THE EFFECT OF GRAFTING ON THE PHYSICAL AND DYEING PROPERTIES OF MODIFIED CELLULOSES

BY

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

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D E D I C A T I O N

Dedicated to Ositadinma Egeonu Ibeagi of the blessed memory.

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F I G U R E S

ABBREVIATIONS

1.	Oxycellulose	Oxycell.
2.	Dimethylol-urea	DMU.
3.	On Weight of Fabric	OWf.
4.	Weight for Weight	W/W
5.	Methyl methacrylate	MMA
6.	Acrylonitrile	AN
7.	Poly(methyl methacrylate)	PMMA
8.	Poly(acrylonitrile)	PAN

A B S T R A C T

Poly(aerylonitrile) and poly(methyl methacrylate) were grafted onto standard and chemically modified celluloses under various conditions using Ceric IV ion as a catalyst.

The effect of grafting on the tensile strength, crease resistance and the dye affinity of the cellulose substrates were investigated. Chemically modified celluloses were obtained by oxidation and cross-linking with various agents using standard procedures.

Dyeing properties of the standard and modified celluloses were obtained using purified Chlorazol Sky Blue FF.

It has been observed that:

a. Oxidation and cross-linking deoreased the tensile strength of the fabric,

b. Metaperiodate oxidation improved fabric crease resistance whereas other forms of oxidation tended to decrease the same property,

c. Cross-linking and grafting decreased the tensile strength of the fabric,

d. Grafting increased the tensile strength of formaldehyde cross-linked standard cellulose, dimethylol-urea cross-linked chromic acid oxycellulose and hypochlorite oxycellulose, but it decreased the tensile strength of standard cellulose, metaperiodate oxycellulose, formaldehyde cross-linked metaperiodate oxy-cellulose and dimethylol-urea cross-linked hypochlorite oxycellulose, and

e. Grafting increased the dye affinity of formal-dehyde cross-linked metaperiodate oxycellulose, dimethylol-urea cross-linked standard cellulose, but it decreased the dye affinity of standard cellulose, dimethylol-urea cross-linked standard cellulose, chromic acid oxycellulose, metaperio-date; oxycellulose, hypochlorite oxycellulose and formaldehyde cross-linked hypochlorite oxycellulose.

CHAPTER ONE

1.1 INTRODUCTION

Cellulose fibres are of great importance in textiles and in allied fields due to their inherent properties such as reasonable tensile strength, water imbibition and high degree of crystallinity.

In order to enhance these natural characteristics and in some cases to impart other new properties, several attempts have been made to modify the structure. Cellulose fibres do not shrink but their disadvantage is that fabrics made of them crease badly.

Whereas protein fibres resist creasing because their molecules are cross-linked together by primary chemical bonds, the weaker Van der Waals' forces and hydrogen bonds in cellulose fibres are incapable of retracting the cellulose chains back to their original positions. It has been proposed that if the amorphous regions could be cross-linked the fibres would become more rigid and slippage of molecules would be minimized.

The first patented cross-linking process by Tootal, Broadhurst, Lee and Co., Foulds, Marsh and Wood involved urea and formaldehyde (1).

Crease resistance and dimensional stability are imparted by polymer network formation within the fibre and by cross-linking adjacent cellulose chains. It is now recognized that application of cross-linking agents to a cotton fabric leeds to decrease in dyeing with direct dyes (2).

According to the generally accepted concepts of dyeing process, practical lack of dyeability may be due to:

i. lack of affinity of the dye to the fibre.
ii. slow rate of diffusion of the dye in the fibre.
iii. inaccessibility of the dye to the fibre.

In order to improve the dyeability and other desirable properties of the cellulosic fabric graft copolymerization of some vinyl polymers onto cotton substrates has been investigated.

1.2 Structure of Cotton Cellulose

It is now generally accepted that cellulose is polymeric with structure shown in Fig. I.

