneer in this field has mentioned that at the time of the invention of crease-resistant finishes, the structure of neither textile fibres nor of synthetic resins was clear. Since these aspects have now been well understood, it would be worthwhile to review briefly the chemistry, morphology and structure of cotton fibres and also the structure of crease-proofing agents.

CHEMISTRY, MORPHOLOGY AND STRUCTURE OF COTTON

Cotton is a plant of the genus Gossypium, is a member of the family Malvaceae or Mallow and of the tribe Hibisceae. The boll of the ripe cotton plant contains seeds to which are attached cotton fibres ranging in size from average length of 0.2 to 2.5 inch and in diameter from 0.001 to 0.005
inch. The fibres have a flattened, twisted, hollow ribbon-like form. The fibre in raw cotton consists mainly of cellulose (85 to 90%) along with impurities like wax, hemicellulose, fatty acids, protein, pigments, moisture and ash. Purified cotton \textsuperscript{8,9} contains 99.5 percent cellulose.

Cellulose owes its name to Anselme Payen, \textsuperscript{10} a French botanist, who investigated the constituents of plant cell walls in the period 1837 to 1842. Cellulose is the chief component of the cell walls of most plants and is a polysaccharide. It is a polymer of \textbeta-D-glucopyranose residues. The manner in which these units are joined in the cellulose molecule is shown in Fig. 1. Thus, cellulose is poly-(1\textarrow{4})-\textbeta-D-glucopyranose. The number of glucose units \textsuperscript{11,12} in native cotton cellulose has been found to be about 5000.

The parallel alignment of the chains of cellulose molecules gives rise to crystalline regions in the cotton fibre. They are oriented regularly to form highly ordered inner or secondary wall. \textsuperscript{13} In the outer or primary wall of the cotton fibre the chains of cellulose molecules are arranged irregularly. The central canal of the fibre is known as lumen which is closed at the tip.

The earlier theories \textsuperscript{14-17} proposed for the crystalline region of cotton fibre were often modified \textsuperscript{18-23}. Amongst these theories \textsuperscript{24-27} proposed in the light of electron microscopy, the "fringed fibril" theory developed by Hearle \textsuperscript{23,25,28,29} is most important and widely accepted. According to this
theory, the crystalline regions are to be regarded as fringed fibrils with the individual chain molecules diverging from the fibrils at different positions along their lengths. It is also evident from the chemical studies by Nair\(^{30}\) and X-ray studies by Patil et al.,\(^{31}\) that the chain molecules pass through crystalline and amorphous regions.

The fibrils are crystalline in nature\(^{32}\) varying in diameter and arranged in concentric cylindrical layers in the wall. They are rather randomly oriented in the primary wall and form regularly aligned right and left handed helices in the secondary wall, with sign reversals occurring simultaneously for all helices of the secondary wall. A model of fibre cell wall showing spiral structure and reversal in growth layers\(^{33}\) is shown in Fig. 1. The cotton fibre follows a similar trend in cell wall structure.\(^{34}\) Recently, Ingram and Morosoft\(^{35}\) have shown that the spiral angle is constant within the range of 20-23°.

Very recently Ingram\(^{36}\) has suggested a model for cotton cellulose with the help of most modern techniques like electron micrography, dark field micrography, and wide- and small-angle X-ray diffraction. He has shown that the fibrils consist of needle shaped crystals separated irregularly along their length by twist and tilt boundaries as shown in Fig. 2.

The macrofibrils with preferred range of width between 1000 to 1200 Å seem to be bundles of microfibrils held together with
CHEMICAL STRUCTURE OF CELLULOSE CHAIN

CONFORMATIONAL STRUCTURE OF CELLULOSE CHAIN

MORPHOLOGICAL STRUCTURE OF THE COTTON FIBRE

Fig. 1
Schematic mode of the twisting and tilting of crystallites in the secondary wall fibrils of cotton

Fig. 2
a lower level of free energy. The microfibrils with a width between 100 and 400 Å are composed of densely packed elementary fibrils of 50 to 60 Å diameter.

The amount of crystallinity as measured from the intensities of X-ray powder diagram was found to be about 70 percent for natural cellulose, about 50 percent for mercerized cellulose and about 40 percent for regenerated cellulose. Crystalline and non-crystalline materials are responsible for strength and flexibility respectively.

Throughout the native fibres, a system of fine and coarse capillaries also exists. The capillary system, permeating the fibre from its surface to the Lumen, is responsible for the accessibility of the native fibres to dyes, swelling agents or other reagents.

**MECHANISM OF CREASE FORMATION AND CREASE RECOVERY OF COTTON TEXTILES**

When a cotton fabric is folded sharply so that a crease is formed, the fibres at the crease are strained. The fibres on the outer side of the bend are subjected to tensile stress and are elongated, while those inside the bend are under compression. Each element of the cotton fibre -- a molecule, a crystallite or a microfibril is also subjected to these forces. Under the influence of the external stress, the strain is thrown on the hydrogen bonds, Vander Waals forces and primary valency bonds. The whole system is disturbed from its equilibrium. The bonds take up the stress and strain,
with the result that some weaker bonds break. The movement of the molecules takes place in the direction of the stress and if they come closer to the other molecules they form new bonds with their neighbours. A new equilibrium is then set up in the system under the applied stress and a new configuration results. When the load is removed, the equilibrium attained by the new forces will be disturbed once again. The strains on the bonds will be no longer in the balanced position. The movement will start again to achieve new equilibrium. New forces formed between the cellulose molecules will oppose the movement. As a result, the original configuration before the stress was applied will not be attained. The fibres do not recover from the strained position and hence a crease is formed. In short a crease can be thought as an irreversible deformation in the fabric due to the application of a stress.

