# RESIN FINISH TO CELLULOSIC FABRICS

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# A C K N O W L E D G E M E N T S

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# A B S T R A C T .

The present study deals with the reactions of formaldehyde, dimethylol urea and two commercial resins, aimethylolethylene urea (ARK NG) and a bis-carboamate derivative (ARK CA) with standard cellulose and various oxycelluloses under varying conditions and the effect of these reactions on the crease recovery and tensile strengths of these celluloses. It has been found that:-

(a) The % add-on of formaldehyde and the other resins to standard and. nitrogen dioxide oxycellulose depend very much on the catalyst used. The efficiency of the catalysts decrease in the order $HCl > MgCl_2.6H_2O > Zn(N0_3)_2.6H_20$ which is related to the acidity of their solutions. It has also been found that divalent metal salts which are generally used as catalysts release hydrogen ions by the binding of the metal ion to the carboxyl groups in cellulose. T he loss in tensile strength is maximum for hydrochloric acid catalyst probably due to hydrolytic degradation.

(b) Oxidation of the cellulose structure with nitrogen dioxide leads to decreases in % add-on of formaldehyde and various other resins. Losses are also observed in

crease recovery angle values and tensile strengths. However, addition of sodium chloride even of as small a concentration as 0.001M to the reaction bath increases the add-on of formaldehyde to both standard and oxycellulose,

(c) Oxidation of the cellulose structure with sodium metaperiodate results in an increase in CRA value even without resin treatment. Higher increase in CRA value is observed when such an oxycellulose was cured at $150^0$ C than when it was "boiled in water. It is thought that cross-1inking occurs through hemiacetal bond formation. Loss in tensile strength is relatively lower than for nitrogen dioxide oxycellulose.

(d) Cross-linking periodate oxycellulose with various resins leads to further increases in CRA values.

(e) Borohydride reduction of periodate oxycellulose produces an increase in resin add-on as would be expected from the increase in available hydroxyl groups. However, decreases in CRA values and tensile strengths were observed.

(f) Most of the above results are interpreted in terms of electrostic forces between positively charged cellulose substrate and similarly charged cross-linking resins.

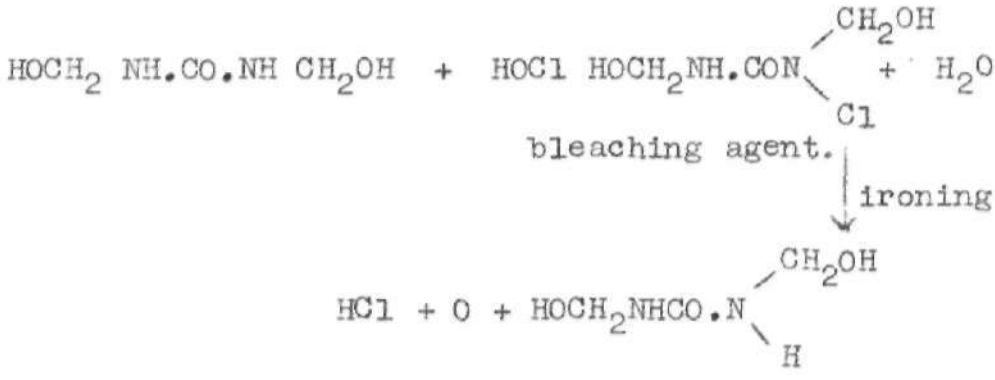
(g) It has also been found that oxidation of the cellulose structure in combination with resin treatments produce fabrics with very high CRA values and accetlble tensile strengths which are also resistant to alkaline degradation. It may be necessary to carry out investigation on a pilot plant scale before any commercial possibilities is exploited.

Chapter 1

# I N T R O D U C T I O N

Native cottons when woven into fabric have a tendency to lose shape and elegance after a single wear and usually do not have good dimensional stability. In an age where smartness and neatness are essential for business and social life and where there is a growing competition from man-made fibres such as nylon, terylene etc. it is natural that attention should be directed to devising ways of obtaining cotton fabrics that combine desired properties with the natural toughness of cotton. The first commercially useful process was perfected by the Tootal Broadhurst Lee Co. in 1932[1]. In this process cotton fabrics were reacted with formaldehyde-urea resin at high temperatures. It was found that these reactions enhanced the ability of cotton fabrics to resist creasing. It was however realized from the onset that crease-proofing of fabrics leads to losses in tensile strength and abrasion resistance. Other problems encountered in these finishing processes is the unpleasant chlorine retention. This problem is common since nitrogeneous resins are used

as finishing agents. Chlorine, usually from bleaching agents and water reacts with primary and secondary amines to form unstable chloroamines. When such chloroamine-containing fabrics are heated as by ironing the fabric, the chloroamines decompose and give off nascent oxygen. This degrading agent can destroy cotton in a single ironing process.




Research efforts have since been directed to improve both dry and wet wrinkle recovery while minimizing the mechanical strength losses. Dry crease recovery is the ability of fabrics to recover from creases in the dry state. This is usually achieved by reacting fabrics with resins at very high temperatures. Wet crease recovery property which allows fabrics to recover from creases in the wet state is achieved by carrying out the process in a swollen collapsed state.

The increase in wet crease recovery is essential for good self-smoothing properties of the fabric in the wet state.

Some articles such as curtains are not exposed to rough usage and therefore it is sufficient if they have good drip-dry properties i.e. good wet wrinkle recovery. An improvement in wet recovery has hardly any serious influence on tensile strength and abrasion resistance.

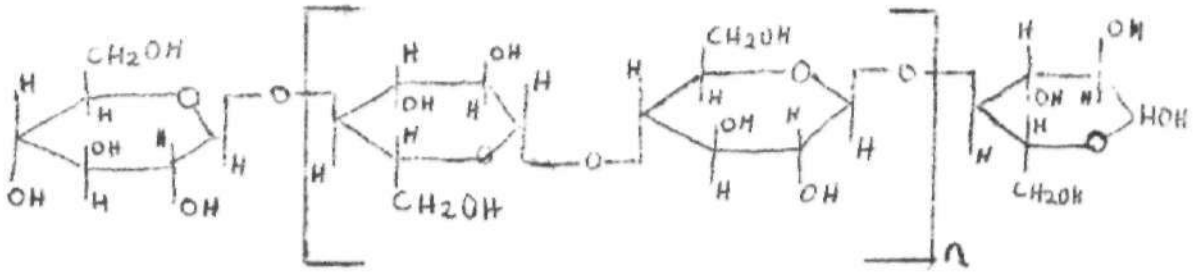
An ideal crease-proofing agent should have the following properties[2]: water-soluble for ease of application, non-toxic, non-chlorine retentive, durable to extremes of washing and produces both wet and dry crease recovery and economically attractive.

Earlier, it was thought that these substances deposit as polymers within the fibre structure thus increasing the crease resistance. It is now recognised that in addition to polymer deposition these resins actually form true chemical reactions with the cellulose chains. This means that the finishing effect obtained would be related to the structure and state of the fabric during and after processing. It is thus appropriate to discuss the structure of Cellulose and the current

theories concerning the finishing process as it relates to the Cellulose Structure.

## 1.2 Structure of Cotton Cellulose

According to concepts generally accepted, cellulose consists of long homogeneous chains of β - D glucose units linked together by 1,4 glycosidic linkage.



There is no evidence that the cellulose structure is branched. The primary hydroxyl group on the sixth carbon atom is most readily available to reagents. The end glucose units are of two types. One contains a hemiacetal group (at the right of the formula) and the other has four hydroxyl groups. The hemiacetal group is a potential aldehyde which can be oxidized to carboxyl group. The anhydroglucose units have a β-configuration, The native cellulose is a family of polysacchrides rather than a single molecular species.

It is a mixture of α-β and γ celluloses, with different proportions of these in different celluloses. α-Cellulose with the highest molecular weight fraction is insoluble after treatment with caustic soda of mercerising strength. The alkali soluble fraction which is reprecipitated on acidification is referred to as β-Cellulose while γ-Cellulose is not precipitated even on acidification.

The macromolecular structure describes the entire polymer molecule or family of molecules in terms of chain length, chain length distribution, chain conformation and chain stiffness. However, the molecular weight and its distribution depends largely on the source, purity of the cellulose and to some extent on the method of determination.

While different samples of cotton cellulose may have the same organochemical structure and the same degree of polymerization yet they may have different physical properties which are due to the differences in the arrangements of the molecules in the fibre substances i.e. due to differences in the degree of crystallinity. Crystallinity is attributed to three dimensional regularity imparted to cellulose by the spatial distribution of the hydroxyl groups which makes

it possible for the chains to associate laterally by hydrogen bonding. As early as 1920 Herzog and Janoke[3] recognised that cellulose gave X-ray patterns. The first unit cell dimensions to be accepted were calculated by Polanyi[4] who postulated a Rhombic Unit Cell with dimensions 7.9 x 8.45 x 10.2Å. A series of investigations by Meyer and coworkers[5] led to the presently accepted monoclinic unit cell with axis a = 8.35Å, b = 10.30Å, C = 7.90Å and angle $\beta = 84^{\circ}$. The unit cell probably belongs to the space group P2 and contains four glucose residues. This structure was confirmed by Gross and Clark[6]. The planes of the glucose units lie in the ab plane and the axis of the cellobiose units are parallel to the b axis of the unit cell. The unit cell is composed of two sets of chains each chain having a two fold screw axis parallel to the b axis of the cell and the set of chains running through the face ac is displaced along the b axis so that one glucose unit occurs in approximately the centre of the cell.

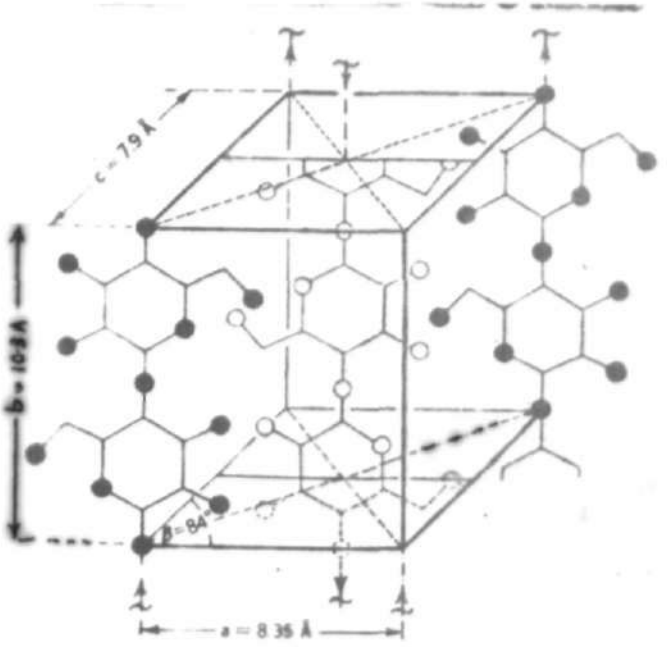



Fig 1 Cellulose model (Meyer and Misch)[6]

The picture which emerges is that cellulosic fibres are composed of long-range order crystalline regions and amosphous regions where the chain molecules are present in random orientation. A gradual transition between the highly ordered regions and the completely disorientated regions with no lines of boundry has been indicated by the results of several investigators[7]. The X-ray patterns of different celluloses depend on the source and history of the samples and at present the following types of X-ray patterns corresponding to

four types of crystal lattice arrangements have been reported. The four crystalline forms of cellulose are designated as cellulose I, II, III and IV.

Table I

| Axis | Cellulose I | Cellulose II | Cellulose III | Cellulose IV |
|---|---|---|---|---|
| a | 8.35 Å | 8.10 | 7.74 | 8.11 |
| b | 10.30 | 10.30 | 10.30 | 10.30 |
| c | 7.90 | 9.10 | 9.90 | 7.90 |
| Angle $\beta$ | 84° | 62° | 58° | 90° |

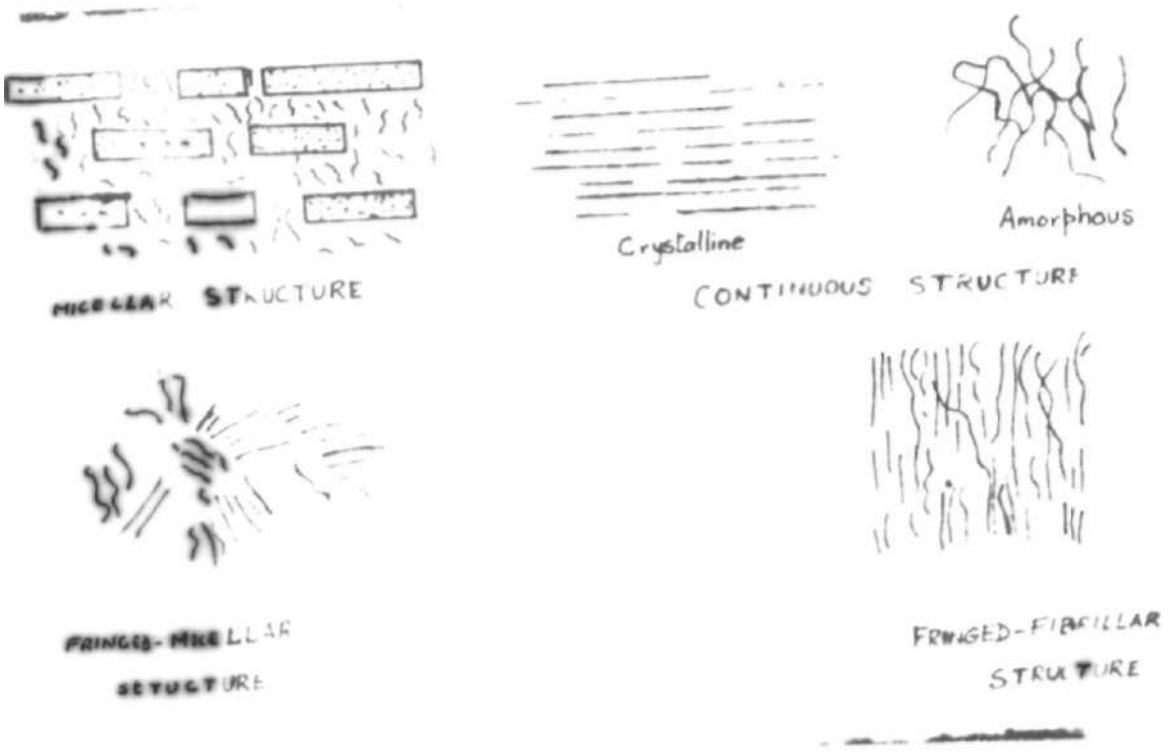
The nature of the crystallites and the manner in which they are built into the fibre constitutes the fine structure discussed below.

