CHAPTER II

REVIEW OF LITERATURE

The review of literature has been discussed in the following subsections :

2.1 General properties of acrylic substances

2.2 Characteristics of acrylamide and formaldehyde

2.3 Effect of finishes on properties of wool and cotton fabrics

2.4 Effect of finishes on permanent setting and durable pressing of the fabrics.

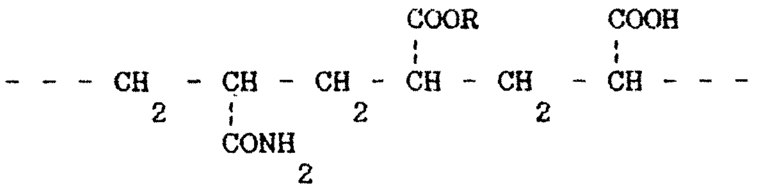
2.1 General properties of acrylic substances

Acrylic substances have often been used for the application to textiles as finishing agents in the form of emulsion polymers. Recently there has been a renewed interest in acrylic compounds. Although acrylic monomers may now be applied directly to textiles, more often the polymer is employed. Application is generally made from water or solvent solution or as an aqueous dispersion (83).

Acrylic compounds belong to the unsymmetrical substituted ethylene class. The acrylic monomers include acrylic and methacrylic acid and their salts, esters, amides and nitriles. Their general representation is $CH2 = \underset{X}{CH}$, where X is like COOH, $CONH_2$ etc. The monomers undergo addition polymerization to form a linear and a long polymer, as shown below :

$$- - - CH_2 - CH - - -$$

Acrylic polymer



$$---CH_2-\underset{CONH_2}{CH}-CH_2-\overset{COOR}{CH}-CH_2-\overset{COOH}{CH}---$$

Acrylic copolymer

These acrylic polymer finishes are thermoplastic in nature, that is these rapidly soften (or melt) with heat and harden upon cooling. Harper (53) has noted that there is no appreciable change in the physical properties of the thermoplastics through repeated heating and cooling cycles. These may be remelted and reshaped as often as possible and as long as the procedure does not introduce charring or degradation to the reworked material.

According to Shapiro (96), these thermoplastic resins have been gaining popularity, since they have become available in the form of aqueous dispersion. These thermoplastic finishes are the dispersion of solid resin particles which when applied from water system will dry to form insoluble films without requiring any curing and washing operations. These not only improve the quality, handle and appearance of fabrics but also enhance the brilliance of colours. It was also pointed out that monomers containing only one double bond give rise to linear polymers and addition of even a trace of monomer having two double bonds (e.g. divinylbenzene butadiene) causes branching between chains and the crosslinked polymer is more resistant to heat, solvents, etc.

Daniel and Vincent (23) investigated that the acrylic emulsions can be cured at room temperature. They crosslink to give durable bonds. Adhesives based on these can be cured without destroying the properties of delicate substrates. Recently polymer emulsions and low temperature catalysts are receiving attention.

Accoring to Nuessle (82), polymers range from methyl methacrylate, the hardest, to 2- ethylhexyl acrylate, the softest. Homopolymers of acrylic acid or acrylamide which are water soluble, will form hard, but continuous films. Most acrylics used for textiles are designed to form a continuous film at 100 °F (38 °C), but for durability it is preferred that the fabric reaches 250 °F (120 °C) for a few seconds. It will then have better cohesion and adhesion.

Acrylic resins have been used as the only fabric finishing agents or as additives with thermosetting resins. These have been utilized to improve tear strength, crease recovery, abrasion resistance and wash and wear behaviour of fabrics. Their important role is also seen in shrinkage contorl (106). These acrylic polymers on other hand are also used to provide body and stiffening in pigment dyeing and printing, and in lamination, upholstery backing and for durable embossed effects. While the use of acrylics in general is gaining importance more in printing, binding and paints etc., acrylamide is more studied for textile finishing.

2.2 Characteristics of acrylamide and formaldehyde

Manufacture of acrylamide monomer

The commercial route of acrylamide has been the hydration of acrylonitrile. In each process, conditions of time, temperature, concentration, inhibitor, pH have been chosen so as to avoid mechanical losses, to increase output and to minimize undesirable side reactions, (57).

Reaction of Acrylamide

Reactions of the acrylamide are of the amide group and of double bond (57).

At the amide function, the reactions of acrylamide include,

(a) hydrolysis to acrylic acid

$$CH_2 = CH - CONH_2 + H_2O \dashrightarrow CH_2 = CH - COOH + NH_3$$

(b) dehydration to acrylonitrile

$$CH_2 = CH - CONH_2 \dashrightarrow CH_2 = CH - CN + H_2O$$

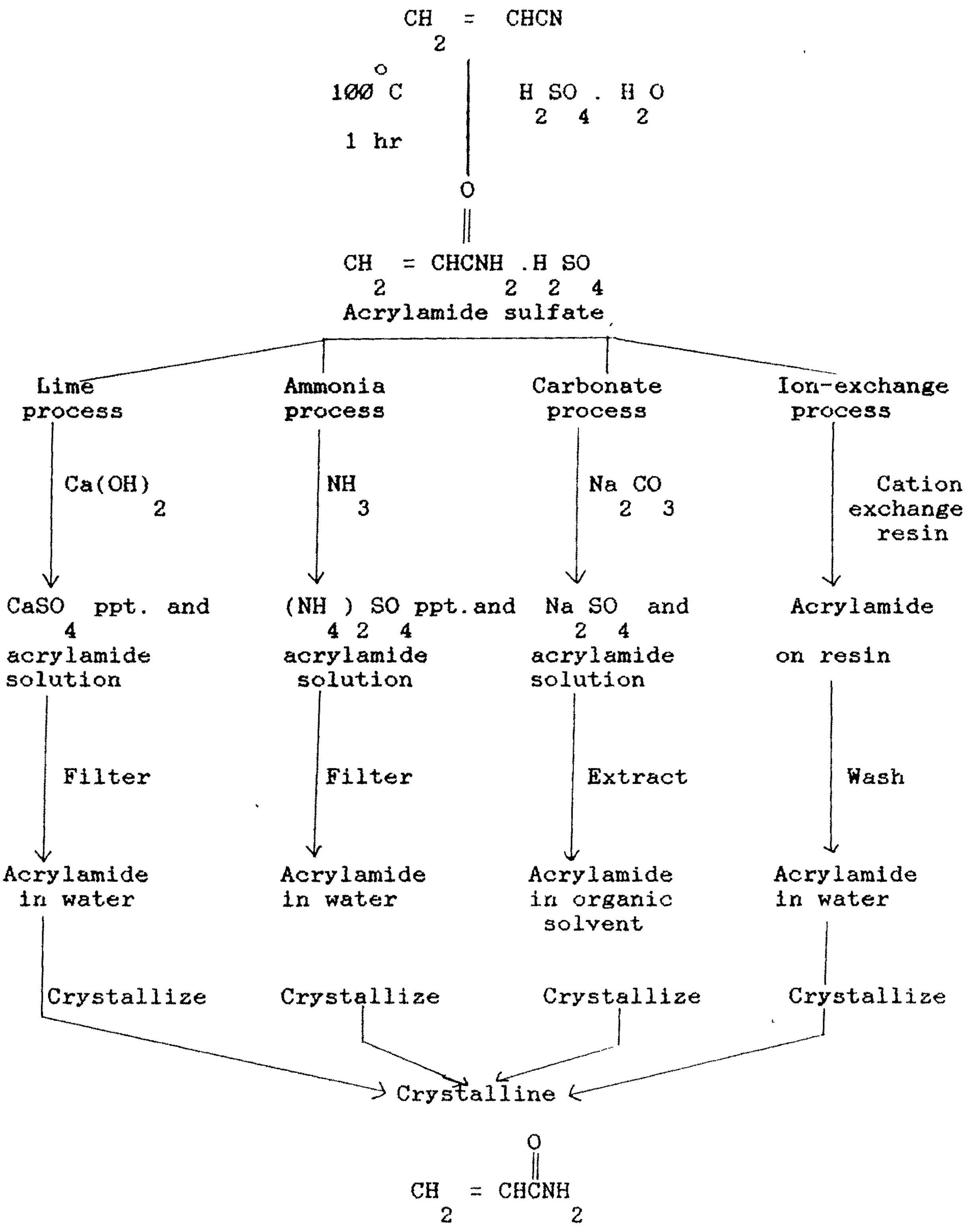
(c) alcoholysis to acrylic esters

$$CH_2 = CH - CONH_2 + ROH \dashrightarrow CH_2 = CH - COOR + NH_3$$

(d) condensation with aldehydes

$$CH_2 = CH - CONH_2 + CH_2O \dashrightarrow CH_2 = CH - CONHCH_2OH$$

At the double bond, the reactions are addition to hydroxy compounds, amines, ammonia, mercaptans, bisulphite ion, etc.