Fabrics made from animal fibres such as wool and Mohair as well as from man-made fibres such as "Terylene" have little tendency towards wrinkling as compared to cellulosic fabrics. The percentage elastic recovery and extensibility of some natural and synthetic fibres are given in Table 2. Terylene, Nylon and Wool possess high elastic recovery and extensibility, while cotton has the least extensibility and very low elastic recovery. This difference in elastic properties is attributed to differences in molecular structure.
TABLE 2

<table>
<thead>
<tr>
<th>Fibre</th>
<th>% Extension</th>
<th>% Elastic recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>Cotton</td>
<td>8</td>
<td>36</td>
</tr>
<tr>
<td>Viscose</td>
<td>21</td>
<td>36</td>
</tr>
<tr>
<td>Silk</td>
<td>26</td>
<td>51</td>
</tr>
<tr>
<td>Wool</td>
<td>38</td>
<td>75</td>
</tr>
<tr>
<td>Nylon</td>
<td>22</td>
<td>91</td>
</tr>
<tr>
<td>Terylene</td>
<td>20</td>
<td>70</td>
</tr>
</tbody>
</table>

Thus, the crease recovery of the fabric depends upon the fibre elastic recovery which can be improved by the introduction of cross-links between adjacent molecular chains in the fibre.

Theories of Resiliency in Resin Treated Textile

"Resin" treatment of cellulosic textiles gives rise to better crease recovery. How exactly the resin brings about observed changes is still controversial. Two theories are prevalent namely (i) resin polymer deposition theory, and (ii) Covalent cross-linking theory.

According to resin polymer theory, the increase in crease recovery is merely due to interstitial deposition of the hard, infusible, amorphous resin polymer, which increases lateral
intermolecular interactions by Van der Waals forces or perhaps by hydrogen bond formation. The cross-linking theory states that the molecules of the creaseproofing agent, which must be at least bifunctional, reacts with OH groups on cellulose chains and form bridges between them. These bridges or cross-linkages are bound to cellulose by true chemical covalent bonds. This theory is supported by an impressive amount of evidence. Moreover, only bifunctional reactants are particularly efficient in improving the resiliency of cellulosic fabrics. For example monomethylolurea and dimethylolurea treated fabrics show vast differences in crease-resistant property. Aben, Stamm and Zollinger have also put forth a direct chemical evidence of the existence of cross-linkages in cellulose treated with bifunctional reactant such as divinylsulphone. By degrading the treated material with 72% sulfuric acid and analysing the products, adducts of glucose units with mono and dimeric sulphone were obtained as degradation products.

In the conventional process, fabrics are impregnated with resin precondensates, dried, and finally cured at elevated temperature. In the structure of the treated cotton fabric there is a combination of normal hydrogen bonds, heat-formed hydrogen bonds, and resin entanglements which provide an elastic network and restrict fibrillar and molecular slippage, reduces swelling and stabilizes the fibres in the configuration prior to curing step. Crease-resistant properties of fabric depends on the number of cross-linkages.
Reactivity of various synthetic resins to cotton fabric depends upon the size and chemical nature of the compound and reaction conditions.

DISTRIBUTION OF CROSSLINKS
In the cross-linking of cotton cellulose, the reversible reactions of hydroxyl groups of cellulose with cross-linking agent is of relevance. Reagents like activated vinyl compounds, carboxylic acids, N-hydroxymethyl compounds, and formaldehyde undergo reversible reaction with hydroxyl groups. It is observed that the following factors are important in determining the site of reaction in the gluco-pyran units:

1. The type of reaction, e.g. reversible or irreversible;
2. The specific nature of the reagent, e.g. molecular size;
3. The reaction medium.

Regarding the attack of the reagent on the glucose unit along the molecular chain, there exists clear evidence that there is a rather pronounced nonuniformity.\(^{48,49}\)

Considering fringed fibril theory where continuous regions of crystallinity are postulated, one would tend to presume that the accessible hydroxyl groups are chiefly of those glucose units that lie on the surfaces of the crystalline regions plus some hydroxyl groups of glucose units which lie in the regions of imperfect order. Thus, accessibility might
be expected to be different for each type of hydroxyl group. It is evident from the data obtained by several workers (a) that heterogeneous reactions of cotton cellulose in weaker swelling media take place to a substantial extent on the surface of microstructural units of the fibre; (b) that there is a selective accessibility of the individual type of hydroxyl groups on the surfaces of these microstructural units; and (c) that there is an interrelationship between the site of attachment of a substituent group at the 2-O-, 3-O-, or 6-O- position in the glucose unit and the site of attachment in or on the micro-structural unit.

Chemical and analytical data have indicated that the conditions which accelerate the rate of reaction or which decelerate the rate of diffusion into the fibre, cause a disproportionate amount of reaction to occur in the peripheral regions of the fibres.

CHEMICAL REAGENTS FOR MODIFICATION OF CELLULOSE

The literature on various reagents used in improving cotton wrinkle recovery is voluminous. The reagents which are used as crease proofing agents are bifunctional or polyfunctional. They are sometimes known as reactants, as they have greater tendency to react with cellulose than with themselves. The number of crosslinking agents can be classified into the following two major groups:

(A) Nitrogenous, and
(B) Non-nitrogenous
These groups can be sub-classified as below:

(A) NITROGENOUS CROSS-LINKING AGENTS
   1. Urea Derivatives
   2. Melamine Derivatives
   3. Cyclic Urea Derivatives
   4. Triazone Derivatives
   5. Uron Derivatives
   6. Epimine or Aziridine Derivatives
   7. Diisocyanate Derivatives
   8. Carbamate Derivatives
   9. Amide Derivatives

(B) NON-NITROGENOUS CROSS-LINKING AGENTS
   1. Aldehyde and Dialdehyde
   2. Epoxides
   3. Chlor-alkyl Compounds
   4. Sulphones
   5. Acetals
   6. Miscellaneous