## 1.3 Fine Structure

In cellulose fibre the three dimensional Unit Cell arrangement of cellobiose unit is repeated in all directions to build up a crystalline region. A cellulose fibre however is not a single crystal; it is a poly-crystalline aggregate consisting of small crystalline regions separated by amorphous or inter-crystalline regions. The term crystalline is used without connoting any particular size, shape, or nature of the boundaries

between crystalline regions. Many theories have been advanced to explain the nature of the crystallites and the manner in which it is built into the fibre[8,9,10]. The presently accepted theory is the fringed fibrillar concept proposed by Hearl[11]. This regards the crystalline region as continuous fringed fibrils made up of molecules diverging from the fibrils at different positions along their lengths. Thus the molecules diverge from their original fibrils, pass through a non-crystalline region and further on get incorporated into another crystalline fibril. During secondary wall development in cotton, fibrils are deposited in a helical manner with constant helical angle with respect to the length and cross-section of the fibre. The presence of these fibrils has been demonstrated by electron microscope[12]. A light scattering[13] microscopic examination of a highly swollen fibre has also revealed a lamellar arrangement of these fibrils in the secondary wall. The angles of the helix which the fibrils make with the fibre axis is referred to as fibrillar orientation and may vary from 20 - 40°. Though the direction of the helix remains constant in all layers at a given point along the fibre lengths, its sense reverses from 30 - 100 times

along the entire lengths of the fibre and this may lead to the numerous convolutions observed and for the extensibility of cotton.




## 1.4 Structure and Finishing Process

One of the major problems encountered in easy-care finishing of cotton is the loss in mechanical properties such as tensile strength and abrasion resistance.
It is then imperative to understand how the structure of cotton cellulose is linked to the finishing process.
From the point of view of the finishing process, the two

important aspects of sturcture are:

(a) The presence of the hydroxyl groups on each glucose unit in the organochemical structure. These play the central role in the cross-linking process. A bifunctional or multifunctional cellulose reactive agent is usually employed. If the cross-linking agent be represented by X - R - X where X is the cellulose reactive group then the cross-linking step can be represented by the equation:-

$$2Cell\text{-}OH + X - R - X \rightarrow Cell - ORO - Cell + 2XH$$

For formaldehyde treatment under acid conditions, Barker[14] proposed the following mechanism of reaction:

$$HOCH_2OH + H^+ \rightleftharpoons HOCH_2\overset{+}{O}H_2 \quad \ldots\ldots (1)$$

$$HOCH_2\overset{+}{O}H_2 \rightleftharpoons HO\overset{+}{C}H_2 + H_2O \quad \ldots\ldots (2)$$

$$HO\overset{+}{C}H_2 \rightleftharpoons H\overset{+}{O} = CH_2 \quad \ldots\ldots (3)$$

$$Cell\text{-}OH + HO\overset{+}{C}H_2 \rightleftharpoons CellOCH_2OH + H^+ \quad \ldots\ldots (4)$$

$$CellOCH_2OH + H^+ \rightleftharpoons CellOCH_2\overset{+}{O}H_2 \quad \ldots\ldots (5)$$

$$CellOCH_2\overset{+}{O}H_2 \rightleftharpoons CellO\overset{+}{C}H_2 + H_2O \quad \ldots\ldots (6)$$

$$CellO\overset{+}{C}H_2 + Cell\text{-}OH \rightleftharpoons Cell\text{-}OCH_2O - Cell \quad \ldots\ldots (7)$$

The existance of the resonance-stabilized carbonium ion (eq. 3) found in this sequence has made this mechanism

more acceptable than the other one proposed by Parikh[15]. In N-Methylol treatments a similar resonance stabilized intermediate is formed

$$R(CO)\ NR\overset{+}{C}H_2 \rightleftharpoons R(CO)\ \overset{+}{N}R = CH_2$$

It had been shown that the hydroxyl groups on the second and sixth carbon atoms of the glucose units are the most reactive in the cross-linking process

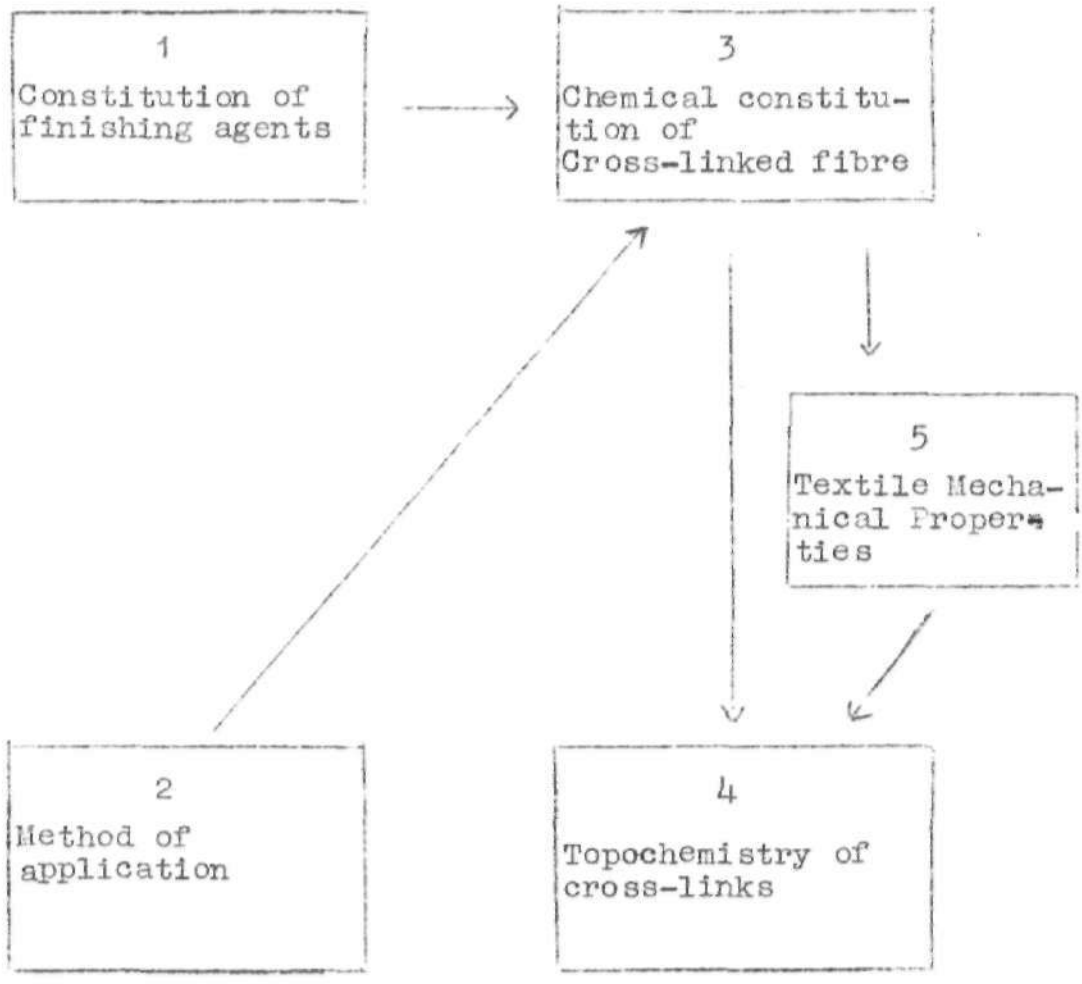
(b) Many properties of cotton fibres especially the mechanical properties e.g. deformation, tenacity and abrasion resistance are due to the fine structure of cellulose. A high degree of fibrillar orientation means high tensile strength and work recovery. The essential feature of the structure of cellulose on which its mechanical properties depend is the net work structure formed by bundles of chain molecules in the non-crystaline regions which link together the crystallites. These crystallites act as "spot welds" and though they contribute to high tensile strength, the characteristic mechanical properties are determined mainly by bond stretching in the non-crystalline regions of cellulose. The relation between orientation and mechanical properties has been analysed mathmetically

and tested experimentally by Herman[16]. The overall but general classification into crystalline and amorphous regions can be used to explain such properties as moisture sorption, dyeing and swelling. From the point of view of the finishing process accessibility of the cellulose structure to the large cross-linking agent molecules is very important. If the cross-linking agents are unable to penetrate uniformly, it will lead to cross-links in only a small region. This destroys flexibility and extensibility of the fibre leading to brittleness and general mechanical strength losses. It is desirable thus to partially open the crystallites by destroying some of the hydrogen bonds so as to achieve a more even distribution of cross-links.

## 2.1 Theories on Cross-linking of Celluloses.

Cross-linking cellulose chain molecules with bi - and poly-functional reagents has become the most important process to impart wash-wear, durable press behaviour to cotton fabrics. It is now generally accepted that the reactions involved in these treatments cause true chemical cross-linking, although there are very few experimental investigations which prove the

chemical nature of these reactions. The block - diagram below shows the areas of research in this field.




An enormous amount of work has been expanded for the improvement of the textile mechanical properties of cotton (block 5) by invention of new chemical reagents and their balanced mixture (block 1) and improvement in

methods of application (block 2). It has only been recently recognised that changes in the textile mechanical properties are not directly related to the methods of application and constitution of the cross-linking agents but that these two factors are linked to other areas of problem. The chemical constitution of the fibre after cross-linking (block 3) and the location of the cross-links within the microscopic and submicroscopic structures of the fibre (block 4). The following problems belong to block 3:

(a) Investigation of the reaction between cross-linking agents and the hydroxyl groups of Cellulose.

(b) determination of the lengths of the cross-links and their effects on the mechanical properties.

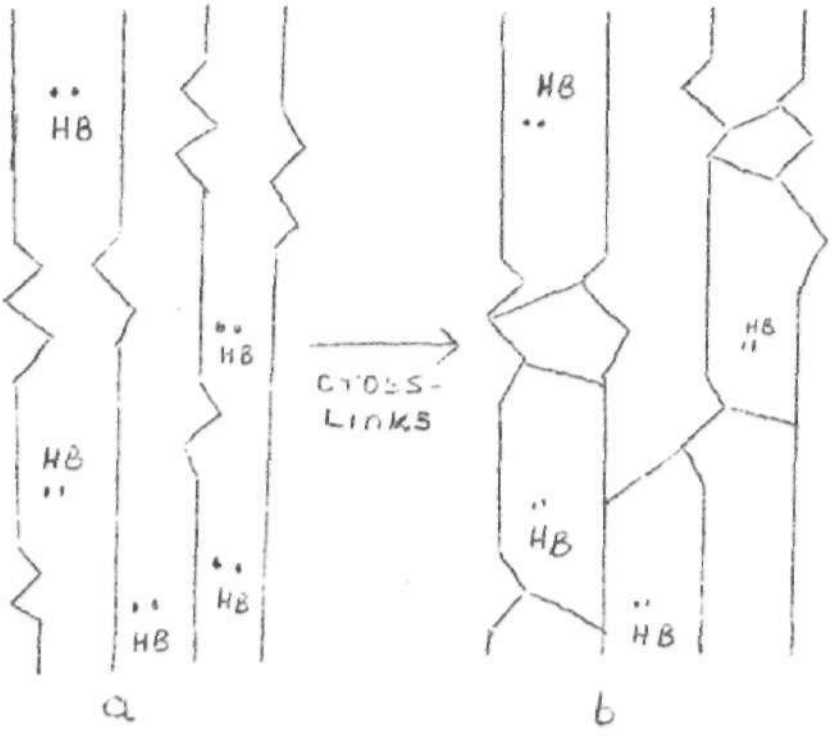
(c) differentiation between grafting and cross-linking and between inter - and intra molecular cross-links.

Intramolecular cross-links between two hydroxyl groups of the same unit belong to block 3 while cross-links between two adjacent or more remote

anhydroglucose units as well as intermolecular reactions are part of the topochemistry of cotton finishing block 4.

It had been shown that the macromolecular structure of cotton can be divided into amorphous and crystalline regions. The crystalline region confers on cotton its toughness while the amorphous region gives it elongation, flexibility, creep and relaxation properties. Because of its greater accessibility most cross-linking occurs in the amorphous region of cellulose.

In the diagram below (a) it is shown that long-chain cellulose molecules are held by strong hydrogen bonds (HB) in certain crystalline regions. There are other regions having no crystallinity. It had been postulated[17] that when chain slippage occurs as in forming wrinkles the structure (a) is incapable of recovering completely to its original state and permanent deformation occurs.




In normal processes of treating cotton with cross-linking agents only about 10% to 15% of cellulose roughly corresponding to the amorphous region is accessible to the reagent. This limited accessibility results in cross-links being concentrated in the flexible region as is shown in (b). While this is desirable for preventing chain slippage and thus producing wrinkle resistance it is on the other hand undesirable for maintaining toughness. Now the original flexible region has become brittle and rigid. Under stress this brittle joint is incapable of distributing an applied load amoung the

various structural elements and this brings about a lowering in tensile strength. This leads to a considerable loss in wear life of the fabric.

