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CHAPTER I
INTRODUCTION

Wash and wear finishes containing formaldehyde are used on cotton and other cellulose containing fabrics to produce crease recovery and durable press effect, thus minimising ironing after laundering. To achieve the desired level of effect, these fabrics are treated with polymeric resins as well as with cross-linking agents, formed by reacting formaldehyde with amine compounds and their derivatives.

Synthetic resins are conventionally classified as A) nitrogenous and B) non-nitrogenous. The nitrogenous resins include 1) dimethylol urea 2) trimethylol-melamine 3) dimethylol ethylene urea 4) propylene urea 5) triazone 6) carbamates and their derivatives. The non-nitrogenous resins include 1) formaldehyde 2) penta-arythritol 3) butadiene-epoxide 4) epi-chlororohydrin and 5) divinylsulphone. The chemical structures of these are given in Table 1. According to Marsh (19) the chief advantages of the resin products are :

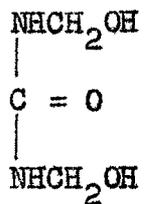
- a) Improved resistance to and recovery from creasing.
- b) Smooth-drying properties after laundering.
- c) Durable effects may be impasted by intermediate mechanical treatment.
- d) Reduced laundry shrinkage.
- e) Increased dry tensile strength and greatly increased wet tensile strength of rayon.

