CHAPTER II

REVIEW OF LITERATURE

Wash and wear finishes has been the subject of interest of many researchers. The related literature has been presented under the following two broad headings.

2.1 Theoretical considerations.

2.1.1 Wash and wear finishing.

2.1.2 Reaction mechanisms.

2.2 Effect of wash and wear finishes on some related properties.

2.2.1 Effect of grafting on properties of fabrics.

2.2.2 Effect of combination finishes on properties of fabrics.

2.1 Theoretical considerations and reaction mechanisms

2.1.1 Wash and wear finishing

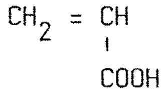
Wash and wear finishing uses a number of compounds which can be divided into thermoplastic finishes and thermosetting finishes.

Thermoplastic finishes: These include compounds formed by addition polymerization and are inherently flexible and durable and do not require curing.[46] They consist of linear molecules accompanied by branching but are not interconnected, i.e. cross-linked from molecule to molecule. These plastics rapidly soften and melt with heat and reharden to rigid materials upon cooling. Generally there is no appreciable change in the physical properties of the thermoplastics through repeated heating and cooling cycles. They may be remelted and reshaped as often as it is practical and as long as the procedure does not introduce charring or degradation to the reworked material.[27]

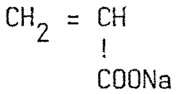
According to Nuessle,[45] polymers range from methyl-methacrylate the hardest, to 2 ethyl hexyl acrylate, the softest. Homopolymers of acrylic acid or acrylamide which are water soluble will form hard, but continuous films. Most acrylics used for textile processing are designed to form a continuous film 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.

Nuessel and Kine[47] described acrylics as subdivision of the unsymmetrically substituted ethylene class, which is composed of resin obtained by polymerization of monomers containing $CH_2=C$ group.

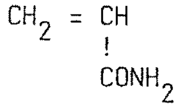
The acrylic monomers include acrylic and methacrylic acid and their salts, like esters, amides and nitriles. Any of these alone or in combination will undergo addition polymerization to form linear polymers.


$CH_2=\underset{COOH}{CH}$

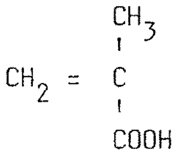
Acrylic acid


$CH_2=\underset{COONa}{CH}$

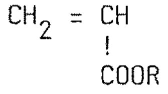
Acrylate salt


$CH_2=\underset{CONH_2}{CH}$

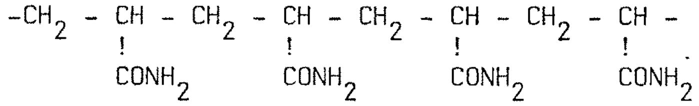
Acrylamide


$CH_2=\underset{COOH}{\overset{CH_3}{C}}$

Methacrylic acid


$CH_2=\underset{COOR}{CH}$

Acrylic ester


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

Polymer of acrylamide

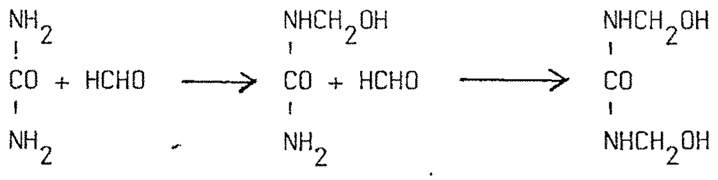
Thermosetting finishes: These include condensation products of aminoplasts.[68] They cannot be reshaped or remelted after they have been cured, set or hardened into a permanent shape. This curing is an irreversible chemical reaction also known as crosslinking which usually occurs during heat.[47]

Thermosetting finishes are (a) nitrogenous type and (b) non nitrogeneous type of finishes

(a) Nitrogenous agents: These include (i) urea formaldehyde, (ii) melamine formaldehyde, (iii) methylol derivatives of cyclic ureas, (iv) triazones and (v) carbamates.[71]

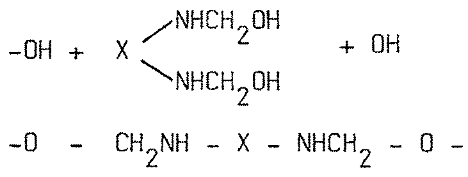
Crosslinking and polymerization are their important reactions. These compounds are used extensively in the finishing of cellulosic fibre fabrics and blends containing cellulosic fibres. For this purpose formaldehyde is condensed with various compounds to produce N-methylol derivatives.

i) Urea formaldehyde precondensate is formed by reacting formaldehyde and urea in the molar ratio of 1.6:1. The reaction takes place as follows.[63]



$$\begin{array}{c}NH_2\\ |\\ CO\\ |\\ NH_2\end{array} + HCHO \longrightarrow \begin{array}{c}NHCH_2OH\\ |\\ CO\\ |\\ NH_2\end{array} + HCHO \longrightarrow \begin{array}{c}NHCH_2OH\\ |\\ CO\\ |\\ NHCH_2OH\end{array}$$

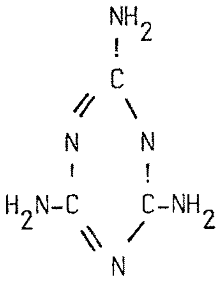
The crosslinking reaction takes place as follows:



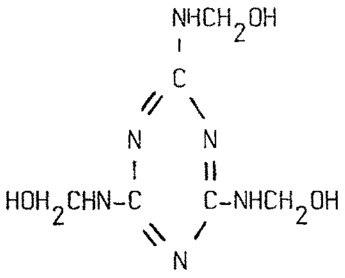
$$-OH + X\begin{array}{l}\diagup NHCH_2OH\\ \diagdown NHCH_2OH\end{array} + OH$$

$$-O - CH_2NH - X - NHCH_2 - O -$$

ii) Melamine or in more precise terminology 2:4:6 triamine 1:3:5 triazine, reacts with formaldehyde to give methylol derivatives.