In 1963 Chipalkatti and coworkers[18] noted that "the problem of tensile strength and abrasion losses remains unsolved". The same conclusion was reached earlier by Tovey[19] in an exhaustive review of the literature. Gordon and Steele[20] noted that in most rubber-like polymers tensile strength rises, passes through a maximum and then falls as the degree of cross-linking increases. Cotton in their opinion has already passed the point of maximum strength obtainable from cross-linking because of its high degree of crystallinity arising from hydrogen bonding. However, Murphy and coworkers[21] have shown the virtual elimination of break and tear strength losses in easy care and permanent press cotton by cross-linking slack-mercerised cotton fibre partially restretched while in mercerisation alkali . This shows that elements of the cotton fibre which normally undergo strength losses during cross-linking are greatly affected by orientation treatments and are thought to be the helical fibrils which make up the windings of the secondary wall. Tensile strength

losses are thus related to the physico-chemical state of the cellulose.

Gagliardi and Wehner[22] proposed that the problem of tensile strength losses can be solved by introducing bulky side groups and finally cross-linking. By increasing the site available for cross-linking there should result a more even distribution of cross-links in the cellulose net work. Secondly the presence of bulky side groups should provide an internal plasticizing effect and further minimize localized stress accumulation in the fibre. They postulated that it is essential to find a suitable pair of monofunctional and difunctional cellulose reactive and swelling compounds such as R - X and Y - R - Y where X and Y are functional groups that can react with cellulose. In another paper[23], they reported their results on using N-Methylol ethylene urea and increasing amounts of the monofunctional N-methylol acetamide (NMA). Satisfactory results were reported. Meimoun and Parisot[24] proposed a topochemical introduction of a polymer into the fibrillar structure of cellulose. The polymer must be elastic, its modulus of elasticity must be less than the initial modulus of the fibre in order not to alter the feel of the fabric. It must not

penetrate the macromolecular structure, and it should preferably be linked to the surface of the elements between which it is able to penetrate. Among the polymers tried, butadiene and isoprene gave satisfactory results. Other works in this field have also been reported[25, 26, 27, 28, 29, 30].

## 2.3 The Role of Catalysts.

In resin finishing of cellulosic fabrics catalysts play a very important role. The more important requirements of these catalysts are briefly indicated below:

(a) The chemical characteristics of the resin precondensate/catalyst mixture should not change significantly for a period of at least a few hours. This implies that the catalyst should not react with the resin at this stage nor the pH of the mixture be so low that premature polymerization or loss of methylol groups take place. The catalyst should also be compatible with a variety of textile auxiliaries such as softener and wetting agents.

(b) The catalyst must be capable of producing

adequate fixation of the resin during curing operations. At the same time slight variation in curing conditions should not seriously influence the final properties of the treated fabric. The catalyst which is used must not give rise to objectionable by-products either in the form of odour or coloured residues or cause hydrolytic degradation.

The emergence of the so-called "phase-separation catalysts"[31] has led to an insight into the role of group II metal salts used as catalysts in the cross-linking of cellulose. These catalysts are group II salts such as magnesium dihydrogen phosphate, calcium hydrogen malonate and zinc hydrogen tartarate at high temperature. The use of mineral acids such as hydrochloric acid may lead to strength losses due to the degradation of cellulose. In some industrial processes neutral group" metal salts such as $MgCl_2.H_2O$ and $Zn(NO_3)_2$ are used as catalysts. In the case of these neutral salt catalysts results indicate strongly that the mechanism of catalysis involves the release of acid at temperatures higher than 140°C. This was confirmed by experimets in which strong concentrations of these

catalysts completely destroyed cotton fabric samples when dried and cured for 5 minutes at 170°C. A recent discovery is the use of mixed catalysts such as the dual mixture of magnesium chloride and sodium fluoroborate. It is proposed that $BF_3$ is released in the dual system which then acts synergically with $Mg^{2+}$ cation to catalyse the reaction[32].

## SCOPE OF PRESENT INVESTIGATION

Cross-linking Cellulose with resins, apart from its chemical interest has become the most important technological process for imparting to cotton fabric durable-press and easy-care properties. Research has mostly been concentrated in developing efficient cross-linking agents, optimization of desirable mechanical properties and chemistry of the process. Little attention has however been given to cross-linking modified celluloses. The present work deals with the study of the effect of oxidizing the cellulose, structure both prior and after resin treatment, on its crease recovery and tensile strength properties. Cellulose is oxidized with various oxidizing agents that are fairly specific in their reactions. The effect of oxidation of hydroxyl groups in cellulose to aldehyde groups and the reduction of aldehyde to hydroxyl on its crease recovery and tensile strength properties is studied. It is hoped that these studies may throw some light on the mechanism of resin finish and also make improvement on the conventional process. No attempt was made here to investigate the utility of the results obtained on commercial scale which should require further investigation on a pilot plant scale.

# Chapter 2

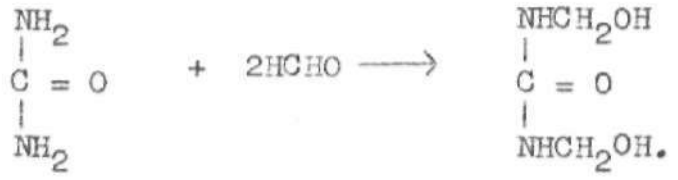
## EXPERIMENTAL METHODS AND RESULTS

### 2.1 Standard Cellulose

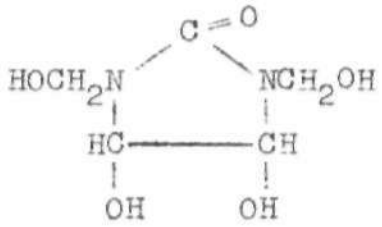
The cotton fabric, 26 picks in the weft and 32 ends in the warp directions per centimeter, was provided by Arewa Textiles Co. It was scoured, bleached and partially mercerised using standard procedure[33]. The purified material is refered to as standard cellulose.

### 2.2 Resins

Throughout these experiments 37% ANALAR grade aqueous formaldehyde stabilized with methyl alcohol was used. The resin dimethylol urea (DMU) was prepared by mixing sixty parts of urea (1 moles) and 170.3 parts of 37% formaldehyde (2 moles) and reacting for 15 hours at 28°C. The pH between 7-8 was maintained by adding sodium hydroxide and buffering with mono sodium phosphate. The resulting dense precipitate of DMU was filtered, washed with anhydrous alcohol and vacuum dried. The equation for the reaction is:



The resin dimethylol dihydroxyethylene urea (ARK NG) with the structure:



and a modified form ARK NGA, together with dimethylol derivative of bis-carbamate with structure:

$HOCH_2.NH.COO(CH_2).O.CO.NH.CH_2OH$

which were supplied by the Hoeschst AG Chemicals Limited Germany were also used in these investigations. All other chemicals used were reagent grade.

## 2.3 Preparation of OxyCellulose Samples.

### 2.3:1 Nitrogen Dioxide Oxycellulose:

The main reaction that occurs when cellulose is allowed to react with Nitrogen dioxide is oxidation of the primary alcohol groups to carboxyl groups[34]. On the basis of oxygen consumption during the reaction Nevel[35] has shown that a small amount of aldehyde groups are also produced by oxidation of the 2:3 glycol group to a dialdehyde.

A solution of Nitrogen dioxide in carbon tetrachloride in the ratio of one of the former to eight of the latter was used. The nitrogen dioxide required for the process was obtained by heating lead nitrate and collecting the gas in a freezing mixture. Standard cellulose cut into 12.5 x 15 cm pieces and weighing about 5 grams were treated with the Nitrogen dioxide solution in a 2 litre quick fitt flask. The material to liquor ratio was maintained at 1:20. The stoppered flasks were mechanically agitated for different lengths of time (see table 2). The oxidized product was separated from the oxidizing mixture, blown with air to remove volatile products, washed twice with carbon tetrachloride and then soaked in frequent exchanges of distilled water until the final washing was neutral to bromothymol blue indicator. It was then carefully dried and conditioned at 65% RH at 28°C.

The carboxyl content of each sample was determined as outlined in section 2.3:2 and the results of carboxyl content shown in table 2.

Table 2

| Weight of fabric Oxidized g | Time of oxidation Hrs | Carboxyl Content m eq/100g Cell. |
|---|---|---|
| 29.95 | 24 | 8.60 |
| 30.03 | 48 | 20.00 |
| 30.06 | 48 | 20.35 |
| 30.04 | 48 | 20.11 |
| 30.03 | 48 | 20.08 |
| 30.11 | 48 | 20.30 |

It can be seen from these values that reproducible results were obtained and it could be safely assumed that oxidation was uniform. All subsequent samples were oxidized for 48 hours using the same material to liquor ratio.

2.3:2 Determination of Carboxyl Content:

The carboxyl groups in oxycellulose can react with the salts of weak acids by an exchange process to release an equivalent amount of the weak acid which can be titrated by sodium hydroxide[34].

$$2Cell - COOH + (CH_3COO)_2Ca \longrightarrow (Cell - COO)_2Ca + 2CH_3COOH$$

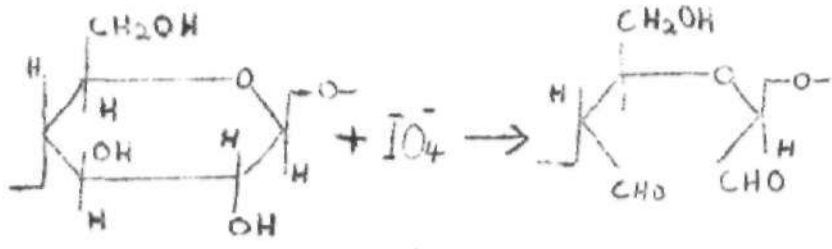
30 mls of 0.5m calcium acetate was added to 0.5 grams of oxidized cellulose in 50 mls of carbon dioxide free distilled water. The resulting mixture was shaken vigorously for 12 hours to ensure the

completion of exchange process. 30 mls aliquots were titrated with 0.1N sodium hydroxide. The carboxyl content was determined using the formula derived by Kenyon.[34]

$$\%\ \text{COOH (by weight)} = \frac{\text{Volume 0.1 NaOH} \times 0.0045 \times 100 \times 8}{\text{Sample weight} \times 3}$$

2.3:3 Periodate Oxy Cellulose

Cellulose can be oxidized by periodate ion, the reaction following the normal malaprade course each unit converted to dialdehyde[36, 37].




Standard cellulose cut into 12.5 x 15 cm pieces of about 5 grams were treated with 0.5M solution of sodium metaperiodate at 28°C at certain time interval. At the end of the reaction the oxycellulose obtained was washed with distilled water till free from acid and vacuum dried. Several samples of oxycellulose were prepared using varying concentrations of periodate

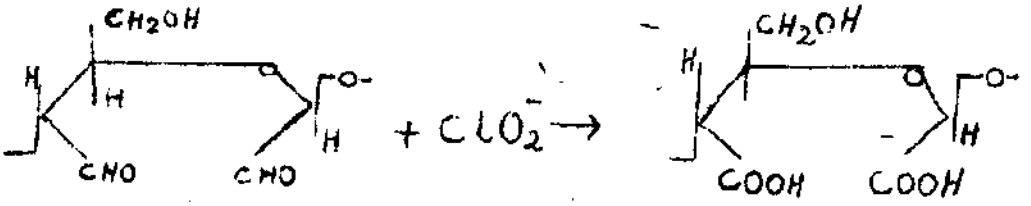
solution and times of treatment. The periodate consumption was determined by neutralizing the oxidizing solution with sodium bicarbonate and treating with excess standard sodium arsenite solution. 10% aqueous potassium iodide was added and the excess arsenite solution was titrated against standard iodine solution. The amount of periodate consumed was determined since[38]

ICC of 0.1N sodium arsenite ≡ 0.0107g $NaIO_4$

from which the percentage oxidation is determined since one anhydroglucose unit reacts with one molecule of periodate.

2.3:4 Oxidation of Periodate Cellulose with $NaClO_2$

Periodate Oxycellulose containing aldehyde groups can be oxidized to carboxyl groups using $NaClO_2$[39]



30 grams of periodate oxycellulose was treated with 0.1N solution of sodium chlorite in 0.5M acetic acid for 72 hours. The flask and content was constantly agitated. The oxidized sample was washed with distilled water, air dried and conditioned at 65% RH at 28°C.

2.3:5 Reduction of Periodate Oxycellulose with Borohydride:

The 2:3 dialdehyde groups of periodate Oxycellulose can be reduced to hydroxyl groups by means of an alkaline solution of potassium or sodium borohydride[40].

$$4\ R_1RC = O + BH_4^- + 2H_2O \longrightarrow 4R_1RCHOH + BO_2^- \cdots\cdots$$

30 grams of periodate Oxycellulose were treated with 0.1M aqueous solution of sodium borohydride in 2 litro quickfit flask. The product was washed dried and then conditioned at 65% RH at 28°C.

2.4 Binding of Magnesium to Standard and Oxycellulose

Magnesium and other divalent metal salts are frequently used as catalysts in cross-linking cellulose with resins. The extent of magnesium binding to carboxyl groups is investigated to find whether this affects its catalytic action since each atom of magnesium

releases two hydrogen atoms. 10 mls of 0.1M of Magnesium Chloride was added to 0.1 gram of Oxy cellulose. This was made up to 50 mls with distilled water and allowed to stand for 12 hours and then titrated potentiometrically with 0.1N NaOH using a Beckman pH meter. The experiment was repeated using standard Cellulose both in the presence and absence of magnesium ions. The titration curves are shown in Fig.7.

It can be seen that the presence of magnesium ions lead to the lowering in pH for both types of Celluloses.

