Ease of wrinkling and tendency to shrinking have been recognised as undesirable properties of fabrics made from natural and regenerated cellulose. It is most desirable that cotton fabrics be produced that will resist wrinkling as well as woolen and worsted fabrics do. The goal of research on the resilience and crease resisting properties of cotton has been to produce fabrics which equal wool and synthetic fibres in these properties with as little sacrifice as possible of the many other desirable qualities offered by cotton. The discovery and large scale production of various synthetic fibres such as nylon, dacron, orlon, acrilan and dynel which gave to the consumer, fabrics which had several desirable properties, have given an impetus to the research to modify the properties of cotton fibre, so that cotton fabrics can have a competitive place in the market.

The first start in this field was made in the year 1928 by Messrs. Tootal, Broadhurst and Lee (15), who patented a finishing treatment of viscose fabrics based on urea formaldehyde and claimed antishrinking and anticrease properties for the finished fabrics. Practice often leaps ahead of theory in industries that possess an advanced technology, and this was true in the case of finishing of cotton with resins. Marsh, one of the inventors of the anticrease process has correctly mentioned that "Neither the structure of textile fibres nor of synthetic resins was clear at the time of the crease resisting invention". (29).
Before considering the application of the resin*, it is relevant to have a clear understanding regarding the structure of cotton fibres, as this will help to understand creasing and shrinking of cotton fabrics and how these two drawbacks can be overcome by the reactions of chemicals occurring within fibres.

Cellulose is a natural high polymer, the building unit of which is an anhydride of glucose. Nature produces this polysaccharide in the form of long chain molecules, possibly by condensation and dehydration of glucose. When observed under a microscope, the cotton fibre appears as a flattened tube showing a spiral effect along its main axis with comparatively thick walls (44). The cross section is bean-like in shape and shows a hollow centre. Fibres which have been swollen by chemical means show bands of fibrils which are slanted at an angle of 20 to 50° along the main axis according to the source of the cotton. When viewed by means of an electron microscope (24, 44, 50, 51), many more details about the fine structure can be obtained. The cellulosic part of the primary walls consists of a network of interweaving fibril strands, 100 - 400 Å in diameter running parallel to the fibre axis on the outside and transverse on the inside. The outermost layer of the secondary wall, known as the

---

* The word resin is a misnomer generally used in literature on textile finishing for monomers, precondensates and for straight chain polymers. Strictly it means a three dimensional cross linked polymer formed by the polymerisation of monomers or precondensates. For the sake of simplicity, however, this popular usage has been continued here.
winding layer, is a continuous sheet made up of alternating narrow and wide bands of fibril bundles. Fibril bundles are about 1000 Å thick and they spiral about the fibre axis. The other layers of the secondary wall are made up of highly packed spirals of microfibrils. The individual layers are about 1000 Å or 5 microfibrils thick. Microfibrils or cellulose micelles are composed of long molecular chains of the repeating units of cellobiose.

Molecular chain formula of cellulose

The units are all bound by 1-4 oxygen bridges. The number of anhydroglucose units in a cotton cellulose molecule has been estimated to average about 5000 (40, 52). One micelle would accommodate 100 - 170 individual chain molecules. Some regions of the fibre are capable of diffracting X-rays in the same manner as three-dimensional crystal lattices. Meyer and collaborators (35, 36, 37) constructed three dimensional basic cell of cellulose in which the cellobiose residues lie parallel to the "b" axis. Mark (28) has shown theoretically that three types of forces namely,

Diagrammatic representation of the entire structure of the cellulose fibre. After A. Frey Wyssling, Naturwiss. 28, 386 (1940).

I. Cellulose Chain, II. Cellulose Lattice, III. Micellar Structure, IV. Fibril, V. Flax Fibre.
hydrogen bonds, van der Waals forces and primary valence forces exist in three different planes of the basic cell of cellulose. As the shortest distance between the centres of the two oxygen atoms of the glucose units is about 2.5 Å, hydrogen bondings occur along the "a" axis within the a - b plane. The strength of the hydrogen bond would correspond to about 15,000 calories per mole. As the shortest distance between hydroxyl groups of parallel chains is 3.8 Å along the c-axis, there are van der Waals forces. Van der Waals forces would correspond to only 8000 calories per mole. Along the b-axis, the primary valence forces exist corresponding to energy of 50,000 calories per mole.