PROCESSES FOR ACRYLAMIDE MANUFACTURE

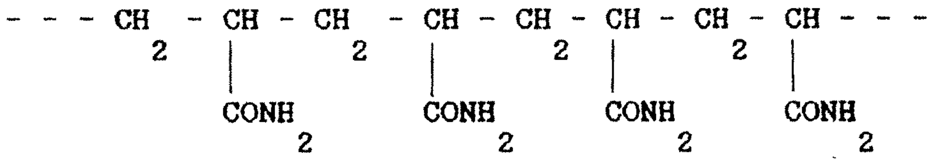
Polymerization of acrylamide

The acrylamide monomer is relatively stable when stored at 10-25 °C. Molten acrylamide polymerizes vigorously with evolution of heat, usually becoming insoluble through loss of ammonia.

$$CH_2 = CH - CONH_2 + HCH = CH - CONH_2 \longrightarrow$$
$$CH_2 = CH - COCH = CH - CO + NH_3$$

Acrylamide is unique in its ability to produce very high molecular weight linear polymer which exhibits strong hydrogen bonding. The viscosity of polyacrylamide in water increases with the molecular weight and decreases with increasing temperature (67). In the presence of free radicals, acrylamide polymerizes rapidly to high molecular weight polymers (94).

Initiators are peroxides, azo compounds, redox pairs,photochemical systems and X - rays. The initiation and termination mechanisms are dependent on the catalyst system. Polymerization in aqueous solution is generally the preferred method because the highest molecular weight polymers are obtained in water. Redox catalysts used for aqueous polymerization are peroxydisulfate with bisulfite, and peroxide with ferrous ammonium sulfate. Ionizing radiation has been extensively used as an initiator for aqueous system as well as for the crystalline monomer (57). Acrylamide has the ability to form soluble polymers of very high molecular weight. Acrylamide monomer undergoes addition polymerization to form a linear polymer thousands of units long,



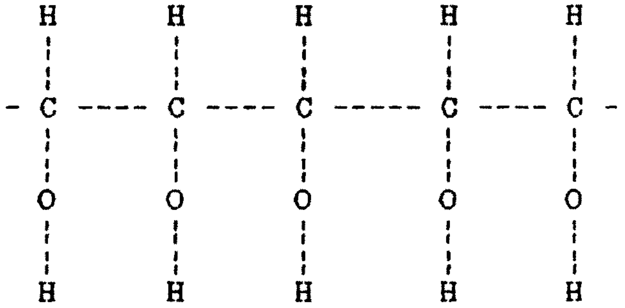
$$---CH_2-\underset{CONH_2}{\underset{|}{CH}}-CH_2-\underset{CONH_2}{\underset{|}{CH}}-CH_2-\underset{CONH_2}{\underset{|}{CH}}-CH_2-\underset{CONH_2}{\underset{|}{CH}}---$$

Solutions of high molecular weight polyacrylamide in water are extremely viscous.

Reaction with formaldehyde

Formaldehyde solutions are slightly acidic with pH 2.5 to 3.5 and this acidity is due to the presence of traces of formic acid (109). The self polymerization of formaldehyde is an exothermic reaction of two types.

$-CH_2-O-CH_2-O-CH_2-O-CH_2-O-CH_2-O-CH_2-O...$ (1)



(2)

$$-\overset{H}{\underset{\underset{H}{O}}{C}}----\overset{H}{\underset{\underset{H}{O}}{C}}----\overset{H}{\underset{\underset{H}{O}}{C}}-----\overset{H}{\underset{\underset{H}{O}}{C}}----\overset{H}{\underset{\underset{H}{O}}{C}}-$$

Reaction of formaldehyde with amides like acrylamide involves the amino group and results in the formation of methylol and methylene derivatives.(67) Acrylamide reacts readily with formaldehyde to form N - methylol acrylamide as given below

$CH_2 = CH - CONH_2 + CH_2O \text{--->} CH_2 = CH - CONH - CH_2OH$

The N - methoylol acrylamide can react with more acrylamide to produce N - methylenebisacrylamide, a tetrafunctional vinyl monomer.

$$CH_2 = CH - CONH - CH_2OH + CH_2 = CH - CONH_2$$

$$CH_2 = CH - CONH - CH_2 - NH - COCH = CH_2 + H_2O$$

N - Methylol groups are introduced by treating a dilute (less than 10%) aqueous solution of polyacrylamide with formaldehyde. Preferred conditions are $40 - 60^{o}$ C for 1 hr. at pH 8 - 10. These solutions are fairly stable, but an insoluble film is formed if the solution is acidified and dried at 100^{o} C.(57).

2.3 Effect of finishes on properties of wool and cotton fabrics

2.3.1 Wool fabrics

Wool belongs to a family of proteins called keratins. The simplest of the proteinaceous components of wool fibre is of polypeptides composed of amino acid residues. It is very hygroscopic and adds warmth. The elastic properties of wool gives it outstanding resistance to and recovery from wrinkles and outstanding drape. The high extensibility with relatively low strength and good wet elasticity are typical characteristics of wool.(108).

Inspite of these excellent properties wool has a great tendency to shrink. Two main types of shrinkage occurs when wool is washed, these are relaxation shrinkage and felting shrinkage. To overcome the shrinkage, there are two ways (i) the degradative treatment and (ii) the additive treatment.

(i) In the degradative treatment, the proteins in the scales of fibres are modified by treatment with e.g. chlorine (Oxidizing), so that scales are softened or their tips removed. This treatment breaks both disulphide crosslinks and peptide chains, and water soluble high molecular weight peptides are produced from proteins in the cuticle without disrupting the epicuticle. Consequently, upon immersion of the wool in water, the cuticle absorbs water and becomes soft. The differential frictional effect is greatly reduced by the softening of the cuticle so that the preferential movement of the fibres is reduced and hence the felting shrinkage.
(ii) The additive treatment entails application of a polymer to the fibre. The polymer masks the scale structure and/or bonds adjacent fibres together (73,52)

Effect of acrylic finishes on properties of wool fabrics

Lipson and Speakman (72) have drawn the attention towards the formation of polymers in wool. They treated wool with a dilute solution of ferrous ammonium sulphate, dried and then treated with a solution of methacrylic acid containing a trace of hydrogen peroxide. Preferential internal polymerization was brought about by the hydroxyl radicals formed inside the fibre when the hydrogen peroxide encountered the ferrous ions. Internal deposits of polymers were capable of increasing wear resistance and reducing the milling shrinkage of woollen materials. If the monomer carries reactive side chains e.g. methacrylamide, internal polymerization followed by crosslinking with formaldehyde causes a striking increase in resistance of wool fibres to extension in water. Though it was not known whether crosslinkages were formed between the polymer and the wool but reaction was useful in strengthening intact fibres and repairing damaged fibres. The maximum resistance to extension with polymer and formaldehyde was noticed at pH of about 5.