TABLE I

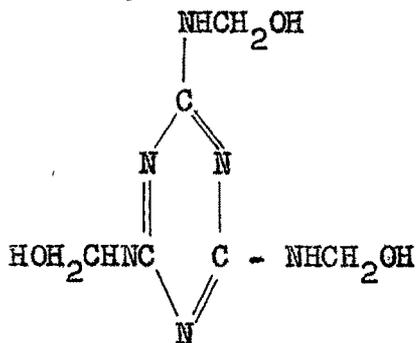
CHEMICAL STRUCTURES OF RESINS

A. NITROGENOUS RESINS

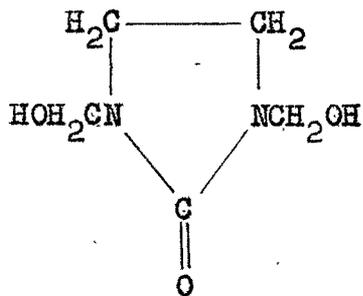
1) DIMETHYLOL UREA



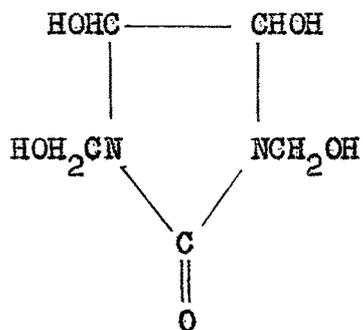
2) TRIMETHYLOL MELAMINE



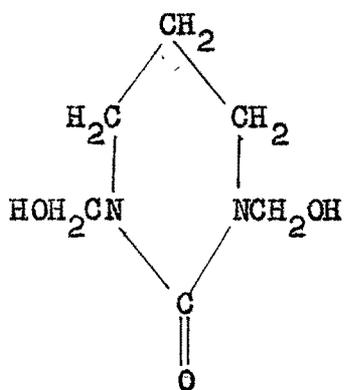
3) DIMETHYLOL ETHYLENE UREA



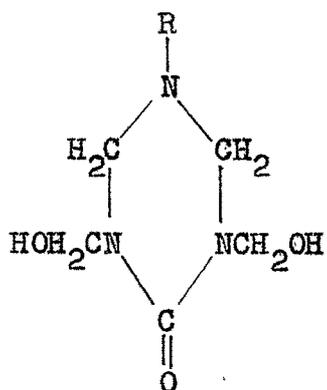
4) DIMETHYLOL DIHYDROXY ETHYLENE UREA



5) DIMETHYLOL PROPYLENE UREA

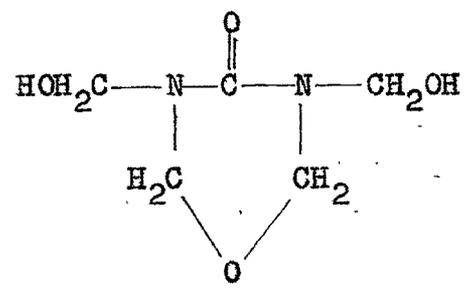


6) TRIAZONE



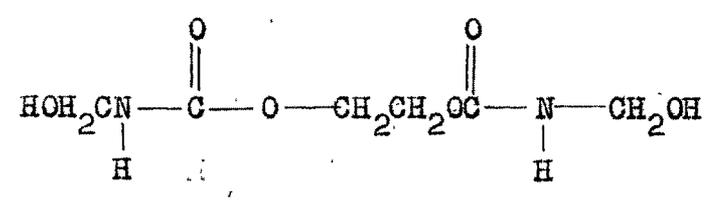
7)

URON



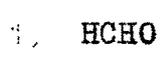
8)

CARBAMATES

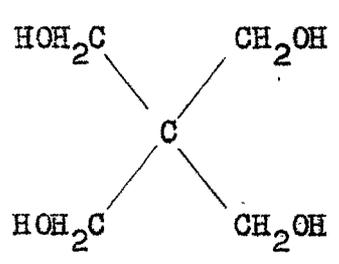


B. NON-NITROGENOUS RESINS

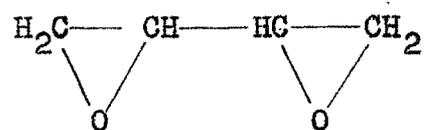
1) FORMALDEHYDE



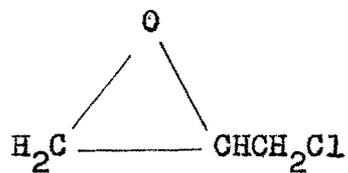
2) PENTAERYTHRITOL



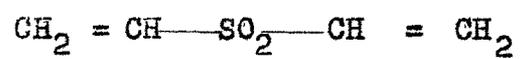
3) BUTADIENE DIEPOXIDE



4) EPICHLOROHYDRIN



5) DIVINYLSULPHONE



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- f) Improved fastness to washing and rubbing of most dyes.
 - g) Decreased water-imbibition and more rapid drying.
 - h) Improved handle and drape of fabrics.
 - i) Increased weight.

Application and Reaction of Resin

The conventional process for resin finishing consists of impregnation with resin, drying and curing at elevated temperature. Some times an after-wash is also given to finished fabrics. The aqueous impregnation solution generally contains the following ingredients, (1) precondensate (8 to 15 percent) (2) additive (1 to 3 percent) and (3) catalyst (1 to 3 percent).

The purpose of the additives is to reduce the stiffness or rigidity by the polymerization of the resin and to improve the strength and abrasion resistance. The acidic catalysts generally used include free acids or latent Lewis acids. The two main requirements of a catalyst for the crease-resisting process are that it should harden resin within reasonable limits of time; three to five minutes and temperature; 130 to 160°C during curing, and it should not interfere unduly with the life of the impregnation bath.

Theoretical Considerations

There are three possible reactions occurring during curing (Reactions I to V, page 8),

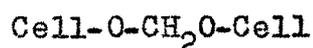
1. Self polymerization of precondensate
2. Cross-linking of resin with hydroxyl groups of cellulose
3. Formation of hydrogen bonding.

The mechanism of crease-recovery is mainly explained with polymeric net work formation and cross-linking with substrate. It is quite possible that all these interactions occur simultaneously or there may be a number of gradual transitions from one into another (19).