(A) NITROGENOUS CROSS-LINKING AGENTS

(1) Urea Derivatives
The first of the crease-proofing agents to be applied satisfactorily on a wide commercial scale was urea-formaldehyde. Urea is capable of condensing with formaldehyde under alkaline medium to give dimethylolurea

\[ \text{H}_2\text{C}-\text{HN}-\text{CO}-\text{NH}-\text{CH}_2\text{OH} \]

I

Dimethylolurea
The methylol compound has two reactive positions: (1) the imino-hydrogen, and (2) the hydroxyl hydrogen. Further condensation can therefore, take place with the elimination of water, hence the 'shelf life' of (1) is not very long, but it can be extended by various devices, such as the addition of hexamine, or by blocking the hydroxyl groups with methyl groups.

\[
H_3COH_2C-HN-CO-NH-CH_2OCH_3
\]

**II**
Dimethoxymethylurea

The main defects of fabrics finished with urea-formaldehyde are extensive strength-losses, chlorine-retention and tendering on bleaching and susceptibility towards hydrolysis. In spite of all these drawbacks, very large quantities of dimethylol urea are still used all over the world, either alone or in admixture with other products of alleged superiority. The cheapness and efficiency of urea-formaldehyde counter balance the cost of new compounds.

(2) **Melamine Derivatives**

The chemical name of melamine is 2:4:6-triamino-1:3:5-triazine; it is a cyclic compound which is interesting to compare with the trimeride of urea. Like urea, melamine reacts with formaldehyde to give methylol derivative, and it is possible to replace all the aminohydrogens; hence it is possible to form hexamethylol melamine. In general, however, trimethylol melamine is the commonest derivative in commercial use.
Like urea formaldehyde, solubility and stability of melamine formaldehyde can be improved by methylation.

The finished fabric has reasonably good resistance to hydrolysis but although it was originally expected that melamine would solve the problem of chlorine-retention damage associated with urea-formaldehyde, these hopes were not completely fulfilled. As is well-known, the problem centres round the formation of chloramides; with melamine, the chlorine is more firmly bound than with urea, but there is a yellowing discolouration of the treated fabric. Melamine is more basic than urea and so, due to buffering action loss in tensile strength is least.

(3) Cyclic Urea Derivatives
(a) Dimethylol ethylene urea: The first of the cyclic urea products to be developed was based on dimethylol ethylene urea popularly called DMEU.
This type of reagent possesses certain inherent advantages in that, as compared to dimethylol urea, there is no imino hydrogen to react with hypochlorite. Furthermore, DMEU is highly reactive, producing good crease recovery, with minimum of reagent; it is argued that DMEU is highly efficient because of its reactivity with cellulose without much tendency to resinify. However, good chlorine resistance requires careful application and the effect may be lost after repeated laundering under alkaline conditions and rapidly lost on acid hydrolysis.

(b) Dimethylol dihydroxyethylene urea: Another cyclic urea of a similar type is dimethylol dihydroxy ethylene urea (DMDHEU).

![Chemical Structure](image)

V. Dimethylol dihydroxyethylene urea

This widely used product gives good resistance to hydrolysis and to chlorine, inspite of its five membered structure. It has been suggested that all the hydroxyl groups react with cellulose with consequent advantage, such as minimum adverse effect on the fastness to light of many dyed fabrics. Stability of the finish has rendered this product attractive for durable-press treatment of garments.
(c) Dimethylol propylene urea: A related compound which is devoid of some of the defects of DMEU is dimethylol propylene urea.

VI. Dimethylol propylene urea

Chlorine-damage resistance in the treated fabric is very good and is retained throughout repeated alkaline launderings; there is still some sensitivity to acid hydrolysis, however. Much of the increased stability of the finish is associated with the presence of six membered ring structure as opposed to five membered ring structure of DMEU. Its use is restricted to high quality goods for special purposes.

(4) Triazone Derivative

Perhaps the cyclic urea reagents that replaced DMEU to a considerable extent are the dimethylol triazones, of which the ethyl derivative is perhaps the most popular.

VII. Dimethylol ethyl triazone
The chief claim for superior results with triazones is on the grounds of resistance to damage by hypochlorite bleach during laundering, for the tertiary amine group of the triazone neutralises the acid formed from the retained chlorine and so prevents degradation of the fabric. Furthermore, the salt formed is decomposed during alkaline washing, so that the tertiary amine group is regenerated to take up acid again when necessary.

In general, however, it was found that the triazones gave poorer crease recovery than other resin treatments, and furthermore, their durability was not as good as that from either melamine formaldehyde or DMEU.

(5) Uron Derivative

Another cyclic urea of commercial interest is the product called bis(methoxy methyl) uron or sometimes simply uron.

Careful preparation is essential for proper chlorine-damage resistance. The outstanding properties obtained by finishing cotton with pure \( N, N' \)-bis (methoxy methyl) uron are explained on the basis of the stability of the uron ring in this agent.
(6) Epimine or Aziridine Derivative

Epimines, like epoxides, are alkylating agents that react with nucleophilic partners. Thus, they can be made to react with the electron-rich groups of native fibres.

\[
\begin{align*}
\text{IX. Carbonyl bisaziridine} & & \text{and} \\
& & \\
\text{X. Tris-aziridinyl triazine}
\end{align*}
\]

Physical and chemical properties of treated fabric depend upon the nature of the finish and number of epimines groups. Fabric treated with (IX) has ion exchange property.\(^5\)

It must be remembered that all derivatives of ethylenimine involve some health hazard\(^5\) and in general, are expensive to prepare.

(7) Diisocyanate Derivatives

There have been many efforts to use the reactive groups in textile fibres, such as the hydroxyl groups in cellulose and poly (vinyl alcohol) and the imino groups in polyamides, to establish within the fibre a polymeric network. Bifunctional diisocyanates used to achieve this purpose.
Reaction of diisocyanates with cotton fabric has been proved by chemical analysis.