## 2.5 Equillibrium Sorption of Formaldehyde

The time required for maximum formaldehyde uptake at 28°C was determined for two different concentrations of formaldehyde in the reaction bath by placing 1.1g of standard cellulose in each of the reaction baths. After the required time elapsed the sample was taken out of the bath, washed with sodium carbonate to neutralize excess acid and washed in several portions of distilled water to remove unbound formaldehyde. For each bath composition the experiment was repeated for different time intervals. The amount of formaldehyde bound in each case was determined as described below and the results are illustrated in Fig. 1.

Table 3

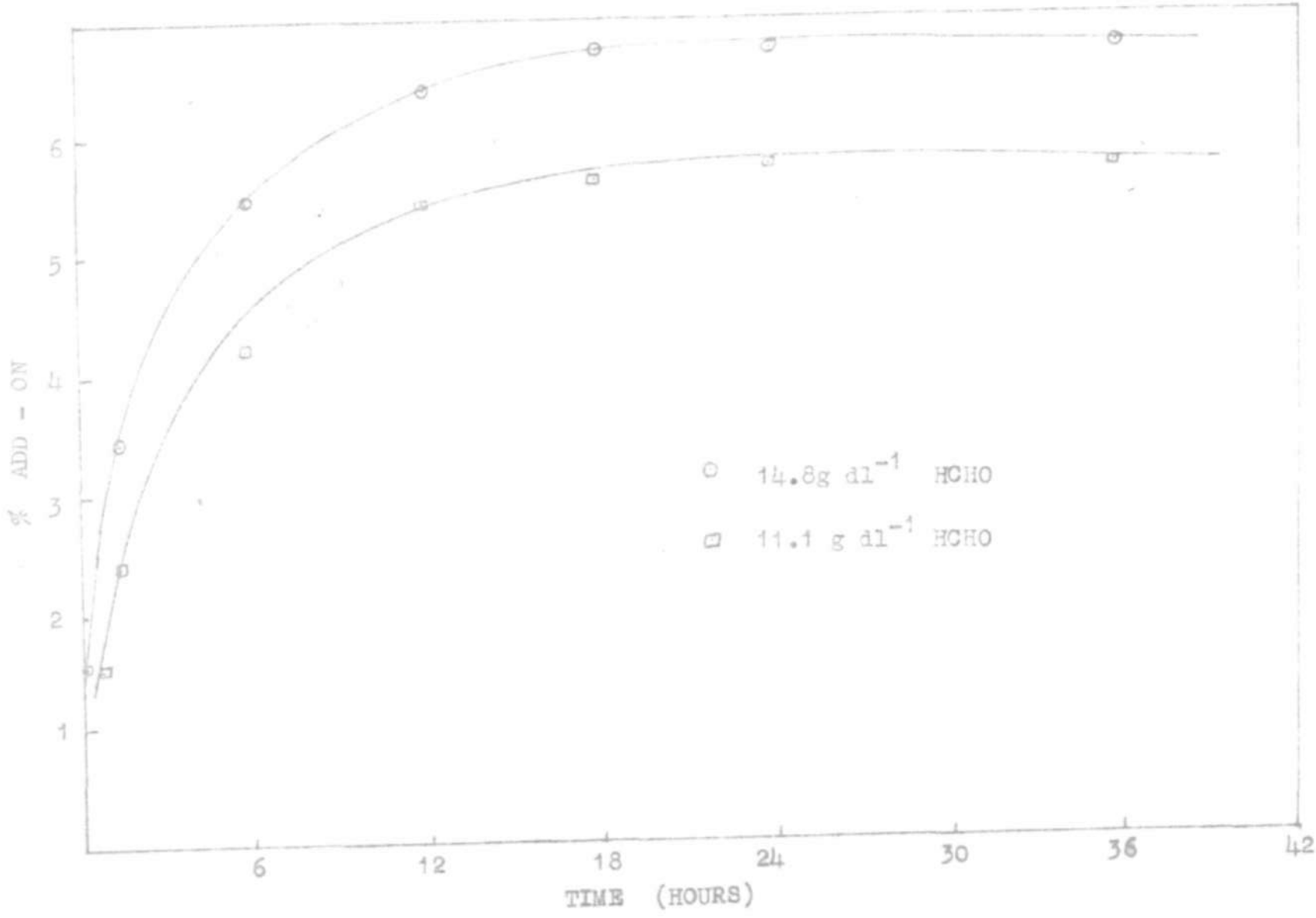
Variation of formaldehyde add-on
to standard cellulose with time of treatment.

Bath composition: HCHO 11.1g/100 mls
HCl 1.74M

Total Volume of bath = 100 mls (Uwof)

| Time of treatment (minutes) | % ADD-ON |
|---|---|
| 5 | 0.03 |
| 10 | 0.09 |
| 15 | 0.37 |
| 20 | 0.79 |
| 30 | 0.79 |
| 40 | 1.01 |
| 50 | 1.24 |
| 60 | 11.53 |
| 70 | 1.71 |
| 80 | 1.80 |
| 90 | 2.25 |
| 180 | 3.26 |
| 360 | 5.25 |
| 720 | 5.48 |
| 1080 | 5.70 |
| 1440 | 5.86 |
| 2160 | 5.85 |
| 2880 | 5.86 |

FIG. 1 VARIATION OF FORMALDEHYDE UPTAKE BY STANDARD CELLULOSE WITH TIME



## Table 4

Variation of Formaldehyde Add-on to Standard Cellulose with Time of Treatment

Bath composition HCHO 14.8g/100 mls

HCl 1.74 m

Total Volume of bath = 100 mls (Uwof)

| Time of treatment (minutes) | % ADD-ON |
|---|---|
| 5 | 0.18 |
| 10 | 0.40 |
| 15 | 1.94 |
| 20 | 1.01 |
| 30 | 1.48 |
| 40 | 1.82 |
| 50 | 2.21 |
| 60 | 2.48 |
| 70 | 2.81 |
| 80 | 3.02 |
| 90 | 3.46 |
| 180 | 5.04 |
| 360 | 5.47 |
| 720 | 6.41 |
| 1080 | 6.84 |
| 1440 | 6.86 |
| 2880 | 6.86 |

## 2.6 Determination of Bound Formaldehyde

The amount of formaldehyde that reacted with cotton fabric was determined by hydrolysis[41]. About 1.1g of formaldehyde treated sample was placed in a distillation flask containing 200 mls of a solution of 5% $H_2SO_4$ and 5% $Na_2SO_4$. 150 mls of distillate was collected in each case. To a 30 ml sample of distillate was added about 10 mls of Schiffs reagent. After standing for 2 hours the formaldehyde was colorimetrically determined by taking the optical density at 550 mμ and comparing with a calibration curve constructed using pure formaldehyde. The Schiffs reagent was prepared by dissolving 0.2g of rosanaline hydrochloride in 120 mls of hot distilled water, cooling and adding 2.0g anhydrous $Na_2SO_3$ dissolved in 2 mls concentrated hydrochloric acid. The amount of formaldehyde bound to 100g cellulose sample (% ADD-ON) was then calculated in each case.

## 2.7 Finishing Standard and Oxycelluloses with Various Resins.

Oxidized and standard celluloses prepared as above were treated with the resins ARK NG, ARKNGA ARK CA and dimethylol urea (DMU).

Fig. 2 % Formaldehyde Uptake by Standard Cellulose using different Catalysts

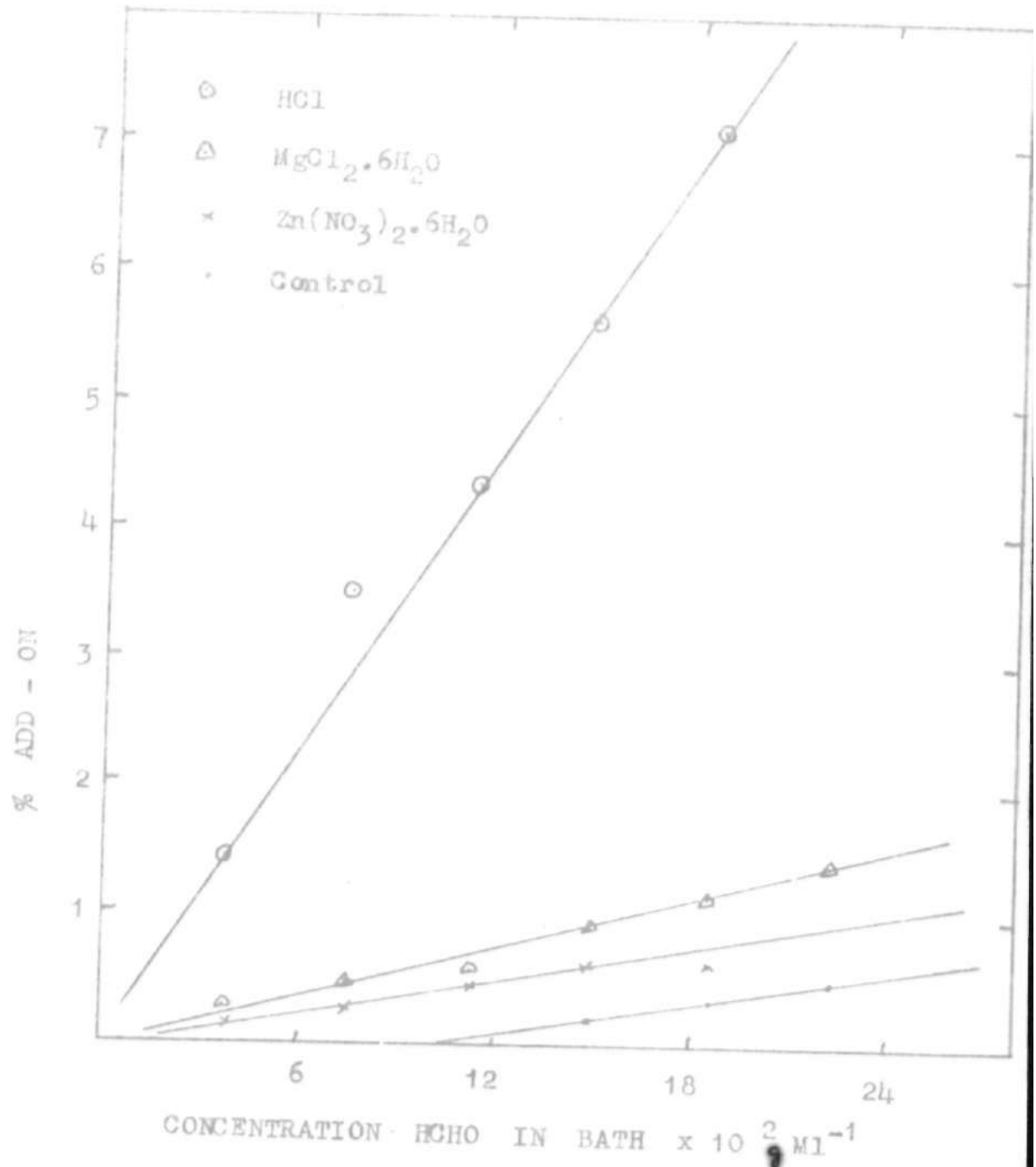
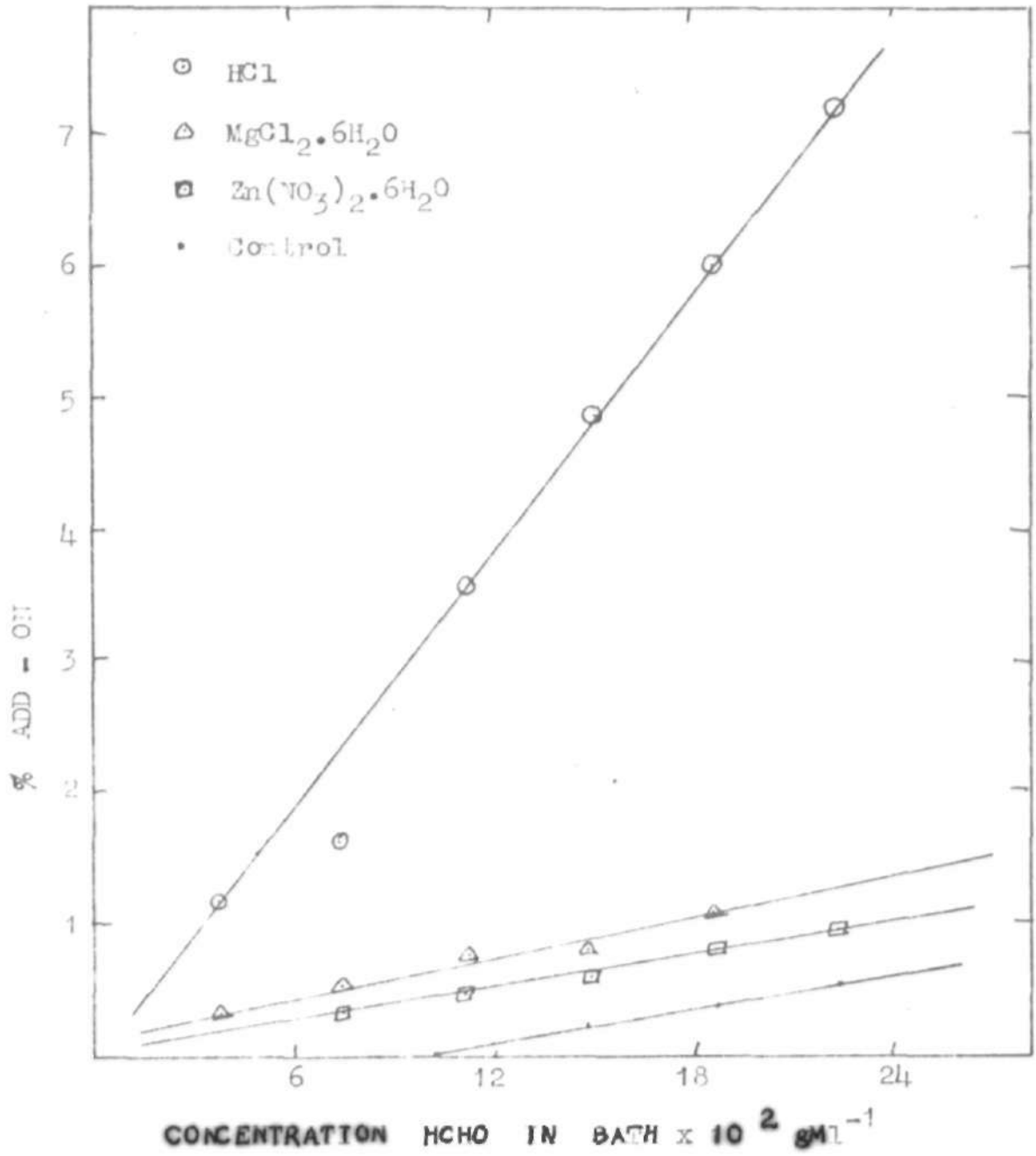


FIG. 3 % FORMALDEHYDE UPTAKE BY OXYCELLULOSE USING VARIOUS CATALYSTS.