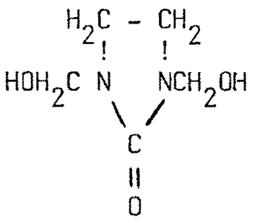
Melamine



Trimethylol melamine

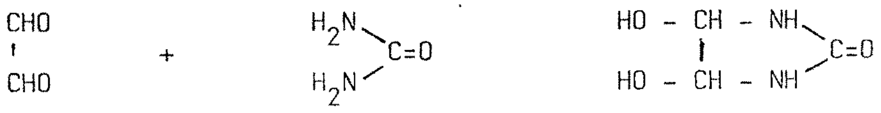
This product is used for wash and wear finishing. The methylol melamines have good storage stability and when etherified with lower alcohols gives finishes with good durability.[71]

iii) Methylol derivatives of cyclic ureas



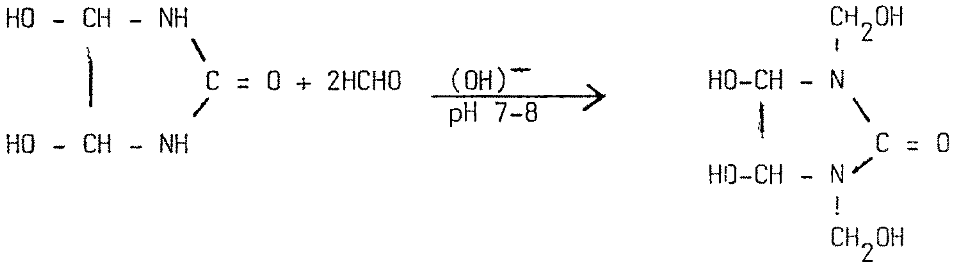
Dimethylol ethylene urea

When glyoxal is reacted with urea under neutral or slightly alkaline conditions for 8-16 hours at room temperature, dihydroxyethylene urea crystallises from the solution.



Glyoxal Urea Dihydroxy ethylene urea

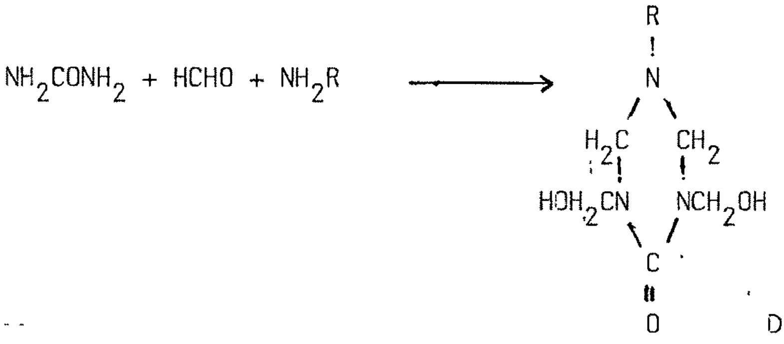
This compound may be dimethylolated with formaldehyde (mole ratio, 1:2) at pH 7-8 (with sodium hydroxide) at room temperature for 8-16 hours.



Dimethylol dihydroxy ethylene urea

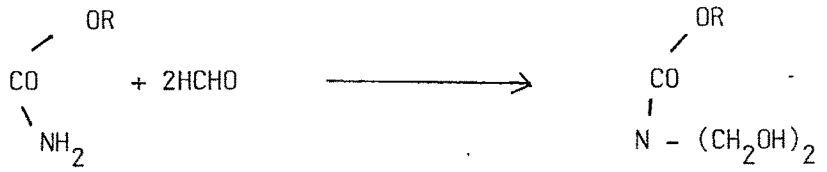
DMDHEU has four hydroxy groups, which are capable of reacting with cellulose, though the N-methylol groups are more reactive than the other two hydroxy groups. N-methylol groups of DMDHEU can crosslink cellulose. The structure has no -NH- group in it and hence does not exhibit chlorine retention.[63]

iv) Triazones are prepared by the reaction of urea, formaldedyde and aliphatic amines. It is possible to vary the nature of the alkyl substituent (R) methyl, ethyl, propyl, butyl and other groups can be used and the basicity of the product can thus be varied



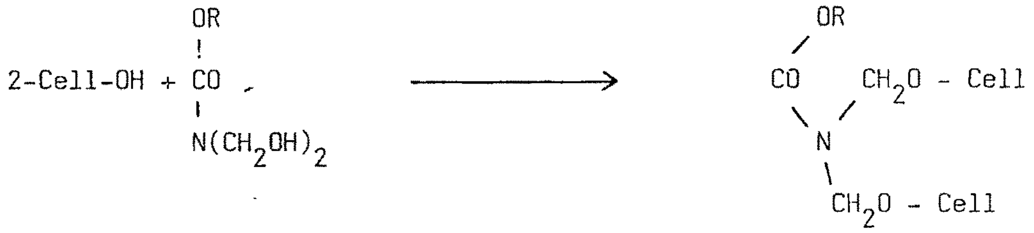
Dimethylol R triazone

v) Carbamates or urethanes can react with two molecules of formaldehyde in an alkaline medium to give a corresponding N,N′ dihydroxy methyl derivative. This product is able to crosslink cellulose molecules under acidic conditions.[71]



N, N′ dihydroxy methyl carbamate

Cellulose molecules under acidic conditions



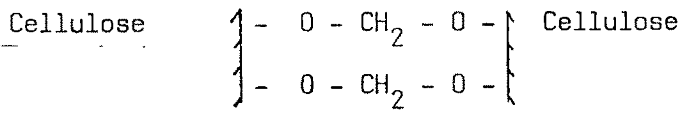
Crosslinked cellulose

The major advantage of the carbamates over other reactants is their resistance to chlorine damage even after multiple commercial or home launderings. When properly cured, wash-wear properties are excellent. The major disadvantages are a tendency to yellow, high free formaldehyde content and high losses in abrasion, tear and tensile strength.[66]

b) Nonnitrogenous agents: These include (1) formaldehyde, (ii) acetals (iii) epoxides and epichlorohydrin and (iv) sulphones.[71]

i) Formaldehyde treatment changes the physical and chemical characteristics of cellulose.[71] High percentage of free formaldehyde in compound will lead to direct formaldehyde reaction with cellulose, thereby forming short crosslinks. During curing, many N-methylol compounds will liberate formaldehyde, crease recovery will be high but fabric strength will be low.[65]

Formaldehyde reacts with hydroxy groups of adjacent cellulose macromolecules thereby crosslinking the molecules.[62]

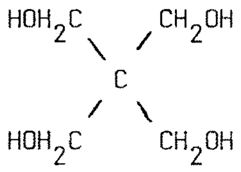


Crosslinking of cellulose macromolecules by formaldehyde

Formaldehyde-cellulose reactions may be summarized as including the formation of hemiacetals under neutral or alkaline conditions. Acetals or formal linkages connect hydroxyl groups in separate cellulose chains.[72,35]

Treatment of cotton fabric with aqueous solution of formaldehyde in presence of formic acid imparts good wet crease recovery to the cloth, without much improvement in dry crease recovery.[71]

ii) Acetals are the reaction products of aldehydes with alcohols under acidic conditions. As in majority of cases the aldehyde used is formaldehyde, the acetals are also known as formals. An important product of the acetal series is pentaerythritol acetal which is prepared by reacting pentaerythritol with formaldehyde.