The relationship between composition of soluble acrylic polymers and shrink - resistance was shown by Bereck(6). Copolymers of butylacrylate, 2-sulphoethylmethacrylate (SEMA), glycidylmeth-acrylate (GMA), 2-hydroxyethylmethacrylate (HOEMA), N-methylol-acrylamide were used. Copolymers of 2-sulphoethylmethacrylate were readily soluble in water above pH 2. The incorporation of self-crosslinking monomers into the copolymer gave considerably better shrink-resist results than the use of external crosslinkers. Copolymers of glycidylmethacrylate, which were cured at or above pH 7, were more effective than copolymers of N-methylolacrylamide, which were usually cured in the presence of strong acidic catalyst. The effect of latter polymers can be considerably improved if the wool is either pretreated or saturated with the acidic catalyst before polymer application. Further investigation showed a good correlation between tensile strength of the polymer films and shrink-resistance. No correlation was found between flexural rigidity and shrink-resist effectiveness. No significant correlation was obtained between swelling of polymer films and shrink-resist effectiveness. Methacrylate improved the tensile strength considerably. Elongation at break increased if butylacrylate content was increased but was reduced after an increase in amount of methylmethacrylate and glycidylmethacrylate (7).

In a recent investigation of grafting with methylmethacrylate on DC. Corona or ferrous ammonium sulphate pretreated wool fabric, Bhalla and Nigam (8) have suggested that ferrous ammonium sulphate pretreated and then methylmethacrylate grafted wool samples did not show any relaxation shrinkage, where as DC. Corona pretreated wool on methylmethacrylate grafting showed slight relaxation shrinkage. The tensile strength of grafted wool fabric increased with increasing concentration, and elongation at break was improved, (5-25%). The percentage weight of methylmethacrylate grafted on ferrous ammonium sulphate increased with increasing concentration for grafting times of 1.5 to 2 hours, but did not occur for three hours methylmethacrylate grafting time. These observations may account for the reduction in disulphide linkages in wool fibres and the formation of ionized thiol groups in excess. Besides grafting, long treatments might have caused crosslinking and polymerization of methylmethacrylate into wool fibres.

The most effcient shrink-resist treatments for wool fabrics depend on the ability of polymers to bond adjacent fibres together effectively, thereby preventing the relative movement of these fibres during washing. An acrylic copolymer of butylacrylate, ethylacrylate and glycidylacrylate (65:25:10) parts by weight were synthesized by an emulsion polymerization for shrink-resist treatment by Jellinek (61). Polyethylene polyamines were used as curing agents. It was reported that epoxy functional acrylic polymer as emulsion conferred an excellent shrink-resist wool when crosslinked by polyethylene polyamine curing agent. The high molecular weight polyethylene polyamine curing agent was required for maximum efficiency. This may be due to superior adhesion afforded by a heterogeneous film with polyamine rich microphase domains. Curing was done at 130°C for 10 minutes. This rate was probably dependent on the mobility and flexibility of the polyamine, which was restricted in branched high molecular weight polyethylenimines.

The wool finishing with aqueous dispersions of self-crosslinking polyacrylates i.e. Primal K.3, H.A.8, H.A. 12 and H.A.16 (in order of hardness) was studied by Feldtman and McPhee (41). The softness of the polymers is generally indicated by the second order transition temperature Tg. Most of the polyacrylates used commercially at present having Tg values in the range of - 30°C (soft) to + 30°C (hard). The reduction in felting, tumble drying shrinkage and pilling, and increases in tensile strength and abrasion resistance were obtained with no significant changes in stiffness, tear strength or wrinkle recovery. However, the hard polymers can be used to obtain imporved washability and durability of wool fabrics, together with increased stiffness and fullness. It was reported that reduced felting was probably due to partial covering of fibre surfaces by polymer, rather than to fibre bonding, but some bonding can occur and this may produce such properties of polymer-treated wool such as reduced pilling and resistance to tumble drying shrinkage. The reactive polyacrylates, applied to wool to inhibit felting, are usually cured with a strong acid catalyst, which promotes crosslinking.

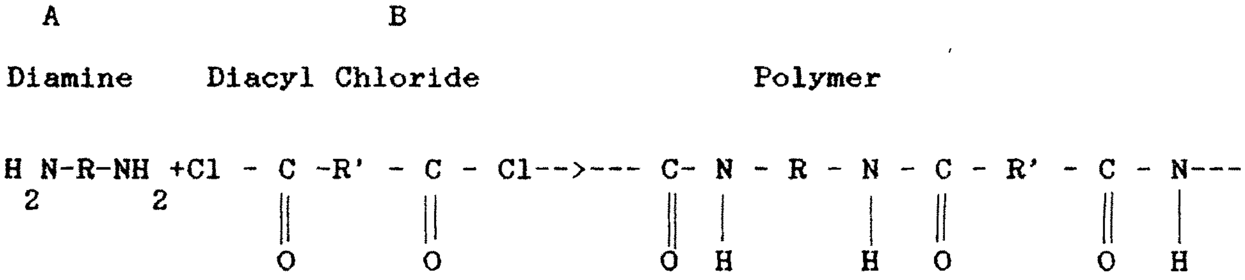
Feldtman and Fleischfresser (38), on the other hand, found that woollen fabrics can be made shrinkproof by the application of polyacrylates and a crosslinking agent, provided that the fabric is first given a reductive pretreatment and then rinsed with water. The main function of the reductive pretreatments including the rinising step is to degrade and clean the surface of the fibre for polymer deposition.

Steiger (103) stated that an acrylic polymer (Rhodex H.A.1) capable of reaction with a thermosetting resin reduced felting shrinkage of wool fabrics. The additive and degradative stabilization processes were compared. It was reported that both the treatments reduced the tendency of wash wool to have an unsightly surface appearance, the acrylic treatment was far superior in minimizing pilling and fuzz formation. The crease recovery was improved by both treatments (chlorination and acrylic polymer) while effect on tear strength was negligible. Tensile strength, however, was reduced by degradative process and was increased by additive process.

Interfacial polymerization of resins in wool

Interfacial polymerization technique consists of bringing a solution of a diacid chloride in an inert water-immiscible, organic solvent, into contact with an aqueous solution of a diamine; polymer is formed almost instantaneously at or near the interface of the two liquid phases.

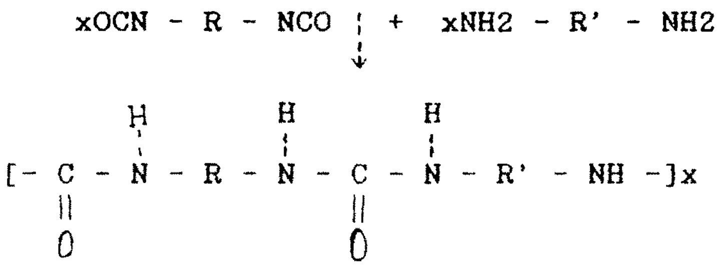
Whitfield et al. (113) stated that through interfacial polymerization, polyamides, e.g., poly (-hexamethylene sebacamide), were fromed on the surface, Fabric was padded consecutively through an aqueous solution of a diamine and a water-immiscible solution of a diacid chloride. polymerization was extremely rapid and no heating or curing was required. The immersion of the diamine-treated fabric into acid chloride solutions resulted in almost instantaneous formation of polyamide resin at the fibre surface as shown below:



$$H_2N\text{-}R\text{-}NH_2 + Cl - \underset{\underset{O}{\|}}{C} - R' - \underset{\underset{O}{\|}}{C} - Cl \longrightarrow --- \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - R - \underset{\underset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - R' - \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} ---$$

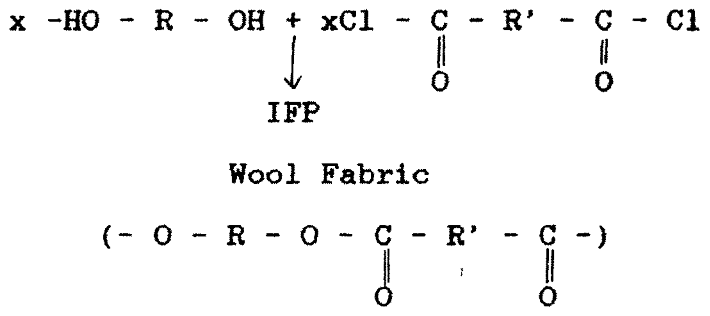
Less than five percent resin on the fabric was required for dimensional stability in laundering. The wool fabrics treated were essentially unchanged in hand, flexural rigidity, break strengh, precent elongation, and chemical resistance, and were improved in wrinkle recovery and smoothness after tumble drying.