The extent of crystallinity of native cotton cellulose as determined by X-ray methods, is about 70-80% (45, 53). In the crystalline areas, long chain molecules lie parallel and are packed in such a close and regular formation that crystal properties result. In other regions, the orientation of the chain molecules is very low and the state of the disorder is such that the material may be regarded as amorphous. If the chains are long enough, they extend through both the regions. Hence the fibre consists of alternating regions of amorphous and crystalline regions, with certain chains running through both the regions. The symmetry and regularity of cellulose molecules in crystalline portions permit adjacent chains to pack closely and the lack of bulky substituents on chains produces greatly accentuated hydrogen bonding between -OH groups of adjacent cellulose chains; whereas the randomness of cellulose chains in the amorphous regions gives rise to weaker attraction.
between -OH groups of cellulose chains. The amorphous areas can be penetrated readily by water and low molecular weight cross-linking reagents. Between the microfibrils there are capillary networks which can be readily reached by colloidal solutions, while the microcapillary structures between the chain bundles of the microfibrils can be reached only by true solutions. The various capillary systems can be made accessible by chemical finishing techniques. The crystalline portions are not accessible to water but can be reached by swelling agents, such as sodium hydroxide or cuprammonium solutions, which can readily break down the hydrogen bonds and van der Waals forces of attraction between the chains and even lead to permanent swelling or molecular disintegration. In the crystalline regions the chain molecules of glucose residues are probably fully extended and they are responsible mainly for tenacity, high modulus of elasticity and resistance toward bending, while the amorphous regions, by their properties of allowing freedom of movement to the molecular chains, account for the flexibility and extensibility of the cotton fibre. It has been suggested that in cotton fibres, extension is also accompanied by untwisting of the fibrillar spirals, the S-twisted spiral sections rotating in one direction and the Z-twisted spiral sections rotating in the opposite direction. As the microfibrillar spiral reversals occur only in the cotton fibre, the extensibility is about twice that exhibited by such other highly crystalline natural cellulosic fibres as flax (49).

Mechanism for Creasing:

When a fabric is folded sharply so that a crease is formed,
the fibres at the crease are placed in a position of strain. The fibres on the outside of the bend are subjected to a tensile stress and are elongated, while those inside the bend are under compression. Somewhere in the middle of the bend, the fibres are neither stretched nor compressed. This is in the neutral plane of deformation. Each element of the cotton fibre—a molecule, a crystallite, a microfibril—is subjected to different forces.

Under the application of external stress, the strain is thrown on the hydrogen bonds, van der Waals forces and primary valence bonds. The whole system is disturbed from its equilibrium. The bonds take up the stress and strain, and some bonds break. The movement of the molecules takes place in the direction of the stress. If they come more closely to other molecules, they form new bonds with their new neighbours. A new equilibrium is then set up in the system under the applied stress, and a new configuration results. The external load is a part of the new equilibrium, since the fibre deforms until the load is balanced by the strain on bonds between its elements. When the load is removed, the equilibrium attained by new forces will be disturbed once again. The strains on the bonds will be no longer in a balanced position. The movement will start once again to achieve a new equilibrium. New forces formed between the cellulose molecules will oppose the movement and as a result the original configuration before the stress was applied, will not be attained. The fibres do not recover completely from their extension, and hence a crease is formed. In short the crease can be thought as a deformation in a fabric due to the application of a stress (usually a bending stress) and due to the inability of the textile
to recover from the strain or deformation completely on removal of the applied stress.

The ability of the textile to recover from strain (or deformation) when the stress is removed is called its elasticity or, more precisely, elastic recovery. The elastic recovery or crease recovery of a textile fabric is affected by its construction and by the construction of the yarns of which it is composed. But the type of fibre which makes up yarn and fabric has a pronounced effect on the fabric's crease-resistance.

Contrary to the ease of creasing tendency of cellulosic fabrics, fabrics made from animal fibres such as wool and mohair, as well as fabrics made from synthetic fibres such as terylene and nylon have little tendency towards wrinkling or creasing. In the following table extensibility and elastic recovery of some natural and synthetic fibres are given (34).

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Extension</th>
<th>Elastic Recovery</th>
</tr>
</thead>
<tbody>
<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>Acetate</td>
<td>29</td>
<td>27</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>

It can be seen from the table that wool, terylene and nylon possess high elastic recovery and extensibility, while cotton has the least extensibility and very low elastic recovery.
This difference in behaviour of cotton and other fibres is attributed to different molecular structures. For example, the elastic behaviour of the wool fibre is explained as follows:

The wool fibres are composed of keratin which is built up from sixteen different amino acids, one of which, cystine, exists as a cross-linkage between two long polymeric polypeptide chains. These cross-linkages account for about 4% of the total weight of wool (38). These cross-linkages will prevent the slippage or sliding of one molecular chain over others. When one such chain is pulled by some stress so that it moves forward, while the other chain is stationary, the cross-linkages will stop the further movement and when the stress is released, they will try to recover from their strained positions and restore the molecular chains to its former position. The high degree of extensibility and recoverability in wool is also explained on the basis of the folded nature of the molecules in keratin. On the application of a stress, these molecules can uncoil from their \( \alpha \)-keratin structure to a highly extended \( \beta \)-keratin structure. When the stress is removed, the fibre structure contracts again to \( \alpha \)-keratin. This behaviour imparts high elasticity to the wool fibres.

Such cross-linkages are normally absent in cellulose, so that once the intermolecular forces have been overcome, the extensibility of cellulosic fibres will be of the non-recoverable type, and crease formation occurs by the mechanism discussed earlier.

Buck and McCord (8) have given typical stress-strain curves for wool and cotton for short time loading, which show that wool
recovers completely from the applied strain while cotton does not.

