STUDIES ON RESIN FINISHING OF CELLULOSIC FABRIC

Thesis Presented to Ahmadu Bello University for Partial Fulfillment of the degree of

MASTER OF SCIENCE (POLYMER SCIENCE AND TECHNOLOGY)

BY

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DEDICATION

This project is dedicated to my wife, Lucy, and my children, Ngita, Hirra, Sajo, and Sarah for their patience and understanding.

ACKNOWLEDGEMENTS

I wish to extend my sincere thanks to Dr. R.T. Shet for his advice and comments in spite of heavy commitments in other directions.

2. I am also grateful to Professor U.D. Gomwalk for providing me with wonderful learning experiences without which this work could not have started.

3. I am also thankful to Arewa Textiles for providing me with the fabric with which I worked and to Gongola State Government I shall remain indebted for sponsoring me on this programme.

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ABSTRACT

The present study deals with the reactions of dimethylol-urea and dimethyloldihydroxy ethylene urea (ARK NO) with standard cotton cellulose under various drying conditions, pad-bath pH, curing temperatures, swelling agents, deposited polymers and added eleotrolyte.

It has been found that:

(a) Drying at room temperature and at 105^{o}C produce fabrics with identical crease recovery angles but the resin add-on is higher with fabric dried at higher temperature.

(b) Curing at 140^{o}C for 6 minutes is as effective as curing at 160^{0}C for 3 minutes using HC1 catalyst,

(c) Compared with magnesium chloride and zinc chloride, sodium hydroxide preswelling produces fabrics with higher crease recovery angles and moisture regain.

(d) Where pad-bath pH is high, the efficiency of the latent acid catalyst is impaired.

(e) Fabrics treated in 10% sodium hydroxide have fairly good tensile strength, crease recovery angles, and moisture regain.

(f) Added electrolyte in the pad-bath facilitates high resin add-on,

(g) Polymer deposition produces fabrics of low moisture regain but high recovery angles.

CHAPTER 1

INTRODUCTION

1.1 The first commercially useful crease proofing process was developed about 50 years ago (1) and based on water-soluble methylol urea compositions. Since then, extensive effort has been directed towards the elucidation of an ideal crease - proofing agent having the following properties: water soluble for ease of application, non-toxic, easily curable, non-chlorine retentive, durable to extremes of washing, minimum reduction of tensile strength or abrasion resistance, produces both wet and dry crease recovery; and of course economical.

1.2 The emergence of man-made fibres has posed the greatest challenge to cotton. Table 1.1 below compares some properties of cotton with those of other common fibres.

Table 1.1: Properties of cotton compared with other major fibres

Properties	Cotton	Wool	Viscose Rayon	Nylon	Polyester
Abrasion resistance	good	fair	fair	excellent	good
Moisture regain at 65% r.h and 20°C	8½%	13½%	11%	4½%	1%
Drapability	fair	good	good	good	fair
Clasticity at 20 C, 65% R.H.					
% Elongation at break	3 - 10	20 - 40	15 - 30	20 - 40	19 - 23
% recovery	75 - 45	99 - 65	82 - 30	100	97 - 80
from % strain	2 - 5	2 - 20	2 - 20	8	2 - 8
Hand	good	good	good	fair	fair
Pilling resistance	good	fair	good	poor	bad
Resilience	poor	good	poor	good	Excellent
Strength (g/denier)	3 - 5	0.8-2	0.7-6	2.5-7.5	2.5-9.5
Strength loss when wet (approx. %)	+ 10	20%	30-50%	15%	0

It is obvious that for cotton to possess universal applicability and maintain its present consumption level in textile industries, research work must be directed towards improving its resiliency and elasticity while maintaining its toughness, absorbancy and hand.

1.3 In the textile industry, several techniques are applied in an attempt to improve the resiliency of cotton. Such techniques include: yarn construction, blending cotton with other fibres having better resiliency and resin treatments. Resin treatment of cellulosic fabrics can improve either dry crease recovery, (DCR), wet crease recovery (WCR) or both. Cellulosic fabrics thus treated, however, suffer from loss in mechanical properties such as tensile strength, tear strength, and abrasion resistance.

1.4 Researches have therefore been directed towards minimizing this loss in mechanical properties. Some of the important areas of research include:

(i) use of new catalysts such as "phase separation" and "mixed catalysts".

(ii) use of different crosslinking agents and variation" of length of cross-links.

(iii) internal plasticization of the cellulose fibrillar structure.

(iv) external plasticization or polymer deposition into the cellulosic fibrils.

(v) Swelling treatment prior to crosslinking.

1.5 The emergence of "phase separation catalyst" (13) has led to an insight into the role of group II metal salts being used as catalyst in crosslinking cellulose with resin. Such catalysts, e.g. calcium hydrogen malonate, zinc hydrogen tartarate, and magnesium dihydrogen phosphate require high temperature when used. In their work, (2) Kraretz et al reported that a mixed catalysts containing magnesium chloride and sodium fluoborate facilitates the crosslinking of cotton cellulose with formaldehyde. Compared with formaldehyde crosslinking process, the dual catalyst system permits operating at lower temperature, shorter curing time and lower concentration of formaldehyde. They observe that the magnesium cation is unique in the dual catalyst system, since other divalent cations e.g. barium and zinc do not act synergistically with fluoborate.

1.6 Crosslinking cotton through graft polymerization has been reported by Sharma and Daruwala (3). These workers grafted fabric samples with binary and ternary mixtures of selected vinyl monomers along with acrylamide using ammonium nitrate as catalyst. In general, satisfactory retention of breaking and tear strength and improved resistance to abrasion was observed. On crosslinking the above grafted celluloses through N-methylol crosslinking agent, improvement in wrinkle recovery noted but accompanied by usual losses in strength and abrasion resistance.

However, when tenary mixtures were grafted at high add-on and crosslinked, a fair retention of mechanical properties was achieved.

1.7 Happer and coworkers (4) have examined the resulting mechnical properties of yarns and fabric treated with polymers of various glass-transition temperatures. Their finding showed that although many polymers were not chemically bound to the cellulose, they were durable as indicated by the relative performance of improvement in crease recovery. They also observed that polymer treatment of yarns improve yarn breaking strength significantly but the overall strength improvement is decreased when yarns are woven into fabric and then crosslinked.