Further investigations were made on interfacial polymerization using polyureas, polyesters, polycarbonates and polyamides (114). Polyureas were formed by the reaction of a diisocyanate in the water immiscible solvent with a diamine in aqueous solution:



$$xOCN - R - NCO + xNH2 - R' - NH2$$
$$\downarrow$$
$$[- \underset{\underset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - R - \overset{\overset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - R' - NH -]x$$

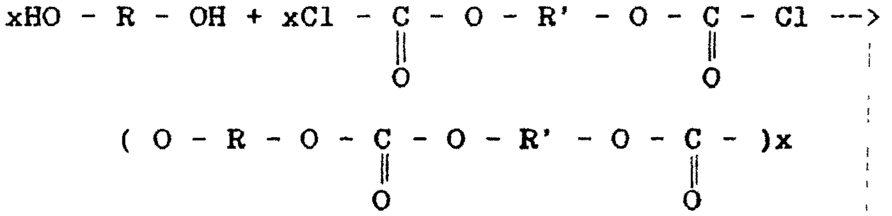
Good shrink-resistance with little modification of wrinkle recovery and flexural rigidity was obtained with one to two percent resin. Reaction of a diol, preferably as its alkali metal salt, by the interfacial technique, (i) with a diacid chloride forms a polyester, and (ii) with a discholoroformate forms a polycarbonate on the wool surface.



$$x\ \text{-HO} - R - OH + x\text{Cl} - \underset{\underset{O}{\|}}{C} - R' - \underset{\underset{O}{\|}}{C} - Cl$$
$$\downarrow \text{IFP}$$
$$\text{Wool Fabric}$$
$$(- O - R - O - \underset{\underset{O}{\|}}{C} - R' - \underset{\underset{O}{\|}}{C} -)$$

(i)

Polyesters and polycarbonates imparted shrink-resistance but not as good as polyureas.



$$x\text{HO} - R - OH + x\text{Cl} - \underset{\underset{O}{\|}}{C} - O - R' - O - \underset{\underset{O}{\|}}{C} - Cl \longrightarrow$$
$$(O - R - O - \underset{\underset{O}{\|}}{C} - O - R' - O - \underset{\underset{O}{\|}}{C} -)x$$

(ii)

Effect of acrylics in combination with epichlorohydrin.

Cook and Riveet (21) used polyamide epichlorohydrin polymer, a polyacrylate, a reactive polyether and two polyisocyanates. Amine pretreatment was given to the wool fabric before the application of polymers, which enhances the shrink-resistance by raising the surface energy of wool. Wool polymer adhesion was improved by pretreatment and hence the shrink-resistance was improved. Feldtman and Mcphee (39) stated that the useful criteria for spreading polymer is that the critical surface tension of wool must be greater than the surface tension of the applied polymer. Chemical pretreatments improve the efficiency of polymer by increasing the critical surface tension of wool. Bateup et al.(5) have also drawn attention to the importance of surface tension for the adhesion of polymers. Srivastava (100) found that acrylamide finish when used on 25% acetone or 25% rectified spirit pretreated wool fabric conferred a good shrink-resistance.

Feldtman and McPhee (40) further suggested that polyamide epichlorohydrin resin reduce felting shrinkage, tumble drying shrinkage and increase tensile strength and abrasion resistance of wool fabric. With acid chlorine pretreated wool only two percent of polymer (on weight of wool) was required for the good penetration of the polymer. The felting of resin treated wool relative to untreated varies only slightly with pH and temperature of the felting solution, in contrast to wool made shrink-resistant by oxidative chemical methods.

The felting shrinkage of chlorinated wool fabric treated with a group of preformed polymers has been investigated by Kamath et al. (65). They used polyamide, polyacrylate and reactive polyurethane on chlorinated wool fabric. The shrinkage values obtained were significantly different from the untreated fabric.

Heiz(56) emphasized the use of chlorine Hercosett process for shrink-resistance of wool over the earlier polymer shrink-resist processes. It was pointed out that with earlier processes there was alteration in handle and physical properties of wool attributable to the relatively high quantities of polymer required, adhesion of the polymer to the wool often inadequate. Crosslinking and condensation system affect the hue and physical properties of wool.

Effect of lubricating and thermosetting finishes on wool

Freeland and Guise (44) used an exhaustion method to shrink-resist unchlorinated wool fabric. Diluted solution of Synthappret BAP (a poly carbamoyl sulphonate),and the acetate salt of Versamine 552 (a C 36- diamine derived from dimerized fatty acids) were used to prepare dispersions. The level of shrink-resistance depend on the polymer, the treatment method, the fabric and the method used to scour the fabric. Fabric treated with Synthappret BAP by exhaustion methods, when compared with padding treatments, had poorer shrink-resistance, fewer and much thinner inter-fibre bonds. Cook and Fleischfresser (19) emphasized the importance of reductive pretreatment before the application of polyether,polyurethane(Synthappret LKF)on wool fabric.

A simple and inexpensive process for conferring a high degree of resistance to shrinkage of wool was reported by CSIRO Division of Textile Industry (42). Fabric treated with a polyurethane dispersion (e.g. impranil DLN or DLH) and a bisulphite adduct of a polyurethane (Synthappret BAP) had a soft handle, reduced pill, and improved dimensional stability and wrinkle recovery.

Several non-crosslinking cationic polymers have been found to improve the shrink-resistance of chlorinated wool. The polymers, applied by exhaustion from neutral to alkaline liquors, did not require a curing operation. In particular, poly (vinylbenzyltrimethyl ammonium chloride), a butylmethacrylate trimethylammoniumethyl methacrylate copolymer, and an octyl methacrylate-trimethylammoniumethyl methacrylate copolymers, were more effective, at low treatment levels, than Hercosett 125(25).

Cook et al. (20) investigated that shrink-resistance can be obtained with silicone polymers. The shrink-resistance depends on inter fibre bonding, rather than on encapsulation of fibres, the effectiveness decreases as the initial viscosity of polymer decreases. The low surface tension of silicone polymers allows to spread spontaneously on wool fibres, which thereby depletes the amount of polymer avilable for inter fibre bonding. The low viscosity polymers spread more readily and account for the relatively poor shrink-resistance. The shrink-resistance obtained with the aqueous silicone emulsion can be improved by adding a small amount of reaction polymer, Synthappret BAP to the formulation(16).

Reactive polyethylene finishes for wool fabric were used by Remy et al.(90). The reactive finishes were either copolymers of methacrylol chloride and ethylene or terpolymers of ethylene, methacrylol, and vinyl acetate. The polymer was applied either by dip-pad-cure method or by exhaustion procedure. The treatment reduced felting shrinkage, increased fabric resistance to acids, alkalies, and strengthened the fabric against breaking and abrasion.

Role of thermosetting in wool

Shrinkage contorl of wool by melamine resins was reported by Maresh and Royer (75). The treated samples were observed under microscope and it was indicated that resin was located at the scale region of the fibre. The fibre bonding played some role in the control of shrinkage. Cook (20) also reported that shrinkage control in wool fabric was conferred by inter- fiber bonding .

McCleary and Royer (78) studied the torsional rigidity and elastic properties of fibre treated with melamine resin and reported that this resin has no effect on the work of extension of a wool fibre. The rigidity was increased because this resin treatment produced a tough sheath of resin around the fibre or sealed the scale. When such a fibre was stretched, the hard cell was fractured and scale between the seal were broken and fibre behaved like original.