(8) **Carbamate Derivatives**
Recently a new type of methylol amide reagents have been used for finishing textiles. These are the dimethylol monocarbamates.

\[
\text{R-O-CO-N}^+\left\{\begin{array}{c}
\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH}
\end{array}\right.
\]

**XII. Dimethylol carbamate**

The finished fabric is exceptionally resistant to both acid and alkaline hydrolysis, as well as to chlorine retention damage. Carbamates are more difficult to apply than is the case with conventional amino aldehyde; a "hard cure" is sometimes necessary for satisfactory results. Ethylcarbamate forms tumor in mice, but methyl and hydroxyethylcarbamates are free from this stigma. Isopropyl carbamates have been found to be the most reactive.

(9) **Amide Derivatives**
The significant feature of amide and carbamate derivatives
is that two methyolol groups are on a single amido nitrogen.

\[ R\ CO\ N\ \overset{\text{CH}_2\text{OH}}{\text{CH}_2\text{OH}} \]

XIII. Dimethylol acid amide.

It is virtually impossible to dimethylolate these bases completely. Formamide, acetamide, isobutyramide and a number of other amides have been shown to impart crease resistance and shrink resistance to cotton fabric. Methylol acrylamide recently achieved a level of commercial importance.

(B) NON-NITROGENOUS REAGENTS

Nitrogen free cross-linking agents have the advantage that they produce an absolute resistance to chlorine and that no fishlike odour remains after finishing treatment. In general, however, the crease resistance effects obtained are not particularly good.

(1) Aldehyde and Dialdehyde Derivatives

The simplest acetalization and cross-linking of cellulose is obtained by finishing with formaldehyde. Roff reviewed the reaction of formaldehyde with cellulose. In the presence of alkalies formaldehyde produces only a temporary change in the physical properties of cellulosic fabrics; while in the presence of acids, formaldehyde forms methylene ether links between the cellulose molecules. According to Heuser, only a very small number of methylene ether links are necessary to
alter completely the physical properties of the fibre. The finishing process can be carried out with formaldehyde in aqueous, nonaqueous or in gaseous form. 65,66

Dialdehyde such as glyoxal, 67 glutaraldehyde, α-hydroxy adipaldehyde impart crease resistance to cotton fabric with strength retention similar to formaldehyde. 68,69 Preferably, they are used in conjunction with a polyhydric alcohol to minimise yellowing. 70

(2) Epoxide Derivatives 71-73

Amongst the new resins for textile uses, are the epoxy resins which contain no nitrogen in the molecule, nor do they contain methylene groups from formaldehyde residue. The reactive grouping in the resin is the simple epoxy group. It is customary to utilise the di-epoxide so as to cross-link the cellulose chain molecules.

![Epoxide Derivative](image)

XIV. Vinylcyclohexene dioxide.

Most promising products could be applied by conventional means in the presence of zinc fluoroborate. The durability of the effect is very good but in spite of high recovery figures, there is a lack of springiness or resilience.
(3) Chloroalkyl Derivatives

In the crease-resisting processes, the use of an alkaline catalyst is not very common, although there are several reactions of cellulose, such as with alkyl chlorides, chloroacetic acid, ethylene chlorhydrin, ethylene oxide and vinyl sulphones, which take place under alkaline conditions. Chloroalkyl compounds always react with cellulose under alkaline conditions. Suitable compounds are 1:3-di-chloro-2-hydroxypropane and epichlorhydrin.

\[
\begin{align*}
\text{CH}_2\text{Cl} \\
\text{HO-CH} \\
\text{CH}_2\text{Cl}
\end{align*}
\]

and

\[
\begin{align*}
\text{Cl-CH}^{\_}_{\text{CH-CH}_2}
\end{align*}
\]

XVI. Epichlorhydrin.

XV. 1:3 dichloro-2-hydroxypropane.

Esters of (XV) have been reported to act as a built-in lubricants.\(^7\)

Treated cotton fabrics exhibit only wet crease recovery; in the dry state, the crease recovery may be worse than that of the untreated goods.

(4) Sulphones

The reaction of divinyl sulfone with cellulose was disclosed in a U.S. Patent issued to Schoene and Chambers in 1950 and assigned to the U.S. Rubber Company.\(^7\)

\[
\begin{align*}
\text{CH}_2 = \text{CH-SO}_2-\text{CH} = \text{CH}_2
\end{align*}
\]

XVII. Divinyl Sulphone.
The reaction of XVII with cellulose is an alkali catalyzed addition of activated olefinic double bonds to active hydrogen, yielding a cellulose ether as the main reaction product. As this is both toxic and lachrymatory, various methods were investigated to overcome these hazards, and one was to form an addition compound with sodium thiosulphate.

The most successful of the sulphone type is based on an extension of the simple compound to a more reactive structure enabling wet recovery to be produced in a very short time, and accelerated about a hundred fold in the presence of sulphites and hydrosulphites. The product is known as Sulfix A and has the following formula:

\[
\begin{align*}
\text{CH}_2\text{-CH}_2\text{-O-SO}_3\text{Na} \\
\text{CH}_2\text{-CH}_2\text{-O-SO}_3\text{Na} \\
\text{CH}_2\text{-CH}_2\text{-O-SO}_3^- 
\end{align*}
\]

(5) Acetal

The associated acetals have offered more promise but their use is very limited.

\[
\begin{align*}
\text{-O-R-O-CH}_2\text{-O-R-O-CH}_2\text{-O-} \\
\text{Acetal Type}
\end{align*}
\]

These acetals function essentially as formaldehyde release agents although the crosslinks may contain residues of the alcoholic component of the acetal.
The properties obtained by treating cellulosic fabrics with blends of epoxy resins and acetals have given a better balance of properties than does either reactant alone.\textsuperscript{83} The acetal reactants\textsuperscript{84} appear to consist of simple monomeric acetals, polymeric acetals of formaldehyde and diglycols or mixture of penta erythritol and the higher dialdehydes such as glutaraldehyde or succinaldehyde.\textsuperscript{85}

(6) \textit{Miscellaneous}

In addition to various compounds described above, interest has also been displayed in the following compounds/processes.

