CHAPTER I

INTRODUCTION

The reaction of cellulose with cross-linking agents, popularly known as "resin finishing", forms the basis for imparting certain desirable properties to cellulosic textiles. In the early stages of its development, resin finishing was mainly applied to regenerated cellulosic fibres with a view to restrict their swelling and to reduce their tendency to shrink and wrinkle. However, resin finishing is being increasingly applied to cotton textiles chiefly because of the need for cotton to compete with the synthetic fibres. Although the cotton fibre possesses various advantages such as good moisture absorption, low static charge development and cheapness, it lacks the crease recovery property exhibited by synthetic fibres like nylon and polyester. The need for improving this property of cotton so that it could approach the performance of the synthetics has provided the real stimulus for resin finishing of cotton.

The first crease resistant finishes were introduced in the 1920s. These were based on aminoplast resins obtainable from the reaction of formaldehyde with urea or melamine.

\[
\text{CO(NH}_2\text{)}_2 + \text{HCHO} \rightarrow \left[\text{-CH}_2\text{.N.CO.NH-}\right]_n
\]

Urea    Formaldehyde    Urea-Formaldehyde resin

\[
\text{C}_3\text{H}_3\text{(NH}_2\text{)}_3 + \text{HCHO} \rightarrow \left[\text{-NH.C}_3\text{.N}_{2}\text{:(NHCH}_2\text{-})_2\right]_n
\]

Melamine    Formaldehyde    Melamine-Formaldehyde resin
These products are applied to the fabric in the form of their precondensates together with an acid donor ("catalyst") and the fabric is subjected to the action of heat when an insoluble resin is formed within the fibre.

The aminoplast resins have several disadvantages such as inadequate storage stability of the precondensate, unsatisfactory washfastness of the finish and "chlorine retention" in the treated fabric. The chlorine retention manifests itself when resin finished fabrics are treated with a bleaching solution containing active chlorine, which readily reacts with the amino or imino groups in the resin forming chloramines.

\[
\begin{align*}
\text{H} & \quad + \quad \text{Cl}_2 \\
\text{H-N} & \quad \rightarrow \quad \text{H-N-Cl} \\
\text{H-N-H+Cl}_2 & \quad \rightarrow \quad \text{H-N-Cl} + \text{HCl}
\end{align*}
\]

The chloramines are not easily removed on washing; during the subsequent drying or ironing of the fabric they decompose to give hydrochloric acid and nascent oxygen. This brings about both hydrolytic and oxidative degradation of cellulose which is reflected in the loss of strength and yellowing or browning of the fabric.

\[
\begin{align*}
\text{H-N-Cl} + \text{H}_2\text{O} & \xrightarrow{\text{Heat}} \text{NH} + \text{HCl} + [\text{O}]
\end{align*}
\]

Further development in crease resistant finishes led to the discovery of the reactant resins. As they lack the
imino hydrogen, they are not susceptible to chlorine retention. 1:3 - dimethylol-2-imidazolidinone or dimethylol ethylene urea (DMEU) belongs to the first of these compounds.

\[
\text{HOH}_2\text{C-N-C-N-CH}_2\text{OH} \\
\text{H}_2\text{C-CH}_2
\]

Dimethylol Ethylene Urea (DMEU)

Reactant resins are mostly bifunctional compounds which react with cellulose and form cross-links between individual structural elements of the fibre. The following formula shows in a simplified manner the cross-linking of cellulose molecules by dimethylol ethylene urea.

\[
\text{Cell O} \text{H} + \text{HOH}_2\text{C-N-C-N-CH}_2\text{OH} + \text{OH} \text{ Cell} \\
\text{H}_2\text{C-CH}_2
\]