Penta erythritol

It is capable of forming not only crosslinkages with cellulose but also polyacetal polymers within the fibre. Although the product imparts good crease resistance to the fabric, it produces considerable losses in tensile strength, tear strength and abrasion resistance.[71]

iii) Epoxides and Epichlorohydrin

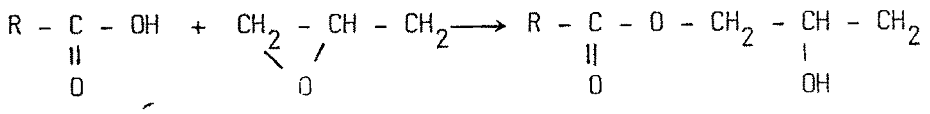
Epoxides have proved to be highly versatile reagents for chemical modification of cotton cellulose by either conventional pad-dry-cure or specialized processes.[9]

Theoretically, any group, R, can be attached to cellulose through a stable ether bond (via an epoxide containing the R group) to impart desired end-use properties to cotton.

Simultaneous application of a diepoxide and fibre reactive dye to cotton by a pad-dry-cure treatment resulted in a crease resistant fabric in which the dye was attached to cellulose through the epoxide group by a linkage stable to acid and alkaline hydrolysis.[9]

The advantage of an epoxy resin are the complete freedom from chlorine retention and stability to hydrolysis under both alkaline and acidic conditions. The epoxy resins are capable of polymerization as well as cellulose crosslinking. However the crosslinking reaction predominates in the presence of cellulose.[71]

The main purpose of adding epoxy resin is to impart crease resistance to the fabric. In general polyepoxides or unsaturated epoxide compounds are used much more often than monoepoxide compound in textile finishing. These compounds react readily with functional groups that possess active hydrogen such as $-NH_2$, -NH-, -COOH, -OH or SH. Reaction occurs as follows[27]:



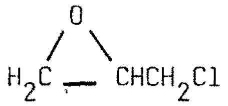
carboxyl group

epoxy compound

A monoepoxy compound, such as epichlorohydrin $\underbrace{O.CH_2.CH}.CH_2Cl$ is formed by the reaction of sodium hydroxide on dichloropropanol

Diepoxide, $\overset{O}{CH_2.CH}.R.\overset{O}{HC.CH_2}$, Glycidyl, $-O-\overset{O}{CH_2.CH.CH_2}$, are typical epoxide compounds[65]

Epichlorohydrin can produce both dry and wet crease recovery to cotton.



epichlorohydrin

It is prepared by the action of sodium hydroxide on α – dichlorohydrin. α -dichlorohydrin is prepared by hydrochlorination of glycol.[71]

Epichlorohydrin is capable of reacting with tertiary amine hydrohydroxide. This reaction removes H^+ and OH^- from the tertiary amine hydrohydroxide to form the free amine. The free amine can react with another mole of epichlorohydrin to form the quarternary salt which in turn reacts with additional epichlorohydrin to form a polymeric substance containing a terminal epoxide group. This polymeric space can then react with another tertiary amine to form a diquartenary salt linking two cellulosic units together.[34]

iv) Sulphones have excellent durability to repeated laundering, are odourless and do not show any chlorine retention. However, some of the sulphones are toxic and cause yellowing of the treated material on curing. This yellowing can be removed by subsequent bleaching.

$CH_2 = CH\text{-}SO_2\text{-}CH = CH_2$

Divinyl sulphone

Divinyl sulphone imparts wash and wear properties to cotton and cross-links two moles of cellulose in presence of alkali, forming a cellulose ether.

$Cell - O - CH_2 - CH - SO_2 - CH - CH_2 - O - Cell$

However, it is volatile, toxic and a very active skin dessicant.[71]

2.1.2 Reaction mechanisms

a) Polymerization reactions

Vinyl addition polymerization are chain reactions, are more complex than condensation polymerization and they are generally more likely to include minor side reactions leading to branching and cross-linking. In vinyl addition polymerization high polymers make their appearance at the outset, duration of the process is determined by the yield of polymer desired and not by the molecular weight required. Addition polymer molecules ordinarily do not respond to further polymerization by interaction with one another. Condensation polymers may be formed from monomers bearing two or more reactive groups of such a character that they may condense intermolecularly with the elimination of a by-product, often water.[17]

Addition polymerization of unsaturated monomers leading to the formation of products of high molecular weight invariably proceeds by chain reaction mechanisms. Primary activation of a monomer M (or a pair of monomers) is followed in rapid succession until the growing chain is eventually disactivated with the net result that a polymer molecule, has been formed from x monomers.

$$M \xrightarrow{\text{activation}} M^{*} \xrightarrow{+M} M_2{*} \xrightarrow{+M} M_3{*} \longrightarrow Mx$$

Each growth step consists of a reaction with a monomer. The majority of polymerization of unsaturated compounds proceeds by free radical mechanism.[17]

Addition polymerization of typical vinyl compound, example ethylene $CH_2{=}CH_2$, leading to the formation of product of high molecular weight invariably proceed by the chain reaction mechanisms. The reactions involved are as follows:

i) The production of a free radical C_6H_5 from the polymerization initiator e.g. benzoyl peroxide.