Phenol formaldehyde,\textsuperscript{86} acetone formaldehyde,\textsuperscript{87} condensates of urea and acrolein and formaldehyde,\textsuperscript{88} polysulfates or polysulfonates of simple hydrocarbons,\textsuperscript{89} process of allylating cellulose and then cross-linking by polymerisation of methyl acrylate,\textsuperscript{90} a highly reactive product derived from acrolein,\textsuperscript{91} biuret,\textsuperscript{92} reactive acrylics,\textsuperscript{93} tris (N-methylol-2-carbamoyl) ethyl amine prepared from acrylamide, ammonia and formaldehyde,\textsuperscript{94} dichloroacetic acid,\textsuperscript{95} grafting of propyl and butyl acrylate,\textsuperscript{96} graftpolymerization of vinyl monomer,\textsuperscript{97} polymerizing of styrene, methyl methacrylate on to cotton with $\gamma$-radiation.\textsuperscript{98}

\textbf{MULTI-PURPOSE FINISHING AGENTS}

During the last few years, research work on resin finishing of textiles has been concerned mainly with the development of versatile finishes or multi-purpose finishes, that is, finishes in which two or more desirable properties are imparted to fabric in a single process.
1. Flame-Proofing with Crease and Rot Resistance

Cellulose fibres impregnated in an aqueous bath containing methylol melamine and a compound of the formula:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{NH-R^2} \\
\text{R'}-\text{P} \\
\end{array}
\]

(Where \( R' \) is alkyl, alkoxy alkyl or halogenated alkyl of 1-4 carbon atoms, \( R^2 \) is \( H \), or alkyl of 1-4 carbon atoms, and \( X \) is \( OR' \) or \( NR^2 \))

together with a catalyst and baked, are rendered the fibres flame-proof without loss in tensile strength.\(^99\)

Chance, Reeves, and Drake\(^100\) obtained wrinkle resistance and flame resistance by treating cotton fabric with the methylol derivatives of tris (2-carbamoylethyl) phosphine and tris (2-carbamoylethyl) phosphine oxide.

Tris (1-aziridinyl) phosphine oxide (APO) polymerized in the fabric using \( \text{Zn(BF}_4\text{)}_2 \) as catalyst produces durable flame retardant, crease resistant and rot resistant fabrics.\(^101\)

Crease resistance, flame resistance and rot resistance can also be obtained, by treating cotton fabric with methylol derivative of dibromocyanoacetamide.\(^102\) Phosphorus containing carboxamides impart high crease resistance and moderate flame resistance.\(^100\) Wide range of phosphorus containing carboxylic acid amide have been patented for flame and rot resistance finishing to cotton fabrics.\(^103\)
A system based on the reaction product of guanidine, dimethyl phosphite and formaldehyde applied by conventional pad-dry-cure process gives fabrics with durable flame resistance and crease resistance.\textsuperscript{104}

Aziridinyl-metal complexes such as tris (aziridinyl) phosphine oxide with Zn (NO\textsubscript{3})\textsubscript{2} give flame resistance, crease resistance and rot resistance to cotton textile.\textsuperscript{105}

Solution (25 to 40\% total solids) containing (THPGH, urea and methylol melamine) in a molar ratio 2:4:1 when applied to cotton fabric, imparted flame and crease resistance.\textsuperscript{106}

Textiles treated with alkylvinyl phosphonium salt,\textsuperscript{107} and aziridinyl complexes with polyvalent metal salts,\textsuperscript{108} have improved crease and flame resistance.

2. Water/Oil Repellency with Crease Resistance

The condensation products\textsuperscript{109} of the reaction of alkyl amine of more than 10-carbon atoms and cyanuric chlorides are padded from chloroform solution on to cellulosic materials previously treated with sodium bicarbonate. After removal of the chloroform the goods are steamed and cross-linking with cellulose occurs to give a water repellent finish.

To impart durable water repellency and crease resistance, the methylol amide of fatty acid\textsuperscript{110} is reacted with secondary amine and the product is converted to the tertiary amine salt. The fabric is impregnated with this salt and cured.
A finish based solely upon perfluoroacidoguanamide is said to impart crease resistance and water and oil repellency.\textsuperscript{111}

For wash and wear combined with water repellent effect, the most satisfactory results are obtained by application of cross-linking together with silicones and their appropriate catalysts, from a single impregnating bath.\textsuperscript{112}

Hydroxymethylated (a) 2-butoxy-4, 6-diamino-S-triazine, (b) 2-butylamino-4, 6-diamino-S-triazine, or (c) 2-n-Octadecylamino-4, 6-diamino-S-triazine in the presence of Zn(NO_3)_2 in methanol,\textsuperscript{113} have also been employed to impart crease resistance and water repellency to the cotton fabric.

The fabric treated with an alkaline aqueous dispersion of an alkyl sulfone and an alcalimethyl salt of an aliphatic hydrocarbon silicocate exhibits crease resistance and water repellency.\textsuperscript{114}

Monomeric guanamines are said to be suitable for imparting crease resistance and water repellency.\textsuperscript{115}

**CATALYST**

Chemical reaction of cellulose hydroxyl groups and mono or polyfunctional reagents takes place in the presence of H\textsuperscript{+} or OH\textsuperscript{-} ion. Free acids, alkali and salts which are able to generate H\textsuperscript{+} or OH\textsuperscript{-} ion at room temperature or at elevated temperature are used. Since they are not found in desired reaction product and remain unconsumed by any of the reactants, they are commonly termed as catalysts. The
alkaline catalysts are effective only with certain reagents such as methylol urea, epoxy, epihalohydrin, etc. Gagliardi examined a large number of alkaline compounds for curing simple methylol urea resins. The compounds which have been found more effective from an industrial point of view are sodium carbonate and quaternay ammonium hydroxides.