1.8 Evidence of seperate origin of strength and crease resistance effects in conventional crosslinking treatments for cotton has been suggested by Murphy and Coworkers (5). Since strength losses during crosslinking can be varied or nearly eliminated without changing wrinkle resistance obtained, strength losses and crease recovery are evidently produced by separate and in some cases independent cross-link mechanisms. The observations of these workers suggest that crease recovery arises from more elementary structural units .. such as crosslinked micro fibrils where tensioning has little effect.

1.9 A concept was presented by Gaghardi and coworker for achieving major improvements in tensile strength, elongation, tear strength, toughness, abrasion resistance and crease resistance cotton fabrics (6). This concept code-named SSX, involved swelling of cotton fabric to increase sites for chemical reaction, introduction of bulky plasticizing side groups and finally crosslinking the distended polymer network to achieve more uniformly placed crosslinks than is possible in existing methods. It was also observed that when crosslinking swellable substituted cellulose much less strength and toughness reduction was produced than was normally obtained in unmodified cotton cellulose.

1.10 Pandley and Nair (7) have reviewed inter-and intra-crystalline swelling of cotton in phosphoric acid. They have discussed the effect of swelling treatment on fibre strength, elongation and other mechanical properties. It is interesting to note that the inter - and intra - crystalline swelling of cotton depends on temperature, concentration of swelling agent, and other factors.

1.11 In their studies, Rowland and coworkers considered the effects upon morphology and physical performance that result from conventional pad - dry - cure crosslinking, crosslinking the fibre in swollen state, simple substitution and polymer deposition (8). They conclude that the development of

resilience may be achieved with conventional cotton fabric and N - methylol reagent through process in which the reagent penetrates through the less accessible regions of the fibre and develope network polymeric crosslinkages.

1.12 In an attempt to minimize losses in strength and abrasion resistance of resin treated cotton fabrics, several other processes have been developed (1, 9,). Importance is attached to better diffusion and uniform distribution of crosslinking molecules in the fibre structure. These processes include: wet fixation, mild cure, steam cure and polyset (10, 11, 12, 13, 2, 14). Fabrics treated by the wet fixation process show considerable penetration and uniform distribution of the crosslinking molecules in the fibre (15). Deep penetration and uniform distribution of the crosslinking agent is attributed to easy diffusion into the swollen structure of cellulose fibres.

1.13 The mechanics of penetration and fixation of crosslinking molecules in cotton fibres is explained by Hollies (15) on the basis of theory of dyeing which involves four steps: (a) swelling of the fibre by water, (b) adsorption of the crosslinking molecule, (c) penetration of the molecule in the swollen structure and (d) fixation of the molecule. The diffusion and distribution of the crosslinking molecules in the fibres is governed by colligative and adsorption properties of the molecules.

The crosslinking reaction itself is governed by the following factors (9): (i) structural features of the crosslinking agent (ii) size, shape, stability in solution and affinity of the crosslinking agent and (iii) the nature, concentration, and distribution of the crosslinking agent in the bulk and in the substrate phase.

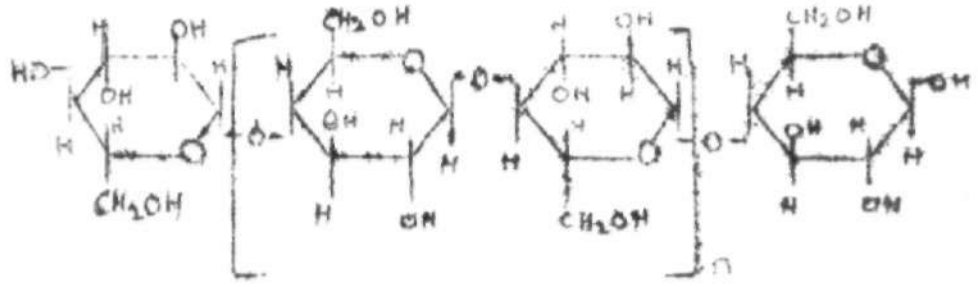
CHAPTER 2

2. Theory of Resin Treatment

2.1 The Structure of Cotton Cellulose

Cellulose is a chain of anhydroglucose rings joined by 1:4 glucosidic linkages but the β - glucose residues are turned over alternately so that the primary alcoholic group in the 6 - position is first on one side of the chain and then on the other.

The length of the chain molecule is considerable and in native cellulose it may be 5000 to 10,000 glucose units but in regenerated



cellulose (viscose) the degree of polymerization may lie between 200 and 700.

The cotton cellulose molecules arrange themselves into regions of lateral order called crystallites and in a less ordered array called amorphous regions.

2.2 Mechanism of resin formation (DMU)

It is of interest to mension the mechanism of dimethyloluurea (DMU) formation. The reaction of compounds containing NH-groups (e.g. urea) with carbonyl compounds (e.g. formaldehyde) are equilibrium reactions.

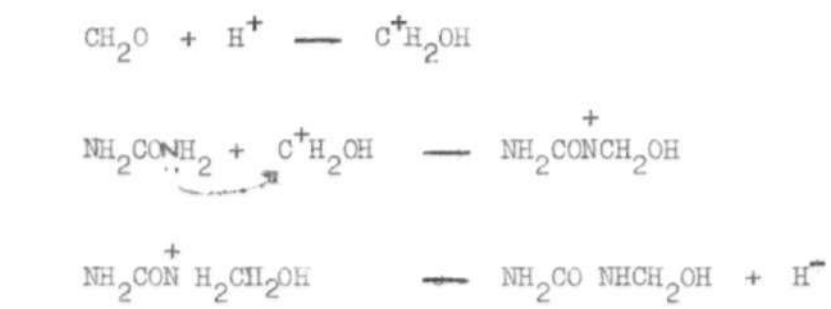
Under basic condition, the mechanism probably involves the abstraction of a proton from the urea (16, 17, 18).







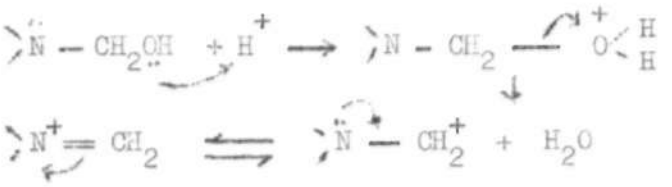
In acid solution the formaldehyde is probably protonated, and the carbonium ion that is formed can then react more easily with the urea.