Initiator - C_6H_5

ii) The addition of C_6H_5 to the vinyl soluble bond to produce a new free radical

$$C_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2CH_2$$

This is known as the initiation reaction.

iii) The addition of this new radical to another monomer molecule.

$$C_6H_5CH_2CH_2 + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2CH_2CH_2CH_2$$

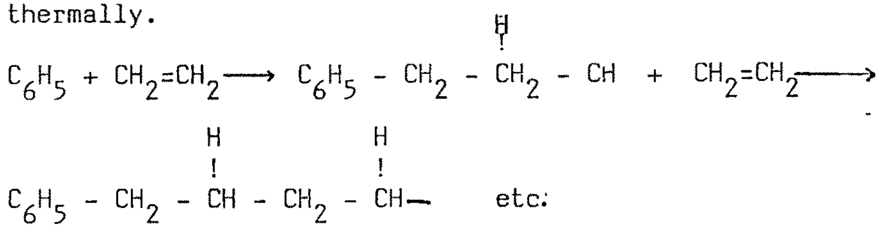
This and similar reactions will further monomer molecules which lead to the formation of a long chain of polymer molecules and are known as propagation reaction.

iv) The termination of the growth of the polymer molecules, usually by the mutual interaction of two of them as for example -

$$C_6H_5(CH_2CH_2)n + C_6H_5(CH_2CH_2)m \longrightarrow C_6H_5(CH_2CH_2)\ m{+}n\ C_6H_5$$

This is referred to as termination reaction.[59]

Free radical polymerization usually are induced by radicals released by a decomposing peroxide, commonly referred to as the catalyst. The initiating free radicals, may be generated photochemically or thermally.



$$C_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5 - CH_2 - \overset{H}{\overset{|}{CH_2}} - CH + CH_2{=}CH_2 \longrightarrow$$

$$C_6H_5 - CH_2 - \overset{H}{\overset{|}{CH}} - CH_2 - \overset{H}{\overset{|}{CH}} - \quad \text{etc.}$$

This explains the polymerization of ethylene induced by free radical in the gas phase.[17]

The commonly employed initiators are organic peroxides such as benzoyl peroxide. These are known to decompose slowly at temperatures of 50 to 100°C with release of free radicals as follows:[17]

$$(C_6H_5COO)_2 \dashrightarrow 2C_6H_5COO \dashrightarrow 2C_6H_5 + 2CO_2$$

Polyacrylamide can be readily prepared by free radical polymerization method using acrylamide as monomer along with suitable initiators.

Polymerization reaction takes place through chain reaction mechanism. Besides the free radical method it can be prepared either by ionic initiated polymerization or by solid state polymerization in which monomer is initiated by gamma rays.[14]

Use of catalysts: The reaction between a fibre and finish is brought in presence of a catalyst. Usually the presence of an alkaline or acidic catalyst for the reactions is essential. The alkaline catalysts are effective only with certain reagents such as methylol urea, epoxy, epichlorohydrin etc.[25] The primary function of a catalyst is to increase the rate of reaction but they do not conform to the classical definition.

These compounds are used in larger amounts and they also take part in the crosslinking reaction, their function is not merely catalytic.[42]

The following classes can be considered as typical.

Acidic catalyst which can be grouped into three groups mainly (i) mineral and organic acids, (ii) ammonium salts and (iii) inorganic salts.[25] The other catalysts are metal salt catalyst, phase separation catalyst, mixed catalyst systems, coreactant systems, alkaline catalyst and self limiting catalysts.[42]

Redox catalytic system involves the use of reducing agents along with initiators during polymerization. The common reducing agents are different metallic salts, sulphites, thiosulphites, pyrogallol, hydroxy acids and hydroxy aldehydes.[14]

"Redox" is a contraction of "reduction-oxidation". The oxidant used is the usual persulphate catalyst and the reducing agent that serves as the activator is usually a sulphoxy compound or a small amount of ferrous salt. Sulphoxy compounds frequently used are sodium metabisulphite, thiosulphite and hydrosulphite. Ferric ammonium sulphate, if needed can be introduced as an activator. Polymerizations are easily carried out with redox systems at room temperature.[52]

Deshpande **et al**[14] reported that polymerization was carried out at 65°C, using 10% acrylamide as monomer and potassium persulphate as initiator. It was observed that addition of sodium hydroxide in the polymerization mixture enhanced its viscosity.

The oxidising catalysts most commonly used for polymerization of acrylic compounds are the water soluble peroxides like hydrogen peroxide, potassium persulphate and ammonium persulphate. Higher concentration of catalyst usually gives higher molecular weight in emulsion polymerization.[43]

Frick and Gautreaux[19] stated that brief exposure of the fabric containing a monomer and initiator to dry heat is the least complicated procedure for polymerization. $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ both radical initiators have proved to be most effective initiators but strength loss of fibre was considerable. This is due to the action of initiator on the cellulose and to the presence of the polymer itself.

Emulsion polymerization:

The major ingredient that go into the making of an emulsion polymer are the monomers, water, catalyst and surface active agent or agents. In this may be added the buffer for pH control, a chain regulator, dispersing agent, thickening agent etc.

The mechanism by which emulsion polymerization takes place can be explained with the ´micelle´ theory. Accordingly, monomer diffuses from monomer droplets through the water phase into micelles formed by the emulsifier and polymerization takes place within these miscelles forming polymer particles that are surrounded by the emulsifier. The site of initiation is the water phase, and is activated by a water soluble catalyst. It is also thought that, in the case of less water soluble monomers, the bulk of the polymerization takes place in monomer polymer particles.

Factors affecting emulsion polymerization:

i) Agitation is an important factor in producing good emulsion. Any agitation that causes foaming is bad. High shear will cause a breaking of the emulsion at the critical tachy stage. Too low an agitator speed or too inefficient an agitator will not rapidly emulsify the monomer being added and will allow pooling of the monomer and result in very poor and grainy emulsions. The best agitation is one in which there is high turbulence and low shear.[52]

ii) pH: The pH also affects the polymerization. It has been found that each emulsion polymerization system appears to have its optimum pH. Vinyl acetate emulsion system has a peak reaction speed at pH5 while a particular butadiene-styrene emulsion system shows a peak at pH11.[17] Dilute solution of acrylic acid and methacrylic acid polymerize faster between pH 2.5-5[39]. Schildknecht[59] stated that redox reaction is the most important reaction in polymerization which yields free radicals by the one electron reduction from the peroxy compound.

Hydrogen peroxide in the presence of ferrous ions initiates polymerization in the aqueous emulsions through generation of hydroxyl radicals.[17]

Fe^{2+} and H_2O_2 mixture is a potent oxidising agent.