The materials were padded with resin solution, together with a wetting agent Velustrol, centrifuged for 1 minute to give about 70% wet pick-up, dried in an oven at 110°C for 4 minutes and then cured at 150°C for 3 minutes. The materials were then conditioned at 65% RH at 28°C and the crease recovery angle (CRA) and tensile strength were determined. All resin treatments were performed using the same methods under the same conditions. The content and concentrations of each padding bath is shown in the appropriate table.

## 2.8 Dry Crease recovery angle and tensile strength Measurements

Rectangular specimens 5cm by 2.5cm were cut from preconditioned fabric to be tested. The specimens were cut parallel to the warp and weft directions. Ten specimens were cut and care was taken to avoid selvedges, end pieces and creased or folded places. The specimen was folded precisely in half so as to give a crease 2.5 cm long and was placed under a weight of 2 kilograms for 2 minutes. The specimen was transfered to the Shirley CRA tester. The CRA was measured after the sample was hanged freely for 2 minutes.

Ten measurements were taken for each fabric sample in the weft and warp direction. The average CRA $(W+F)^{\circ}$ was determined. All measurements were taken with the shirley CRA tester in a specially constructed cabinet which maintains the testing atmosphere at 65% RH.

Tensile strength measurements were performed using Instron machine model 1026. Measurements were performed on 2.5 cm strip at cross-head speed of 50mm/min, chart speed 100mm/min at gauge length 12.5cm using load cell 1026 CM with range 0-50 Kg. Ten measurements were performed for each specimen and the average break load calculated. Results for CRA and breaking loads are given in appropriate tables.

Table 5

Effect of External bath Concentration of Formaldehyde on its Add-on to Standard Cellulose using different Catalysts

(a) Catalyst 1.74M HCl

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 1.44 |
| 6.4 | 3.49 |
| 11.1 | 4.43 |
| 14.8 | 5.65 |
| 18.5 | 7.13 |
| 22.2 | 8.61 |

(b) Catalyst 2.5% $MgCl_2.6H_2O$

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 0.30 |
| 6.4 | 0.41 |
| 11.1 | 0.64 |
| 14.8 | 0.91 |
| 18.5 | 1.11 |
| 22.2 | 1.45 |

Table 5(c)

Catalyst 2.5% $Zn(NO_3)_2.6H_2O$

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 0.14 |
| 6.4 | 0.25 |
| 11.1 | 0.45 |
| 14.8 | 0.60 |
| 18.5 | 0.60 |
| 22.2 | 0.91 |

FIG. 4 % FORMALDEHYDE UP-TAKE BY STANDARD AND OXYCELLULOSE USING HCl CATALYST.

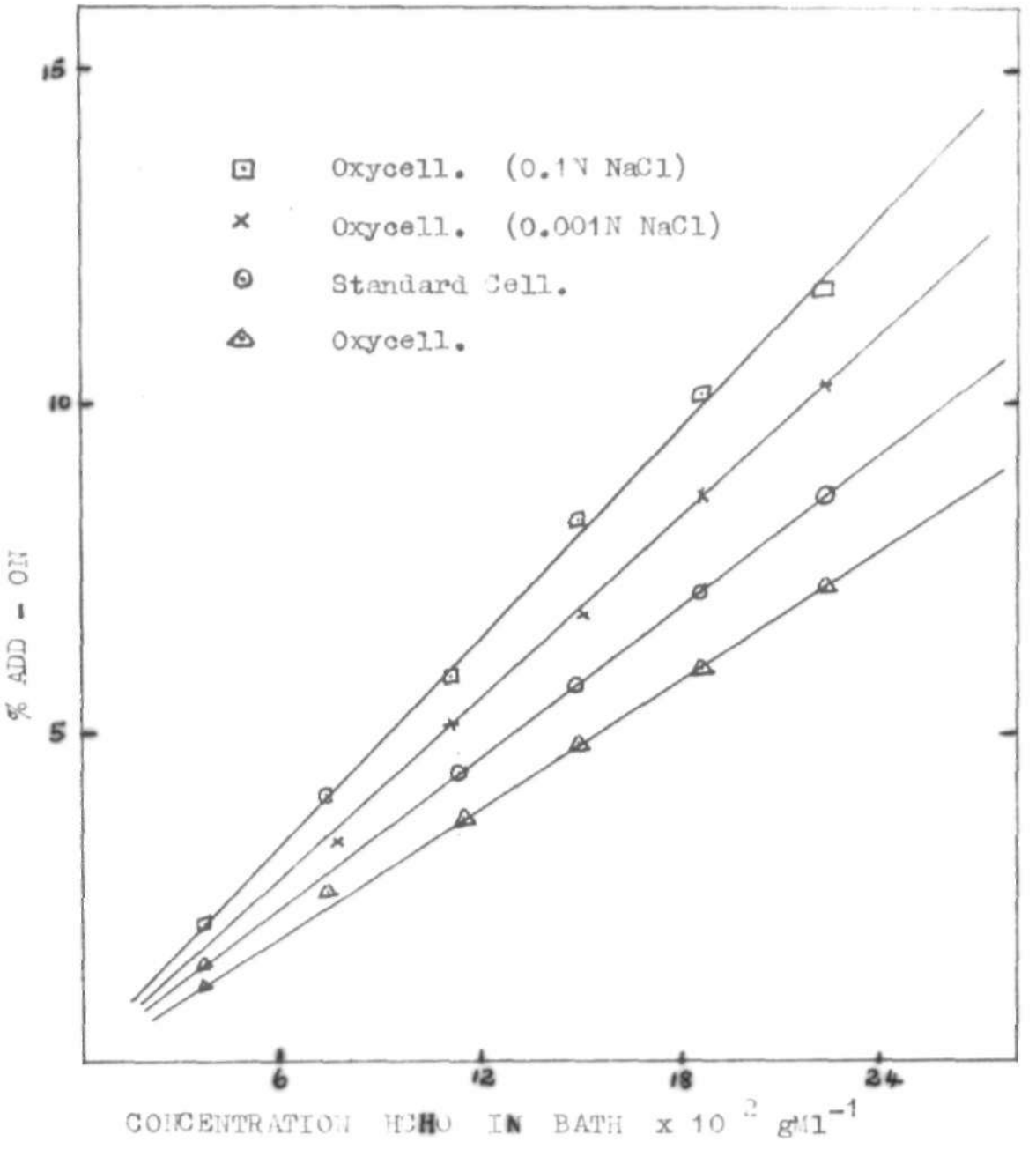


Table 6

Effect of External Bath Concentration of Formaldehyde on its Add-on to Nitrogen Dioxide Oxycellulose using different Catalysts

(a) Catalyst 1.74M HCl

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 1.16 |
| 6.4 | 1.63 |
| 11.1 | 3.89 |
| 14.8 | 4.85 |
| 18.5 | 5.99 |
| 22.2 | 6.93 |

(b) Catalyst 2.5% $MgCl_2.6H_2O$

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 0.32 |
| 6.4 | 0.35 |
| 11.1 | 0.50 |
| 14.8 | 0.61 |
| 18.5 | 0.80 |
| 22.2 | 0.93 |

Table 6(c)

Catalyst 2.5% $Zn(NO_3)_2\ 6H_2O$

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 0.24 |
| 6.4 | 0.54 |
| 11.1 | 0.48 |
| 14.8 | 0.75 |
| 18.5 | 1.03 |
| 22.2 | 1.85 |

FIG. 5 % Formaldehyde Uptake by Standard and Oxycelluloses using magnisium Chloride Catalyst.

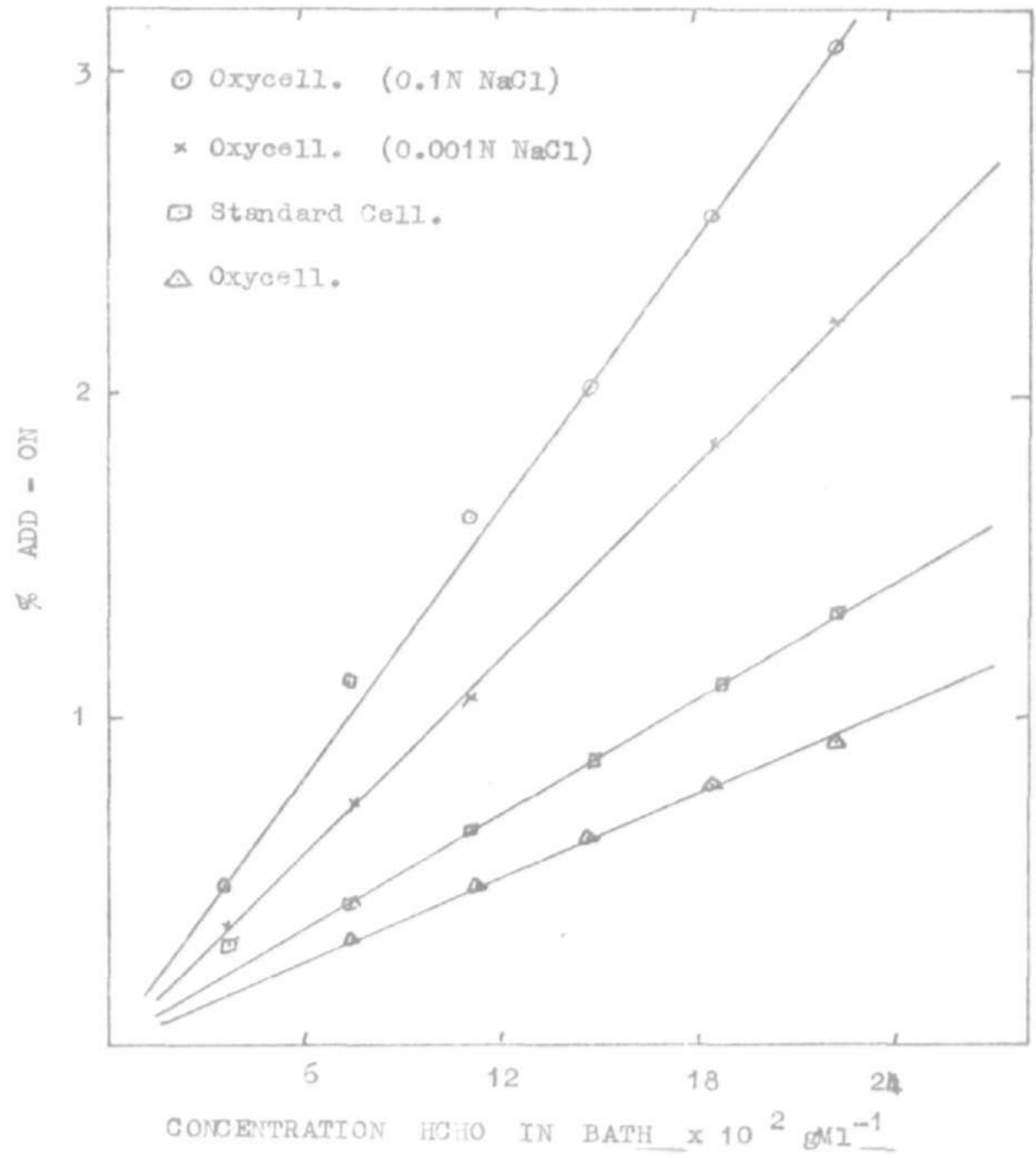


Table 7

Effect of External Bath Concentration of Formaldehyde on its Add-on to $NO_2$-Oxycellulose in the presence 0.1N NaCl Using different Catalysts

(a) Catalyst 1.74M HCl

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 2.01 |
| 6.4 | 4.03 |
| 11.1 | 6.04 |
| 14.8 | 8.21 |
| 18.5 | 10.15 |
| 22.2 | 14.95 |

(b) Catalyst 2.5% $MgCl_2.6H_2O$

| HCHO Concentration g/100 mls | % ADD-ON |
|---|---|
| 3.7 | 0.48 |
| 6.4 | 1.12 |
| 11.1 | 1.63 |
| 14.8 | 2.37 |
| 18.5 | 2.55 |
| 22.2 | 3.26 |

FIG. 6 % FORMALDEHYDE UP-TAKE BY STANDARD AND OXYCELLULOSES USING ZINC NITRATE CATALYST.