The various cross-linking agents for cellulose which are available today, fall under two main categories viz. (a) nitrogenous and (b) non-nitrogenous. Some of the most important of these cross-linking agents are listed below.
(a) Nitrogenous cross-linking agents:

\[
\begin{align*}
\text{1:3 - dimethylol-2-imidazolidinone} & & \text{1:3 - dimethylol-4:5-dihydroxy-2-imidazolidinone} \\
\text{Dimethylol Ethylene Urea (DMEU)} & & \text{Dimethylol Dihydroxy Ethylene Urea (DMDEU)} \\
\text{1:3 - dimethylol pyrimidinone} & & \text{Dimethylol tetrahydro-5-ethyl-s-triazine-2-one} \\
\text{Dimethylol Propylene Urea (DMPU)} & & \text{Dimethylol Ethyl Triazone (DME2)} \\
\text{Bis-(Methoxymethyl) Urea} & & \text{Dimethylol Mono Carbamate}
\end{align*}
\]
(b) Non-nitrogenous cross-linking agents:

\[ X-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{CH}_2-\text{CH}_2-X \quad (\text{where } X = \text{Na}_2\text{SO}_4, \text{Na}_2\text{SS}, \text{\textsuperscript{\alpha}-substituted Diethyl } \text{CH}_3\text{COO}, \text{or other sulphones}) \]

\[ -\text{O-R-OCH}_2\text{O-R-OCH}_2\text{O} - \]

Acetals

\[ \text{Cl-CH}_2-\text{CH-CH}_2-\text{Cl} \]

\[ \text{OH} \]

Dichloro propanol

Theories on the mechanism of improved crease recovery properties imparted by various treating agents:

Two major theories have been put forward to explain the improved crease recovery of cellulose fabrics treated with resin precondensates: the cross-linking theory and the resin deposition theory. It was at one time believed that the improvement in crease recovery properties resulting from treatment of cellulosic textiles with resin precondensates was due to the formation of a resilient coating around the fibres. While some evidence supporting this has been reported (1), it has been shown that under conditions obtained in conventional treatments, the precondensates do not coat the fibres, but penetrate into the fibres more or less uniformly (2,3). Furthermore, it has been observed that treatments with polymerised compounds, which
cannot penetrate the fibres but form resin deposits on the fibre surface, impart no crease recovery to the fabrics; on the contrary they make the fabric stiff and consequently increase its tendency to wrinkle (4,5,6). The resin deposition theory was suggested mainly because the early treatment agents were resin precondensates which can form three-dimensional polymers under conditions used in treating cotton. However, many resin formers which are not capable of reaction with cellulose do not improve crease recovery when introduced inside cellulosic fibres and caused to polymerise (7,8,9). Certain precondensates believed to be incapable of cross-linking cellulose, when applied with alkaline catalysts, have been found to improve crease recovery. However, the extent of improvement obtained under these conditions is not generally high and not fast to washing. Moreover, the possibility that such compounds as dimethylol urea can cross-link with cellulose even under alkaline conditions cannot be ruled out (10,11,12,13,14).

According to the cross-linking theory, molecules of cross-linking agents - which must be at least bifunctional - react with the hydroxyl groups of cellulose chains and form bridges between them. These 'bridges' or cross-links are bound to cellulose by covalent bonds. The cross-link theory is supported by a considerable amount of evidence (15). Treatment with compounds which give water soluble materials
when polymerised themselves result in improved crease recovery properties durable to washing (16). Further, the crease recovery of cellulose can be improved by treatments with compounds which are not resin formers (17,18,19). Polymerisation of ethyl acrylate in allylated cotton improves crease recovery, by polymerisation within untreated fibres which cannot be cross-linked by the acrylate, does not produce an improvement (20,21). The treated fibres are not soluble in cellulose solvents (22,23) indicating that the hydroxyl groups on cellulose chains are blocked (24,25). Unlike cotton treated with monomethylol urea which cannot cross-link cellulose, fibres treated with dimethylol urea do not disintegrate into thin sheets of microfibrils upon beating in water in a blender but break into short thick chunks of cellulose several layers thick suggesting the presence of interfibril and interlayer cross-links (26,27).

Fine-Structure of Cellulose:

In order to understand why resin deposition or cross-linking of cellulose causes an improvement in its crease recovery properties a brief description of cellulose fine-structure is necessary.