Function of methylated melamine-formaldehyde resin in controlling shrinkage of woollens was noted by Stock and Salley (104). They reported that when tensile hysterisis cycles were performed before and after resin treatment, the behaviour remained unchanged. The directional frictional test revealed a significant decrease in directional coefficient as a consequence of the treatment.

2.3.2 Cotton fabrics

Modification of cotton cellulose

Cellulose can be modified by four methods to improve the performance of fabrics (30).

(i) By preparing cellulose derivatives as cellulose ethers and esters, but this has a disadvantage of affecting the desirable properties of cellulose adversely.

(ii) By preparing crosslinked cellulose with different resin treatments. This is a well established method of obtaining durable press garments, but cellulose chains become part of three dimensional net work, with the result the cotton material becomes stiffer, more rigid and loses some of its useful properties.

(iii) Cellulose modification can be done by preparing branched cellulose using graft polymerization technique. This imparts to cotton certain desirable properties without adversely affecting the useful properties. The free radical may be formed onto the cellulose molecules, by exposing the cellulose to high energy radiation by treating it with aqueous solution of selected ions, such as ceric ions, or by thermally decomposing peroxide in contact with cellulose.

(iv) However, this method (iii) is expensive and an alternate method is, <u>in situ</u> polymerization. Here simple monomers can be applied with suitable catalytic system using conventional processing route that is pad - dry - cure.

Effect of acrylics on properties of cotton fabrics

Deshpande and Chavan (30) reported the in situ polymerization of acrylic acid, acrylamide and their mixture. Free radical polymerizing catalysts (potassium persulphate and sodium thiosulphate) were used. The crease recovery angle and breaking strength were comparable with conventional resin finishing treatments. The stiffness was foud to be variable with different treatments. The free radical polymerization using same concentration of redox initiators was found to be very fast in case of acrylic acid in comparison to acrylamide. The stiffness was therefore found to be more in case of acrylic acid treatment. It was also noticed that the stiffness depend on the time interval between preparation of padding bath and actual padding process. Higher the interval, stiffer the sample because the free radical polymerization starts in the bath itself. The add-on with various treatments was found to vary berween 6 to 13%. The excessive add-on confirms the deposition of polymer on the surface and inside.

Reaction products from acrylamide and dialdehyde were investigated by Frick *et al.* (46) as finishing agents to give cotton wrinkle resistance and durable press properties. The effectiveness of these products was less than that of conventional amide formaldehyde agents. Discoloration of the fabric was caused. This finish from glyoxal and acrylamide had greater resistance to acid than the most common formaldehyde free finish. Ryan (92) has pointed out that the precise nature of crosslinks may differ with different finishing agents and may involve not only covalent linkages but also hydrogen bonds and Van der Waals forces.

Formaldehyde reactive compounds were used by Gonzales *et al.*(50). Prior to crosslinking the cellulose polymeric acrylamide affected the crosslinking reaction of formaldehyde and cellulose. The polyamide increased the wet crease recovery and decreased the dry crease recovery in comparison with fabrics crosslinked only in the presence of formaldehyde. A certain degree of crispness was imparted to finished fabrics. Approximately three times as much formaldehyde remained in pretreated fabrics than those crosslinked only with formaldehyde.

Lamprinakos and Sookman (71) and Taylor and Hurwitz (106) noted that polyacrylate copolymer emulsion improved the tear strength and hand of cotton fabrics. This was largely mechanical, caused by immobilization of the yarn structure.

An acrylic acid polymer and oxalic acid renders woven cotton fabrics crease resistant while retaining or improving its tear strength and pliability. This was achieved by impregnating the sheeting with a mixture of the monomers (or polymers) of two resins and polymerizing the two resin by the action of oxalic acid to produce a tough pliable resinous film on the cotton fabrics. The impregnating mixture comprises an aldehyde urea resin and an acid stable polyacrylate resin (74).

Effect of reaction of N-methylolacrylamide in cotton fabrics

Some researches on polymerization crosslinking of N-methylolacrylamide in cotton fabrics are reviewed below:

Crosslinking with methylolacrylamide was explored by Gardon (48) and it was observed that the acid catalyzed application of N-methylolacrylamide to cellulose led to formation of acrylamidomethyl ether groups. It was indicated that only 6-hydroxyl was etherified. Partially acrylamidomethylated cotton can be crosslinked without changing the bulk of the sample by saturating the pendant double bonds either through alkali catalyzed addition of cellulosic hydroxyls or by anionic or free radical catalyzed homopolymerization. A free radical catalyst, such as ammonium persulphate, causes homopolymerization of the acrylamidomethyl ether groups. Wet state treatment with an alkaline catalyst causes addition of hydroxyls to double bonds, and dry state treatment with alkaline catalysts can result in either or both of these reactions. To obtain highest attainable crase recovery in cotton, it is necessary to introduce one crosslink per four to five accessible anhydroglucose units. Crosslinks produced by alkaline catalysis caused greater losses in tensile strength than those produced by free radical catalysis. Wet and dry tensile strength losses with increasing degree of cross linking followed the same trend but the wet strength losses were more than the dry ones. The reduction in the breaking elongation due to crosslinking was roughly proportional to the tensile strength loss.

The _in situ_ polymerization of N - methylolacrylamide (NMA), acrylamide (AM) and tetrakis (hydroxymethyl) phosphonium chloride THPC was tried by Warburton (110). A very favourable balance between crease reovery and tensile strength was obtained when crease recovery angle was less than 260°. However, beyond this angle, strength loss increased rapidly although with increasing crease recovery. The durable press ratings for overhead lighting were between 3 and 3.5, which was very good but not excellent. Soft film forming acrylic polymers used in conjunction with a crosslinking agent have been reported to improve the balance of crease recovery, tensile strength and abrasion resistance of durable press fabrics (54).

Polymerization-crosslinking of N-methylolacrylamide (NMA) in cotton was explored by Rowland *et al.* (91) to find out the factors critical to the achievement of resilience with superior retention of strength and abrasion resistance in the fabric. Persulphate catalyst simultaneously initiated, both polymerization and crosslinking reaction of N-methylolacrylamide (NMA) in cotton fabric. With dry cure reaction the textile performance properties of the resulting durable press cotton were comparable to the application of agents such as DMDHEU. Wet cure reaction at or above 100°C resulted in low resilience, high retention of strength and increased stiffness, the last attributed to fibre bonding in yarns.

Cotton fabric treated with N - methylolmethacrylamide was compared to corresponding products treated with N-methylolacrylamide. It was found that N-methylolmethacrylamide imparted high levels of resilience, together with superior retention of strength. The preferred balance between resilience and retained strength was realized when N-methylolmethacrylamide and N-methylolacrylamide are prepared with a CH_2O/ amide ratio of 1.0 and applied from solutions containing 11.4 and 10% solids respectively (99).

Gonzales and Rowland (51) reported that the experimental reagent systems, N-methylolacrylamide plus phosphate salts, N-methylolmethacrylamide, N-methylolmethacrylamide plus phosphate salts and N-methylolpolyethyleneurea showed different rates of recovery from creasing in laundering, tumble drying, compared to cotton finished with coventional crosslinking reagents. The durable press fabrics treated with experimental reagents recovered from creasing more slowly in initial period (6 sec.) but more rapidly in the second period of measurements (1 min.) than those treated with conventional reagents.

A simultaneous treatment of cotton fabrics with 4,5-dihydroxy-1,3 -dimethylethyleneurea and an acrylate copolymer was studied by Yamamoto (115). When acrylate copolymer with low glass transition temperature (below -22^{o}C) and high molecular weight (above 10^{5}) were used with the crosslinking agent, the treated fabrics had an excellent level of crease resistance and tensile strength. Good durability to repeated launderings, resistance to hydrolysis, wash and wear rating, shrink-resistance were obtained on the resin finished cotton fabrics. No formaldehyde was detected during processing or from the resin treated fabrics thus produced.