The reactivity of these N - methylol compounds is due to the nitrogen atom in the α - position, which facilitates condensation reactions with compounds containing acidic hydrogen, e.g. hydroxyl group on cellulose or with NH-group of urea itself.

Under acid condition DMU reactivity is easier by the fact that only water which has little energy, has to be eliminated instead

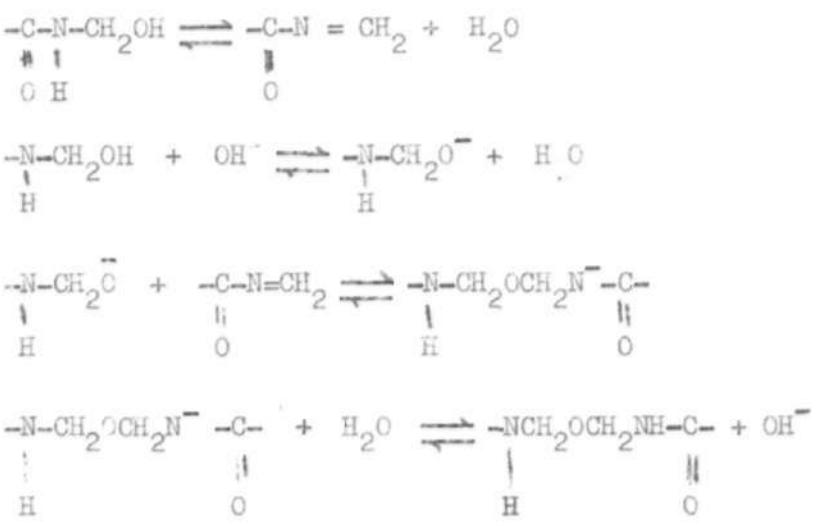
of the hydroxyl ion that is eliminated under basic condition.



The resonance stabilized imonium - carbonium ion plays a decisive part in the reaction scheme. It then reacts with acidic hydrogen.



Under basic conditions the following mechanism of condensation has been suggested (25).



2.3 Resin reactions on cellulose

The condensation reaction on cellulose is normally carried out under acidic condition and it is generally accepted that the final resin contains methylene bridges and other products (19). When a

resin treated fabric is subjected to curing at 150°c for 4 minutes, polymerization and crosslinking occur in a deswollen state and the following reaction takes place (9).

a) Decomposition of the metal salt ; catalyst

$$2\ MgCl_2 6H_2O \longrightarrow Mg_2OCl_2 + 5H_2O + 2HCl$$

b) Protonation of the crosslinking molecules

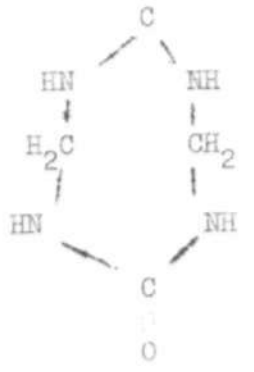
$$RCONHCH\ OH + H^+ \longrightarrow RCONH\ \overset{+}{C}H_2 + H_2O$$

c) Crosslinking reaction

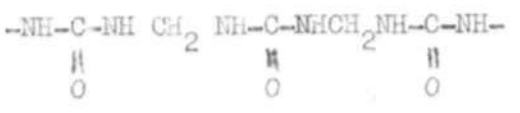
$$RCONH\ \overset{+}{C}H_2 + CellOH \longrightarrow RCONH\ CH_2O\ Cell$$

Other reaction products that are possible include (19):

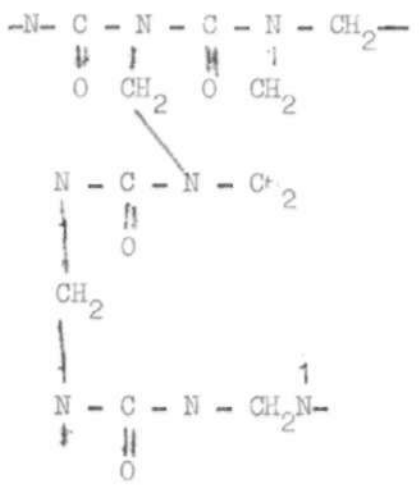
a) Cyclic polymers



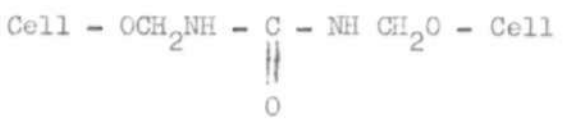
b) Linear polymers



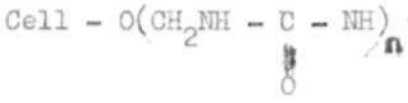
c) Crosslinked polymers



d) Monomeric cellulose crosslinkages



e) Linear polyner crosslinked to cellulose:



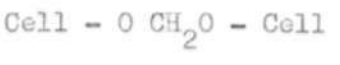
f) Crosslinked polymer also crosslinked to cellulose (see type c):

g) Linear polymer linked to cellulose at one end only:



h) Crosslinked polymer linked to cellulose at one end only (see type c):

i) Methylene crosslinks between cellulose molecules:



j) Polyoxymethylene crosslinks between cellulose

Cell - O $(CH_2O)_n$ - Cell

k) Polyoxymethylene chains linked to cellulose at one end only

Cell - O $(CH_2O)_n$ CH_2OH

l) Oxymethylene polyners

$HOCH_2(O\ CH_2)_n\ OCH_2OH$

The main reaction products are types (b)through (i)

2.4 Effects of swelling on penetration

It has already been pointed out that the crystalline areas of the cotton fibre are not accessible to resin molecules. Swelling action on cellulosic fabric is an important technique that opens the fibres and hence allows uniform distribution of crosslinks in the fibrillar structure. At low concentration of swelling agents, the swelling agents penetrate between microstructural units, but at high concentrations they penetrate into crystalline elementary fibrils by breaking hydrogen bonds between cellulose chains (22). When swelling agent is removed, hydrogen bonds are reformed but permanent changes in morphology and fine structure are effected.