The reaction of all N-methylol resins with cellulose is catalyzed by acid. The acidic catalysts generally used are either organic acids or Lewis acids. The catalysts can be grouped as follows:

(1) Mineral and Organic acids
(2) Ammonium salts
(3) Oxidizing agents
(4) Inorganic salts

Mineral and Organic Acids
In the early days of resin finishing free acids were widely used. The first patent mentioning the use of urea-formaldehyde claims the use of three percent tartaric acid on the actual weight of the resin. The free acids as such have very limited application because they give poor bath stability by polymerizing the precondensate rapidly. Free acids find some use in the various processes of cross-linking cellulose with formaldehyde, under different conditions of swelling and in vapour phase reactions.
Ammonium Salts

Ammonium salts, if heated sufficiently, lose ammonia leaving the free acid which act as a catalyst. They have a number of disadvantages. They promote odour formation and with certain resins, they increase chlorine retention. Recently, it has been claimed that the mixture of oxalic acid with ammonium chloride can be used as a catalyst to give excellent wash and wear finishes. Amine salts are generally the hydrochlorides of aliphatic amino alcohols. The most popular type is catalyst AG which probably contains 2-methyl 2-amino propanol hydrochloride. Other types in use are morphine hydrochloride, 2-amino butanol phosphate and triethanolamine hydrochloride. These catalysts are claimed to have no odour formation and chlorine retention defects.

Oxidizing Agents

Hydrogen peroxide or peracetic acid may also be used as a catalyst in resin finishing. Hydrogen peroxide or peracetic acid oxidize free formaldehyde to give acids.

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O}_2 & \longrightarrow \text{HCOOH} + \text{H}_2\text{O} \\
\text{CH}_3\text{COOH} + \text{HCHO} & \longrightarrow \text{CH}_3\text{COOH} + \text{HCOOH}
\end{align*}
\]

The formed formic acid then functions as a catalyst. At room temperature, hydrogen peroxide in the resin bath produces formic acid only at a slow rate, so that good bath stability is obtained. However, such catalysts have not been exploited for commercial resin finishing.
Inorganic Metal Salts

Inorganic metal salts are widely used as catalysts because they give better storage stability to the resin bath and to the resin-treated but uncured fabrics than organic acids and ammonium salts. Amongst other advantages of metal salts are their very low volatility, absence of undesirable odour, no yellowing of the treated fabrics and minimum damage to the fabrics.

Inorganic metal salts normally used as catalysts are zinc chloride, zinc nitrate, magnesium chloride, aluminium chloride, etc. In general, the metal salts develop acidity either due to hydrolysis in solution or due to thermal decomposition.

\[ 2\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{Mg}_2\text{OCl}_2 + 5\text{H}_2\text{O} + 2\text{HCl} \]

\[ \text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{ZnO} + 2\text{HCl} + \text{H}_2\text{O} \]

Kullman et al.\textsuperscript{130,131} found that N-methylol amides, in the presence of metal salts, react slowly with cellulose at room temperature. Frick et al.\textsuperscript{132} have shown that the reaction at room temperature results in a better strength retention as compared to the reaction at high temperature. It has been claimed\textsuperscript{133} that cotton fabrics with high degree of wrinkle resistance and with little or no reduction in moisture absorptivity may be produced by using a mixture of magnesium chloride and sodium chloride as catalyst.
A process of textile fabric finishing is described, in which the mixture of Lewis acid type metal salts and organic acid is used as catalyst. Recently, Frick et al. showed that a mixture of certain metal salts and carboxylic acids form highly active catalysts for cross-linking of cellulose with formaldehyde or methylol amide agents. The mixtures exhibit synergistic catalytic activity. Carboxylic acids which are hydroxy or alkoxy substituted on the α- or β- carbon have been found effective, whereas unsubstituted acids are not. The catalytic activity of the combination of magnesium chloride hexahydrate and citric acid in a weight ratio of 2 to 3 is a typical example of such catalysts. A number of such catalytic combinations are also patented. Mixed catalytic systems based on Mg salts have also been studied in the ATIRA Laboratories. Increased catalytic activity is explained on the basis of complex formation between the acid or its salt and the polyvalent metal ion with the liberation of the protons. The reaction rates of the combined catalysts are much faster than those obtained when metal salts alone are used. Some of the advantages of these catalysts are:

1. Curing temperature as low as 125°C could be used without sacrificing the efficiency of the resin cure.

2. Since the reaction can be carried out during the drying stage, very high wet crease recovery can be developed at this stage effectively, when sufficient moisture is present in the fabric.
(3) The low temperature cure gives better retained tensile and tear strengths, better abrasion resistance and a better balance of wet and dry crease recovery.

(4) On account of the reaction commencing at the drying stage, resin migration problems are avoided.

(5) On account of the effective pH control, formaldehyde odour is substantially minimized during processing.