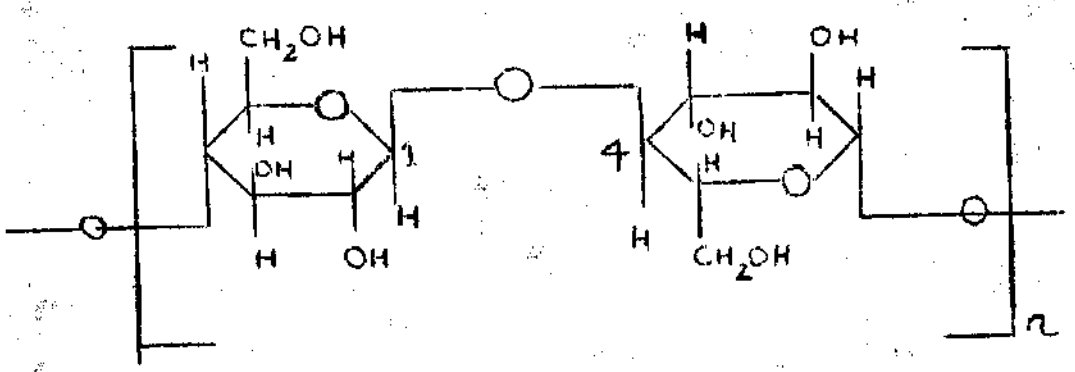
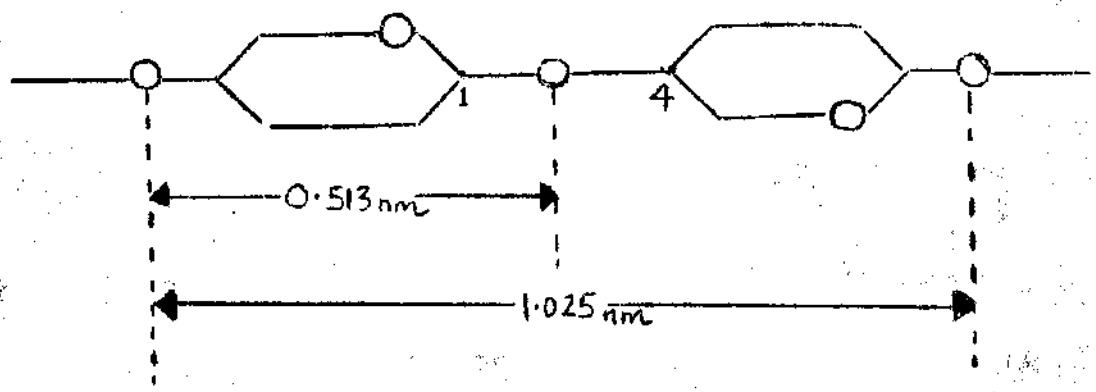


Fig. I Cellobiose unit



Confirmation of the above structure was obtained by analysis of the cellobiose unit using X-ray diffraction.

Preston et al (3) have shown that cellobiose consists of two β - glucose molecules that are linked at the 1, 4 carbon atoms. The primary hydroxyl group on C-6 atom is most readily accessible for reactions. Variation in the physical properties of cellulose is attributed to the differences in the degree of crystallinity. Crystallinity is in turn attributed to dimensional regularity imparted to cellulose chain by spatial distribution of the hydroxyl groups. These hydroxyl groups enhance lateral association of cellulose chains by hydrogen bonding (4,5,6).

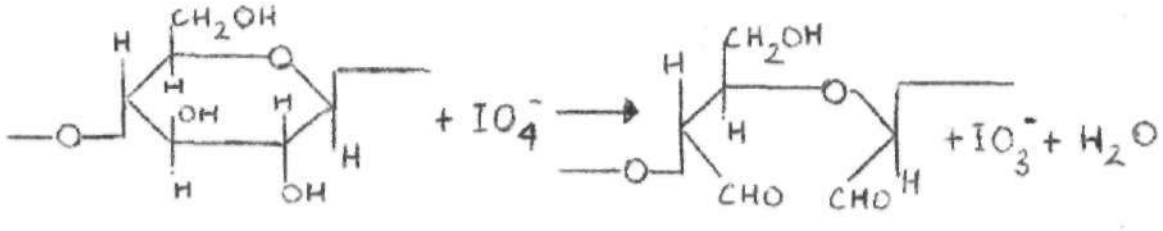
Cotton fibres are now believed to be composed of long range order of crystalline regions and amorphous regions where the chain molecules are in random orientation. There is also a gradual transition between the highly ordered regions and the completely unorientated regions with no marked boundary between the two regions (7). X-ray patterns of cellulose reveal four types of crystal lattice arrangements which are designated

Cellulose - I, Cellulose - II, Cellulose - III and Cellulose - IV. Classification is based on axial dimensions of the crystalline lattices, and the value of β - angle of the lattices. These crystallites constitute the fine structure. The fringed fibrillar concept proposed by Hearle (8) regards the crystalline region as a continuum that trespasses the non-crystalline region to join another fibril. This concept has been confirmed by electron and light-scattering microscopic examinations of highly swollen cotton fibre (9,10).