In cotton, its strength is derived from the crystallites while flexibility and extensibility are determined by the amorphous regions. The amorphous regions act as areas in which slippage can occur, allowing transfer and relief of stress. However, crosslinking in these regions prevents such slippage and results in a less perfect

distribution of the applied stress, leading to localized stress and consequently early failure.

Rayon on the other hand has an intrinsically weak, less ordered fine structure, The molecular chain is much shorter and easily torn apart. Insertion of crosslinks into such a system has the effect of increasing the cohesiveness of the whole.

2.5 Damage due to retained chlorine

Conventional finishes based on dimethylolurea contained NH-groups that could form a chloramine when the treated fabric was exposed to hypochlorite bleaching:

$$-NH- + HOCl \longrightarrow -NCl- + H_2O$$

With urea formaldehyde resins, the chloramine itself is colourless, but decomposition occurs on subsequent ironing of the fabric, with formation of hydrochloric acid and nascent oxygen: (see eqn. below). These conditions result in scorching of the fabric and chemical degradation of the cellulose: On the other hand, DMDHEU has no -NH- group and is therefore free from chlorine retention.

$$-NCl- + H_2O \longrightarrow -NH- + HCl + (O)$$

CHAPTER 3

Scope of Investigation

In recent years, cotton has suffered an unprecedented challenges from man-made fibres. Housewives prefer fabrics with reduced labour in home laundering. The cost of labour on commercial laundering has risen. The general taste of fabrics in the market is for an easy wear as well as an easy care fabrics. The man-made fibres respond better to modern taste.

Attempts have been made to improve the resiliency of cotton by resin treatments involving the following techniques: pre-swelling treatments, use of phase separation catalysts, mixed catalysts, and plasticization.

The resin treated fabrics suffer tremendously from loss of tensile strength and abrasion resistance. It has been suggested that tensile strength losses are partly due to the embrittlement of the cellulose molecules caused by crosslinking of cellulose chains and partly due to hydrolytic degradation of cellulose.

The present investigation is aimed at understanding the causes for strength loss at various stages of resin treatment of cellulosic fabrics. The effect of drying and curing temperatures on crease recovery and tensile strength of the resin treated fabric were examined. The effects of swelling and polymer deposition prior to resin treatment of the cotton fabric were also . . investigated.

CHAPTER 4

4. EXPERIMENTAL

4.1 Fabric description and purification

The cotton fabric was obtained from Arewa Textile Ltd., Kaduna in a scoured, bleached and mercerized form. It has 20 picks by 40 ends per centimeter. It was further purified by boiling it for 30 minutes in 0.01% sodium carbonate solution and finally washing it three times in warm water, and dried in air. The fabric so prepared is refered to as standard cellulose.

4.2 Swelling treatments

Various swelling agents were used: sodium hydroxide, zinc chloride and magnesium chloride. The concentrations of the swelling agents and the methods of application were stated in appropriate sections.

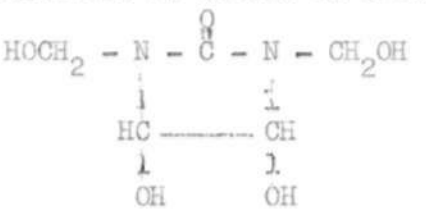
200 ml of swelling agent were applied to each sample (1:15 fabric to liquor ratio) and the wet pick-up adjusted to 70%.

4.3 Resin preparation of dimethylolurea (DMU)

The DMU was prepared by mixing sixty parts of urea (1 mole) and 170.3 parts of 37% formaldehyde (2 mole). The mixture was left to react for 15 hours at 28°C. The pH of 7 - 8 was maintained by adding sodium dihydrogen phosphate. The resulting dense precipitate was filtered, washed with absolute alcohol and vacuum dried. The equation of the reaction is:



The dimethyloldihydroxy ethylene urea (DMDNEU) was obtained from Hoeschst Nigeria Ltd. under the commercial name "ARK NG". The structure of DMDNEU is shown below:-



4.4 Resin finishing of standard cellulose

10% resin solution was prepared in water with the following additives: 10% catalyst (based on weight of resin) and 1% surface active agent — "Teepol" (also based on weight of resin). 150 ml of resin mixture were used in padding each fabric sample - 17 cm x 44 cm (warp x weft) and weighing about 15 g (without the 70% pickup after swelling treatments). The resin treated fabric was adjusted to 100% pick-up, dried and cured. The cured fabric was washed in 300 ml of 0.01% soda ash containing 0.01% Teepol at 50°C and warm water thrice before drying in air. The soda ash washing was done to remove surface resins that would not contribute in improving the fabric resiliency.

The composition of padding bath, drying and curing conditions are shown under appropriate tables.

The catalysts used include zinc nitrate, magnesium nitrate and dilute hydrochloric acid.

The dried resin-treated fabric was conditioned for 48 hours at 65% r.h and 20°C. The conditioned fabric was used for the following tests or determinations: resin estimation, moisture regain, crease recovery angles (wet and dry) and breaking load.

4.5 Resin estimation from fabric

The method of determining the resing add-on is that recommended by Technical Committee 'D' of the Textile Institute (23). Resins were removed together with acid - soluble substances which may be present either in the finish or in the fibre. The total loss of mass was assumed to represent the amount of resin finish. A mass of test specimen of approximately 2g and a moisture specimen of 1g were accurately determined. The test specimen was placed in 500 ml round bottomed flask with standard joint socket B24, 200 ml of 0.02N HCl were added and boiled under reflux for one hour. The liquid was decanted through crucible of porosity 2, the residue washed in 100 ml water at 80°C twice and once in 100 ml of 0.1% sodium bicarbonate solution. The specimen was again washed with 100 ml water at 80°C. All washings were filtered through crucible. The specimen was thentransfered to the crucible and again washed with 100 ml water at 80°C. Each wash was allowed to stand for 2 minutes before applying vacuum. The moisture specimen was dried in a tared weighing bottle at the same time as the crucible containing the residue at 105 ± 2°C to constant weights, after

cooling them in dessicator.