MECHANISM OF CROSS-LINKING

The mechanism of reaction between formaldehyde and cellulose has been studied by a number of workers.\textsuperscript{141-147} Generally, it is accepted that the hydrated formaldehyde is protonated and dehydrated to furnish the electrophilic species which subsequently combines with anionic sites of cellulose. Since these reactions are reversible, the principle of microscopic reversibility\textsuperscript{148} requires that this should also be the mechanism of hydrolysis of cross-links. Parikh\textsuperscript{149} suggested that protonation of cellulose initiates the reaction and furnishes the electrophilic species. Mehta \textit{et al}\textsuperscript{150} suggested the formation of a carbonium ion on cellulose as the rate determining step in the mechanism for cross-linking. Cellulose absorbs formaldehyde rapidly on accessible hydroxyl to form hemiformals\textsuperscript{151} which react relatively slowly to form cross-links.\textsuperscript{152} Cross-links may be formed from cellulose hemiformals in two ways (i) reaction of cellulose hemiformal carbonium ion with cellulose hydroxyl (Equation, 1, 2) to form monomeric or dimeric cross-link and (ii) reaction of cellulose carbonium ion...
generated as a result of reaction of acid on cellulose with the cellulose hemiformals (Equation 3).

\[
\text{Cell}^+\text{O.CH}_2\text{OH}^+ \rightarrow \text{Cell}^+\text{O.CH}_2\text{O.CH}_2^+ - \text{H}_2\text{O} \rightarrow \text{Cell}^+\text{O.CH}_2
\]

\[
\text{Cell}^+\text{O.CH}_2^+ + \text{HO.Cell} \rightarrow \text{Cell}.\text{O.CH}_2.\text{O.Cell} + \text{H}^+
\]  

\[
\text{Cell}^+\text{O.CH}_2 + \text{HO.CH}_2.\text{O.Cell} \rightarrow \text{Cell}^+\text{O.CH}_2.\text{O.CH}_2.\text{O.Cell} + \text{H}^+
\]

\[
\text{Cell}^+ + \text{HO.CH}_2.\text{O.Cell} \rightarrow \text{Cell}.\text{O.CH}_2.\text{O.Cell} + \text{H}^+
\]

According to Vail\textsuperscript{153} the acid catalysed reaction of N-methylol agents with cotton proceeds through a series of reversible steps in which the formation of a resonance stabilized intermediate is considered to be the rate determining step. Thus, the formation reactions are:

\[
\text{RCONHCH}_2\text{OH} + \text{H}^+ \rightarrow \text{RCONHCH}_2\text{OH}^+\]

\[
\text{RCONHCH}_2\text{OH}^+ \rightarrow \text{RCONHCH}_2 + \text{H}_2\text{O}
\]

\[
\text{RCONH.CH}_2 + \text{Cell.OH} \rightarrow \text{R.C.NH-CH}_2.\text{O.Cell}^+
\]

\[
\text{RCONH.CH}_2.\text{O.Cell}^+ \rightarrow \text{RCONHCH}_2.\text{O.Cell} + \text{H}^+
\]

In the N-methylol agents, the hydroxyl groups are always beta to an activating group such as a carbonyl group or a triazine ring. Base-catalyzed eliminations are quite generally observed for beta-hydroxy ketones, nitriles, esters, and
sulfones and should occur with N-methylolamides also. The first step would be removal of an alpha-proton by base (B), followed by splitting off of the beta hydroxyl group as a hydroxyl ion.

\[
\text{HOCH}_2\text{NH}_2\text{C}_2\text{R} + B \rightarrow \text{HOCH}_2\text{N}_2\text{C}_2\text{R} + BH
\]

\[
\text{HOCH}_2\text{N}_2\text{C}_2\text{R} \rightarrow \text{HO} + \text{CH}_2 = \text{N}_2\text{C}_2\text{R}
\]

The resulting imine (I) is an alpha, beta-unsaturated compound and should undergo a base-catalyzed Michael-type 1,4-addition to cellulose.

\[
\text{Cell-CH} + B \rightarrow \text{Cell-O} + BH
\]

\[
\text{Cell-O} + \text{CH}_2 = \text{N}_2\text{C}_2\text{R} \rightarrow \text{Cell-OCH}_2\text{N}_2\text{C}_2\text{R}
\]

\[
\text{Cell-OCH}_2\text{N}_2\text{C}_2\text{R} + BH \rightarrow \text{Cell-OCH}_2\text{NH}_2\text{C}_2\text{R} + B
\]

Trimethylolmelamine, dimethylol urea, monomethylol acrylamide cross-link cellulose at unusually moderate temperatures, in the range of 105°-125°C, in the presence of dilute alkalis like sodium hydroxide, sodium carbonate and bicarbonate.

PROPERTIES OF RESIN FINISHED COTTON TEXTILES

Resin finishing of fabrics has its own advantages and disadvantages. These are as follows:
Advantages

**Improved crease recovery and crease retention properties:**

This is the most important quality that resin finishing imparts to the fabric, which is now able to recover from wrinkles formed during wear and washing. In most cases, the fabrics are manipulated so as to preserve the flat state and recovery from creasing is merely the return to the flat state. If, however, the goods are creased, pleated, embossed before the final curing step in the process, then the fabrics will tend to return to these distorted configurations on removal of imposed stress.

**Improvement in fabric drape:**

Draping ability of cotton, linen and rayon goods is improved by the resin finishing process. Improving drape does not need as high a resin fixation as that required in crease resistant finishing. Certain dress and curtain goods can often be recognised at a glance as resin finished from the way they 'hang' or drape.

**Ease of washing and ironing:**

Improved crease resistance and better crease retention help the consumer to use the treated fabrics for garments and apparels which can be washed and dried easily and the trouble of heavy ironing is avoided.

**Improved Dye fastness:**

Resin treatment improves the fastness to washing of many direct dyes. The light fastness of many direct and vat dyes, however,
is adversely affected by resin treatment. Three exhaustive studies report the effect of resin treatment on the fastness properties of different dyes. 155-157

Rot-Resistance:
Because of the wide range of materials conferring bacteriostatic or fungistatic properties on textiles, it might be expected that textiles treated with various after-treatments designed to confer other properties would have also a measure of bacteriostasis. This is true of fabrics subjected to drip-dry processes, particularly those using triazines or having a high concentration of free formaldehyde; fire-proofing finishes, particularly those using tetrakis (hydroxymethyl) phosphonium chloride-melamine; melamine-formaldehyde, cationic softeners, and some water-repellent finishes. 101, 158-163

Disadvantages
Tensile Losses:
The highest strength is attained in a fibre when the flexibility of its structure is high enough to permit full distribution of load and yet not so high that failure can occur by slippage of the structural elements past each other. In cotton, applied load is not fully distributed among structural elements of the fibre. Failure appears to occur by consecutive breaking of those structural elements that carry the brunt of the load; it propagates through the fibre by passing from one area of stress concentration to another. When the cotton fibre is cross-linked, the flexibility of its structural components is
decreased. Consequently, the degree of load distribution possible is also diminished, and the treated fibre fails at lower loads. Fabric tensile strength reflects the tensile strength of its component fibres.