The concept of the covalent cross-linkage between cellulose and resin, which has some similarity to methylene or oxymethylene linkage in the reaction between cellulose and formaldehyde, was revived by Cameron et al. (24). The existence of cross-bonds in resin finished viscose was suggested on the basis of water imbibition value, insolubility in cuprammonium hydroxide solution, increase in elasticity and reduction in extensibility. According to authors, a greater part of the material is deposited between the molecules of cellulose in the amorphous resin of the fiber; the change in fiber properties, however, is due mainly to a much smaller amount of reactant actively cross-bonding adjacent molecules. The true picture of the crease resisting effect is probably between the extremes of the simple cross-link and the interstitial resin. It was concluded that the modification of the fiber involves an increase in elasticity and a decrease in plasticity, and this is the basis of the crease recovery of the treated fabric.

REACTIONS AND LINKAGES OF FINISHING AGENTS

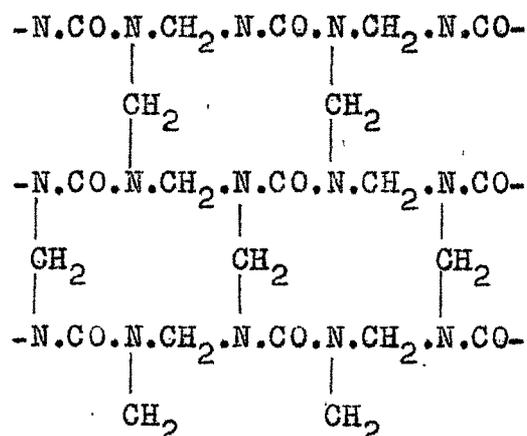
(1) Cross-linkage of cellulose with formaldehyde



Reaction I

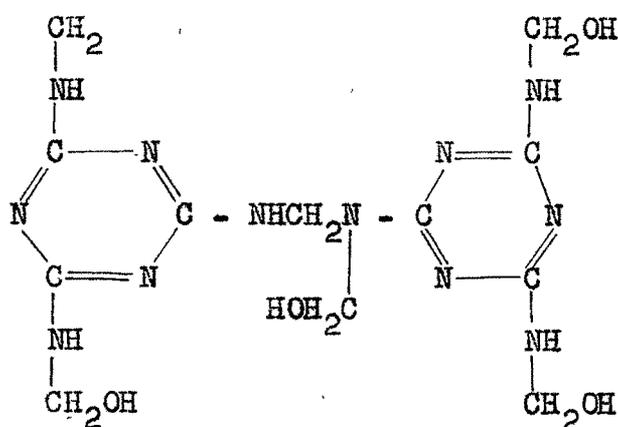
(2) Short methylene bridge

Three dimensional polymeric net work of urea-formaldehyde



Reaction II

(3) Polymeric net work of melamine formaldehyde

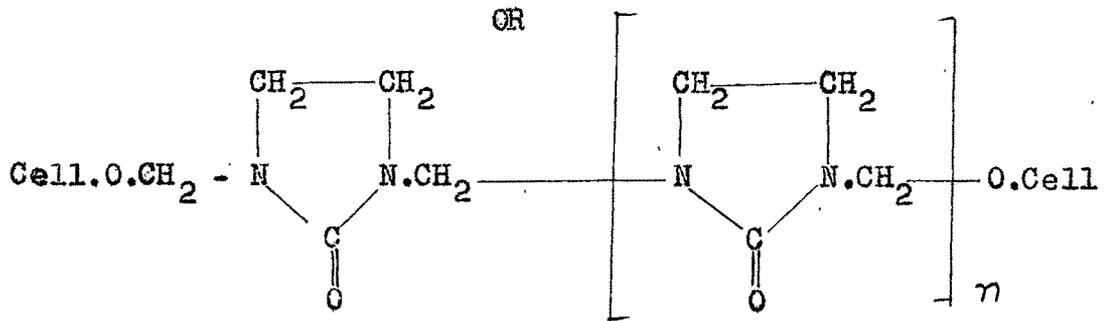
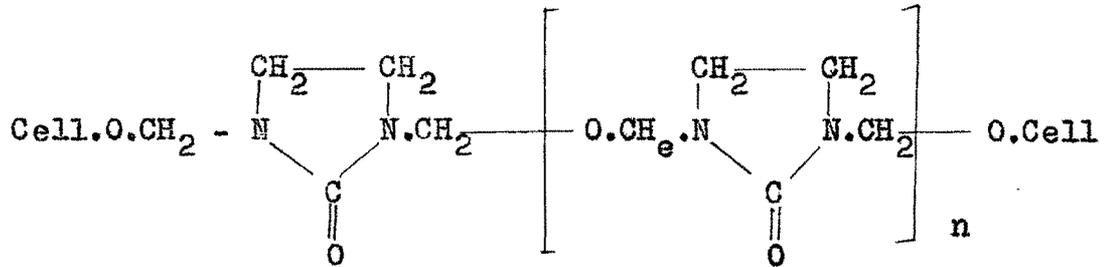