Graft polymerization/radiation of acrylics on cotton fabrics

Graft polymerization of acrylamide onto cotton fabric using ceric ammonium nitrate as catalyst have been investigated by Kamogawa and Sekiya (66). Fabric was impregnated with acrylamide monomer and ceric ammonium nitrate. The polyacrylamide grafted fabric thus produced was extracted with hot water, and methylated with formaldehyde. The fabric was then padded with acid catalyst and crosslinking material. This trial was made to impart a durable crease proofing effect to the polyacrylamide grafted fabric by the incorporation of crosslinks between graft chains of different cellulose molecules by means of a methylene-bisamide linkage ($-CONHCH_2HNOC-$). Excellent crease resistance was obtained. The acid cure of methylolated polyacrylamide- grafted fabric alone or in conjunction with adipamide offered the best durability to both acid extraction and laundering, due to the formation of a durable methylene-bisamide linkage between graft chains. However, the strength loss was due to the formation of short methylene crosslinkages between cellulose molecules by free formaldehyde.

Demint (29) reported that the radiation induced interaction of acrylonitrile with cyanoethylated cotton probably involves grafting of side chains of acrylonitrile at the site of the cyanoethyl groups. The extent of interaction is dependent on the degree of substitution of cotton and on radiation dosage. With an increase in the degree of substitution from 0 to 1.3, the amount of interacted monomer increased about four fold. There was an increase in delayed elastic recovery and elongation-at-break and a decrease in permanent set.

Vinyl monomers along with acrylamide onto cotton using ceric ammonium nitrate as catalyst and subsequently polyacrylamide grafts were methyolated <u>in situ</u> and crosslinked by Sharma and Daruwala (97). Except in case of acrylamideacrylonitrile treatment, finished fabrics showed good wrinkle recovery properties accompanied by satisfactory retention of breaking and tear strength. The finish was suitable for the deferred cure process with minimum evolution of formaldehyde. When the grafted samples were crosslinked through N-methylol cross-linking agent, improvement in wrinkle recovery properties were accompanied by usual losses in strength and abrasion resistance. When tertiary mixtures containing ethylacrylate, acrylamide and acrylonitrile were grafted at higher polymer add-ones, and fabric was crosslinked through the conventional agents, very good abrasion resistance along with good strength retention was achieved.

Two alternative radiation chemical means for crosslinking chains with N-methylolacrylamide yield improved crease recovery. Special advantages have been noted for the chemical grafting followed by radiation crosslinking. Wet and dry crease recovery angle increased with increasing add-on of N-methylolacrylamide but only a minor improvement was noted in the absence of radiation. With increasing radiation doses the wet and dry crease recovery angles continually increased (101).

Dasgupta (24) observed a permanent chemical bonding rather than a mere deposition, between the grafted polymer and the fibre. It is accepted that chemical crosslinking within the cotton fibre is one of the basic requirements for improving wrinkle resistance. The grafting process results in crosslinking and intermolecular bonding and therefore, brings about increased crease recovery. Grafted cotton with mixed monomers exhibited high tensile strength, increased crease recovery, good dimensional stability, highest dye acceptability, resistance to micro-organisms and water and excellent handling properties.

Dimensional stability or shrinkage control of cotton Fabrics

Irvin (50) reported quite early in 1959 that the chemical crosslinking agents, similar to those used for improving crease resistance properties of woven cotton fabrics, could be used to stabilize about half the inherent shrinkage of a knitted fabric and would also provide the significant improvements to their wash-wear appearance. Marsh (76) has pointed out that the crease resisting finishes also have the tendency to reduce shrinkage during washing and that a resin concentration of seven percent crosslinking agent is adequate. Additional increases in resin did not contribute significantly to either shrinkage-control or durable press rating, but did result in further losses in strength.

Shrinkage-control for cotton and cotton-polyester blend knitted fabrics has been investigated by Black (10). Acrylic with modified glyoxal based crosslinking agent was used.

Additional effect of heat setting was also noted. The resin treated condition made fabric more stable than does heat setting. The excellent shrinkage value after finishing, in cotton was assumed by the cotton crosslinking agent. Frick et al.(45) pointed out that the adducts of glyoxal with urea, 1-3, dimethylurea, and methyl carbamate can be used as formaldehyde free finishing agent for shrink-resistant, wrinkle resistant and durable press cotton. These adducts are less effective than the usual methylolamide finishing agents. A small amount of formaldehyde with glyoxal can increase the effectiveness. These agents are more effective on the fabrics where less crosslinking is required.

Frick and Verburg (47) reported that laundry shrinkage in knitted fabrics of cotton or cotton-polyester was reduced by a combination of chemical crosslinking and preshrinkage treatments. Preshrinkage during finishing was induced by compression either before or after crossliking, and by either wet or dry relaxation after crosslinking. DMDHEU with magnesium chloride hexahydrate or with zinc nitrate hexahydrate was used. It was noticed that the shrinkage and strength decreased with increased crosslinking. The increased stability by crosslinking treatments led to the reduction in unrecovered extension after repeated high strain or after prolonged low strain.

Studies on cotton/wool blend fabrics

Harper and Mehta (55) studied the application of crosslinking agents and polymers to cotton/wool blends. The effect of catalyst on performance levels was investigated and role of polymers in improving the dimensional stability and wet wrinkle recovery was elucidated. Polymers included were polyacrylate, ethylene-vinyl acetate copolymers, an aqueous polyethylene emulsion, and mixture of polyurethane and polyurathane prepolymers (Synthappret BAP and Impranil DLN). The effectiveness of cotton/wool blend with crosslinking agents depends on the use of proper catalyst system. Magnesium chloride was an efficient catalyst, where as zinc nitrate and carboxylic acids were considered less effective. Shrinkage on laundering was reduced. The use of a crosslinking formulation together with a surface polymer gave a further improvement in shrinkage control, lowering the shrinkage to just 3.0 - 3.6% with 60/40 cotton/wool blend fabric.

O'Connell et al.(84) reported the application of DMDHEU to wool blend fabrics after stabilizing the wool against felting shrinkage using the Wurlan process. The Wurlan treatment consisted of dip - pad application of hexamethylene diamine followed by a dip pad of sebacoly chloride to form an interfacially polymerized polyamide coating on the fibres. The Wurlan treated fabrics were completely stable to washing. There was only one percent change in area after four washes. But 100% fabric treated with equivalent amounts of DMDHEU could not be made resistant to felting shrinkage. The strength of wool/rayon blend was retained better, while wrinkle recovery, fabric weight and area shrinkage appeared better in wool/cotton blend fabric.

While neither the Wurlan nor the DMDHEU treatment has a marked effect on 100% wool, both affected some cellulosic properties. Further investigation was made on fabrics constructed from lends containing 50% wool/40%rayon/10% nylon. The tensile and tear strengths of all treated blend fabrics were significantly reduced by the cellulosic crosslinking treatements (85).

Mehta (79) reported that the reductive setting-pretreatment, utilizing sodium bisulfite solution increased shrink- resistance of finished 50/50 cotton/wool blend knit fabrics without severely damaging strength properties. DMDHEU along with acrylic and polyurethane finishes improved the shrink-resistance of pretreated fabrics.

Thorsen and Ash (107) found that DMDHEU reduced shrinkage in 70/30 and 50/50 wool-cotton blend fabrics, but ozone pretreatment was necessary to confer an appreciably high shrink-resistance. Ozone treatment of 100% cotton did not affect its laundering shrinkage, and the shrinkage imparted to cotton-wool fabric by DMDHEU was not altered by ozone treatment. Ozone increased the strength of 100% wool fabric and decreased the strength of DMDHEU treated 100% cotton. Ozone increased the total reflectance of fabrics increasingly with increased cotton content. DMDHEU increased the yellowness of wool and wool, blend fabrics due to formaldehyde release, the larger the percentage of wool in the blend, the greater the amount of yellowing.