The cotton fibre is a complex, well-ordered unit which is generated during the growth cycle of the cotton
plant in the form of a long, hollow tube, approximately 20 microns in width by 25,000 microns (1 in.) in length. 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 (28). The primary wall is very thin (ca. 0.1 micron thickness); and accounts for only 5% of the weight of the fibre. The secondary wall is quite thick (varies from ca. 1 - 5 microns) and is composed of successive layers (lamellae) of cellulose. The shape of the fibre cross section resembles that of a kidney bean. 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. It is known that the secondary cell wall contains about 95% of the cellulose of the fibre. This secondary wall appears to be a continuous structure but on swelling, it readily separates into radial lamellae that are about 0.1 micron thick and are apparently continuous throughout the length of the fibre (29). The lamellae are made up of about five layers of microfibrils. These smaller structures are nearly parallel and arranged spirally about the fibre axis. The direction of the spiral reverses frequently. These facts become evident when an expanded portion of the cross section of the fibre is examined under great magnification using an electron microscope (30,31,32,33).
The microfibrils are composed of cellulose molecules which in turn consist of D-glucopyranosyl units joined together in a linear chain:

\[
\begin{align*}
\text{H} & \quad \text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{H} & \quad \text{OH} & \quad \text{CH}_2\text{OH} \\
\text{H} & \quad \text{CH}_2\text{OH} & \quad \text{H} & \quad \text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH} & \quad \text{H} & \quad \text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{H} & \quad \text{OH}
\end{align*}
\]

The units are bound together by \(1\rightarrow4\) \(\alpha\)-oxygen bridges.

The number of anhydro glucose units in a cotton cellulose molecule has been estimated to average about 5000 \((34,35)\). One microfibril or cellulose micelle would contain 100 - 170 individual chain molecules. Some regions of the fibre can diffract X-rays in the same manner as three-dimensional crystal lattices. The extent of crystallinity of native cotton cellulose as determined by X-ray methods is about 70 - 80% \((36,37)\). In the crystalline areas long chain molecules lie parallel and are packed in such a close and regular fashion that crystal properties result. In other regions the order of chain molecules is very low and the state of disorder is such that the material may be regarded amorphous. If the chains are long enough, they extend through both regions. Hence the fibre consists of alternating
regions of amorphous and crystalline regions with certain chains passing through both the regions. The symmetry and regularity of cellulose molecules in the crystalline regions permit adjacent chains to be packed closely and the lack of bulky substituents on the 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 regions can be penetrated readily by water and low molecular weight cross-linking agents. Between the microfibrils there are capillary networks which can be readily reached by colloidal solutions, while the microcapillary structure between the chain bundles of the microfibrils can be reached only by true solutions. The various capillary systems can be made accessible by suitable chemical finishing techniques. The crystalline portions which are not accessible to water can be reached by swelling agents like sodium hydroxide which 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 \( \beta \)-glucose residues are probably fully extended and they are responsible mainly for tenacity, high modulus of elasticity and resistance towards bending, while amorphous regions by their property
of allowing freedom of movement to molecular chains account for the flexibility and extensibility of the cotton fibre.

Mechanism of creasing:

As already mentioned, the highly ordered regions in cellulose fibres are interspersed with zones where the degree of order is low. In the less ordered zones, the chain molecules, elementary fibrils and microfibrils are very mobile because of low cohesion between individual units. When such a disordered region is subjected to an external tensile stress, the fibre elements are straightened out till the stress is uniformly shared.

The same process occurs when a fibre is bent. Along the outer arc of bending, the stresses cause a plastic deformation, while there is a deformation due to compression along the inner arc. When the stresses causing the bend are removed, the fibre elements remain in their above position i.e. the bend remains. It will thus be clear that an elastic deformation of the bending i.e. a return to the original position after the removal of the stress can be achieved by eliminating the displacement of the structural elements with respect to one another. This permanent fixing of the disordered regions is attained through resin deposition or cross-linking of cellulose. An analogy often
employed in this context is that of a bicycle tube: an
almost empty bicycle tube can be easily bent and remains
in this position without showing any tendency to return to
its original position. However, when air is pumped into
the tube, it becomes elastic and returns to its original
shape on removal of external stress. The same analogy
can be employed for cross-linked cellulose also, if one
considers the tube to be stiffened by internal bonds (38).