Gagliardi and Gruntfest (18) have shown experimentally by plotting a stress-strain curve for 150x40 filament viscose that increasing elastic recovery of cellulose fibres by treatment with crease proofing agents, produces fabrics which have a high degree of wrinkle resistance. They further state that "The formation of such cross-linkages reduces the extent of internal molecular slippage, which is responsible for the creep or plastic flow at high stress application, and increases the Hooke's law region in the fibres i.e. the amount of true elasticity." Cooke et al (11) have found from the study of measurements of elasticities at low extensions of fabrics treated with melamine formaldehyde and urea formaldehyde that elasticity of the fabric is obtained by an increase in the elasticity of the fibres which is carried through the yarn and finally to the fabrics. Hamburger, Platt and Morgan(26) have concluded that high immediate elastic deflection at low average tensile strains is an important fibre property in determining the
crease recovery of the fabrics.

This shows that crease proofing of cotton can be based on increasing the elastic recovery of the fibres by adding new forces of attractions by formation of cross linkages between adjacent chains in the amorphous regions of cellulose.

Grease Proofing Agents:

The simplest compound that can bring such modification in the cellulose fibre is free formaldehyde. It has been known since 1906 that formaldehyde reacts with cellulose in presence of strong acid catalysts and forms methylene cross-links with cellulose (12).

\[ \text{Cell.} \cdot \text{O-CH}_2\cdot \text{O-Cell.} \]

The treated product has improved crease recovery, greatly reduced water imbibition and improved dimensional stability. Formaldehyde has not been used widely because of its volatility and excessive losses in strength of the treated fabric. Recently interest has been shown in the reaction of formaldehyde with cellulose in wet condition (without drying and curing). This reaction produces a high wet crease recovery with slight losses in tensile strength (21, 32, 43).

A large number of other compounds has been synthesised for the purpose of achieving the same general effects produced by formaldehyde but with greater ease of application and more uniform fibre modification. Most of these compounds are condensation
products of formaldehyde and amines or amides.

Methylol urea compounds were the first resin precondensates used commercially for improving wrinkle resistance (15). Urea and formaldehyde react together in aqueous solution at room temperature under neutral or faintly alkaline conditions to give methylol ureas.

\[
\begin{align*}
\text{NH}_2 & \quad + \quad \text{HCHO} & \quad \rightarrow \quad \text{NH} \cdot \text{CH}_2 \text{OH} \\
\text{CO} & \quad \quad \text{CO} & \quad \quad \text{NH}_2
\end{align*}
\]

Monomethylol urea (MMU)

\[
\begin{align*}
\text{NH}_2 & \quad + \quad 2\text{HCHO} & \quad \rightarrow \quad \text{NH} \cdot \text{CH}_2 \text{OH} \\
\text{CO} & \quad \quad \text{CO} & \quad \quad \text{NH}_2 \quad \text{NH}_2
\end{align*}
\]

Dimethylol urea (DMU)

During the reaction, the viscosity of the solution increases and free formaldehyde content decreases. DMU can be obtained as a dense white precipitate after 24 hrs. Both MMU and DMU can undergo further condensation slowly in solution, and at a much more rapid rate on heating. MMU can give

\[
\begin{align*}
\text{NH} \cdot \text{CH}_2 \text{OH} & \quad \text{CO} + \text{H}_2 \text{O} \\
\text{CO} & \quad \text{NH}_2 \quad \text{NH}_2
\end{align*}
\]
Similar reactions can occur with DMU also. These compounds when applied to cellulose, in their monomeric water-soluble form, penetrate into the accessible regions of cellulose and under the application of heat with acidic catalysts, they are believed to react with hydroxyls of cellulose through their N-methylol groups. They may also polymerise and form the resin by the mechanisms discussed later on. It has been shown by X-ray diffraction pattern that the resins are deposited in between the fibrils and also between the microfibrils of the cellulosic fibres (7). The same conclusion has been drawn by observing under microscope the cross sections of treated fibres dyed with acid dyes (7).

As there are four functional groups present in DMU, viz. two imino groups (\( \text{\textgt{NH}} \)) and two N methylol groups (\( \text{\textgt{N.CH}_2\text{OH}} \)), it can polymerise extensively in presence of acidic catalysts. Nuessele et al (41) have described nine such possible modes of reaction, taking into account the formation of liner or three dimensional polymers and their possible reactions with cellulose.

\[
\begin{align*}
2 \text{\textgt{N.CH}_2\text{OH}} & \rightarrow \text{\textgt{N.CH}_2\cdot N + H}_2\text{O} \\
\text{\textgt{N.CH}_2\text{OH} + \text{\textgt{NH}}} & \rightarrow \text{\textgt{N.CH}_2\cdot N + H}_2\text{O}
\end{align*}
\]

\[
\text{Cellulose-OH + } \text{\textgt{HO.CH}_2\cdot N} \rightarrow \text{\textgt{Cell.O.CH}_2\cdot N}
\]
From these basic reactions, nine different reactions are shown below:

1. Cyclic dimer \( \begin{array}{c} \text{M} \\ \text{M} \end{array} \)
2. Linear polymer \(-\text{M-M-M-M-}\)
3. Thermoset polymer \(-\text{M-M-M-} \\ \text{M-M-M-M-} \)
4. Simple cross-links
5. Linear polymer, cross-linked to cellulose
6. Thermoset polymer cross-linked to cellulose
7. Monomer linked only to one cellulose chain
8. Linear polymer, linked only to one cellulose chain
9. Thermoset polymer, linked only to one cellulose

Reactions 4 to 9 are shown diagrammatically in Figure where \( \text{M} \) = dimethylol urea residue.