2.4 Effect of finishes on permanent set or durable press of fabrics

2.4.1 Mechanism of setting wool

The long polypeptide chains that form the bulk of the interior of the wool fibre are held together by a number of bonds. Hydrogen bonds and disulphide crosslinks play an important role in setting. Hydrogen bonds are broken very easily by wetting or by steaming the wool. Some will reform in new positions on drying or cooling. These new bonds are sufficient to hold a deformed fibre in its new position while it remains dry but on wetting they are broken again and the fibre tends to return to its original configuration due to the restoring forces of the more stable hydrogen bonds and of the covalent -S-S- bonds. Durable setting requires that the restoring forces of these bonds be balanced or removed. The most important mechanism for wool setting is the rearrangement of both hydrogen and disulphide bonds, under the influences of heat and moisture to form a stable structure. The rearrangement of the -S-S- (disulphide bonds) occur via an interchange between the -S-S- bonds and free ionised thiol groups (S-). The rate of interchange and hence of setting is increased by reducing or alkaline reagents that split -S-S- bonds to produce more thiol groups. (12,33,112).

Stabilization of set in wool fabrics

Loss of set in wool fabrics during washing occurs because the hydrogen and disulphide bond rearrangements can still take place and are reversed during washing (12). Therefore another setting must be prevented in laundering. This can be achieved only if thiol-disulphide interchange is inhibited by stabilizing treatments such as, (i) removal of thiol groups with thiol removing reagents, (ii) by using reactive polymers, (iii) by crosslinking reagents, (iv) by addition of stabilizing reagents to wash liquor (17,28,35,27).

Reaction sequence for permanent press effect

Cook and Delmenico (18) pointed out that shrinkproof and set wool can be given a permanent press finish by treatments that prevent molecular rearrangements during laundering. The basic method for producing permanent press wool garments involves shrinkproofing plus setting plus stabilization. Any stabilizing treatment will give a high level of set stable to laundering, if prior setting is adequate. A slightly lower level of initial setting can give better results if the stabilizing treatment involve both crosslinking and thiol removal. Introduction of crosslinks berfore setting, even if the fabric is in the required configuration during crosslinking, will contribute to the loss of the desired shape during laundering because the crosslinks are in the wrong configuration at the molecular level.

Jones (63) pointed out that prolonged steaming of wool in the presence of reducing agents, alkalies, produces set that is stable to machine washing by lowering the thiol content of the wool and thus inhibiting thiol disulphide interchange rather than by secondary effects, such as crosslinking or denaturation.

Polymer application for set stabilization in wool fabrics

It has been reported by Feldtman and Fleischfresser (36) that set wool inhabits loss of set during machine washing and tumble drying. It was emphasized that the fabric be kept in the required configuration during the curing operation, the polymers may be applied before setting is carried out. Self-crosslinking polyacrylates, polyamide epichlorohydrin, polyurethane were padded. These preformed polymers due to their size confined to the surface of fibers. These polymers applied to wool do not interfere directly with thiol-disulphide interchange but stabilize set by physically constraining the fabric to the set configuration.

It was further noted that the rate of loss of set in wool fabric during washing increases rapidly with the temperature of wash liquor. The application of preformed polymers to the set wool significantly retards this loss of set, especially at lower temperatures, where softening of the polymer is be less than at higher temperature. (37)

De Boos <u>et</u> <u>al</u>. (26) emphasized the use of acrylic reagents in wash liquor. It was reported that acrylic reagents act as thiol blocking agents and help in retention of set. Halogenated acetic acid (e.g. chloroacetic acid) also used as thiol blocking agent to improve retention of set. Crosslinking agents especially formaldehyde increases the retention of set.

The simultaneous stabilization of set and shrinkproofing of pre-chlorinated wool fabric can be achieved by the condensation of a di-isocyanate with a polyamine or a polyalcohol across the wool liquid-phase boundary. This has been suggested by Jones and White (64). Polymers derived from the reaction of the polyamine with diacid chlorides or bis (chloroformates) failed to stabilize the set and produced statisfactory shrink-resistance only when formed by condensation at a liquid-liquid interface. Polymers derived from the reaction of a polyamine with divinyl sulphone, epichlorohydrin, or formaldehyde failed to shrinkproof the wool and also lowered the set stablility produced by the action of divinyl sulphone, epichlorohydrin or formaldehyde alone. The mechanism of set stabilization by polymers was emphasized due to fibre encapsulation and inter fibre bonding.

Jones (62) suggested that the most practical method for producing high degree of shrink-resistance, set stability and wet wrinkle recovery is by the application of a polymer to the garment using a polyurethane elastomer. A small degree of permanent improvemet in the dry wrinkle recovery was obtained.

Combining the two operations, first by spraying the garments with a solution containing disulphide and a crosslinking resin and then steam pressing and finally heat curing was attempted by CSIRO Division of Textile Industry (32). But this process did not give set stabilization because a crosslinking resin could not be found which combined the necessary properties of lack of reactivity with bisulphite, and low reactivity with wool in steam pressing conditions, but yet sufficient reactivity with wool to form crosslinks during heat curing.

Sello and Tesoro (95) described a process by which setting and stabilization can be carried out concurrently. Alkaline setting with potassium carbonate combined with crosslinking with an activated vinyl compound was used. But it was necessary to press the pretreated fabric while wet in order to ensure good crease retention after washing.

A new permanent-press process was developed, for wool which involved treating the fabric with an aqueous dispersion containing (a) a glycidol-capped polyurethane prepolymer,(b) an adduct of sodium bisulphite and glyoxal, (c) N-methylol acrylamide and (d) magnesium fluoborate as catalyst. Slacks made from treated fabric were sprayed with water, steam-pressed for 60 seconds, dried and heat cured at 150-155 ^{o}C for 10-15 minutes. Steam pressing step sets the wool via the normal bisulphite-initiated thiol disulphide interchange mechanism and curing step cured the polymer, to cause crosslinking of wool by glyoxal released from its adduct with bisulphite and also to cause vinyl polymerization of the N-methylol acrylamide within wool fibres.(32)

2.4.2 Durable press or permanent-press effect in cotton fabrics

Like wool, cellulosic fibres cannot be just set, since only weak hydrogen bonds contribute to dimensional stability. The initial stress relaxation is readily brought about by e.g. steam pressing, the extensive stabilization that is required is usually achieved by the use of fibre crosslinking agents with appropriate catalysts (112).

Durable pressing of cotton fabrics in flat form has been emphasized by the use of polymer, crosslinking agents and immediate curing (110,115). But for durable pressing of garments deferred cure process has been reported (till the fabric is converted into the garment) (68,22,50).

Pensa _et al_. (87) described a process for permanent setting of cellulosic fabrics. In this the reactive chemical system present on the fabric is partially reacted (i.e. the reagent is reacted with cellulose without significant polymerization) to form a stable intermediate which is capable of further reaction under suitable conditions. Results support the hypothesis that a large number of crosslinking agents can react with cellulosic fabrics in the following manner :

I Cell - OH + X - R - X --> Cell - O - R - X

II Cell - O - R - X + Cell - OH --> Cell - R - O - Cell.

X-R-X represents a crosslinking agent containing two reactive groups, X, which can be reacted with cellulose to yield an intermediate cellulose ether virtually free of crosslinks as shown in reaction I. The intermediate products can be washed and stored, and yields a crosslinked product when heated in presence of a catalyst (as shown in reaction II).

Durable press finishing of cotton with N-methylolacrylamide using non-peroxide polymerization was presented by Welch (111), using the water-soluble azo compound 4,4'-azobis (4-Cyanovaleric acid) and its salts as nonoxidative free radical polymerization initiators. Two stage curing at 110° and 160° was used to induce vinyl polymerization, followed by cellulose crosslinking in the presence of zinc salts. The wrinkle recovery angle was improved and the durable press ratings of 4.0 - 4.2 was obtained. Hurwitz (58) stated that methylolacrylamide and methylolmethacrylamide when used as two stage crosslinking resin, the N-methylol group reacted with cellulose like methylol urea of other methylol amides under acidic catalysis. The vinyl unsaturation could then be catalyzed to form a vinyl polymeric structure by free radical catalysis including radiation.