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO$

In presence of a vinyl compound, the reaction is completed by Fe^{2+} and by the monomer as follows[59]:

$HO + Fe^{2+} \longrightarrow Fe^{3+} + OH^-$

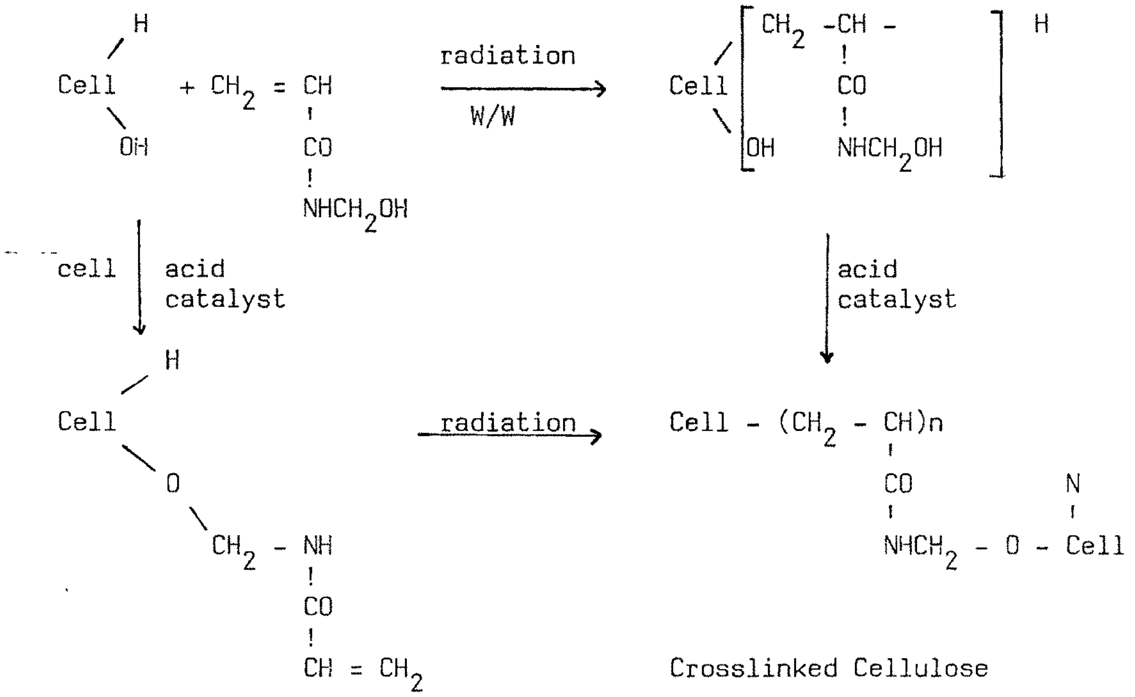
$HO + CH_2{=}CH_2 \longrightarrow HOCH_2 - CH_2$

Other peroxy compounds can behave similar to hydrogen peroxide in this reduction reaction. The persulphate ion with Fe^{2+} is a strong oxidising solution whereas temperature of 50°C and above are required for the initiator of a solution or an emulsion polymerization by persulphate alone, very rapid polymerization are induced at room temperature by the Fe^{2+} and $S_2O_8^{2-}$ in mixtures. Here presumably the SO_4 ion radical is available.[59]

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{--} + Fe^{3+} + SO_4^{\cdot -}$$

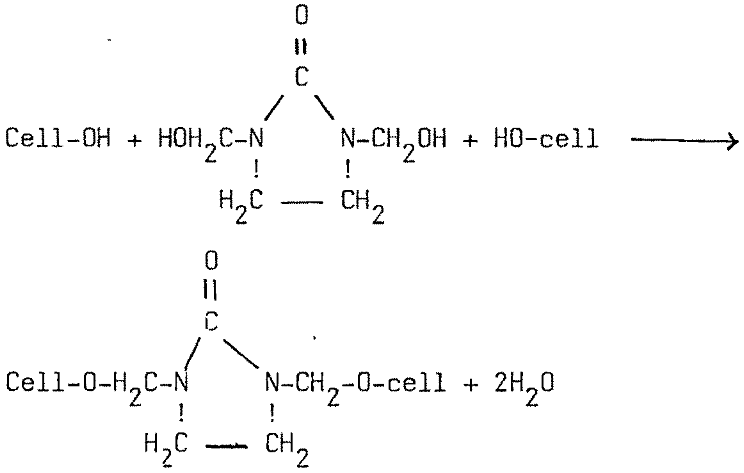
b) Crosslinking reactions

Cellulose is crosslinked with N-methylol acrylamide by radiation and the following reaction takes place.[67]

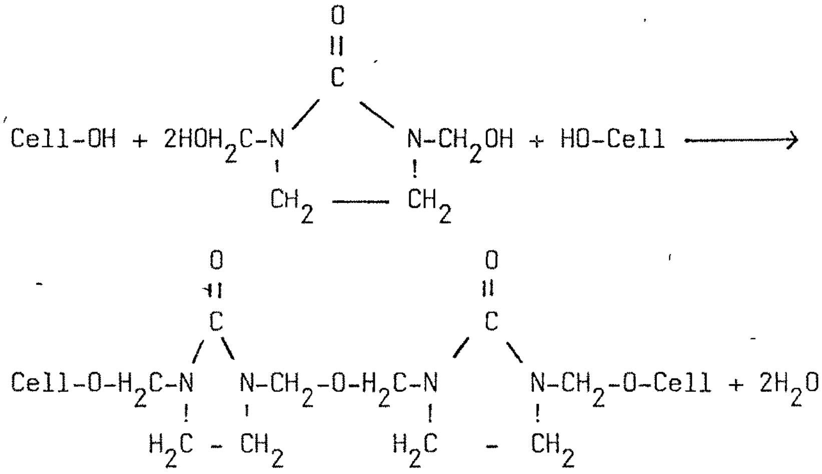


The crosslinking reaction between cellulose and dimethylol ethylene urea approximates the following.[57]

i)



ii)



N-methylol acrylamide under acid conditions reacts with rayon cellulose in the following manner.[21]