**Tear strength losses:**
The decreased mobility of cross-linked structural elements decreases fibre extensibility. Tear-strength losses exhibited by the treated fabrics may be due to this factor, though it has also been suggested that the finishes increase friction between threads, and the resulting higher resistance to slippage is responsible for tear strength reduction.\textsuperscript{164-167}

**Losses in abrasion resistance:**
Reduction of fibre extensibility may also be responsible for the lower abrasion resistance of treated fabrics.\textsuperscript{168-171} Abrasion losses seem directly proportional to extensibility losses. The wear life of crease resistant finished fabrics is comparatively lower than untreated fabrics.

**Decreased moisture sorption:**
The amount of water imbibed by the fabric at equilibrium is reduced from 40 percent to about 20 percent by resin treatment. The resin treated fabric also shows decreased moisture sorption. The fabric for apparel purposes are expected to imbibe perspiration and evaporate it out. Lower water imbibition and moisture sorption of the resin treated garments lead to discomfort during wearing.
Chlorine damage:
When fabrics crease-proofed with compounds containing hydrogen bearing nitrogen atoms are bleached with hypochlorites, chloramide compounds can be formed by substitution of chlorine on the nitrogen. These compounds are thermally unstable. On application of heat, as in ironing, they disintegrate, and hydrochloric acid is formed in the fabric. The damage is due to acid hydrolysis and possibly to oxidation of cotton cellulose.

METHYLOL AMIDES AS FINISHING AGENTS
N-methylol formamide and N-methylol acetamide are reported to be hydrolysis-resistant wash and wear finishes for cotton fabric.\textsuperscript{172} Methylolated formamide and higher fatty acid amides\textsuperscript{173} and their mixture with methylol urea; N,N'-dimethyl-
N,N'-dimethylol adipamide,\textsuperscript{174} N,N-dimethylol propionamide containing various activating substituents in the $\beta$-position,\textsuperscript{175} dimethylol derivatives of linear bisamides and glyoxalmonoaamid reaction product\textsuperscript{176} have also been used as crease resistant finishes for cotton fabric. Methylol stearamide or stearamido-methylpyridiniumchloride\textsuperscript{177} and methylated methylol melamine import crease and abrasion resistance properties to cotton textiles. Phosphorus containing N,N-dimethylol carboxylic acid amides\textsuperscript{178} improve crease recovery and produce flame resistant finish, which is fast to washing and dry-cleaning. Methylol derivative of fluorinated amides also have been used as water and oil repellents for cotton fabric.\textsuperscript{179-180} Methylol derivatives of acrylamide and methacrylamide have been
reported to impart crease resistance with minimum of chlorine retention damage to cotton fabric.\textsuperscript{181-188}

Thus, it appears that during the last few years, there has been great interest in the development of multifunctional finishes. A satisfactory multifunctional finishing agent should contain, in addition to cross-linking groups, other substituents which will impart additional desired properties. The compound should have a low molecular weight so that the desired properties can be conferred on the fabric at low add-on levels. In this context, the methylol derivatives of substituted acid amides present interesting possibilities and seem to offer an attractive and simple way of imparting multiple finishes to cotton. Chance \textit{et al}\textsuperscript{102} synthesized dibromocyanacetamide and by treating cotton fabric with its methylol derivative, obtained crease resistance, flame resistance, and rot resistance.

After the synthesis of an acid amide with suitable substituents, the next important reaction in the synthesis of the finishing agent is its methylolation. The methylolation of an amido compound presumably proceeds through nucleophilic substitution. All methylolations are generally accelerated by alkali. In an alkaline medium, formaldehyde and anion of the amido compound determine the rate and extent of the reaction. The substituents in the amido compounds are expected, therefore, to play an important role in the electron displacement. Vail \textit{et al} have studied the extent of the reaction in alkaline solution.
of formaldehyde with formamide, acetamide, bisformamide and bisacetamides. Since proton abstraction is a necessary prerequisite for methylolation, the reaction should be enhanced in the presence of a stronger base. In order to ascertain the various types of influences on the methylolation of acid amides, the present study was undertaken. By means of model compounds, the relationship between chemical constitution and the rate and extent of methylolation have been studied. The compounds used in this study were selected because of their structural characteristic and not because of their ability to impart wash and wear properties to the cotton fabrics. With this in view the following acid amides were synthesized: Formamide, acetamide, propionamide, butyramid, isobutyramid, trimethylacetamide, dimethylaminoacetamide, glycolamide, lactamide, mandelamide, chloroacetamide, bromoacetamide, \( \beta \)-chloropropionamide, trichloroacetamide, \( \alpha, \beta \)-dibromo N-hydroxymethyl propionamide, \( \alpha, \beta \)-dibromocinnamamide, 2:4:5-trichlorophenoxyacetamide, 2,4,6-tribromophenoxyacetamide and cyanoacetamide.

Methylolation of some of the above cited acid amides containing various electron-releasing and electron-withdrawing substituents has been carried out with formaldehyde in the presence of sodium hydroxide and triethylamine. The relative rates and extents of methylolation of these acid amides have been studied. Methylol acid amides have been evaluated as textile finishing agents.