The loss of mass was expressed as a percentage according to the equation:

$$\text{Loss of mass } (\%) = 100 \left(\frac{W_1 M_2}{W_2 M_1} - 1 \right)$$

Where W_1 = mass of test specimen before extraction

W_2 = mass of test speciment after extraction and oven dried

M_1 = mass of moisture specimen

M_2 = mass of moisture speciment after oven drying

4.6 Measurement of moisture regain

The moisture regain of each resin treated sample was determined (7) by conditioning a specimen of about 1g for 48 hours at 20°C and 65% r.h, over-drying the conditioned specimen at 105°C to a constant weight and calculating the regain from the expression:

$$\text{Moisture regain } (\%) = \frac{A - B}{B} \times 100$$

Where A = conditioned mass at 65% r.h. and 20°C

B = dry mass of specimen alter oven-drying at 105°C

4.7 Crease recovery angle (CRA) measurements

The method described below (23) is recommended by International Organization for Standarzation (I.S.O.) replacing earlier methods in use.(24) Rectangular specimen, 5.0 x 2.5 cm were cut from the sample: 20 in warp direction and 20 in weft direction. The

specimen were taken not less than 50mm from the selvedges. Creased, wrinkled, bent or deformed parts of the sample were also avoided. The cutting of weft and warp specimens must be distributed all over the sample. The specimen were conditioned at 20°C and 65% r.h for 48 hours, after which the test specimen was folded and maintained in this state for 5 minutes under a load of 2 kg. The creasing load was then removed, the specimen was allowed to recover for a period of 5 minutes and the dry crease recovery angle (DRA) measured using Shirley crease recovery Tester. The determination was done for ten warp specimen and ten weft specimen.

The experiment was repeated to determine the wet crease recovery angles (WRA) for ten warp and ten weft specimen soaked in distilled water for five minutes.

4.8 Measurement of breaking load

Each specimen was 25 mm by 100 mm gauge length. Ten specimen were tested on each fabric sample. The fabric strip was mounted on an Instron machine at constant rate of extension with gears at 100 mm/min and 200 mm/min chart speed. A load cell of 0 to 50 kg was used. The breaking load of each of the ten specimen were recorded on the Instron graph and the average calculated. The stress at break was calculated from the expression below:

$$\text{Breaking stress} = \frac{\text{Force at break}}{\text{Cross-sectional area}}$$

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Effect of varying the drying conditions of the resin padded fabric

It was intended to see how the even distribution of resin inside the fabric could be affected by drying temperature. The pad bath pH of 1 was made by addition of dilute HCl which is an effective curing catalyst at that concentration.

The standard cellulosic fabric of 44cm x 17cm was padded in 10% DMDHEU containing 0.1% Teepol (surface active agent) and the bath adjusted to pH. 1 by dilute HCl. The fabric samples were dried at 100% pick-up under the following conditions: room temperature ($25^{\circ}C$), $75^{\circ}C$ and $105^{\circ}C$ to the same moisture content. The results are tabulated under Table 5.1. The cured fabric had average thickness of 3.1×10^{-4}cm.

Table 5.1 shows high crease recovery angles, over 60% loss of strength, high resin add-on and more than 2% loss of moisture regain.

It is observed that the crease recovery angles are not affected by drying conditions. There is, however, a slight increase in resin add-on with increase in drying temperature. This observation is consistent with the fact that two competative reactions simultaneously take place: crosslinking reaction and condensation reaction. The higher, the drying temperature, the

Table 5.1 Effect of drying temperature on resin treated fabric

Drying Temperature	DCR (W + F)°	WCR (W + F)°	Breaking Load kg	Breaking Stress $x10^7 N/_{M^2}$	Resin Add-on (%)	Moisture Regain (%)
Room temp. (25°C)	265	255	10.5	1.30	5.69	4.75
75°C	270	256	10.2	1.29	5.93	4.70
105°C	265	255	10.2	1.29	6.33	4.70
Untreated	102	99	36.2	4.58	-	7.03

Table 5.2 The effects of curing at different conditions

Curing temperature	DCR (W + F)°	WCR (W + F)°	Breaking Load kg	Breaking Stress $x10^7 N/_{m^2}$	Resin Add-on %	Moisture Regain %
110°C for 10 minutes	160	155	22.5	2.84	3.10	5.93
130°C for 8 mins.	218	224	11.5	1.44	4.86	5.41
140 C for 6 mins.	240	235	10.5	1.33	5.56	5.02
150°C for 4 mins.	265	245	10.2	1.29	6.33	4.70
160°C for 3 mins.	265	254	10.2	1.29	6.34	4.76
Untreated	102	99	36.2	4.58	-	7.03

more favourable the condensation reaction. Thus, the higher resin add-on, is not followed by more loss of tensile strength or higher recovery angles. Drying at low temperature may favour more even diffusion of resin molecules into the pores of the cellulose (9). The moisture regains are comparable for the three temperatures.

5.2 The effects of temperature of curing

It was intended to observe the optimum curing temperature with the resulting fabric having a good balance of mechanical properties.

The standard fabric samples (17cm x 44 cm) were padded in a pad-bath of the same mixture as under paragraph 5.1, dried at 105°C for 8 minutes and cured under the conditions stated below. The average thickness of each fabric was 3.1×10^{-4}m. The results of measurements are tabulated under Table 5.2.

It is observed that no effective curing is done below 140°C and the curing at 140°C for 6 minutes is almost as effective as that at 160°C for 3 minutes. The resin add-on increases with increasing temperature while the moisture regain follows an opposite trend.

The poor resin add-on below 140°C is due to the incomplete condensation and crosslinking reactions due to the low temperature. The loss in moisture regain is expected as more cellulose hydroxyl

groups are crosslinked to the resin molecule at higher temperature. The above observations are in agreement with that of Madan and coworkers (26) who observed that a curing temperature of 140°C for 4 minutes is as effective as 160°C for 3 minutes. Both drying and curing conditions are essential steps to obtain high crease recovery angles.

5.3 Effect of Pad bath pH

To determine the effect of pH of the pad bath on the resulting fabric mechanical properties, the fabric was padded in pad baths of various hydrogen ion concentration.

The standard fabric was padded in resin solution as under paragraph 5.1 but the pH was varied from 1 to 4. At 100% resin pick-up the fabric samples were dried at 105°C for 4 minutes. The effects of pad bath pH are tabulated under Table 5.3.

The crease recovery angles decrease with increasing pH while the breaking load increases with increasing pH. There is also an increase in moisture regain consistent with decrease in resin add-on with increasing pH. The decrease in crease recovery angles from pH 2 to 3 is rather sharp, and the decrease in add-ons is only marginal.