Reaction III

Linear Condensation

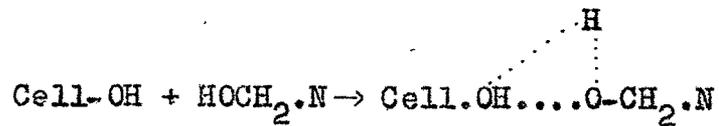
- (4) Cross-linking of cellulose with methylol-cyclic ethylene-urea.

Cellulose + methylol cyclic ethylene urea



Reaction IV

- (5) Formation of hydrogen bonding :



Reaction V

Benerito et al. (10) have also drawn attention to a number of factors which cannot be explained on the basis of cross-linkage theory. They suggested a series of points which should be considered to explain the mechanism of resiliency, the most important of which are (a) the original overall hydrogen-bonded network of native cotton and the importance of the tightly bound water in the network, (b) the realization that a new hydrogen bonded network must be formed simultaneously as the original is broken either by use of solvents or reactants capable of breaking and making new hydrogen bonds if the fiber properties of cotton are to be maintained.

Carter (12) suggested, that the desirable effects are achieved by the introduction of covalent cross-links and not by the internal deposited polymer resulting from the self condensation reaction of the dimethylol cross-linking agents. All aspects of this question have not been resolved, but it has been shown that only a small fraction of the reagent which is added to the fiber is involved in covalent cross-linking.

The reactions during a chemical modification have been studied by Rollins et al. (30) via electron microscopy. By examining fiber fragments and thin cross-sections after treatment with cellulose solvents which dissolve the unreacted cellulose, one can locate the cross-linked regions. Observation of cross-linked cotton in this way showed that the

periphery of the fiber may be crosslinked before the centre. Fibers, uniformly reacted in the wet or swollen state, can swell extensively in a solvent but will not dissolve.

Properties Introduced by Wash and Wear Finishing

Crease recovery increases with increasing percentage of resin up to a limit, while the strength decreases with increasing concentration of resin. There exists a simple relation between recovery and decrease in strength, as given by Marsh (19) and Nikerson (23). A review of the effects of various products on cotton fabrics has been given by Nuessle (25). According to Nuessle, for efficiency of recovery on a basis of resin concentration, dimethylol ethylene urea is best followed by trimethylol melamine and then dimethylol urea, in all cases, the increase in recovery was accompanied by a fall in tearing strength; the resins can be arranged in the reverse order for the loss in strength.

In a study on wear life of easy-care cotton fabrics Neelakantan et al. (22) have reported that these should have sufficient durability to alternate wear-and-laundrying cycles in order to meet the stringent demand of consumers. The direct method of assessing this durability is by service tests, which are tedious, time consuming and expensive. Two different ways of assessing the wear resistance of garments were suggested. In the first, the wear resistance has been obtained from statistically planned wear trials, in the second set of data

the wear resistance is obtained in terms of the number of repeated laundering cycles. The results indicated that, inspite of complexity of the phenomenon of wear, it is possible to draw conclusions on the wear performance of a fabric from a knowledge of its initial tear strength and elongation. There was no need to include the laboratory assessment of abrasion resistance. They further suggested the need to identify other fundamental parameters that are related to the fabric wear life.