Delayed curing for durable press effect

Kullman *et al*. (68) favoured the deferred curing of cotton fabrics impregnated with crosslinking agent and catalyst. Cotton goods were impregnated with the finishing agent and catalyst and were dried at a relatively low temperature, sufficient to remove water but below a temperature which would cause substantial crosslinking. The treated fabrics were cut and sewn into garments and pressed to introduce creases and smooth areas where desired, and then cured to complete the crosslinkage of the cellulose while the garments are in the desired shape. The creases as well as the smooth drying characteristics, are thus durably fixed in the garment through chemical reaction. Dimethylol ethyl carbamate gave better results than dimethylolethyleneurea, urea formaldehyde, dimethylol ethyltriazone, dimethylol hexahydropyrimidinone and methylated methylol melamine.

Effect of formaldehyde treatment was also noted. Chance et al.(13) noticed that cotton treated in the swollen state with formaldehyde and hydrochloric acid gave good wet crease recovery. If formaldehyde wet cotton is impregnated with catalyst and heat the dry wrinkle recovery is greatly improved. Kullman and Coworkers (68) used this process with a delay period between the catalyst impregnation step and the heat treatment step. After storage fabrics were pleated, ironed and cured at 160°C. Even after three months there was improved crease recovery angle. But the effectiveness decreased with prolonged storage. Though appearance rating was fairly constant for samples stored before heat treatment but was somewhat poorer that that of the samples heat treated immediately. This finish showed a complete immunity of the fabric to chlorine damage because of its non - nitrogenous nature.

Deferred cure processes for durable process has also been stated by Alexander (1). He reported that DMDHEU with a delayed action catalyst after padding and drying remained almost completely dormant for a period of 90 days and then can be cured at 165°. Though this meets the requirement of coloured fabrics but not recommended for white because of its poor resistance to chlorination. Dimethylolpropyleneurea is found useful on white fabrics. The delayed action catalysts only should be used because free acid type catalyst would initiate cure during storage or tend to cure rapidly on the pressing. The best catalysts are metal salts, which yield their acid during the high temperature. With the use of reactive acrylate polymers the wrinkle recovery angle has slightly decreased in case of 100% cotton and increased in

85/15 cotton/nylon blend. Other investigators have also reviewed the deferred cure process for permanent press (49,105).

Two techniques for applying crosslinking resins to selected regions of fabric structure have been developed by Cooper et al.(22) (i) coating the back of the fabric with solution containing the crosslinking reagent, and (ii) impregnating fabric with a crosslinking agent, drying then applying a catalyst inactivator to the face of the fabric. These produce fabrics after curing with the face consisting essentially of untreated cotton. After twenty cycles of washing and tumble drying the preferentially crosslinked fabrics have wash - wear appearance ratings equal to those of conventionally crosslinked fabrics.

National Cotton Council of America (89) utilized the recuring process after adding catalyst. Fabrics were padded, cured, made into garments and again cured. Though the creases so introduced were not as durable to the laundering as those which are set on the fabric in an initial cure but found comparable to woollen and worsted fabrics. Main emphasis was directed towards recuring the cloth which has been treated with dimethylol cyclic ethyleneurea (CEU) formulation. If initial curing was hard curing, then recuring gave poor results but if mild curing temperature was used in first curing, recuring could be carried out more successfully. The crosslinking of CEU or a polymer of CEU to the cellulose was through a methylene ether linkage. Two mechanisms of recuring were reported : (i) The acid catalyst solution may be hydrolysing the crosslinking resin by breaking the methylene ether linkage, and then forming new crosslinks.

(ii) The recuring step merely completes or further cures a partially cured cellulose fabric by reacting unbound resin. Some of the CEU which is bound to the cellulose by only one linkage, leaving a second free methylene group to react with cellulose on recuring.

Durable press performance of wool - cotton blend fabrics

Pardo and Co - workers (84) evaluated the wool, cotton or rayon and nylon blend fabrics. For durable press performance after treating with a shrink - resist process (WURLAN Interfacial polymerization) for the wool component and by a delay cure crosslinking procedure DMDHEU for the cellulosic component. They reported that blend with rayon or cotton gave almost the same durable press performance. The plain weave fabrics performed slightly better than the twill weave fabrics with respect to appearance retention, but twill weave was slightly superior in textile and tear strength retention.

O'Connell et al. (85) revised the Pardo's experiment. They reported that fabrics become yellow when temperature above 300^{o} F was used in curing is related to reactive decomposition products from DMDHEU released at this temperature. Carbamates or dimethylolpropyleneurea will be useful to reduce the yellowness. They reported that excellent durable press properties can be possessed by a combination of treatments consisting of wool shrink - proofing and cellulosic crosslinking.

Thorsen and Ash (107) found that DMDHEU alone does not improve the durable press properties of 100% wool fabric, but they are slightly improved in the 70/30 wool - cotton, somewhat improved in the 50/50 wool - cotton, and markedly improved with the 100% cotton fabric. It was emphasized that with the 70/30 and 50/50 wool - cotton fabrics there is marked improvement if the ozone and DMDHEU treatments are combined.

Harper and Mehta (55) used DMDHEU and polymer finishing for durable press on cotton - wool blend fabrics with good crosslinkings on 60% cotton 40% wool twill fabric, durable press ratings were from 3.5 - 3.8 and wrinkle recovery angle was about 300°. With DMDHEU the maximum durable press rating obtained was 3.8 when magnesium chloride was used as catalyst. With a mixture of DMDHEU and polymers the maximum durable press rating was 3.7, which was obtained with 10% DMDHEU and 5% ethylene - vinylacetate copolymer.

Mehta (79) reported the durable press finishing of cotton wool blend knitted fabrics. The pretreatment of knit fabric improved the appearance through subsequent resin finishing. The finished goods exhibited good durable press apperance even after repeated wahsing.

Skirt as an experimental garment

Application of the finish for pleat retention in this work, was assessed with the help of a skirt, which is a commonly used garment. The related review of such applications is noted below :

CSIRO Division of Textile Industry (112) developed the methods available for setting durable pleats in skirts. Autoclave steaming, atmospheric pressure steaming and steam press, etc. were used to introduce pleats. It was also reported that certain reactive polymers, when cured on the garment in the required shape, are capable of maintaining the shape while the free-hanging garment is set in steam.

A permanent press finishing process with Oligan SW [poly (alkyleneoxide) backbone chain] has been in commercial use for some time for making pleated skirts and men's slacks from both, woollen and worsted fabrics. The fabric was treated with Oligan SW. It followed the normal routine for skirt making in which the fabric was pleated between paper formers and steamed in an autoclave (32).

Shaw (98) also studied skirt pleating, but no flat setting was made; skirt panels were cut out, hemmed and pleated between pleating papers. Setting was carried out by steaming the pleated panels in an autoclave using steam pressure of 15 lb/in^2. It is an advantage to have some relaxation shrinkage in fabric, which is to be made into pleated skirts, so that it will shrink and tighten the pleating paper. This prevents the cockling that sometimes occurs during pleat setting.

Cooper <u>et al</u>. (22), used preferential crosslinking methods and delayed curing process for durable press pants cuffs. Kullman <u>et al</u>. (68), favoured the deferred curing of cotton fabrics impregnated with crosslinking agents e.g. dimethylol ethyl carbamate and a catalyst. Treated fabrics were cut and sewn into garments and pressed to introduce creases and then cured to complete the crosslinking of the cellulose.

The different styles of skirts, in fashion at one or other time, were reviewed by Patel (86), who has noted that the present trend is of skirts with pleats, gathers or tucks at a particular position. On the basis of the above interpretation, a simple skirt with knife pleats in the centre was chosen, to study the retention of pleats.