Dry and wet crease recovery:

The "natural" crease recovery property of cellulose
largely depends on the "natural" hydrogen bonding between
its structural elements. Heating which removes moisture
and increases hydrogen bonding improves crease recovery
of cellulose. However, only the dry crease recovery is
improved in this manner since hydrogen bonds are susceptible
to rupture by moisture. The dry-only recovery exhibited
by cellulose oxidised with periodic acid may also be the
result of the formation of water-sensitive bonds (39).

Conventional methods which introduce covalent cross-links
into the fibres improve both dry and wet crease recovery
of the products. The wet crease recovery is generally
lower but since cellulose is nearly as accessible to
cross-linking agents as it is to water, this difference
is small (40).
Wet-only crease recovery:

Making cellulose more accessible to moisture appears to improve its recovery in wet state, but not in the dry state. For instance, partial phosphonomethylation results in the fabric having high wet crease resistance with hardly any improvement in the dry crease recovery (41). The wet recovery may depend on the internal pressure generated by swelling forces similar to the deformation recovery of a hose filled with water under pressure.

The internal pressure mechanism may also contribute to improvement in recovery obtained by wet-reaction processes. The reaction takes place on swollen fibres and side chain and intramolecular cross-linking is possible (42,43). It has been suggested that cross-links introduced by wet reaction processes are located in regions of some lateral order; they therefore impose no restraint on chain and fibril slippage in dry fibres, in which slippage takes place primarily in the highly disordered regions. However, these cross-links stabilise the swollen structure and restrain slippage when the fibres are wet (Fig. 1).

Marsh (44) has interpreted the wet-only recovery in terms of taut and loose structures. Cross-links introduced by wet-reactions process restrict chain and fibril mobility only as long as the fibre is distended and distances between its structural elements are high. When the fibre dries,
Fig. 1. Diagrammatic representation of dry-cure process (A and B) and wet-reaction process (C and D). (Reproduced from Textile Res. J. 31, 198 (1961).
Fig. 2. Diagrammatic representation of a wet-reacted fibre structure. A: water swollen, distended exhibiting crease recovery; B: dry, collapsed exhibiting no crease recovery. (Reproduced from Textile Mfr. 85, 294 (1959).)
there is no restraint on slippage, because the whole structure collapses and its elements become less cohesive (Fig. 2).

Optimum dry and wet crease recovery:

Cross-linking of cotton at intermediate states of distention (neither fully swollen nor completely collapsed) results in products with better properties for most normal uses than treatments at either extreme (45, 46). Such fabrics have lower swelling capacity and lower wet recovery than those reacted in the swollen state but have also dry crease recovery. Compared with dry cured fabrics, they are more absorbent and have higher wet crease recovery. High dry and wet crease recovery can also be obtained by conventional resin treatment of fabrics previously reacted in the swollen state (47).

Reeves (48, 49) has explained the formation of wet and dry crease recovery properties on the basis of cross-linking cellulose at lamellar, microfibrillar and molecular levels. According to him, lamellae are relatively easy to separate and hence slippage between these structures could occur when extension or compression forces are applied. Slippage could also be expected to occur between microfibrils. These structures are somewhat more difficult to separate than lamellae but they are considerably more numerous.
Therefore, even minute movement between microfibrils could become significant when the entire cotton fibre is considered. If the cellulose chains that are cross-linked happen to be in different microfibrils, then the two microfibrils represented by the two cellulose molecules are bound together. In all probability, the cellulose chains taking part in the cross-linking reactions will be at or near the surface of the microfibril unless a long cross-linking agent is used. Because of the accessibility and relative distances involved, microfibrils should be readily cross-linked. Lamellae can be bound together through the same process; but cross-linking of lamellae is more likely to occur when the fibre is in a relatively collapsed or unswollen condition.