Fetouh et al. (16) experimented on improving properties of Egyptian cotton with urea-formaldehyde resin finishes. They reported that efficiency of the precondensate depends on urea/formaldehyde ratio. It improved crease recovery but dropped the tensile and tear strength, because strength loss increased as portion of formaldehyde was increased. Increasing amount of formaldehyde were tried, aiming to increase the effect to produce at a low add-on of solid resin. They found that raising urea/formaldehyde 1: 2.8 with addition of cationic softening agent gave optimum increase in crease recovery with the least possible losses in wear and tear strength.

In a study conducted by Daruwalla et al. (15) different catalyst systems with N-methylol resins were studied. Sulphamic acid either alone and in combination with other catalysts, magnesium-chloride, citricacid and ammonium-sulphate was examined. Three different curing methods were used, a) hot

air cure b) steam cure and c) rapid cure. Results indicated that the extent of hydrolysis of cellulose resulting from the use of sulphamic acid is much lower as compared with that of hydrochloric acid and more or less equal to or slightly lower than that of both breaking and tearing strengths of fabrics finished to the same level of dry-wrinkle recovery, improvement either by rapid cure or steam cure technique is greater than that observed with the pad-dry-cure method of application. Sulphamic acid has been found to be an effective catalyst and enables satisfactory levels of wrinkle recovery improvement and wash and wear ratings.

Achwal (3) in a review report on recent developments in finishing suggested that special techniques of finishing are necessary to enhance other wearing properties of cotton fabrics such as dimensional stability, ability to recover from wrinkles, the wear life of medium and cheap quality fabrics for common man. For the purpose bifunctional cross-linking, N-methylol type agents are widely used. To overcome the draw backs of loss of strength and abrasion resistance the use of film forming additives are recommended.

There are, in general, two main methods for modifying a resin finishing process, apart from the use of a specially selected type of resin, with a view of reducing the magnitude of the adverse effects, namely, (a) use of a softening agent and (b) use of a swelling treatment (19).

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Softeners have been used with beneficial results in respect to tearing strength; it is probable that they act as lubricants enabling the fibers to slip on one another and then take up the tearing stresses more or less together, the improvement in abrasion resistance and crease recovery being relatively less. The softening agents are more often added to the precondensate liquor depending upon their compatibility. It is also possible to use a wide choice of softening agents as an after-treatment. Since thorough washing is important to remove the externally deposited resin, it is also equally important to have the beneficial effect of softener fast to laundering. Nuessle et al. (26) have presented reviews which deal with the importance of softening agents and their effects in wash and wear finishing.

Moncrieff (21) reported that inclusion of thermoplastic additive in the resin bath preserves fiber strength considerably. This if suitably chosen and present in right quantity, does not have any great effect on anti-crease properties of cotton fabric. He studied the effect of thermoplastic additives namely, 1) synthetic latex, 2) polyacrylamide, 3) acrylic emulsion and 4) polyvinyl-alcohol. N-Methylol acrylamide was used as main resin component. The results showed that 0.5 percent concentration of polyvinyl alcohol served as best additive quantity whereas other thermoplastic additives needed about one percent concentration. It was explained that polyvinyl alcohol film is harder, more brittle and less springy than

others. In the curing cross-linking of thermoplastic additive with the fiber and with polymerized methylol acrylamide was suggested.