$CH_2=CH-CO-NH-CH_2-OH + H^+ \longrightarrow CH_2=CH-CO-NH-CH_2 + H_2O$

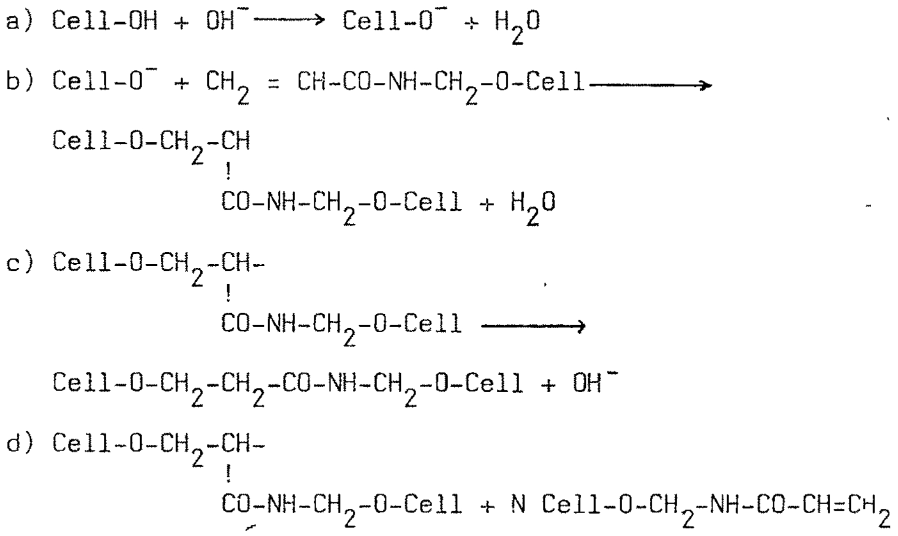
$CH_2=CH-CO-NH-CH_2^+ + HO-Cell \longrightarrow CH_2=CH-CO-NH-CH_2-O-Cell+H^+$

Under alkaline catalyst treatment of the acrylamidomethyl cellulose in the absence of other reagents caused addition of the cellulosic hydroxyl to the double bonds forming crosslinks of the following nature:

$Cell-O-CH_2-NH-CO-CH_2-CH_2-O-Cell$

It was noted that cotton pretreated with acrylamide in alkaline medium is more responsive than untreated cotton to acid catalyzed formaldehyde crosslinking.

When partially substituted acrylamidomethyl cellulose is treated with an alkaline catalyst, reaction can be initiated by ionizing either the free hydroxyl groups or the acrylic groups. In the first instance, the following sequence of reactions is possible



a) $\text{Cell-OH} + \text{OH}^- \longrightarrow \text{Cell-O}^- + H_2O$

b) $\text{Cell-O}^- + CH_2 = \text{CH-CO-NH-CH}_2\text{-O-Cell} \longrightarrow$

$$\text{Cell-O-CH}_2\text{-}\underset{\substack{|\\ \text{CO-NH-CH}_2\text{-O-Cell}}}{\text{CH}} + H_2O$$

c) $$\text{Cell-O-CH}_2\text{-}\underset{\substack{|\\ \text{CO-NH-CH}_2\text{-O-Cell}}}{\text{CH-}} \longrightarrow$$

$$\text{Cell-O-CH}_2\text{-CH}_2\text{-CO-NH-CH}_2\text{-O-Cell} + \text{OH}^-$$

d) $$\text{Cell-O-CH}_2\text{-}\underset{\substack{|\\ \text{CO-NH-CH}_2\text{-O-Cell}}}{\text{CH-}} + \text{N Cell-O-CH}_2\text{-NH-CO-CH=CH}_2$$

Polymeric cellulose crosslinks

2.2 Effect of wash and wear finishes on some related properties

Frick and Gautreaux[18] studied the crosslinking reaction at low temperature on cotton. Different concentrations of a solution of dimehylol ethylene urea with zinc nitrate hexahydrate as catalyst, was applied to cotton and tested for wrinkle recovery angle and for breaking strength. Maximum wrinkle recovery angles (and so presumably maximum extent of crosslinking) were reached in 40 to 90 days. Highest ultimate value for recovery angles was obtained with lowest relative humidity. With dimethylol ethylene urea and zinc nitrate the crosslinking reaction was also examined at 70°C, a temperature intermediate between normal curing temperature and room temperature. Higher strength by 5-10% was observed as compared to that obtained at normal curing temperature. A wrinkle recovery angle of 145° was obtained from 8% dimethylol ethylene urea in two hours; this wrinkle recovery angle was near the 150-160° which is the maximum reached during normal curing.

Treatment of the fabric with dimethylol ethylene urea makes the fabric crease resistant and fast to laundering. However, the drawback of treatment with this agent is that the tensile strength of cotton fabric is reduced by 20-30% in warp and by 40-50% in the weft direction.[57]

Pandya[49] studied the effect of formaldehyde resin with certain adducts (polyethylene glycol, diethylene glycol and polyvinyl alcohol) on the physical properties like tensile strength, elongation and wrinkle recovery of cotton. The results showed that with all the treatments, elongation was reduced in comparison with the untreated fabric. Crease recovery increased with urea formaldehyde alone due to the crosslinking between cellulose and the substrate but on addition of adducts the crease recovery angle decreased and stiffness increased.

Robert and Bruno[55] treated cotton and polyester/cotton blended fabrics of various proportions with dimethylol dihydroxyethylene urea (DMDHEU) using a conventional pad-dry-cure technique to know if any reactions occured between the polyester and crosslinking agent and also whether cotton fibres in the blends are over crosslinked.

They concluded that, a treatment with DMDHEU (from 6.8 percent to 9 percent) is adequate to produce acceptable durable press performance in the all cotton fabric. They further stated that treatment with higher level of crosslinking agent failed to generate additional improvement in durable press ratings. Excessive crosslinking did not significantly improve the resiliency of the cotton fibres and lowered certain strength characteristics particularly abrasion resistance.