Benerito (50,51) has reviewed the current theories explaining dry and wet crease recovery in cotton with well-documented experiments in support of each and has cited observations not predicted by these theories. A new theory consistent with all experimental facts is presented in terms of the hydrogen-bonded structure of cotton cellulose, the modern hydrogen-bonded structure of water and inter-relations between cotton or chemically modified cotton and water. On the basis of this theory, it is concluded that consideration should be taken not only of cross-linking cellulose at the molecular, fibrillar or lamellar levels and of the degree of
swelling of cotton fibres at the time of reaction, but also of the structure of water as well. The reagents and chemical modification of cotton affect the structure of water which in turn affects the conformation of chemically modified cotton.

Durability of the finishes:

The improved crease recovery properties imparted to cellulose by treatment with polyfunctional cellulose-reactive compounds are durable. Some of the finishes can be removed only under conditions in which the fabric itself would disintegrate while others are affected by repeated washing especially under highly alkaline conditions and by the acid treatment which is common in some laundries (52). According to Reeves, Vail and Frick (53) the electron displacement effects of substituent groups caused by induction and resonance in the amido-methylol compounds are related to their ease of hydrolysis: Electron-releasing groups attached to either the amido nitrogen or the carbonyl carbon facilitate acid hydrolysis; while electron-attracting groups hinder hydrolysis.

Strength losses:

It is well known that cotton fabrics exhibit losses in strength after crease-proofing treatments. A part of this loss can be ascribed to acid damage, although according to Marsh, the apparent damage cannot be ascribed to that caused
by acid or oxidising agents since on removing the resin it is possible to restore the original physical properties of the cellulosic material (54). However, it is likely that the same changes which lead to higher crease recovery also cause a decrease in strength properties of the fabric.

Tensile strength losses:

Gordon and Steele (55) advance the view that there is a high degree of cross-linking in amorphous cellulose material. They make use of the theory put forward by Bueche (56) on the effect of cross-linking on the strength of rubberlike polymers. According to this theory, the tensile strength of a rubberlike polymer increases initially as the degree of cross-linking increases, passes through a maximum and decreases at high levels of cross-linking. The loss in tensile strength of cellulosic material as crease recovery improves due to cross-linking is ascribed to a high degree of cross-linking of a cellulose material beyond the maximum in the tensile strength - cross-link density relationship. O'Brien and van Loo (57) have however suggested a theory involving a relatively low degree of cross-linking based on the rate of wrinkle recovery improvement with time of reaction. This requires then, a different explanation for tensile strength losses which occur as the crease recovery of cotton is improved. For this, they have considered the accessible regions of cellulose as the weak link which
controls the strength of cotton (58). The strength of cotton can then be attributed to a considerable number of hydrogen bond cross-links and perhaps molecular entanglements in this region. A reduction in the number of these hydrogen bond cross-links will cause a decrease in the strength of the fibre. According to the theory developed by these workers, for the reaction of crease resistant finishes with cotton only a small fraction of the agent is involved in the formation of covalent cross-links with the balance being taken up in the formation of intra-molecular or intra-chain bridges of some sort. This intra-molecular bridging would reduce the possibilities of hydrogen bond cross-linking of cellulose molecules. The result would be the formation of a covalent cross-link at the expense of a number of hydrogen bond cross-links. The bond energy of a C-O bond such as that resulting from the reaction of a methylol compound with cotton is 70 kcal. The inter-molecular cohesion of a C-O...H-O-C link such as for the hydrogen bonds in cellulose is 14 kcal/mole; energies of such H-bonds may be smaller (59). The tensile strength contributed by a bond is proportional to bond energy. If the formation of a covalent cross-link results in the elimination of more than five hydrogen bond cross-links between cellulose molecules, the result will be a loss in strength. If only a small fraction of a cross-linking finish is involved in the formation of covalent cross-links
and a larger part of it forms intra-molecular bridges which interfere with the normal hydrogen bond cross-linking of cellulose molecules, a considerable loss in strength is to be expected.