The problem regarding the polymerisation of DMU within fibres is still controversial. More details will be discussed in the next chapter.
Monomethylol urea can form a resin within the cellulosic fibre, and can react with only one OH group of the cellulose molecule. There is no possibility of cross linking with cellulose chains as postulated for DMU.

\[
\begin{align*}
\text{O}_n & \quad \text{NHOCH}_2\text{NH.C.NH}_2 \rightarrow \text{HO (CH}_2\text{NH.C.NH)}_n + (n-1) \text{H}_2\text{O} \\
\text{O}_n & \quad \text{Cell.OH} + \text{HOCH}_2\text{NH.C.NH}_2 \rightarrow \text{Cell.O.CH}_2\text{NH.C.NH}_2 + \text{H}_2\text{O}
\end{align*}
\]

Efficiency of urea formaldehyde precondensates as crease proofing agents, depends mostly on the ratio of urea to formaldehyde. Monomethylol urea has low crease proofing efficiency but little effect on the hand and strength of the fabric, while dimethylol urea gives high crease recovery to the fabric but produces a marked deterioration in its hand and wear properties. In practice therefore, a molar ratio of 1 urea to 1.5 - 1.8 of formaldehyde is generally used.

Main disadvantages with the use of UF resins, are poor bath stability, poor wash fastness under severe conditions of washing, susceptibility to acid and alkaline hydrolysis of the resin, and high strength loss due to chlorine retained from laundering bath containing active chlorine. It is believed that chlorine is retained by the urea resin through formation of a chlorimide or chloramine by replacement of hydrogen at an active amino nitrogen in the resin molecule.

Dimethylol ethylene urea was developed to overcome two of the major drawbacks of urea formaldehyde resins, namely poor washfastness and high chlorine retention. Cyclic methylol urea compounds
are tetra-substituted derivatives of urea in which the two nitrogen

\[
\text{HOH}_2\text{C}.\text{N}.\text{CO}.\text{N}.\text{CH}_2\text{OH} \quad \text{Dimethylol ethylene urea} \\
\text{CH}_2-\text{CH}_2 \\
\text{(1, 3-bis hydroxymethyl)} \\
-2- \text{imidazolidone}
\]

atoms are connected by a carbon chain. Dimethylol ethylene urea (DMEU) is the most widely used compound in industry. Due to the presence of only two functional groups, DMEU can form only linear and not three dimensional polymers as DMU. (11). The possibility of cross-linking with cellulose is thus much greater with this resin(54). Hence it is also known as reactant type resin. Because of this higher efficiency of cross linking, DMEU treated fabrics can have high crease recovery at low additions. DMEU solutions have excellent storage stability at room temperatures and pad baths containing catalysts are more stable than those of urea resins. It has been found recently that under certain conditions, DMEU can produce some chlorine retention. The conditions leading to chlorine retention by DMEU treated fabrics have been discussed later on.

Triazone compounds sometimes described as modified ureas possess a closed ring structure obtained by reacting dimethylol urea with an alkyl amine (9).

\[
\text{HOCH}_2\text{NHCONHCH}_2\text{OH} + \text{RNH}_2 \rightarrow \text{NH} - \text{CO} - \text{NH} \\
\text{Dimethylol urea} \quad \text{Alkyl amine} \\
\text{Triazone}
\]
The triazone may further be reacted with formaldehyde to yield a methylol triazone condensate which can undergo condensation to form polymers.

\[
\text{Methylol triazone}
\]

They are less susceptible to chlorine damage and acid hydrolysis, because of the tertiary nitrogen in the molecule. Their main drawbacks are low efficiency, discolouration at high temperatures used in commercial curing, and susceptibility to odour formation.

Melamine formaldehyde compounds are prepared by reacting melamine with formaldehyde. By varying the ratio of reagents, one may vary the degree of substitution, that is the number of methylol groups in the final product (25).
Compared to MMO and DMU, MF is more stable to storage, but is still not sufficiently so, for prolonged storage at room temperatures. Similar reactions as with MMO and DMU can occur with MF also, leading to products of high molecular weight and low water solubility. The MF monomers can undergo the same type of condensation and cross linking reactions as the UF monomers. A linear and a ring polymer, are shown below (11).