The N-methylol crosslinking agents, i.e. dimethylol alkyl triazone (TAE), DMDHEU and methylol melamine formaldehyde (MMF) were used as crosslinking agents on cotton fabrics. The catalyst included analytical reagent grade zinc acetate dihydrate for polymerization and reagent grade zinc nitrate hexahydrate for crosslinking. Nonionic polyethylene emulsion was used as fabric softener. An ionic product based on alkylaryl sulphamate was used as a wetting agent. It was seen that zinc acetate catalyst caused predominantly homopolymerization of N-methylol resins during crosslinking reactions with hydroxyl groups of cellulose. However a stronger catalyst such as zinc nitrate was necessary for crosslinking reaction with hydroxy groups of cellulose at a high temperature. The use of two different catalysts in the polyset process serves a dual purpose. One was to form homopolymers of resin to avoid extensive crosslinking and the other was to activate the crosslinking cellulose at elevated temperature with available N-methylol resins.[48]

Two alternative radiation/chemical means for crosslinking chains with N-methylol acrylamide yield improved crease recovery. Special advantages have been noted for the chemical grafting followed by radiation crosslinking. It was found that wet and dry crease recovery angles increased with increasing add-on of N-methylol acrylamide but only a relatively minor improvement was noted in the absence of radiation. With increasing irradiation doses the wet and dry crease recovery angles continually increased.[67]

Reaction products from acrylamide and glyoxal or glutraldehyde have been used as finishing agents to give cotton wrinkle resistance and durable press properties to cotton. These reaction products serve as examples of adducts from aldehydes and an amide with an electron withdrawing acryl group. The effectiveness of these products was less than that of conventional amide formaldehyde agents but about equal to that of presently available formaldehyde-free agents. This finish from glyoxal and acrylamide had greater resistance to acid than the most common formaldehyde-free finish.[20] As pointed out by Ryan[56] the precise nature of crosslinks may differ with different finishing agents and may involve not only covalent linkages but also hydrogen bonds and Vander waals forces. The covalent bond crosslinking in the wet state, or highly swollen state if swelling is due to media other than water will result in wet crease recovery and crease retention. Whereas covalent bond crosslinking by dry curing at elevated temperature will result in dry crease recovery and crease retention as well as substantial degree of wet crease resistance and crease retention.

Satyanath[58] conducted a study on the effect of acrylic polymer on physical properties of cotton and polyester blend fabrics. Polyacrylamide finish improved wrinkle recovery more in case of polyester/cotton as compared to cotton fabric. Tensile strength was maintained with both cotton and the polyester blend and was in fact slightly increased. Increase in strength was associated with a reduction in elongation. After washing, wrinkle recovery was the same for cotton fabrics indicating durability of finish.

A study using acrylic finish by Divya[15] showed that cotton cambric and polyester/cotton fabrics showed an improved wrinkle recovery and an ease of ironing. Two catalysts used were ammonium persulphate and hydrogen peroxide. Ammonium persulphate was a better catalyst than hydrogen peroxide. Hydrogen peroxide being weak and oxidative, a larger part was given off at the predrying stage.

Asnes **et al**[5] described that wash and wear appearance increases when vinyl monomers are added in the polymerisation step, and the added monomers influence strength retention. Acrylic monomers in various forms have been used to impart desirable properties in both natural and synthetic fibers. They have been used to render fabric crease resistant while retaining or improving its tear strength and pliability.

Mathur[37] and Bali[7] studied the stress-strain behaviour and the changes in stiffness and wrinkle recovery by application of acrylic and polyvinyl acetate finishes on cotton and cotton/polyester blend fabrics. Different concentrations (0.5, 1.0, 2.0, 4.0 and 8.0%) of the finish were padded and cured at 130°C for 10 minutes. The results revealed that with acrylic finishes there was an increase in wrinkle recovery whereas with increasing concentration of polyvinyl acetate finish there was a decrease in wrinkle recovery and an increase in stiffness. Tensile strength of fabrics improved at lower concentration, while at higher concentrations it decreased. Elongation of treated fabrics (upto 4% of finish) was higher than that of untreated fabric.

Lamprinakos and Sookman[31] and Taylor and Hurtwitz[69] noticed that polyacrylate copolymer emulsion improved the tear strength and hand of durable press cotton fabrics. This was largely mechanical, caused by immobilization of the yarn structure. Grace[24] has also indicated that natural or synthetic polymer fabrics when treated with an aqueous dispersion of an oxidised high density ethylene polymer have durably improved tear strength and lustre.

According to Taylor and Hurtwitz[69] acrylic polymers are internally plasticised and thus provide any degree of flexibility. In addition fairly good tear strength is imparted to cellulosics and synthetic webs. Acrylonitrile lattices when used as bonding agents also provide good tear strength.

An acrylic acid polymer and oxalic acid renders woven cotton fabric 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 resins by the action of oxalic acid to produce a tough pliable resinous film on the cotton fibres. The impregnating mixture comprises an aldehyde urea resin and an acid stable polyacrylate resin.[34]

Majumdar[33] reported that polymer finish improved the transfer printing of cotton whether alone or in blend. The finish imparted thermoplastic nature to the non-thermoplastic fibre cotton and made it receptive to the disperse dyes. Cotton fabric finished with acrylic emulsion and printed with paste containing polyvinyl alcohol showed more transfer printability. Good colour retention was observed after washing when fabrics were finished.

Pensa **et al**[50] described a process for permanent setting of cellulosic fabrics. In this the reactive chemical system present on the fabric is partly 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:

$$\text{I} \quad \text{cell-OH} + \text{X-R-X} \longrightarrow \text{cell-O-R-X}$$

$$\text{II} \quad \text{cell-O-R-X} + \text{cell-OH} \longrightarrow \text{cell-R-O-cell}$$

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 product can be washed and stored, and yields a crosslinked product (as shown in reaction II) when heated in presence of a catalyst.

2.2.1 Effect of grafting on properties of fabrics

Studies on grafting of acrylic acid and acrylonitrile onto polyester using the technique of initiation by gamma radiation as well as benzoyl peroxide, have shown that the degree of grafting is dependent on the time of treatment and concentration of the initiator, and the monomer, as well as on the irradiation doses. The nature of grafted fibre substance remained the same irrespective of the grafting technique. Increase in moisture regain of polyester from 0.4 to 1.22 and 4.6 percent was achieved by grafting with acrylonitrile and acrylic acid respectively.[29]

Dasgupta[12] 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 improved wrinkle resistance. The grafting process results in crosslinking and intermolecular bonding and it should therefore, bring about increased crease recovery. It was concluded that grafting of single vinyl monomers on cellulose took place through the various hydroxyl groups of the cellulose and the breaking of the vinyl bonds of the monomer to form only methyl linkages.

Kumar **et al**[30] stated that during the course of grafting monomers in the liquid state either pure or in aqueous solutions undergo simultaneous homopoloymerisation tending to form a sticky product as well as the loss of monomers and, therefore, it is necessary to add a retarder in the grafting solution to avoid this parasitic homopolymerisation.