Several workers (60, 61, 62) claim that it is possible to decrease tensile losses and even to increase the tensile strength of cotton fabrics by applying tension during the treatment. In this case the cross-links improve the load distribution because they form in the fibre subsequent to the alignment of its elements under stress. There are also considerable data in the literature which indicate that the loss in tensile strength is almost directly proportional to the improvement in crease recovery. This suggests that tensile strength data might be included in the quantitative theory of the effect of wrinkle-resistant finishes on properties of cotton (63).

Tear strength losses:

The decreased mobility of cross-linked structural elements decreases fibre extensibility as well as uniform load distribution. The loss in tear strength exhibited by the treated fabrics may be due to the decreased fibre extensibility, 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 (64, 65, 66, 67). There is a striking
analogy between the mechanism responsible for tensile and tear strength losses. In both cases, it is the decreased ability of the structure to distribute an external load among a large number of its elements. Tensile losses result from poor load distribution among structural elements of the fibre. Tear strength loss results from a decrease in the ability of yarns to share the applied load. As a tear progresses in the fabric, new yarns come under stress. When fibre elongation and inter-fibre slippage are lowered, fewer yarns can accumulate at the point of tear propagation, and less force is required for the tear to continue.

Fibres cross-linked under tension have low extensibility. and while tension during treatment improves fabric tensile strength, tear strength may suffer additional losses. On the other hand, lubricating agents, which increase the ability of fibres and yarns to rearrange under load and share stresses, improve the tear but may lower the tensile strength of fabrics.

Losses in abrasion strength:

The lower abrasion resistance of treated fabrics shown by laboratory tests may also be the consequence of the reduction in fibre extensibility (68, 69, 70, 71). Abrasion losses seem directly proportional to extensibility losses.
However, it has been found that as the load used in testing decreases, the difference between untreated and treated fabrics diminishes, until under a certain load, they are of the same level; at very low loads, the treated fabric shows a higher abrasion resistance than the untreated. The reason for this seems to be that fabric resistance to abrasion is affected not only by fabric extensibility but also by elastic recovery. At high loads, efficient distribution of stress among many fibres is of primary importance. The reduced extensibility of treated fibres prevents good stress distribution, and such fabrics fail at a higher rate. At low loads, the increased elastic recovery of treated fabrics becomes significant and treated fabrics exhibit higher abrasion resistance than untreated ones. Since in normal wear garment stresses are low and since at low load the loss of extensibility is compensated for by an increase in elastic recovery, the results of common laboratory abrasion tests are not dependable indicators of actual wear life of a garment.

Incorporation of rubber lattices or other thermoplastic materials to crease proofing formulations has been found to improve wear properties of treated fabrics (72, 73, 74, 75).
Catalysts:

The reaction between various crease proofing agents and cotton cellulose may take place simply on heating the impregnated fabric, but the time required is long and the durability of the finish is poor. Therefore, compounds which accelerate the reaction and stabilise the finish are necessary. Because their primary function is to increase the rate of the reaction, these compounds are commonly referred to as catalysts, although they are often used in amounts which indicate that their function is not merely catalytic.

By definition, a catalyst is a compound which accelerates a chemical reaction without itself entering into the reaction. A wide variety of chemicals have been used as catalysts in promoting reactions between the cross-linking agent and cellulose. These can be divided into two general groups as follows:

(a) Acids:
   Organic acids
   Inorganic acids.
(b) Latent acids:
   Ammonium salts
   Amine salts
   Metal salts.