MF has a higher basicity than UF and it hydrolyses at a slower rate in acids and alkalis.
By methylation of methylol melamine, the stability to storage at room temperature is increased to a considerable extent. The presence of \( >N\cdot CH_3 \) groups instead of \( \sim NH \) groups, reduces the number of reactive groups from 6 (3 \( >NH \) and 3 \( -CH_2OH \)) to only 3 methylol groups. This reduces the possibility of polymer formation and increases the possibility of cross-linking with cellulose. Another important consequence of this structural change is the immunity to chlorine retention as the hydrogen at the imino group is replaced by the \( CH_3 \) group. Cyclic triazines are similar to methylated methylol melamine but their structures are not known with certainty.

The guanamines are substituted amino triazines which contain only two reactive \( NH_2 \) groups instead of three as in melamine (6). In the structural formula for the guanamines shown, \( R \) may be \( H \) for formoguanamine, \( C_6H_5 \) for benzoguanamine, \( CH_3 \) for acetoguanamine, and \( CH_3(CH_2)_16 \) for stearoguanamine. The guanamines form methylol condensates similar to, but more hydrophobic than, the methylol melamines.
Halogenated aliphatic or alicyclic compounds such as glycerol-1,3-dichlorohydrin, glycerol-1,2 dichlorohydrin, glycerol 1,3 dibromohydrin, and epichlorohydrin (1,2 epoxy-3-chloropropane), are used to produce cross linking of cellulose molecules. In these compounds there are at least two halogen atoms on different C atoms, both capable of forming epoxide rings with at least one hydroxyl group also present in the same molecule. The reaction, which is claimed to be complete in a few minutes at 90°C in presence of an alkaline catalyst, is believed to occur in the following stages (22).

\[
\begin{align*}
\text{Cellulose} - \text{OH} & \quad \text{ClCH}_2\text{-CHOH-CH}_2\text{Cl} \\
\downarrow \text{NaOH} & \quad \text{Glycerol 1,3 dichlorohydrin} \\
\text{Cellulose ONa} & \quad \text{CH}_2\text{-CH}_2\text{-CH}_2\text{Cl}. \\
\end{align*}
\]

It is claimed that the finish is permanent and resistant to prolonged washing and repeated laundering. The finished fabric does not retain chlorine on laundering.

Recently a new class of epoxy resins has been introduced (46).
These resins are characterized by the presence of an epoxide ring, absence of nitrogen and absence of formaldehyde. They are free from the usual problems associated with the nitrogen-formaldehyde types of resins. The replacement of the easily hydrolyzable methylene-nitrogen linkage by the more stable carbon-carbon linkage in the epoxy resins, gives a much more washfast finish.

Being free from N, their chlorine resistance is permanent unlike the chlorine resistance of N-formaldehyde resins which develop chlorine retention upon repeated hot alkaline washings.

Chemically, these resins contain two epoxy groups linked through an intermediate group \( R \) which can be a hydrocarbon, a polyhydric phenol, a polyhydric alcohol or an inorganic acid such as phosphoric acid.

\[
\begin{array}{c}
\overset{O}{\text{C}} - \overset{C}{\text{H}} - \overset{R}{\text{CH}} - \overset{\text{CH}_2}{\text{O}} \\
\end{array}
\]

Among other compounds proposed for use as crease proofing agents, are thiourea formaldehyde (7), formamide-formaldehyde, hydantoin formaldehyde (7), tetra-methylol acetylene-diurea (7) and bis-hydroxymethylamides of dicarboxylic acids (2). Recently di- and polyisocyanates (22) have been introduced as cross-linking reagents for cellulose. These compounds have not achieved significant use in industry. Their chemical structures are given below:
Thiourea formaldehyde

\[
\begin{align*}
\text{CS} & \quad \text{NH} - \text{CH}_2\text{OH} \\
\text{NH}_2 & \\
\end{align*}
\]

and

\[
\begin{align*}
\text{CS} & \quad \text{NH} - \text{CH}_2\text{OH} \\
\end{align*}
\]

Hydantoin-formaldehyde

\[
\begin{align*}
\text{OC} & \quad \text{N} - \text{CH}_2\text{OH} \\
\text{CO} & \\
\text{H}_2\text{C} & \quad \text{N} - \text{CH}_2\text{OH} \\
\end{align*}
\]

Tetra methylol acetylene diurea

\[
\begin{align*}
\text{HOCH}_2\text{-N-CH-N-CH}_2\text{OH} & \\
\text{CO} & \quad \text{CO} \\
\text{HOCH}_2\text{N-CH-N.CH}_2\text{OH} & \\
\end{align*}
\]

Bis-hydroxy methyl amides of dicarboxylic acids

\[
\begin{align*}
\text{HO.CH}_2\text{NH.CO(CH}_2)_n\text{CO.NH.CH}_2\text{OH} & \\
\end{align*}
\]

Hexamethylene di-iso-cyanate

\[
\begin{align*}
\text{O=C=N-}(\text{CH}_2)_6\text{-N=C=O} & \\
\end{align*}
\]

Catalysts:

The crease proofing agents are polymerised or reacted with the cellullosic fibres in presence of certain compounds. As their primary function is to increase the rate of the reaction, these
compounds are commonly referred to as catalysts. However, they are often used in amounts which indicate that their function is not merely catalytic. These catalysts belong to the following groups:

(1) Mineral and organic acids
(2) Ammonium salts
(3) Amine salts
(4) Inorganic salts (such as magnesium chloride and zinc nitrate referred often as metal salts in literature)
(5) Oxidising agents
(6) Alkaline catalysts

Mineral and organic acids were the first catalysts used for curing (i.e. polymerizing) amino resins. They have very limited application because they give poor bath stability by condensing the precondensates rapidly.