Grafting of acrylic and vinyl monomers on to the synthetic fibres can be accomplished either chemically or by means of ionising radiation. In the former case, the fibres are preswollen in a suitable solvent, then freed from the solvent and treated with the monomer containing initiator like benzoyl peroxide. On heating, the benzoyl peroxide decomposes to give a free radical which extracts a hydrogen atom from the fibre and creates another free radical. The monomer reacts with the latter, forms a short chain and terminates by extracting hydrogen atom from another chain. In this process, the free radical from benzoyl peroxide can also directly react with the monomer and cause homopolymerization. This is an undesirable reaction as it would not only waste the precious monomer but also would necessitate homopolymer removal from fibre.

In the radiation initiated method, two approaches are possible. Free radicals can be generated initially in the solid state at low temperatures in the absence of oxygen and then treated with the monomer for formation of a chain on the backbone. Alternatively, the free radicals can be generated by the radiation in the presence of oxygen to form the relatively stable peroxy radicals. These, when treated with monomers and heated, form short chains on the polymers.

Chemical method of grafting vinyl monomers onto synthetic fibres gave higher homopolymerization than radiation method and hence latter is preferable.[54]

Bonnefis and Puig[8] on the basis of their study on grafting by direct irradiation of polyester fibres in contact with aqueous solution of acrylic acid, have shown that grafted fibres containing upto 40 percent polyacrylic acid have interesting properties with respect to moisture uptake, static electrification and affinity with basic dyes while mechanical properties are unaffected. The most useful grafting ratio has been found to be between 15 and 20 percent. Both hydrophillic and antistatic characteristics were found to increase by the conversions of acid grafts to corresponding metal salts.

In a study on grafting of acrylic acid and methacrylic acid onto polyesters, Rao and Coworkers[53] have shown that ferrous ammonium sulphate (in case of acrylic acid) and copper sulphate (in case of methacrylic acid) are the best additives capable of inhibiting polymerization without affecting the grafting process.

Achwal[2] has also stated that hydrophillicity can be imparted to polyester fabric by grafting of acrylic acid, methacrylic acid as monomers.

Sharma and Daruwalla[61] grafted fabric samples with a binary and tertiary mixture of selected vinyl monomers along with acrylamide onto cotton using ceric ammonium nitrate as catalyst from aqueous solution or emulsion. Subsequently polyacrylamide grafts were methylolated in-situ and crosslinked. Except in the case of acrylamideacrylonitrile treatment, finished fabrics showed good wrinkle recovery properties accompanied by satisfactory retention of breaking and tear strength, and also very much improved resistance to abrasion.

Grafted cotton fabric with-mixed monomers exhibited high tensile strength increased crease recovery, good dimentional stability, higher dye acceptability, resistance to microorganisms and water, and excellent handling properties.[12]

The ceric ion method of grafting acrylic acid to cellulose was extended to rayon filaments. The fibre samples were pretreated with an aqueous solution of ceric ammonium sulphate. This was followed by a washing step to remove excess ceric solution at the fibre surfaces. The grafting reaction was carried out in toluene to reduce homopolymer formation. Grafting yields of approximately 40% were obtained with grafting efficiencies in excess of 92%.[36]

Acrylamide and dially-dimethyl ammonium chloride in presence of a catalytic system comprising of ammonium persulphate and sodium dithionite was copolymerized on the surface of polyester fabric. The finish was found to impart durable antistatic and hydrophillic properties to the fabric without any deterioration of its basic properties.[32]

Mittal and Trivedi[40] reported that soil release finishes on mixed polymers of acrylic acid are used for polyester blends. Acrylic soil release finish are hydrophillic and anionic in nature. Hydrophillicity of the finish helps in reducing the affinity of the finish for hydrophobic soils. These finishes are used on light and medium weight fabrics.

2.2.2 Effect of combination finishes on properties of fabrics

Browne[10] suggested that the dimethylol derivatives of the condensation products of two moles of acrylamide with one mole of ethylene glycol, when used as a crosslinking agent for cotton, gave higher wet than dry wrinkle recovery and permitted greater retention of strength than the conventional dimethylol ethylene urea crosslinking agent.

Crease resistant cotton fibrics have been produced by use of N-methylolacrylamide prepared from acrylamide and formaldehyde. Wrinkle recovery, shrinkage and reduction in tear strength are dependant on the acrylamide formaldehyde ratio. The treatment was found to be stable to six standard washings.[3]

Phadke[51] conducted a study on the effect of thermoplastic and thermosetting finishes on properties of cotton and polyester blend fabrics after treatment with different concentration ratios of DMDHEU and acrylic finishes. It was observed that combination finishes assisted each other in improving wrinkle recovery. Acrylic finishes in increasing amount not only helped to improve wrinkle recovery but also helped to retain or to improve tensile strength. They caused apparent bridging up of the cellulose chains. Their presence, minimised the loss in strength when used in combination with DMDHEU.

Influence of the finish was seen to be more with increasing content of cotton in fabrics which was explained, as the finish reacting with cellulose. No effect was thus noticed on polyester. Equal proportion of acrylic and DMDHEU finish was found to be the optimum combination finish.

Abrams and Sherwood[1] have stated that 70 parts of polymeric latex and 30 parts of resin formaldehyde application imparts improvement in the fabric properties. This improvement due to the use of latex resin formulation is not brought about just by the reduction in concentration of the urea formaldehyde but because polymeric latex plays a definite part in the improvement in breaking strength, abrasion resistance, bursting strength and hand.

Garvey[22] studied the changes in the physical properties of resin treated fabrics resulting from the addition of elastomers, thermoplastic resins, thermosetting resins, repellents and softeners to a normal thermosetting resin finishing bath. It was found that the physical properties were modified by the addition of these materials. Some of the agents markedly increased the tear strength, abrasion resistance and wrinkle recovery of resin treated fabric.

Nuessle[44] found out that crease recovery of cotton fabrics may be greatly enhanced by treatment with thermoplastic (polyvinyl alcohol and polyacrylate) and the thermosetting (urea formaldehyde etc.) resin formers and reactants. Improved recovery is always accompanied by a loss in tear strength; and in order to obtain high crease recovery value with maximum tear strength, it is necessary to select a finish and to include a softner in the treatment.