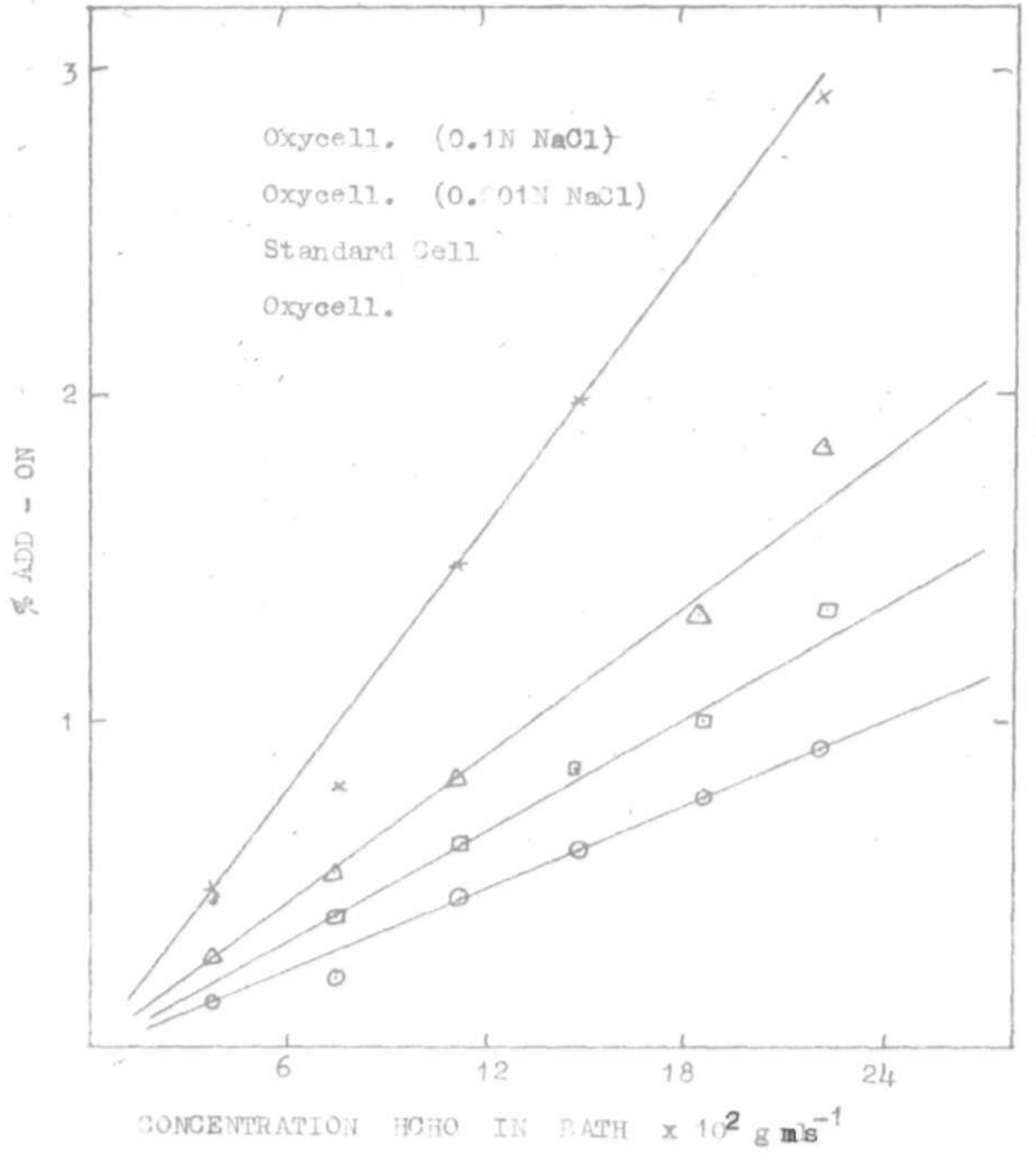


FIG. 7 POTENTIOMETRIC TITRATION OF STANDARD AND OXYCELLULOSES IN PRESENCE OF $Mg^{2+}$ ION

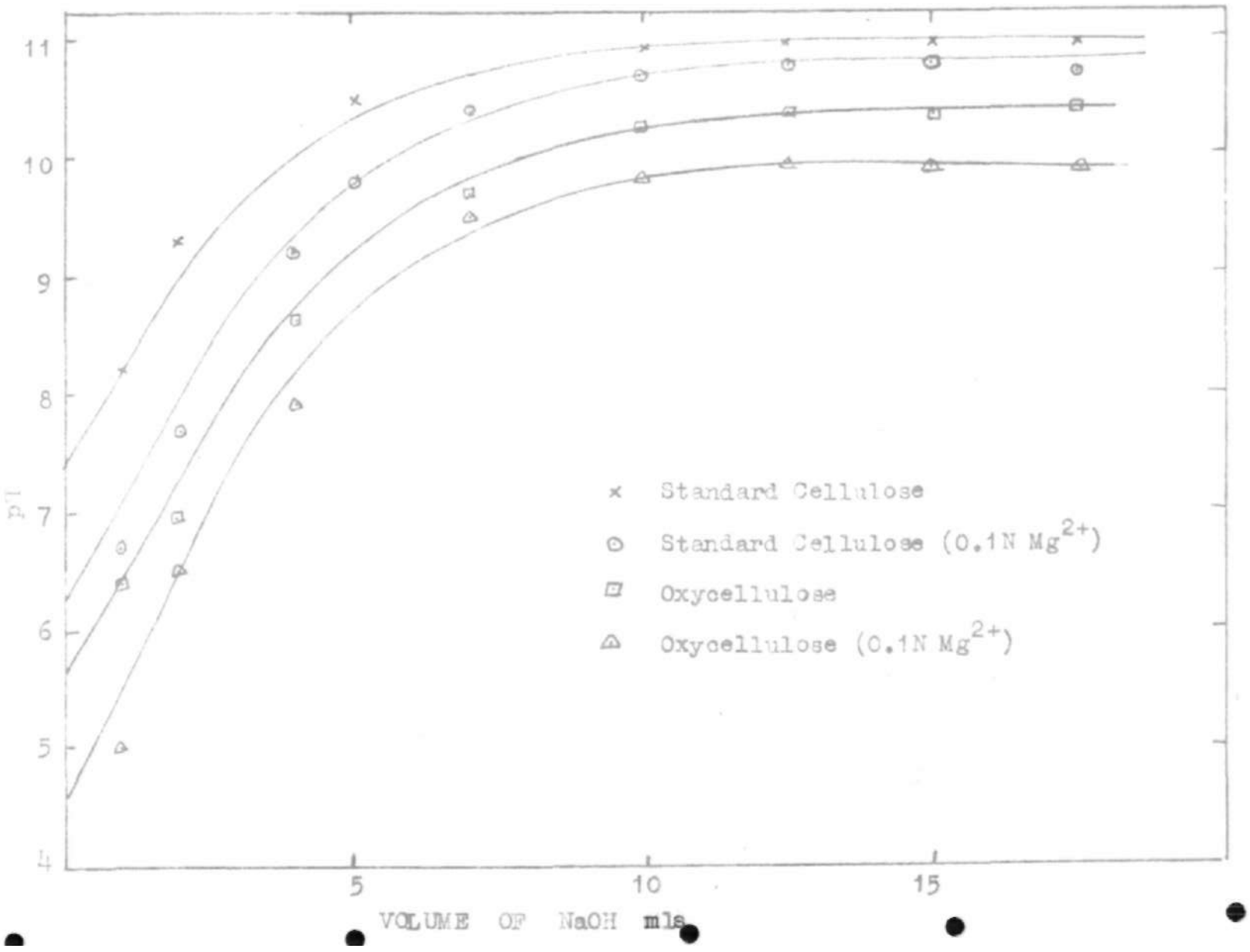


Table 8

Cross-linking Standard and $NO_2$- Oxycellulose with Dimethylol urea DMU

Bath Composition: DMU 3% Owf.
Vel.1% "
Dried 110°C/4 min Cured 150°C/3 min

| Type | Catalyst | % | % ADD-ON | CRA (W+F) | Breaking Load Kg. |
|---|---|---|---|---|---|
| Standard Cellulose | HCl | 12.5% | 6.25 | 254.1 | 6.10 |
| | $MgCl$ | 2.5% | 3.28 | 214.5 | 12.50 |
| | $Zn(NO_3)_2$ | 2.5% | 4.04 | 210.5 | 13.25 |
| Control | | | | 159.2 | 15.22 |
| | HCl | 12.5% | 3.98 | 230.6 | 3.92 |
| OxyCell. | $MgCl_2$ | 2.5% | 2.10 | 208.1 | 2.88 |
| | $Zn(NO_3)_2$ | 2.5% | 2.18 | 198.5 | 2.60 |
| | HCl | 12.5% | 12.10 | 237.1 | 1.03 |
| OxyCell. | $MgCl_2$ | 2.5% | 8.00 | 210.7 | 2.92 |
| 0.1N NaCl | $Zn(NO_3)_2$ | 2.5% | 9.01 | 207.1 | 2.88 |
| Control | | | 151.8 | | 3.86 |

Table 9

Cross-linking Standard and $NO_2^-$ Oxycellulose with ARK NG

Bath Composition ARK NG 10% Owf.
Vel. 1% "
Dried 110°C/4 min Cure 150°/3 min

| Type | Catalyst | % | % ADD-ON | CRA (W+F)° | Breaking Load Kg |
|---|---|---|---|---|---|
| Standard Cellulose | HCl | 12.5% | 9.00 | 292.2 | 5.39 |
| | $MgCl_2$ | 2.5% | 5.32 | 271.7 | 8.36 |
| | $Zn(NO_3)$ | 2.5% | 4.32 | 257.3 | 8.56 |
| Control | | | | 159.2 | 15.22 |
| Oxycell. | HCl | 12.5% | 8.50 | 260.1 | 1.58 |
| | $MgCl_2$ | 2.5% | 3.97 | 239.9 | 3.00 |
| | $Zn(NO_3)$ | 2.5% | 3.31 | 221.8 | 3.75 |
| Control | | | | 151.8 | 3.86 |
| Oxycell. | HCl | 12.5% | 16.51 | 278.0 | 1.67 |
| 0.1N NaCl | $MgCl_2$ | 2.5% | 11.31 | 262.6 | 2.56 |
| | $Zn(NO_3)$ | 2.5% | 10.41 | 232.1 | 2.16 |

Table 10

Cross-linking Standard and $NO_2$ Cellulose with ARK CA

Bath Composition ARK CA 10% Owf
Vel 1% "
Dried 110°C/4 min Cured 150°C/3 min

| Type | Catalyst | % | % ADD-ON | CRA (W+F)° | Breaking Load Kg |
|---|---|---|---|---|---|
| Standard Cellulose | HCl | 12.5% | 12.30 | 255.1 | 1.48 |
| | $MgCl_2$ | 2.5 | 7.13 | 248.3 | 4.95 |
| | $Zn(NO_3)_2$ | 2.5 | 5.21 | 233.0 | 5.68 |
| Control | | | | 159.2 | 15.22 |
| Oxycellulose | HCl | 12.5% | 9.60 | 220.4 | 1.74 |
| | $MgCl_2$ | 2.5% | 4.72 | 215.3 | 2.54 |
| | $Zn(NO_3)_2$ | 2.5% | 4.38 | 202.5 | 3.68 |
| Control | | | | | |
| Oxycellulose | HCl | 12.5% | 17.31 | 233.7 | 1.63 |
| 0.1N NaCl | $MgCl_2$ | 2.5% | 11.96 | 228.0 | 2.63 |
| | $Zn(NO_3)_2$ | 2.5% | 10.89 | 214 | 3.58 |

Table 11

Cross-linking Periodate Oxycellulose with Formaldehyde

Catalyst 2.5% $MgCl_2.6H_2O$ (Owf)

| HCHO Concent. g/100 soln. | % ADD-ON | CRA | Breaking Load Kg |
|---|---|---|---|
| 3.7 | 0.03 | 231.4 | 8.70 |
| 6.4 | 0.03 | 230.2 | 8.46 |
| 11.1 | 0.02 | 237.9 | 8.32 |
| 14.8 | 0.03 | 233.7 | 8.56 |
| 18.5 | 0.04 | 231.2 | 8.53 |
| 22.2 | 0.06 | 230.4 | 8.26 |
| Control | | 231.9 | 8.74 |

Table 12

Effect of boiling and curing Periodate Oxycellulose on Mechanical Properties

| % Oxidation | Process | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|---|
| 10 | Boiled | 225.5 | 5.21 |
| 10 | Cured | 234.2 | 8.36 |
| | Control | 233.9 | 8.97 |
| | Boiled | 215.0 | 7.27 |
| 4.5 | Cured | 248.0 | 10.86 |
| | Control | 236.0 | 10.28 |
| | Boiled | 200.1 | 12.32 |
| 1.0 | Cured | 209.3 | 12.44 |
| | Control | 188.8 | 12.58 |
| Standard Cellulose | | 159.2 | 15.22 |

Table 13

Effect of Cross-linking different Cellulose with DMU.

Bath Composition 3% DMU
1% Velustrol

Dried 110°C/4 min. Cured 150°C/3 min.