The decrease in add-ons are small when compared with the fall of crease recovery angles as pH increases. This is due to the fact that the condensation reaction is more favoured at

Table 5.3 Effect of pad bath pH on fabric mechanical property

Bath pH	DCR (W + F)°	WCR (W + F)°	Breaking Load (kg)	Breaking Stress $\times 10^7 N/m^2$	Resin Add-on (%)	Moisture Regain (%)
1	265	245	10.2	1.29	5.33	4.70
2	243	232	12.0	1.52	5.50	4.75
3	225	204	18.0	2.27	5.42	5.13
4	215	204	19.0	2.40	5.30	5.15

high pH than at low pH whereas at low pH the crosslinking reaction may be more dominant. The increase in moisture regain from pH 1 to pH 4 may be due to the increase in number of free hydroxyl groups on the cellulose molecule that have not participated in crosslinking reaction.

These observations are consistent with earlier work by Madan and coworkers (9). They observed that above pH 2.5 there is a rapid fall of crease recovery angles and at pH 2.5 an optimum balance of crease recovery and strength losses are obtained. The poor tensile strength at pH 1 compared with that of pH 4 may be due to the hydrolytic degradation of the acid catalyst.

It is reported that cotton assumes a zero charge at pH 2.8 (20, 21). It is negative above this pH and positive at pH lower than 2.8. At the initial stage of curing, the thermodynamics of the system shall favour condensation polymerization of the resin rather than crosslinking. When the magnesium chloride must have released adequate H^+ ions to lower the pH below 2.8 the crosslinking reaction takes off (for $MgCl_2$ catalyst).

5.4 The effects of preswelling treatments

Swelling agents do open the cellulose microstructure so that resin molecules are distributed uniformly inside the cellulose pores. On curing, the resin treated fabric should have more favourable mechanical properties.

The standard fabric of 17cm x 44cm was swollen in 10% aqueous solutions: sodium hydoxide, magnesium chloride or zinc chloride for 10 minutes. Where sodium hydroxide was used as swelling agent, the swollen fabric was washed twice in fifteen times its weight of water and finally in 150 ml of 0.1% acetic acid. The fabric was adjusted to 70% pick-up before treatment in mixture of 10% DMDHEU, 1% $MgCl_2$ catalyst 0.1% surface active agent (Teepol), dried and cured as under paragraph 5.1. The swelling effects are shown under Table 5.4.

It is observed that the crease recovery angles are higher for the swollen fabrics than that of the unswollen fabric, whereas the breaking loads and the resin add-ons are comparable. On treatment with a swelling agent there is a gain of 1% in moisture regain over unswollen fabric. The HCl-cured fabric has poor moisture regain but much higher crease recovery angles than the fabrics cured with magnesium chloride.

The slight increase in moisture regain is due to decrystallizing action of the swelling agent on cotton microstructure. The swelling action is sufficient to break the secondary forces and thus open the cellulose crystallites for the resin to penetrate (27). The regions which are normally inaccessible now become accessible to water molecules even after the curing treatment via the free hydroxyl groups on the anhydroglucose units.

Table 5.4 The effects of swelling agents on fabric

Swelling Agent	DCR (W + F)°	WCR (W + F)°	Breaking Load (kg)	Resin Add-on (%)	Moisture Regain (%)
Sodium Hydroxide	215	224	19.0	4.67	6.17
Zinc Chloride	210	218	19.5	5.19	5.89
Magnesium Chloride	208	214	20.0	5.41	5.71
Unswollen					
- HCl cure	265	245	10.2	6.33	4.70
- $MgCl_2$ cured	200	192	20.5	5.24	5.15



The wet recovery angles are slightly higher than the dry recovery angles. This has earlier been observed by Madan and coworkers (26). The improvement obtained in the WRA is because the initial chemisorption reaction was carried out in the swollen state in the presence of the latent catalyst. The recovery angles of the fabrics cured by $MgCl_2$ are lower than that cured by HCl. This may be due to the fact that the $MgCl_2$ catalyst is not as efficient as the HCl.

5.5 *Effect of residual alkali on curing efficiency*

It was of interest to observe to what extent, the efficiency of the latent acid catalyst was impaired by residual alkali.

The standard fabric (44cm x 17cm) was swollen in 10% sodium hydroxide solution for 10 minutes. The alkali swollen fabric was washed in water to pH 12, pH 9, pH 5 and pH 4, the pick-up adjusted to 70% before padding in 10% DMDHEU as under paragraph 5.4, dried and cured. The effects are under Table 5.5.

It is observed that the crease recovery angles for pH above 5 is poor. The increase in resin add-on with decreasing pH is not reflected in the moisture regain. The breaking load falls more drastic than the moisture regain.

Table 5.5 The effect of residual alkali on resin treated fabric

Washed in water to pH	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
12	125	124	3.54	31.0	6.83
9	160	162	3.83	29.5	6.52
5	215	218	4.49	23.5	6.27
4	215	224	4.67	19.0	6.17

Table 5.6 Effect of NaOH concentration for preswelling treatment

Concentration of NaOH (%)	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
5	202	212	4.56	19.5	5.92
10	215	224	4.67	19.0	6.17
15	212	225	5.04	16.9	5.96
20	210	227	5.47	14.0	5.82

The poor resin add-on above pH 5 washings may be explained by the fact that the hydrogen ion catalyst efficiency is impaired under alkaline condition. The observation confirms that the condensation reaction on cellulose is normally carried out under acidic condition.

5.6 Effect of sodium hydroxyde concentration by swelling treatments) on fabric properties

It has been established that preswelling action affects the properties of resin treated fabric (see section 5.6). The dependence of such properties on concentration of the swelling agent was examined. The swelling agent used is sodium hydroxide. The catalyst used is magnesium chloride, being much milder than hydrochloric acid.

The standard fabrics were swollen in different concentrations of sodium hydroxide for 10 minutes, washed twice in ten times its weight of water and once in 150 ml of 0.1% acetic acid, adjusted to 70% weight pick-up before padding in 10% DMDHEU (as in section 5.4) dried and cured. The results are tabulated under Table 5.6.

It is observed that the crease recovery angles are not improved after the use of 10% NaOH. The resin add-on increases slightly with increase of swelling agent but the reduction in tensile strength is much more dramatic. The moisture regain has not changed appreciably.