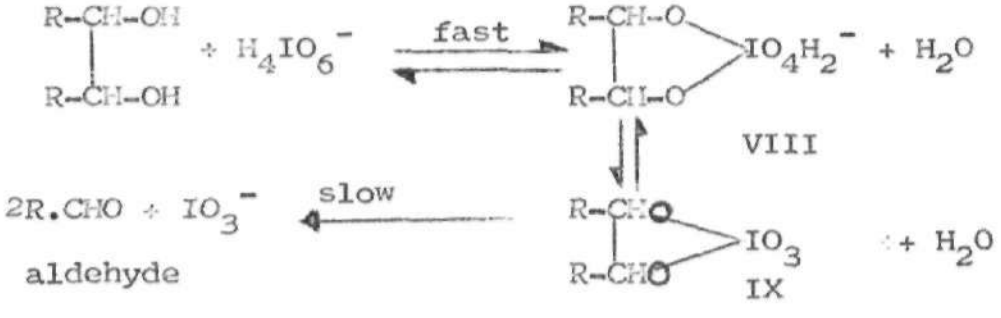
1.3 Oxidation of Cotton Cellulose

1.3.1 Metaperiodate oxidation

Oxidation of cotton cellulose by metaperiodate under suitable conditions leads to the conversion of anhydro-D-glucose units to dialdehyde units. Metaperiodic acid oxidation has been shown by Jackson and Hudson (11) to follow the normal Malaprade course where each chain unit converts to 2,3 dialdehyde unit:



The oxygen consumption of metaperiodate oxycellulose is equal to the percentage of the chain units that have been oxidized, according to equation of the oxidation reaction. The mechanism of oxidation of cellulose by metaperiodate is believed to consist of a rapid formation of a univalent anionic ester VIII which is readily dehydrated to IX. IX structure decomposes slowly and unimolecularly to the final products by intramolecular rearrangement:



Exhaustive studies of properties of metaperiodate oxycellulose by Davidson (12) reveal the presence of aldehyde groups in the oxidized chains due to their high copper reducing power and extreme alkaline sensitivity.

1.3.2 Chromic acid oxidation

The mode of attack on cellulose by metaperiodates

and nitrogen dioxide has been found to be reasonably specific (13). They are able to react with both amorphous and crystalline regions of the material without destroying its fibrous form. Results obtained from these specific reactions are applied in the interpretation of the more complicated reactions that are associated with such industrially important oxidants as hypochlorites and chromic acid. Oxidation of cellulose by aqueous chromic acid (dichromate in dilute sulphuric acid) leads to a progressive increase of both reducing and acidic properties (14). Uronic acid determination (15) suggests that the majority of the carboxyl groups formed are at C-6 atom. Chromic acid oxycellulose differs from most other oxycelluloses in that they retain much smaller mechanical properties. Chromic acid oxycellulose is therefore characterised by high copper number and low methylene blue affinity, which indicate high aldehyde and low carboxyl contents.

1.3.3 Hypochlorite oxidation

Oxidation of fibrous cellulose by hypochlorite has been shown by Clibbens Et al (16) to depend on the pH of the solution. In alkaline solution where the

effective oxidant is the hypochlorite ion, the reaction is very slow, and it gives rise to acid oxycelluloses of low reducing power. In mildly acidic solution (pH 3-5) in which the effective oxidant is undissociated hypochlorous acid, the reaction is also slow but it gives rise to highly reducing oxycelluloses which contain few acid groups.

In neutral (or nearly neutral; pH 7.4) solutions which contain both hypochlorite ions and hypochlorous acid, the oxidation is maximum and oxycelluloses with both acidic and reducing properties are produced (17).