Catalyst 2.5% $MgCl_2$ $6H_2O$

| Type | % Add-on | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|---|
| Na Oxycellulose (Control) | | 182.7 | 5.29 |
| Na Oxycellulose (DMU) | 4.8 | 198.8 | 6.79 |
| $NO_2$ Cellulose | | 153.2 | 3.80 |
| Periodate Cell (Control) | | 233.9 | 7.85 |
| Periodate Cell (DMU) | | 264.8 | 8.37 |
| Borohydride Reduced Oxycellulose } Control | | 145.0 | 3.92 |
| " DMU | | 212.0 | 4.89 |
| Standard Cellulose | | 159.2 | 15.22 |

Table 14

Effect of Cross-linking different Cellulose with ARK NG

Bath Composition 10% ARK NG
1% Velustrol
Dried 110°C/4 min. Cure 150°C/3 min.
Catalyst 2.5% $MgCl_2.6H_2O$

| Type | | % Add-on | CRA (W+F)° | Breaking Load Kg |
|---|---|---|---|---|
| Na Oxycellulose (Control) | | | 182.7 | 5.29 |
| Na Oxycellulose (ARK NG) | | 13.14 | 202.6 | 5.29 |
| Periodate Cell (Control | | | 233.9 | 7.85 |
| Periodate Cell (ARK NG) | | 9.49 | 272.6 | 8.71 |
| Borohydride Reduced Oxycellulose | Control | | 145.1 | 3.92 |
| " | (ARK NG) | 16.45 | 225.1 | 7.30 |

Table 15

Effect of ARK NG Cross-linking on Periodate Oxycellulose

Bath Composition 10% ARK NG
1% Velustrol

Dried 110°C/4 min Cured 150°C/3 min

Catalyst 2.5% $MgCl_2.6H_2O$

| Type | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|
| Standard Cell. | 159.2 | 15.22 |
| Standard Cell. (ARK NG) | 262.7 | 13.42 |
| Periodate (0.01M/4 hr) Cellulose | 196.78 | 11.45 |
| " " (ARK NG) | 264.7 | 10.54 |
| Periodate (0.05M/3 hr) Cellulose | 211.6 | 10.28 |
| " " (ARK NG) | 294.1 | 9.54 |
| Periodate (0.05M/6 hrs) Cellulose | 233.9 | 10.15 |
| " " (ARK NG) | 297.3 | 9.72 |

Table 16

Effect of degree of Oxidation on ARK NG Cross-linked Cellulose Using 2.5% $MgCl_2.6H_2$ Catalyst

(a) Oxidized with 0.01M $NaIO_4$ for 6 Hours

| % ARK NG in Bath | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|
| 15.0 | 268.5 | 11.76 |
| 10.0 | 275.9 | 11.54 |
| 7.5 | 295.5 | 9.66 |
| 5.0 | 279.0 | 9.10 |
| 2.5 | 249.3 | 10.52 |
| 1.0 | 224.6 | 11.58 |
| Control | 198.8 | 12.58 |

(b) Oxidized with 0.03M $NaIO_4$ for 6 Hours.

| % ARK NG in Bath | CRA (W%F)° | Breaking Load Kg. |
|---|---|---|
| 15.0 | 211.8 | 8.95 |
| 10.0 | 237.6 | 9.33 |
| 7.5 | 280.5 | 8.71 |
| 5.0 | 273.6 | 9.04 |
| 2.5 | 253.5 | 9.40 |
| 1.0 | 247.4 | 9.90 |
| Control | 219.8 | 10.28 |

Table 16c Oxidized with 0.05M $NaIO_4$ for 6 Hours.

| % ARK NG in Bath | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|
| 15.0 | 253.5 | 8.71 |
| 10.0 | 264.9 | 8.66 |
| 7.5 | 283.4 | 7.98 |
| 5.0 | 281.4 | 8.43 |
| 2.5 | 276.9 | 8.79 |
| 1.0 | 252.0 | 8.98 |
| 0 | 233.9 | 9.47 |

(d) Oxidized with 0.10M $NaIO_4$ for 6 Hours

| % ARK NG in Bath | CRA (W+F)° | Breaking Load Kg. |
|---|---|---|
| 15.0 | 254.8 | 8.54 |
| 10.0 | 300.0 | 8.44 |
| 7.5 | 308.0 | 7.16 |
| 5.0 | 302.0 | 8.42 |
| 2.5 | 297.1 | 8.63 |
| 1.0 | 261.1 | 8.89 |
| Control | 243.4 | 9.08 |

Table 17

Effect of Alkaline treatment on Resin Finished Periodate Oxycellulose

| | |
|---|---|
| Periodate Cellulose Oxidized | 0.05M/6 Hours |
| Bath Composition | 10% ARK NG |
| | 1% Velustrol |
| | 2.5% $MgCl_2.6H_2O$ |
| Dried 110°C/4 min | Cured 150°C/3 min. |

| Concentration $Na_2CO_3$ | CRA(W+F)° | Breaking Load Kg. |
|---|---|---|
| 10% | 269.4 | 8.69 |
| 5% | 262.1 | 8.72 |
| 1% | 265.1 | 8.59 |
| Control | 264.9 | 8.66 |

# Chapter 3

## D I S C U S S I O N

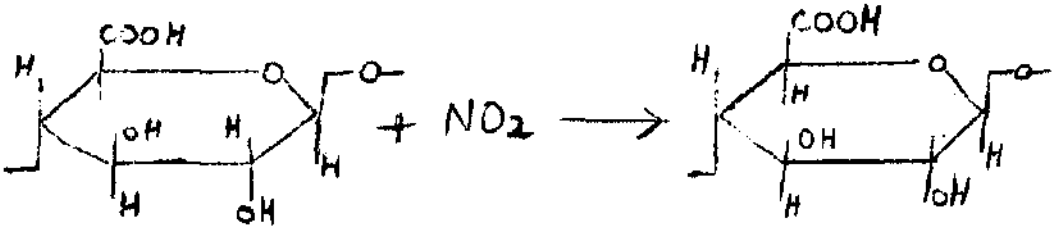
3.1

Reaction between formaldehyde and cellulose can occur under two different conditions:- (a) When cellulose is in a collapsed state. In this case cellulose is impregnated with formaldehyde in the presence of a catalyst, dried, and cured in an oven at high temperature of about 150°C and (b) in the swollen state. This is when cellulose is simply immersed in acid solution of aqueous formaldehyde for a certain time and temperature. Some work has been reported on sorption of formaldehyde by standard and modified celluloses. Beltzer[42] has observed that oxycelluloses absorb large quantities of formaldehyde. Roff[43] studied sorption of formaldehyde by standard cellulose from its aqueous solution and concluded that reaction between cellulose and formaldehyde is governed by pH, concentration, temperature and the time of immersion. Datye and Nabarh[44] investigated sorption of formaldehyde by various celluloses and observed that it decreases with

decreasing amount of secondary hydroxyl groups and increase in the number of carboxyl groups but is independent of the number of primary hydroxyl and aldehyde groups in the cellulose. None of the workers have however correlated the formaldehyde sorption behaviour of cellulose to crease recovery angle and other mechanical properties. Fig. 1 shows the uptake of formaldehyde with time of treatment. Two different concentrations were used. It can be seen that in both cases formaldehyde uptake increases rapidly at first followed by a slow increase until a maximum is reached. After about 24 hours no change of add-on with time is observed. The initial rapid add-on may correspond to reaction in the more accessible region. The subsequent slow increase may be due to reaction in difficultly accessible regions. It can also be seen that no decrease in add-on is observed with length of treatment. This clearly shows that no acid hydrolysis of cellulose takes place during this time as otherwise the amount of the accessible fraction would be decreased thereby decreasing the add-on with time of treatment.

Fig. 2 and Fig. 3 shows the variation of percentage add-on of formaldehyde to standard and nitrogen dioxide

oxycellulose with concentration of formaldehyde in the reaction baths. Oxidation of the cellulose with nitrogen dioxide mainly converts the hydroxyl groups on the sixth carbon atom to carboxyl groups.




However, Nevell[45] has shown that in the formation of oxycelluloses containing one carboxyl group per unit chain; 2.35 atoms of oxygen per unit chain were consumed instead of the expected 2 atoms. It was postulated that the extra 0.35 atom of oxygen per unit represents oxidation of the 2:3 glycol groups to dialdehyde. Thus Nitrogen dioxide oxycellulose contains a small but definate amount of aldehyde groups. The oxycellulose used contains 20 m moles of COOH per 100 grams cellulose (see section 2·3·1). On the bases of 2.35 atoms of oxygen consumption per chain unit, the oxycellulose should contain 7 m moles of aldehyde groups per 100 gram celluloses.

Comparing Fig. 2 and 3 shows that nitrogen dioxide oxidation leads to about 15.6% decrease in formaldehyde uptake as compared with standard cellulose when hydrochloric acid is used as catalyst. The same order of decrease is also observed when magnesium chloride and zinc nitrate are used as catalyst. Datye and Nabar[46] have attributed the decrease in formaldehyde uptake to the decrease in the number of secondary hydroxyl groups. However, calculations based on the present work show the decrease in hydroxyl content to be of the order of 1.2% which cannot explain the observed loss in add-on of 15.6%. It appears that this decrease can be explained on the basis of an electrostatic effect. In acid solutions aldehyde groups from oxidized celluloses can acquire a proton which is resonance stabilized

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

It is also known that hydrated formaldehyde and hemiformals obtained by reaction between formaldehyde and methyl alcohol

$$CH_3OH + HCHO \longrightarrow CH_3OCH_2OH$$

also acquire protons in acid solutions[47, 48].

Thus we now have the situation in which both a relatively rigid substrate (oxycellulose) and the formaldehyde or hemiformal moities are positively charged. Thus in the absence of any counterions the absorption of formaldehyde molecules would be retarted due to electrostatic repulsion between them. However, in the presence of added counterions there should be an increase in the sorption of formaldehyde. A counterion such as $Cl^-$ ion would surround the positively charged groups in cellulose thus shielding them from the approaching $HOCHOH_2^+$ and thereby facilitating sorption. The results in Fig. 4 seem to agree with this postulate. It can be seen that there is a dramatic increase in about 20.2% and about 44.7% in add-on when in the presence of 0.001 and 0.1N sodium chloride. Roff[43] also observed this phenomena when reacting formaldehyde with standard cellulose in the presence of neutral salts. He observed that the increase in add-on depends on the concentration of the added neutral salt. Roff attributed this increase as due to unspecified physical causes. Similar increase in add-on of DMU and ARK NG by oxycelluloses in the presence of added neutral salts such as sodium chloride were also observed as can be seen from data in tables 8 - 10.

These results are discussed later. It can be seen further that the % add-on depends on the catalyst used. Hydrochloric acid is the most efficient since it leads to large formaldehyde uptake. The order of relative efficiency is $HCl > MgCl_2 > Zn(NO_3)_2$. However because of the possibility of acid hydrolysis divalent metal ions could be better catalysts.

## 3.2 Binding of Magnesium to Celluloses.

Divalent metal salts particularly magnesium chloride are generally used as catalysts in cross-linking cellulose with formaldehyde and other resins. Since these reactions are acid catalysed the study of binding of magnesium to standard and oxycelluloses with subsequent release of hydrogen is of interest. Nitrogen dioxide oxycellulose contains carboxyl groups on the sixth carbon atom and standard cellulose acquires carboxyl groups during the process of purification by scouring and bleaching[49]. Magnesium may bind to carboxyl groups according to the reactions:

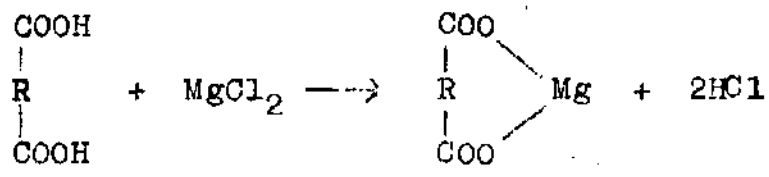
$$2\ \text{Cell} - \text{COOH} + Mg^{2+} \longrightarrow \text{Cell} - C(=O)\backslash Mg/ C(=O) - \text{Cell} + 2H^{+}$$

and

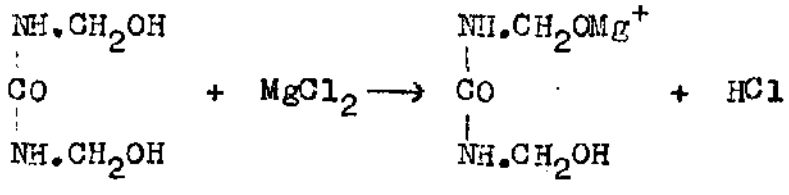
$$\text{Cell} - \text{COOH} + Mg^{2+} \longrightarrow \text{Cell} - C(=O)\backslash OMg^{+} + H^{+}$$

Fig. 7 shows the titration curves for standard and nitrogen dioxide oxycellulose in the presence and absence of magnesium chloride. The addition of magnesium lowers the pH for both types of celluloses. However, the pH was lowered to a greater extent in the case of nitrogen dioxide cellulose probably due to the greater number of carboxyl groups. The mechanism by which divalent metal ions catalyse the cross-linking of cellulose is not clear. Since cross-linking of cellulose with resins has been accepted as acid catalysed, most workers have suggested that divalent metal ions somehow release acids under curing conditions of about 150°C. Mehta and Gupta[50] have shown that mixed catalysts of dicarboxylic acids and neutral salts such as magnesium and sodium chlorides release mineral acids at high temperatures which would then catalyse the

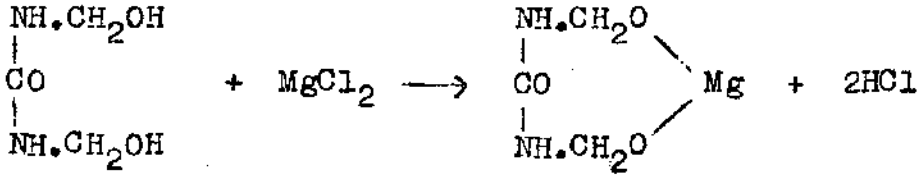
reaction. They suggested the reaction as



in which the higher volatility of halogen acids compared to those of organic acids is reponsible for their displacement. This work suggests that binding of magnesium ions to cellulose chains may contribute to acid release characteristic of metal salts that are generally used as catalysts. Magnesium ions can also react with dimethlol resins that are used as cross-linking agents. Dimethylol urea for example could undergo the following types of reactions at high temperatures.



or the Cyclic product



which of these reactions takes place in preference to

the other and to what extent is difficult to say.

## 3.3 Effect of modifying the structure of Cellulose on its Crease recovery and Mechanical properties

### 3.3.1 Effect of Nitrogen dioxide Oxidation on Resin Finishing of Cellulose:

It is well known that the final properties of Cellulose after Cross-linking depends on its state and structure after and before cross-linking. In an exploration of the relation between structural features and performance qualities of a fabric, Rowland and Bullock[51] emphasized the importance of the structure of the reaction residues after cross-linking. Bullock and Guthrie[52] provided data indicating that an increase in conditioned crease recovery angle occurs when carboxymethyl cellulose (D.S 0.05-0.10) as cross-linked with formaldehyde in the vapour state. Mackelvey and coworkers[53] have also shown that substitution of cellulose structure with various acyl groups produced fabrics with increased wet and dry CRA values. They attributed this to internal plasticizing effect of the long acyl groups.