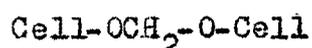
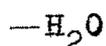
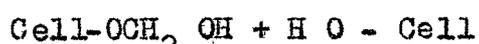
In another research work in the department Pandya (27) studied the effect of starch (0.5%), diethylene-glycol (1%) polyethylene glycol-400 (1%) and polyvinyl alcohol (1%) as additives alongwith urea-formaldehyde (10%). The finishing treatment was given by two step process. First, the cotton fabric was padded with resin solution containing catalyst and dried. In the second step the dried sample was repadded with the additive, dried and then cured at 140°C for five minutes. Samples treated with urea-formaldehyde alongwith additives showed an increase in both wet and dry tensile strength compared with urea-formaldehyde. Increase in breaking elongation was also observed. However a decrease in the crease recovery angle was observed with resin-additive treatments. In the case of starch and polyvinyl alcohol the decrease in the wrinkle recovery was attributed to the film forming nature of the additive, while with glycols the lubricating action was contributed. With resin-additive treated samples an increase in water-retention was also observed.

Properties Introduced by Formaldehyde and Their Importance

As cross-linking agent for cellulose, formaldehyde has established itself because of the ease of application, ready

availability, low cost and fastness to washing. Although it has quite a few advantages, its disadvantages are also many the major ones being odour and toxicity.

Reactions with formaldehyde has been studied by Meyer et. al. (20). It was found formaldehyde under acidic conditions react with cellulose to produce stable methylene ethers or formals (oxymethylene bridge).



The stable oxymethylene bridges alters both the physical and chemical properties to a marked degree. Principal changes include reduction in swelling on exposure to water, increase in elastic recovery and stiffness.

Walker (33) suggested that only a small percentage as much as 0.1% of formal linkages are necessary to effect radical modifications in physical properties of cotton fabric. These formal linkages connect hydroxyl groups in separate cellulose chains. A ring closure involving neighbouring hydroxyl groups in the same glucopyranose unit is believed unlikely since the resultant deposition of atom would lead to strained and complex rings. It is the location of oxymethylene bond in the fine structure of the cellulose which is

the controlling factor rather than the chemical nature of the bath on the physical properties.

Singh et al. (32) studied the role of moisture in cross-linking reaction of formaldehyde. The results showed that the extent of fiber swelling at the time of cross-linking can affect the cross-link distribution throughout the fiber cross section which in turn determine the chemical and physical properties of final product.

Watanable et al. (34) also studied the role of moisture in cross-linking of formaldehyde. The results showed that relation between bound formaldehyde and crease recovery was not affected by fabric moisture content for dry-crease recovery. The changes in wet-recovery was reported. Wet and dry recovery are affected when moisture content goes above 15%, because the decomposition speed starts to exceed the cross-linking speed at high moisture content.

Segal et al. (31) attributed the loss of strength by formaldehyde cross-linking to embrittlement of cotton fiber arising from inability of the fiber microstructural unit to distribute stresses because of restriction of movement imposed to cross-links. The losses have also been attributed to a combination of this embrittlement together with molecular degradation of cellulose.

Techniques and Mechanisms used to Reduce
Free and Liberated Formaldehyde

The formaldehyde containing thermosetting resin finishes impart good wash and wear and durable press effects but not free from drawbacks. The treated material shows loss in strength and abrasion resistance. Apart from these, the resin treated fabrics are also known for their chlorine retention, free formaldehyde and fishy odour (17).

Recently attention is drawn on presence of free formaldehyde in resin treated fabrics. Virtually all the amino-formaldehyde durable press finishes for cotton are considered as potential sources of formaldehyde. Formaldehyde vapours are present during textile finishing, garment finishing so also during distribution, retailing and final use. Liberation of formaldehyde during storage conditions was also reported. With growing awareness of health hazards all over the world, problems about sensitivity of human beings has been reported. The formaldehyde is reportedly responsible for most cases of contact dermatitis from clothing finishes (1).