Many organic acids have been used as catalysts; e.g. oxalic, maleic, tartaric and citric. Degradation of the fabric is
usually a little greater with these acids than with some of the milder agents available. Among the inorganic acids, boric acid has been used to a considerable extent especially in Europe. In "moist cure" processes, as in Knittex POM III process, cross-linking of cellulosic fabrics is done in the presence of free acid at low temperatures with control of moisture content of the fabric in a standard atmosphere. Better strength-crease recovery relationships are claimed with this method (76). However, most inorganic acids cause excessive degradation unless used in controlled amounts and conditions and thus salts with latent acid-forming properties are preferred. The resin bath stability with such salts is also improved because of a reduced tendency of the resin to polymerise prior to application to the fabric.

The ammonium salts of phosphoric, sulphuric, and hydrochloric acids have been used to a considerable extent because of their latent acidity but have, of late, largely given way to newer catalysts. The main draw-back of ammonium salt catalysts is the development of fishy odours in the resin treated goods. The reaction of formaldehyde and ammonia under acidic conditions at high temperature produces a characteristic fishy odour (77). It has been found (78) that formic acid or its salt is necessarily present in the formation of trimethyl amine which is the main constituent of fishy odour:
The odour will be removed by a thorough after-wash, although this may be uneconomical at times.

The acid catalysts in common use today fall generally into two classes viz. amine hydrochlorides and inorganic metal salts. The amine hydrochlorides are usually alkanol amine hydrochlorides. A considerable number of other primary and secondary amine hydrochlorides have been used as catalysts. Inorganic salts such as magnesium chloride and zinc nitrate have gained widespread popularity in recent times in wash and wear finishing. These salts are generally used at high curing temperatures and produce excellent crease recovery properties. During curing, they undergo thermal decomposition producing free acid and metallic oxide.

\[2\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = \text{MgOMgCl}_2 + 2\text{HCl} + 11\text{H}_2\text{O}\]

\[\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} = \text{ZnO} + 2\text{HNO}_3 + 5\text{H}_2\text{O} .\]

One of the chief advantages in the metal salt catalysts lies in the retention of basic residues, such as the oxides as shown above, by the fabric after the curing treatment has been completed. These residues act as buffers against the acid produced on ironing the treated fabric after bleaching with hypochlorite solution. These buffers tend to be retained very tenaciously by the fabric even after repeated washings. Metal salt catalysts are important in minimising chlorine
retention damage in another connection; the DMEU finish should be non-chlorine retentive but poor results are sometimes encountered especially after storage. This has been examined by Bacon, Smith and Hughes (79) who have studied amine hydrochloride, magnesium chloride and zinc nitrate. They found that zinc nitrate gave optimum resistance to chlorine damage but caused discoloration (yellowing) at high curing temperatures so that magnesium chloride was preferred. Smith (80) examined the effects of organic acids ammonium salts and metal salts as catalysts on the deterioration of chlorine resistance property during storage and found that the best results were obtained from a 'hard cure' with magnesium chloride at 160°, but at a temperature of 140°, zinc nitrate was found to be quite effective.

Irvine, Simons and David (81) have suggested a mixture of magnesium chloride and aluminium chloride as a mild cure catalyst, which is claimed to be effective and practical for resin curing.

Foster (82) has examined the effect of the concentration of amine hydrochloride over the range of 1 - 16% on the resin solids. According to him, above 3% of DMEU on the fabric, there is no improvement in recovery with over 3% of the catalyst expressed on resin solids, but there is an increase in tensile and tear strength losses. An increase in catalyst
concentration does not seem to offset deficiencies in time or temperature of cure. In a later publication, Foster (83) showed that with a constant concentration of 9% solids in the bath the recovery increased as the logarithm of the catalyst concentration up to a maximum of 0.3% amine hydrochloride in the impregnating bath.

Frick, Kottes and Reid (84) have compared the action of 0.5% solutions of ammonium sulphate, an alkanolamine hydrochloride and zinc nitrate in solutions of 7% DMEU; they found that the ratio of formaldehyde to ethylene urea in the finished fabric changed with the catalyst and concluded that ammonium sulphate gave a greater proportion of bound but not cross-linked material and zinc nitrate gave the highest amount of cross-linking as supported by chlorine retention data.