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]
\[ \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{H}^+ + \text{C}_2\text{O}_4^- \]

However, they can be used successfully by choosing particular combinations of acid and buffers or mixtures of acids. A mixture of boric acid and tartaric acid is used widely in Europe with UF resins.

The work of Battye, Marsh, Tankand, Watson, and Wood (30) suggested the use of ammonium salts of strong acids which develop the correct acidity only on drying. These salts produce resin baths with an initially high pH, but their reaction with
formaldehyde lowers the pH with time. Consequently the resin starts condensing in solution and settles out as a precipitate. These catalysts function by two mechanisms (1) hydrolysis of the salt to liberate free acid, and (2) reaction with the free formaldehyde in the resin bath to give the free acid and hexamethylene tetramine.

\[ \text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} + \text{H}^+ + \text{Cl}^- \]

\[ 4\text{NH}_4\text{Cl} + 6\text{HCHO} \rightarrow \text{C}_6\text{H}_{12}\text{N}_4 + 4\text{H}^+ + 4\text{Cl}^- + 6\text{H}_2\text{O} \]

The residual products resulting from the use of ammonium catalysts in curing may be:

(1) The original salt left unreacted
(2) Hexamethylene tetramine formed as shown above
(3) Various methyl amines formed by a reductive alkylation of ammonia by formaldehyde, in the presence of reducing agents (42, 14)

\[ 2\text{NH}_3 + 3\text{CH}_2\text{O} \rightarrow 2\text{CH}_3\text{NH}_2 + \text{CO}_2 + \text{H}_2\text{O} \]
Monomethyl amine

\[ 2\text{NH}_3 + 6\text{CH}_2\text{O} \rightarrow 2\text{(CH}_3\text{)}_2\text{NH} + 2\text{CO}_2 + 2\text{H}_2\text{O} \]
Dimethylamine

\[ 2\text{NH}_3 + 9\text{CH}_2\text{O} \rightarrow 2\text{(CH}_3\text{)}_3\text{N} + 3\text{CO}_2 + 3\text{H}_2\text{O} \]
Trimethylamine

(4) Aminomethyl derivatives of the resin

As these catalysts impart limited bath stability and produce fishy odours, associated with methyl amines as shown in
reaction (3), their current usage is limited.

Alkanolamine salts are considered to be an improvement over the ammonium salts. These are generally milder catalysts and have been used to various extents with different types of resins such as urea, ethylene urea and melamine formaldehyde resins. At high temperature and on reaction with formaldehyde they give a weaker base so that its salts may be hydrolysed. They are latent acid catalysts as they give lower pH only at the temperature of curing. Ordinary primary amine salts are not used because they react immediately with formaldehyde, lower the pH, and give poor bath stability. The mode of the reactions is as follows (17).

\[
(HOCH_2CH_2)_3N \cdot HCl \xrightarrow{\text{hydrolysis}} (HOCH_2CH_2)_3N + H^+ + Cl^- \\
RNH_2 \cdot HCl \xrightarrow{\text{hydrolysis}} RN = CH_2 \cdot HCl + H_2O \xrightarrow{\text{hydrolysis}} \\
+ HOH \quad RN = CH_2 + H^+ + Cl^- .
\]

Inorganic metal salts such as magnesium chloride and zinc nitrate are the most recently developed catalysts for amino textile resins. They are effective for all resin types and are especially recommended for use with the melamine and dimethylol ethylene urea resins. Being salts of weak bases and strong acids, they hydrolyse and liberate the free acid.

\[
MgCl_2 + 2H_2O \xrightarrow{\text{hydrolysis}} Mg(OH)_2 + 2H^+ + 2Cl^- \\
Zn(NO_3)_2 + 2H_2O \xrightarrow{\text{hydrolysis}} Zn(OH)_2 + 2H^+ + NO_3^- .
\]
With metal salts there would be less hydrolytic degradation of cellulose by acid liberated during curing, as the basicity left by the metal residues would counteract acidity. For the same reason, the fabrics cured with metal salts as catalysts give less chlorine damage.

The exact role played by the metal salt catalysts in imparting high cross-linking efficiency of the resins with cellulose is still uncertain. Whether the liberated acid or the metal complex formed by chelation of the polyvalent metal ion with the resin is effective in polymerizing and cross-linking the resin is yet to be established.