It is interesting to note the trend of loss of tensile strength with increasing concentration of swelling agent. It has been observed that 16% (4M) sodium hydroxide exhibits maximum osmotic pressure (28). Since swelling is quite high, it is unlikely that cellulose does extend in a Hookean fashion and that yield point is exceeded at higher concentrations of NaOH. The decrystallization and swelling of cellulose therefore create some internal strains which are not totally eliminated on crosslinking. Hence the fabric shows a decrease in tensile strength with increase in swelling due to sodium hydroxide concentration.

The increase in resin add-on with almost constant crease recovery angles is simply due to polymer deposition which may have contributed only a little to the loss of tensile strength.

5.7 Effect of time of contact of swelling agents and the fabric

It would be recalled, the requirement for good penetration of resin molecules is to open the crystallites of the cellulose with a swelling agent. The required time for such structures to be opened shall depend on concentration of swelling agent as well as time of contact with the cellulose molecules.

In order to observe the effects of time on swelling, two swelling agents were used: magnesium chloride and sodium hydroxide.

Table 5.7. Effect of time of swelling fabric in 10% NaOH solution

Time of Swelling (min)	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
0	200	192	5.24	20.5	5.15
1	205	214	4.25	20.0	5.47
10	215	224	4.67	19.0	6.17
30	214	227	4.80	15.7	6.23

Table 5.8 Effect of time of swelling fabric in 10% $MgCl_2 . 6H_2O$

Time of Swelling (min)	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
0	200	192	5.24	20.5	5.15
10	208	214	5.41	20.0	5.71
30	191	217	5.38	19.5	5.79
60	194	220	5.39	18.5	5.68
600	198	216	5.38	18.5	5.70

The standard fabrics were padded in 10% sodium hydroxide for various times, adjusted to 70% pick-up and after washing as done under paragraph 5.4, and paddled in 10% DMDHEU, dried and cured.

Other samples of the standard fabric were also padded in 10% magnesium chloride for different times, adjusting the wet pick-up to 70%, before padding in 10% DMDHEU, dried and cured. The effects are shown under Tables 5.7 and 5.8.

Under Table 5.7, it is observed that there is a moisture regain of about 1% when swelling time increases from 0 to 30 minutes. The tensile strength falls by up to 25% but the add-on is only slightly increased. The crease recovery angles are slightly increased. The wet recovery angles are higher than the dry recovery angles.

However, under table 5.8, the moisture regain and resin add-on are not appreciably affected. There is a slight fall of breaking load with increasing time of swelling. The wet crease recovery angles are slightly higher than their dry counterparts.

The swelling time in sodium hydroxide affects the tensile strength. The same argument advanced under paragraph 5.6 explaining the loss of tensile strength with increasing concentration may be used here. The time of contact of the fabric with magnesium chloride has only slight effects on the tensile strength.

The higher value of the wet recovery angles is due to the fact that the initial chemisorption was carried out in the swollen state.

5.9 The Effect of electrolyte on the sorption of DMU and AMDHEU

The resin DMU is linear but DMDHEU is of ring structure. The sorption of these resins was observed with the aim of noting if there is structural effects in their sorption with sodium chloride electrolyte using magnesium chloride catalyst. It was also intended to investigate the electrolytic effects of the two resins after having added sodium chloride.

The standard fabrics were swollen in 10% sodium hydroxide for 10 minutes washed twice in water and finally in 0.1% acetic acid. With 70% wet pick-up the fabric was padded in 10% DMU containing 1% magnesium chloride catalyst and 0.1% surface active agent and various concentrations of sodium chloride. The padded fabrics were dried at 100% pick-up for 8 minutes at 105°C and cured at 150°C for 4 minutes. The experiment was repeated with 10% DMDHEU substituting DMU. The effects are tabulated under Tables 5.9 and 5.10.

In the case of DMU, there is a large increase of resin add-on at as low concentration of sodium chloride as 0.01N (or 0.058%) and it stabilizes immediately. In the case of DMDHEU the increase in add-on is not that rapid and it comes

Table 5.9 Effect of NaCl electrolyte on DMU sorption

Amount of NaCl in resin	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
0.00 N	218	229	4.55	20.0	5.05
0.01 N	220	232	6.14	19.5	4.84
0.10 N	225	230	6.30	18.5	4.75
1.00 N	220	234	6.35	18.5	4.75

Table 5.10 Effect of NaCl electrolyte on DMDHEU sorption

Amount of NaCl in resin	DCR (W + F)°	WCR (W + F)°	Resin Add-on (%)	Breaking Load (kg)	Moisture Regain (%)
0.00 N	215	224	4.67	19.0	6.17
0.01 N	220	236	4.70	19.0	6.14
0.10 N	228	234	5.31	18.5	6.21
1.00 N	230	237	5.40	18.0	6.21

to limiting value of 5.40%. The crease recovery angles are slightly increased with both resins. The tensile strength are also slightly affected by the electrolytes in both resins. The DMDHEU treated fabric maintains a better moisture regain than the DMU treated fabric.

The crease recovery angles do not agree with the increase in resin add-on of both Tables 5.9 and 5.10. The explanation to this may be due to a lot of the deposited resin do undergo some condensation polymerization without necessarily getting crosslinked with cellulose hydroxyl groups.

The above observation is in agreement with that of Madan and coworkers (26) who observe effects of chemisorption of DMDHEU in the presence of $MgCl_2$ in the concentration range of 1 - 2 M. They explained this effect in terms of modification of the water structure by the ionic solutes. Dissolved ions are assumed to carry water molecules. The hydrated ion, by virtue of strong electrostatic field, forms an envelope of a molten zone in which there is more orientation disorder than in the hydration zone as well as in bulk water.

When cellulose is immersed in water, the water initially absorbs onto the cellulose surface, forming a monolayer of strongly bound water molecules. The energy of interaction of this water with cellulose is of the order of magnitude as for hydrogen bonding (29). It is thus possible to expect, in a

system containing cellulose, magnesium chloride, (or another electrolyte) water, and crosslinking compound, that the charged magnesium ion probably disturbs the monolayers of water molecules adsorbed on cellulose surface. This disturbance in the adsorbed water molecules will increase with increasing electrolyte concentration and, in effect bring the crosslinking molecules into closer contact with the surface. As a result of it, the activity of surface hydroxyls of cellulose and the hydroxyls of crosslinking agent is accentuated.