Japan has been a pioneer in formaldehyde-cellulose researches. They have laid down maximum specifications for the amount of formaldehyde to be present in the fabric depending on the use of the fabric and the age group for which it is intended (1). The group specifications of formaldehyde are as given below :

GROUP	FORMALDEHYDE LIMIT	TEXTILES
I	Less than 1000 PPM	Ladies, gents and children over garments, school uniforms, pull-overs, lining materials
II	Less than 300 PPM	Blouses, polo and open shirts, pajamas, under-shirts etc.
III	(a) Less than 75 PPM	Underwears, hand gloves, socks etc.
	(b) Zero PPM	All textiles for children below the age of two years.

Additives are generally used in resin finishing bath to reduce rigidity of treated fabric and thus improving the strength and abrasion resistance. In an attempt to reduce free formaldehyde apart from the modification of resin additives are also used. These act as either binder or scavenger. The use of additives for the purpose should be carefully considered as these may also modify the functional properties of substrates.

Achwal et al. (1) studied optimisation of processing conditions during finishing of cotton fabrics with N-methylol agents to get minimum free formaldehyde on finished fabric using different additives. In the study dimethylol urea (DMU), dimethylol ethylene urea (DMEU) and dimethylol dihydroxy

ethylene urea (DMDHEU) were used. The free formaldehyde content on fabric was analysed at three stages, pad, dry and cure. Liberated formaldehyde on storage was determined using extraction method followed by acetylacetone method. The three additives studied for use in the pad bath were sodium sulphite, dicyandiamide and urea. From the study it was concluded :

1. The free formaldehyde content of commercially finished cotton fabrics with N-methylol type agents is normally very high (> 1500 PPM).
2. Washing of finished fabrics reduces the free formaldehyde content substantially, which however, increases on storage.
3. Addition of urea to finishing bath reduces free formaldehyde content of finished fabric. Spraying of urea, however, will be practically useful to reduce free formaldehyde.
4. Getting 75 PPM of formaldehyde will not be possible by using common methylol type and getting zero PPM can be met only with non-nitrogenous agents.

Andrews et al. (8) studied variables that influence formaldehyde release from cotton finished for durable press. The variables studied were 1) influence of catalyst 2) influence of cross-linking agent 3) influence of available formaldehyde and 4) influence of free formaldehyde in the pad bath. It was concluded that concentration of cross-linking agent

its ratio with catalyst are important in determining formaldehyde release in finished fabric. Formaldehyde release decreases with decreasing agent concentration and increases with decreasing catalyst concentration. Damage from retained chlorine in the Scorch test was parallel to the relationship and reflects a common mechanism for both relationships. For most agents formaldehyde release cannot be predicted from pad bath concentration.

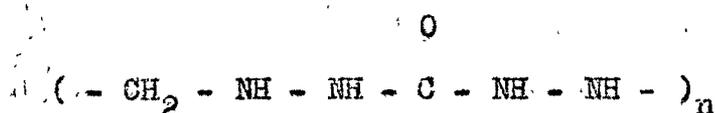
In another study Andrews et al. (7) reported a new approach to reducing formaldehyde release from cotton and cotton blend fabrics finished for durable press and that is the addition of polyhydroxy alcohols to the pad bath. Polyhydroxy alcohols used were, ethylene glycol, diethylene glycol, propane-diol, polyethylene-glycol-300 and polyvinyl alcohol - 1400. The resin, N-methylol type along with the additive was applied using pad-dry-cure method. The effect of different catalysts, zincnitrate, zinc-chloride and magnesium chloride was also studied. Formaldehyde release was determined using AATCC test method 112-1978. It was reported that at the conditions used, the glycols do not interfere appreciably with cross-linking reaction between methylol-amides and cotton. Glycols reduced formaldehyde liberation values by one-half to one-third. However investigators were of the opinion that the mechanism involving the reactions between the polyols, cross-linking agents and cellulose are too complex.