Schroeder and Condo (85) have made a detailed study of the catalytic activity of fluoroborates and sulphates. As shown by earlier work on latent catalysts from organic bases, the catalytic activity depends on the strength of the basic metal i.e. the weaker the base the better is the catalytic activity. They conclude that the activity of the bath is not the factor determining the catalytic activity; what is of importance is the acidity of the material at the time of cure.
Ziifle, Berni and Bensrito (86) have investigated cellulose - DMEU reaction in the presence of "good" and "poor" catalysts and have suggested that the catalyst enters into the reaction forming a complex with DMEU through the formation of nitrogen-to-metal bonds. In addition, crease recovery properties and chlorine retention of treated specimens are dependent upon the catalyst concentration and a critical catalyst concentration is indicated at which maximum cross-linking, maximum crease recovery and minimum chlorine retention are obtained. In a later paper (87), these workers have given data from infra-red absorption spectra of the treated cotton products which are in agreement with those obtained in earlier work.

O'Brien and van Loo (38) have studied the effect of catalyst and catalyst concentration on the reaction rates of resins with cellulose. They have put forward a theory considering metal salt catalysts to act as Lewis acids forming an activated complex with the cellulose reactant, which is consistent with the data obtained on the effect of catalyst concentration on the rate constants.

Recent work on catalysts and scope of present work:

In recent years, a number of factors have combined to increase the importance of catalyst selection for resin finishing. For example, higher levels of crease recovery are now required and this demand reduces the tolerances
allowable in processing conditions. The advent of permanent-press finish has given new impetus to the study of the catalytic system in resin finishing. The excessively high temperature and long time required with catalysts like magnesium chloride create a number of problems particularly in curing complicated structures like garments. The high temperatures required have always been a problem for control of fabric degradation under low pH conditions obtained at the curing stage. Attempts have been made earlier to control the pH during padding and subsequent heat treatments particularly while treating cellulosic textiles with formaldehyde, e.g. by making use of mixed catalytic system such as magnesium nitrate, strontium nitrate and citric acid to control the drop in pH at curing stage (89). In another case, Mg-EDTA chelate is used along with magnesium chloride to raise the pad bath pH to 6.0 (90). Attempts to lower the temperature of cure have also been made using urea and magnesium chloride (91). Other salt mixtures such as aluminium chloride - magnesium chloride mixtures described by Irvine, Simons and Davids (loc.cit.) have also been investigated. Mixtures of organic acids and salts which act as Lewis acids have been used by Parsons and Mona (92) with hydrazide-formaldehyde agents and by Hushebeck (93) for all formaldehyde containing agents. Pierce and Frick (94) have used citric acid with magnesium chloride to reduce the temperature of cure to as low as 60\(^\circ\). In this case, one has
to control carefully the rapid drop in pH during heat
treatment of the fabric. An interesting application of
magnesium chloride in combination with dibasic acid salts
has been briefly reported by Berni et al for use in their
poly-set process to effect simultaneous cross-linking and
polymerisation of selected N-methylol compounds (95).

The phase separation catalyst system developed by
Burkitt et al and patented by Tootal of U.K. also uses
a mixed catalytic system consisting of magnesium chloride
and sodium dihydrogen phosphate (96). It is different from
the above cited examples in that the actual catalysis here
is controlled by the magnesium dihydrogen phosphate produced
in situ exhibiting phase separation on heating and/or
concentration, whereby pH is suddenly reduced to facilitate
reaction between cellulose and the cross-linking agent at
the desired stage of heat treatment.

The present work deals with a novel system of catalysts
developed as a result of an extensive study of inorganic
metal salts, which are used as catalysts in the cross-
linking reactions (97). The study has shown that the
catalytic properties of inorganic metal salts like magnesium
chloride can be considerably improved by mixing with weak
organic acids, their partial or complete salts. The mixed
catalysts have a number of advantages in terms of controlling
the reaction at desired levels. These possibilities, the probable mechanism of the mixed catalysts and their application in resin finishing are discussed in the subsequent chapters.
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