Yabani (30), however used electrostatic effects in explaining the increase in resin add-on in the presence of electrolyte. The bleached and mercerized cellulose has some of its hydroxyl groups oxidised to aldehyde groups. In an acid solution, the aldehyde groups on cellulose acquire proton which is resonance stabilized:

$$\text{Cell} - \text{CHO} \xrightarrow{H^+} \text{Cell} - \text{CH} = \overset{+}{\text{O}}\text{H} \longleftrightarrow \text{Cell} - \underset{+}{\text{CH}} - \text{OH}$$

The resin also acquires proton. Thus, a situation is created where both the cellulose and the resin are positively charged. In the absence of counterions the absorption of formaldehyde molecules would be retarded due to electrostatic repulsion. A counterion such as Cl^- ion would surround the positively charged groups in the cellulose and hence shielding them from the approaching $\text{N-CH}_2\text{-}\overset{+}{\text{O}}\text{H}_2$ and thereby facilitating

sorption. The results under Tables 5.9 and 5.10 also agree with this postulate.

The high resin add-on with DMU may be due to the more simple linear structure of DMU (compared with DMDHEU) which facilitates more of it to be diffused into the cellulose pores. The high moisture regain with fabrics treated with DMDHEU may be due to the bulky ring structure of the DMDHEU which renders the cellulose macromolecules to remain decrystallized even after curing treatments.

5.10 Effect of polymer deposition and resin treatment

Polymer additives have been used extensively to improve crease recovery characteristics of cellulosic fabrics.

Two separate treatments were studied: one was to deposit the polymer, dry and cure the fabric; and the other was to deposit the polymer, apply DMDHEU resin, dry and cure the fabric.

The standard fabric 17cm x 44cm was swollen in 10% zinc chloride, padded to 100% pick-up, dried for 5 minutes at 105°C and cured at 150°C for 10 minutes. The polymers used are tabulated with the results under Table 5.11.

Another standard fabric (17cm x 44cm) was swollen in 10% zinc chloride solution and padded to 100% pick-up after when

Table 5.11 Effects of polymer deposition only

Type of polymer on fabric	DCR (W + F)°	WCR (W + F)°	Fabric Thickness x 10^{-4}m	Breaking Load (kg)	Breaking Stress x 10^{7}N/m^{2}	Moisture Regain (%)
Polyethylene glycol	110	109	3.2	38.0	4.66	4.70
Polyvinyl alcohol	107	108	3.5	37.5	4.19	4.74
Polyacrylamide	107	122	3.2	39.5	4.84	5.02
Carboxymethyl cellulose	109	132	3.2	38.0	4.66	4.94
None	102	99	3.1	36.2	4.58	7.03

Table 5.12 Effect of polymer deposition and resinification

DMDHEU resin with polymer on fabric	DCR (W + F)°	WCR (W + F)°	Fabric Thickness x 10^{-4}m	Breaking Load	Breaking Stress x 10^{7}N/m^2	Moisture Regain (%)
DMDHEU only	215	220	3.1	20.5	2.62	5.65
Polyethyleneglycol	228	230	3.2	18.0	2.21	3.81
Polyvinylalcolhol	220	235	3.5	23.0	2.58	4.23
Polyacrylamide	224	230	3.4	17.5	2.02	3.85
Carboxymethyl-cellulose	201	228	3.4	17.5	2.02	4.16
None	102	99	3.1	36.2	4.58	7.03

it was padded in 5% polymer dispersion to 100% pick-up before padding in 150 ml of 10% DMDHEU and 1% zinc nitrate catalyst and 0.1% surfactant to 70% pick-up, dried at 100°C for 5 minutes.and cured at 150°C for 4 minutes. The experiment was repeated for all the polymers under Table 5.12 and the results also shown there.

In Table 5.11, the crease recovery angles and tensile strength are slightly increased. The moisture regain has fallen by more than 2%.

The low moisture regain may be due to the presence of condensed polymer on the cellulose surface and thus shielding the entrance for the moisture. The reasons for the slight increase in crease recovery have been proposed by Rawls and coworkers (31). They concluded that the polymer characteristics necessary for improved crease resistance are high elastic recovery, low glass transition temperature and low permanent set. Differences among these may help explain the relative performance of various classes of polymers.

On the other hand, Table 5.12 shows that the crease recovery angles are high and the tensile strength has fallen for some by about 50%. The moisture regain ... values are also low.

The high recovery angles may be due to the total effects of the resin and polymer. There is a little increase in wet

recovery angles. Detailed relationships among polymer deposition morphology, and performance characteristics are not simple to interpret; the nature of the bulk polymer in the fibre pores or on surfaces, the association of hydrogen bonding of the polymer with cellulose surface and the friction or lubricity conferred to fibre surfaces may be important (8). The low moisture regain is due to the decreased accessibility of the cellulose to moisture by the polymer deposit.

5.11 Conclusion

a) Drying temperature is important and its effect on resin add-on slightly observed. Drying at higher temperatures give higher add-ons without corresponding increase in crease recovery angles.

b) The pad-bath pH determines the electrical nature of the cellulose and at high pH the efficiency of the latent acid catalyst is impaired.

c) Curing at 140°C for a longer time is as effective as curing at 160°C for 3 minutes.

d) Sodium hydroxide of mercerizing strength, 5 to 30% can swell cellulose appreciably. However, for a good balance of mechanical properties, 10% sodium hydroxide is favourable at 10 minutes swelling time.

e) Time of swelling also affects the mechanical properties of the resinified fabric. Swelling time of ten minutes has good balance of properties. The above observation is not apparent when the swelling agent is magnesium chloride.

f) Preswollen resin treated fabric has at least 1% moisture regain over unswollen treated fabric.

g). The presence of electrolyte (e.g. sodium chloride) in the resin facilitates high resing add-ons with slight increase in crease recovery angles. The good moisture regain is not affected by the high add-ons.

h) Polymer deposition and resinification provide fabrics with good crease recovery angle but poor moisture regain.

i) The loss of tensile strength has been observed in all the techniques studied. However, a better retension of tensile strength is achieved by pre-swelling treatments.

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