Reeves et al. (29) have studied formaldehyde release in formaldehyde and resin treated fabrics. The purpose of the study was to determine whether less formaldehyde is released from formaldehyde treated fabrics than N-methylol treated fabrics with respect to total formaldehyde. The total formaldehyde analysis indicated that the dimethylol dihydroxy ethylene urea (DMDHEU) finish may be slightly less durable than the formaldehyde finish fabrics. Progressive loss of formaldehyde was observed during repeated launderings with DMDHEU finishes, whereas with formaldehyde finished fabrics rapid decrease of free formaldehyde was observed and arrived more quickly at a low level of free-formaldehyde. Furthermore washing virtually eliminated formaldehyde release from formaldehyde treated fabrics.

In an attempt to reduce formaldehyde release in durable finishes of cotton textiles, Cashen (13) studied the effect of carbonylhydrazide as an additive. Dimethylol-dihydroxy-ethylene urea (DMDHEU), Dimethylol ethylene urea (DMEU) methyl carbamate and ethyl carbamate were used as cross-linking agent along with zincnitrate catalyst. The introduction of two percent or more carbonylhydrazide to the resin bath DMDHEU caused almost instant gelling due to polymerization. For pad-dry-cure the samples were dipped and nipped at approximately 85 percent pick up. The dried samples were cured at 160°C for three minutes. With higher concentration of carbonylhydrazide (2 percent) the two step process was used, the fabric was treated first

with cross-linking agent of catalyst as above and dried. In the second step the dried sample was padded with additive solution, dried and then cured. The cured samples were analysed for formaldehyde release before and after wash.

In the above study it was suggested that in acid medium formaldehyde and carbonylhydrazide react subsequently producing a Schiff base - $\text{CH}_2 = \text{NNHCONHNH}_2$, Hypothetically the carbonylzone readily undergoes polyaddition through methylene bridges to form a polymer having the structure -



The polymer possesses active hydrogen atom that can be methylated with formaldehyde and subsequently grafted to cellulose. Thus reducing free formaldehyde. The decrease in formaldehyde release was observed without serious adverse effect on durable properties or strength.

In another study Cashen (14) studied the effect of carbonylhydrazide (8.6%) addition to commercial preparation of unbuffered dimethylol-dihydroxy-ethylene urea (45%). The accelerated formaldehyde release and arrest of formaldehyde release was promoted by series of three hour incubation in a precision scientific-forced draft oven at 60°C. The formaldehyde-carbonylhydrazide insoluble solid which was formed from commercial DMDHEU resin was separated by use of an Automatic-servale super speed centrifuge, type SS-3, at 15,000 RPM. The alternate incubation and centrifugation was carried out

without further addition of carbonylhydrazide for seven times. The modified DMDHEU-M was then diluted and applied on cotton by pad-dry-cure method. Free formaldehyde was determined by the A.A.T.C.C. sealed jar method 112-1975 with colour developed in chromotropic acid. Tests were also conducted, treating cotton with 10 percent DMDHEU with one percent carbonylhydrazide directly to the pad bath. It was reported that free formaldehyde content in both carbonylhydrazide applications was reduced to 243 PPM by incubation and centrifugation compared to 1,044 PPM associated with conventional finish. It was further reported that free formaldehyde associated with a finish obtained with the modified resin can be further lowered if 0.2 or 0.5 percent carbonylhydrazide is added to the pad bath.

Recently, Hunsucker *et al.* (18) studied the effect of alkyl nitro alcohol in combination with dimethylol dihydroxy ethylene urea (DMDHEU) on formaldehyde release properties. The alkyl nitro alcohol was added directly to the pad bath. The catalyst used, with a buffered and non-buffered DMDHEU, were 'hot' magnesium chloride and zinc nitrate. Substantial (35 to 59%) lowering of formaldehyde was observed in all formulations, however, lower level of formaldehyde was achieved with zinc nitrate catalyst in both buffered and non-buffered systems. The durable press properties of the fabric treated not significantly different. There was no increased discoloration on the fabric. The nitro alcohol used in the formulation is non-sensitizing and mutagenic.