Oxidising agents such as hydrogen peroxide or peracetic acid have been suggested as catalyst for the UF resins (17). They oxidise free formaldehyde present in the resin to formic acid, which acts as the real catalyst.

\[ \text{HCHO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HCOOH} \rightarrow \text{H}^+ + \text{COOH}^- \]

\[ \text{HCHO} + \text{CH}_2\text{COOH} \rightarrow \text{CH}_2\text{COOH} + \text{HCOOH} \rightarrow \text{H}^+ + \text{COOH}^- \]

This type of catalyst has not been tried commercially.

Alkaline catalysts such as sodium carbonate and sodium bicarbonate have been used with UF resins by Gagliardi (17). He shows that the same degree of crease recovery and better shrinkage stabilization can be obtained as compared with the
usual acid catalysts. Here no problems of bath stability are encountered. Murakami (39) has commented that the alkaline catalysts used by Gagliardi are in effect latent acid catalysts due to a Cannizzaro reaction between the catalyst and free formaldehyde present during curing.

Steele (47) has shown the mechanism of acidic and basic condensation of the resins as follows:

**Acidic condensation:**

\[ -N\text{-CH}_2\text{OH} + HA \quad \text{fast} \quad \leftrightarrow \quad -N\text{-CH}^+ + H_2O + A^- \]

\[ -N\text{-CH}^+ + H-\text{N}^- \quad \text{slow} \quad \leftrightarrow \quad -N\text{-CH}_2\text{-N}^- \]

\[ H \quad \text{fast} \quad \leftrightarrow \quad -N\text{-CH}_2\text{-N}^- + HA \]

**Basic condensation:**

\[ -\text{CO}-N\text{-CH OH} \quad \leftrightarrow \quad -\text{CO}-N=\text{CH}_2 + H_2O \]

\[ -\text{N\text{-CH}_2OH} + OH \quad \rightarrow \quad -\text{N\text{-CH}_2-0} + H_2O \]

\[ -\text{N\text{-CH}_2-0} + -\text{CO-N=CH}_2 \quad \rightarrow \quad -\text{N\text{-CH}_2-O-CH}_2-\text{N-CO-} \]

\[ -\text{N\text{-CH}_2-O-CH}_2-\text{N-CO-} + H_2O \quad \rightarrow \quad -\text{N\text{-CH}_2-O-CH}_2-\text{NH-CO-} + OH \]
Application:

The resin monomers are dissolved in water in the required concentration and a suitable catalyst is added. The quantity of catalyst depends on the nature and strength of the catalyst, curing temperature and the resin used. The fabric to be treated should be clean, dry, free from sizing and as free from strain as possible. Generally a mercerised fabric is selected for better absorbency of the resins. The padding is done in a two-or three-bowl padding mangle giving one or two nips between an ebonite and a soft rubber bowl. The squeezing pressure is adjusted to give a wet pick up of approximately 70 to 80% so that the resin monomer can penetrate inside the fibres. Recent work has shown that even with moderate pressures in padding or by application of the resin by spraying (4) penetration within the fibres takes place, provided the resin is of a low molecular weight. After padding, drying is done at a temperature of about 110°C for about 5 to 10 minutes. During the initial drying phase, pH conditions begin to change and formaldehyde is evolved as polymerisation occurs. It has been observed by Alvasker and Turner (1) that increasing concentration of formaldehyde vapours in the surrounding atmosphere appeared to retard the further condensation of hydroxymethyl ureas. A sufficient exhaustion of air is kept to avoid excessive accumulation of formaldehyde vapour and moisture. During drying, the solution on the surface of the fabric and of the individual fibres gets dried, producing a gradient from
within the fibre to the fibre surface. This causes a tendency for migration of resin to the fibre surface. This resin migration is minimised by using moderate drying temperatures. After drying, curing is done in a separate polymerizer at a temperature ranging from 140°C to 180°C for about 5 to 2 minutes. The fabric is cured in a completely relaxed state. The width and length of the fabrics during this thermosetting operation determine the final stabilization of the fabric. The optimum curing temperature and time depend upon the nature of the fabric, resin and catalyst used.

The cured fabric is then given a thorough washing treatment under slightly alkaline conditions. This wash removes the various decomposition products of the resin and catalyst formed during curing and minimises any dangers of development of obnoxious odours and of the degradation of the resin due to presence of acidity left by the catalyst residue.

Properties of the Finished Fabric:

The most important changes in the cellulosic fabrics produced by these finishing treatments are improved crease recovery, reduced water imbibition and improved dimensional stability. These changes are brought about either by the entanglement of a hard amorphous polymer formed within cellulose fibres (26,31,34) or by the formation of cross links between the monomeric or lower polymer form of the resin and the cellulose molecule (10,27,19,48).
mechanism of improvement of crease recovery by resins has already been discussed earlier in the introduction.