However little work has been reported on the effect of oxidizing the cellulose structure before and after cross-linking. Table 7 shows the effect of oxidizing the cellulose structure with nitrogen dioxide prior to cross-linking with diemthylo urea (DMU). There is a general direct relationship between the percentage add-on of DMU and the crease recovery angle. The crease recovery angle is highest when hydrochloric acid is used as the catalyst. Data also show that increases in % add-on and CRA generally lead to losses in tensile strengths. It further shows that oxidation of cellulose leads to a considerable lowering of % add-on and a drastic loss in tensile strength. The decrease in add-on is in agreement with similar decreases observed in formaldehyde absorption. The loss in tensile strength however could not be altogether due to stiffening of the structure due to resin treatment as the values for control in the absence of resin also indicate a very large loss. A plausible explanation of this large loss may be hydrolysis of the cellulose by nitric acid which could be produced from nitrogen dioxide oxidant and moisture from the fabric. Results in table 7 show that addition of 0.1M sodium chloride leads to an increase

in add-on but without increase in CRA values. The increase in add-on could be due to shielding by $Cl^-$ ions of the positively charged groups as proposed and explained in the previous sections. Increase in add-on should have shown a corresponding increase in CRA values. This however is not observed. This suggests that intramolecular reaction between resin and hydroxyl groups on the same chain could be significant. The resins could also be deposited in the accessible region of the fabric causing brittleness and loss of fabric strength. Both the above modes of reaction while leading to increase in add-on will hardly affect the CRA. Results in Table 8 and 9 show similar behaviour for commercial resins ARK NG and ARK CA. These commercial resins lead to greater add-on than DMU. This may probably be due to differences in molecular sizes of the various resins and also the difference in concentrations used.

### 3.3.2 Effect of periodate Oxidation on resin finishing of Cellulose:

Oxidation of the Cellulose structure with nitrogen dioxide leads to a decrease in CRA values and tensile strength. It had been postulated that these losses may

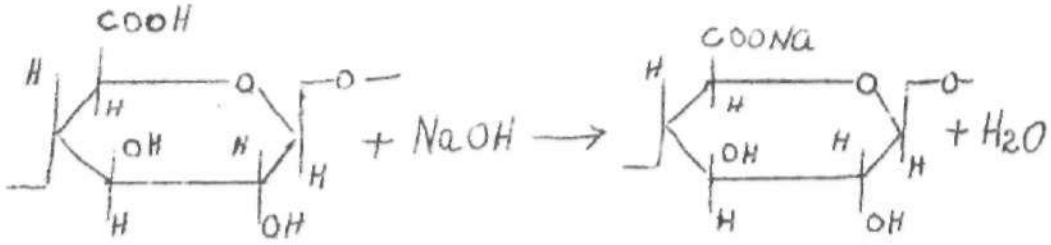
be due to hydrolysis of the cellulose. In this section the effect of oxidation of the cellulose structure with sodium metaperiodate is considered. Oxidation of the Cellulose structure with sodium metaperiodate leads to the breaking of the 2:3 bonds and production of dialdehyde in these positions. The aldehyde groups from one chain could react with hydroxyl groups from another chain leading to hemiacetal cross-linking which may lead to increase in the ability of the fabric to recover from creases. In order to investigate this "built in" cross-links in oxycellulose, cellulose oxidized to varying degrees was boiled in water for 30 minutes or dried and cured for 4 minutes at 150°C, and the CRA and tensile strength were determined. The results are shown in Table 12. It can be seen from the values of the control that oxidation with sodium metaperiodate leads to increase in CRA values. The higher the state of oxidation the greater the CRA values but there seems to be a levelling off at higher degree of oxidation. General losses in tensile strengths which increase with increase in the state of oxidation is also observed. These results also show that curing the periodate oxycellulose at 150°C even in the absence of cross-linking agents leads to very high CRA values,

which increase with the degree of oxidation. The CRA and tensile strength values for boiled oxycellulose are lower than those for the cured samples. This clearly indicates that more hemiacetal cross-links between adjacent chains are formed under dehydrating conditions.

$$\text{Cell} - OH + \text{Cell} - CHO \longrightarrow \text{Cell} - \underset{\displaystyle OH}{\underset{|}{CH}} - O\ \text{Cell}$$

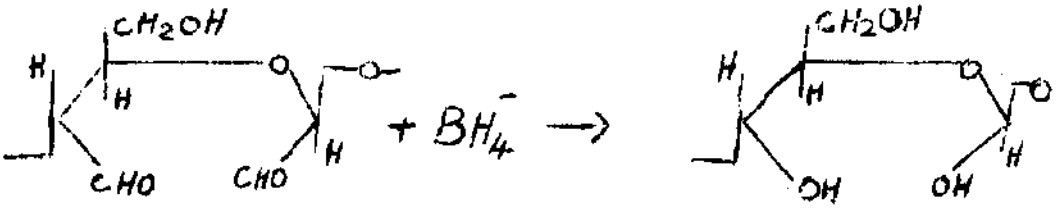
Lower tensile strength values are observed for boiled samples inspite of lower CRA values. This may be due to hydrolytic degradation under boiling conditions. Losses in tensile strength in periodate oxycelluloses are comparatively lower than those of nitrogen dioxide oxycellulose. While tensile strength loss is apparently inherent in the oxidation process its actual value is probably increased by easing of the strain due to opening of the anhydroglucose unit as a result of oxidation.

Tables 13 and 14 show results of investigation on various modified celluloses. The sodium carboxyl cellulose was prepared by reacting nitrogen dioxide oxycellulose with sodium hydroxide.




The sodium carboxy-cellulose will be fully ionised as a result of which an overall negative charge will be carried by the cellulose chain. However, since in resin finishing acid liberating catalysts are used it is doubtful how much of this negative charge would be retained by the fabric, but clearly the nett positive charge as a result of protonation of the aldehyde groups on the fabric would be much less than it would have been in the absence of carboxylate anions prior to resin treatment. This could result in reduction of repulsive forces between cellulose chain and the positively charged cross-linking moieties, leading to an increase in add-on. Results in Table 13 show that % add-on of both DMU and ARK NG are higher for COONa oxycellulose than COOH oxycellulose. This increase is also reflected in high CRA values of the sample. However, no significant change in tensile strength is observed.

Periodate oxycellulose was reduced by borohydride treatment and was then cross-linked with various resins. The aldehyde groups are reduced to hydroxyl groups, the reaction can be represented as:



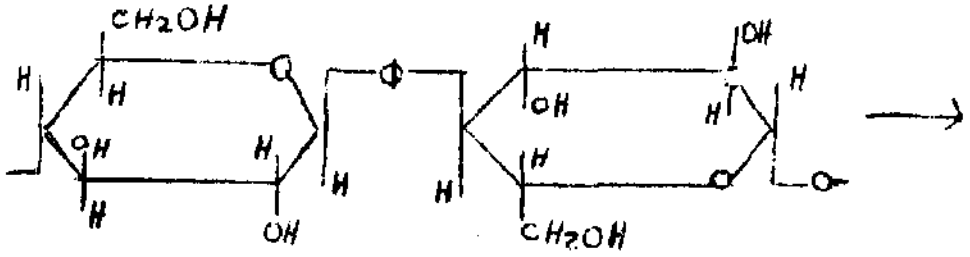
The results of cross-linking borohydride reduced oxycellulose are given in Tables 13 and 14. For ARK NG cross-linking, the % add-on is 16.45 as compared to 9.49 for periodate oxycellulose. Increase in add-on could be due to increase in hydroxyl groups as a result of reduction, the accessible hydroxyl groups can now react with resins. Moreover conversion of aldehyde groups to hydroxyl groups which are less readily protonated should lead to a decrease in electrostatic repulsion and hence an increase in add-on. Crease recovery angle values increased from 145.1° to 225.1° for borohydride oxycellulose while the increase for periodate oxycellulose is from 233.9° to 272°. Similar results are obtained for DMU treatment. The higher add-on of both DMU and ARK NG by borohydride treated oxycellulose does not seem to be

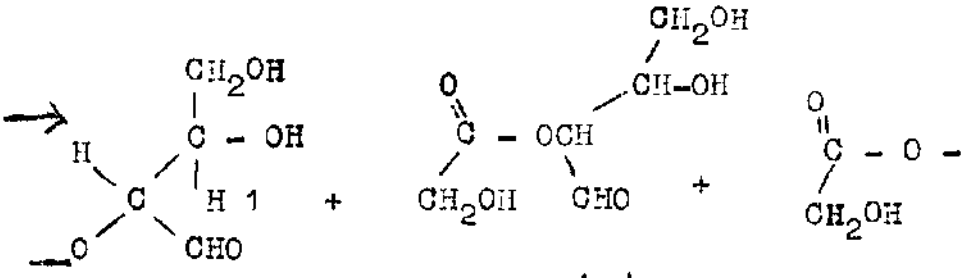
in tune with the CRA which are lower than those for periodate oxycellulose. It is thus clearly apparent that the periodate oxycellulose acquires cross-links other than from resin treatment. These as explained earlier could be hemiacetal links. No significant change in tensile strength is observed as a result of cross-linking borohydride reduced oxycellulose but the actual process of converting the aldehyde groups to hydroxyl groups leads to substrantial loss in tensile strength which is apparently due to hydrolytic degradation.

Celluloses of different degrees of periodate oxidation were prepared and then treated with ARK NG and 2.5% magnesium chloride catalyst. Results are shown in Table 15. The results indicate increases in CRA values of both resin treated and untreated samples. Oxidation with 0.05M sodium periodate for 6 hours gave CRA value 233° which increased to 297.3 after treatment with the resin. The breaking load dropped from 10.15kg to 9.72kg after treatment with resin. Ordinarily such a high CRA value (297.3) should have led to high loss in tensile strength. This shows that oxidation of the cellulose structure prior to cross-linking brings some release of strain in the cellulosic chain molecules.

To study this effect of release in strain on mechanical properties and CRA values cellulose fabrics were treated with ARK NG of various concentrations from 1-15%. The fabrics were prepared by the pad-dry-cure method and then oxidized with sodium metaperiodate of varying concentrations to bring about different degrees of oxidations. Results are given in Table 16. In all cases CRA values increase as ARK NG concentrations increase reaching a maximum at about 7.5%. Oxidation leads to increase in CRA values. Such high CRA values unavoidably should have resulted in much lowering of the tensile strength. This is not the case. It thus appears that oxidation leads to removal of strain from the fabric.

It is well known that oxidation of cellulose with periodate leads to products which are easily degraded by alkaline treatment. Pascu[54] has shown the mechanism of this degradation involving the formation of intermediary





degradation products

Cellulose fabric is subjected various times during its life to such alkaline treatment during laundering etc. Cellulose fabrics oxidized with 0.05M sodium periodate for 6 hours and cross-linked with 10% ARK NG solution dried and cured were subjected to alkaline treatment to investigate the effect if any of alkaline degradation. They were boiled with $Na_2CO_3$ solution of various strengths ranging from 1% to 10% for 5 minutes and the CRA and breaking loads were determined. Results are shown in Table 17. It can be seen that CRA values are not altered by alkaline treatment and further the strength of the fabrics were not affected. This shows that cross-linking due to hemiacetal and resins are fast to laundering. But the most interesting result of cross-linking with resin is to produce stable periodate oxycellulose. It therefore can be concluded that resin treatment in combination with periodate oxidation gives

fabric with higher crease recovery which is fast to laundering and the fabric resistant to alkaline degradation.

It must be admitted that resin treatment of fabrics to improve their desirable qualities is a complex process depending on the type of resin, state of the cellulose fabric before and after treatment and also on other auxiliaries such as catalysts and wetting agents. It had been found during the course of this work that oxidizing the cellulose structure using various oxidizing agents has profound effects on mechanical properties. Periodate oxidations generally lead to increases in CRA values probably due to hemiacetal formation while other types of oxidation produce lowering in CRA values. It is also observed that most processes of oxidation produce substantial losses in tensile strength. It might be worthwhile to discuss two conflicting theories pertaining to the mechanism of cellulose cross-linking. Parikh[15] has suggested that the mechanism involves protonation of the cellulose hydroxyl groups:

$$\text{Cell} - OH + H^+ \rightleftharpoons \text{Cell}(OH_2)^+$$

$$\text{Cell}(OH_2)^+ + CH_2(OH_2)_2 \rightleftharpoons \text{Cell}-O-CH_2OH$$

$$\text{Cell}(OH_2)^+ + \text{Cell}-O-CH_2OH \rightarrow \text{Cell}-OCH_2O-\text{Cell}$$

Barker[14] has however suggested that the mechanism involves protonation of the resin which can be resonance stabilized

$$HOCH_2OH + H^+ \rightleftharpoons HOCH_2\overset{+}{O}H_2$$

$$HOCH_2\overset{+}{O}H_2 \rightleftharpoons HOCH_2^+ + H_2O$$

$$HOCH_2^+ \rightleftharpoons HO{=}CH_2^+$$

The present investigation seems in line with the Barker mechanism. It however appears that the cellulose chain also carries positive charges not as suggested by Parikh but mainly due to protonation of the aldehyde groups which cellulose acquires in the process of purification or deliberate oxidation. This is indicated by the increase in add-on when sodium chloride is added to a reaction bath. Parikh and coworkers have not given a specification of their standard cellulose regarding CHO and COOH content. It is likely that the farbic used by Parikh had high aldehyde content and therefore his hypothesis that cellulose is positively charged may be justified. Barker did not observe any add-on with ethylene glycol as was expected from the Parikh model.

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