The various factors involved in crease recovery for a particular fabric are proportion of resin to fibre, type of resin and catalyst, and drying and curing conditions (11). The degree of wrinkle recovery per unit of resin concentration differs with each type of resin. However, for metal salt catalysts, if crease recovery is related to the molecular concentration of the resin in the fabric, the behaviour of different resins is very similar. For a given resin add-on, ethylene urea finishes give the highest crease recovery, modified melamine resins show somewhat lower values while urea resins give the lowest crease recovery (11).

Reduced Water Imbibition and Dimensional Stability:

When a cellulose fibre is immersed in water, it absorbs or imbibes water. The water is accommodated in the amorphous regions, and as the crystallites are unchanged, the molecular chains in the amorphous regions move apart. This results in the swelling of cellulose fibres which produces shrinking of the fibres. Introduction of the resin in the amorphous portion of the cellulose prevents such separation of the molecular chains, so that the resulting system takes up less water i.e. its imbibition is reduced and thereby its dimensional stability is increased. Shrinkage control of the fabric can be achieved in various degrees by all the amino textile resins, when applied to cellulosic fibres. Shrinkage control is an extremely
important commercial advantage, which is sometimes ignored by the emphasis on improved crease recovery. Wardell (55) says that "use of synthetic resins through stabilizing shrinkage made available more yards for a critical civilian shortage of fabrics during World War II." Fischer (13) mentions that "resin treated rayons did not shrink as much during mechanical shrinkage as did the untreated and in some cases, the yardage saved actually offset the cost of the resin treatment." Resin treated fabrics due to their lower holding of water also dry at a quicker rate than untreated fabrics.

Strength:

It has been shown that for each specific resin, either of the polymerizable or reactant type, the decrease in tear and tensile strength follows the increase in crease recovery which, in turn, depends on the quantity of the resin applied.

As the cotton fibre is highly oriented, the extension is due to the micellar slippage. The presence of resin, whether cross linked or entangled between the micelles, prevents the slippage of the cellulose chains and thereby reduces the extensibility of the fibres. This results in the loss in tensile as well as tear strength of the cotton fabrics. The original strength of the fabric can be regained if the resin is removed carefully by acid hydrolysis (19). This means that the loss in strength is not due to the chemical degradation of the cellulose
molecules, but due to the mere presence of the resin which brings about changes in fabric properties as discussed earlier. Finishes based on ethylene urea give the highest strength loss for a given resin weight, while those based on urea show the lowest.

Another consequence of the decreased extensibility of the resin treated fibre is the reduced abrasion resistance.

 Chlorine Retention:

When fabrics crease proofed with compounds containing amino or imino groups are bleached with hypochlorite solutions, chloramine or chloramide compounds can form by substitution of chlorine on the nitrogen.

\[ \text{NH} \rightarrow \text{N.Cl} \xrightarrow{\text{heat}} \text{HCl}. \]

These compounds are thermally unstable and on application of heat as in ironing, they liberate hydrochloric acid. Strength of the fabric decreases because of hydrolysis of cellulose by the acid liberated on ironing. As the extent of chlorine retention depends on the number of \(\text{NH}\) groups in the fibre-resin product, it is very high with condensation products of urea or melamine with formaldehyde. Dimethylol ethylene urea which does not contain any chlorine retentive \(\text{NH}\) groups still gives chlorine retention to varying extents if stored under humid conditions or given an acid souring. Fabrics treated with non-nitrogenous compounds such as the epoxides and acetics, do not retain chlorine at all and exhibit no chlorine damage.
Effect on Fastness of Dyes:

It has been found that with many direct dyes the fastness to washing is improved by resin treatment, with some it is unaffected, whereas with other dyes, it is adversely affected. The light fastness of many direct and vat dyes is affected by resin treatment. It has been shown that the number and position of \(-\text{OH}\) and \(-\text{NH}_2\) groups in direct dyes influence the effect of resin treatment on light fastness (3). Increasing molar ratio of urea:formaldehyde increases loss of light fastness. For vat dyes the following mechanism has been proposed for explaining the decrease in light fastness (5). Peroxide formed by exposure to light of the photo-sensitive dyes generates free \(-\text{CH}_2\) radicals from the resins which cause an irreversible reduction of the quinonoid link in the dye. In support of this mechanism, it was found that a free radical and peroxide inhibitor, diallyl phthallate, was effective in reducing fading. Fading increases more or less linearly with time.

According to a recent study, resins (20) and reactants can be classified into four groups in a decreasing order of their effect on the light fastness of dyes:

1. Dimethylol ethylene urea
2. Guanylurea formaldehyde
3. Melamine formaldehyde, triazines, ketone-aldehydes, epoxy resins and epoxy DMEU blends
4. Urea resins and tetramethylol glucoluril
Odour Formation:

The fabrics treated with aminoresins, particularly with UF resins and ammonium salt catalyst, develop an unpleasant fishy odour on storage under humid conditions. The fishy odour is due to the formation of alkylamines as discussed earlier. The alkylamines are water soluble and can be removed by an afterwash.

Rot Proofing:

The resin treated fabrics are less sensitive to bacterial decay or rotting. This may be due, in part, to the reduced capacity of the resin-treated cloth for imbibing water.
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