1.4 Theories on Cross-linking

Although the mechanism of cross-linking of cotton cellulose with resins is not fully understood, the process is based on the presence of the hydroxyl groups on each of the anhydro-D-glucose unit. If the bifunctional cross-linking agent is represented by the formula X-R-X, where X is the cellulose reactive group, then the cross-linking reaction may be represented by the equation: $2Cell\text{-}OH + X\text{-}R\text{-}X \rightarrow Cell\text{-}O\text{-}R\text{-}O\text{-}Cell + 2H\text{-}X$

Because of the usual slow rate of cross-linking reactions in alkaline medium, the reactions are acid-catalysed. For cross-linking reaction of formaldehyde with cellulose under acid conditions, Barker (18) proposed the following mechanism:

$$HOCH_2OH + H^+ \rightleftharpoons HOCH_2O^+H_2$$

$$HOCH_2\dot{O}H_2 \rightleftharpoons H\dot{O}CH_2 + H_2O$$

$$HO\dot{C}H_2 \longleftrightarrow H\dot{O}{=}CH_2 \qquad (1)$$

$$Cell\text{-}OH + H\dot{O}CH_2 \rightleftharpoons Cell\text{-}O\text{-}CH_2OH + H^+$$

$$Cell\text{-}OCH_2OH + H^+ \rightleftharpoons Cell\text{-}O\text{-}CH_2\dot{O}CH_2$$

$$Cell\text{-}O\text{-}CH_2\dot{O}CH_2 \rightleftharpoons Cell\text{-}O\text{-}\dot{C}H_2 + H_2O$$

$$Cell\text{-}O\text{-}\dot{C}H_2 + Cell\text{-}OH \longrightarrow Cell\text{-}O\text{-}CH_2\text{-}O\text{-}Cell + H^+ \qquad (2)$$

The existence of the resonance stabilized carbonium ion (I) makes this proposal more acceptable than that of Parikh (19). The general expression for cross-linking reaction between dimethylol-urea (DMU) and cellulose in acid medium is as shown:

$$HOCH_2.HN\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH.CH_2OH + 2Cell\text{-}OH$$

$$\xrightarrow{H^+} Cell\text{-}O\text{-}CH_2\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}CH_2\text{-}O\text{-}Cell + H_2O$$

1.5 Theories on Grafting

It has been recognized that ceric salts form effective redox systems in the presence of organic reducing agents such as alcohols, thiols, glycols, aldehydes and amines (20). The oxidation-reduction produces Cerous ions and transient free radical species capable of initiating vinyl polymerization.

Duke et al (21, 22) have shown that Ceric salts form complexes with alcohols and glycols, and that the disproportionation of these complexes is the rate determining step of the reaction.

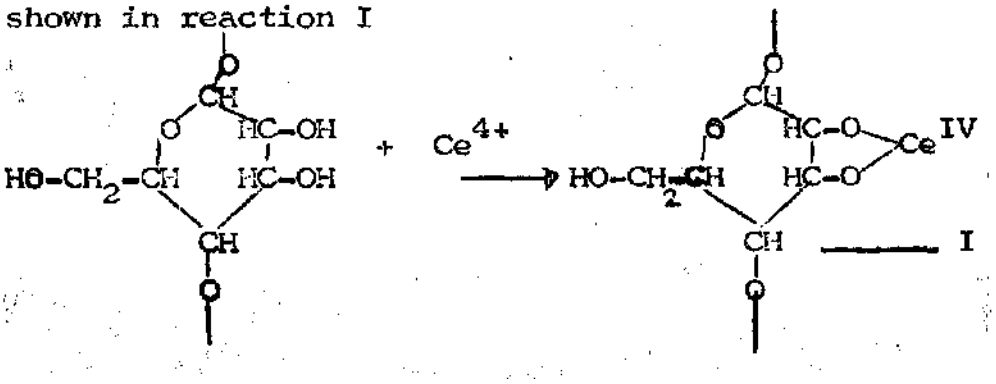
Mino and co-workers (23,24) have observed that C_1-C_2 bond in the glycol is cleaved during oxidation reaction with Ce IV ion, and that grafting onto cellulose involved cleavage of the C_2-C_3 glycol bond.

Terasaki and Matsuki (25), Cumberbirch and Holker (26), and Arthur et al (27) have also postulated glycol bond cleavage in cellulose grafting initiated by Ce IV ion. For alcohols (20, 28, 29) the mechanism of reaction is generally expressed as: $Ce^{4+} + RCH_2OH \rightleftharpoons B \rightarrow Ce^{3+} + H^+ + R\dot{C}HOH$

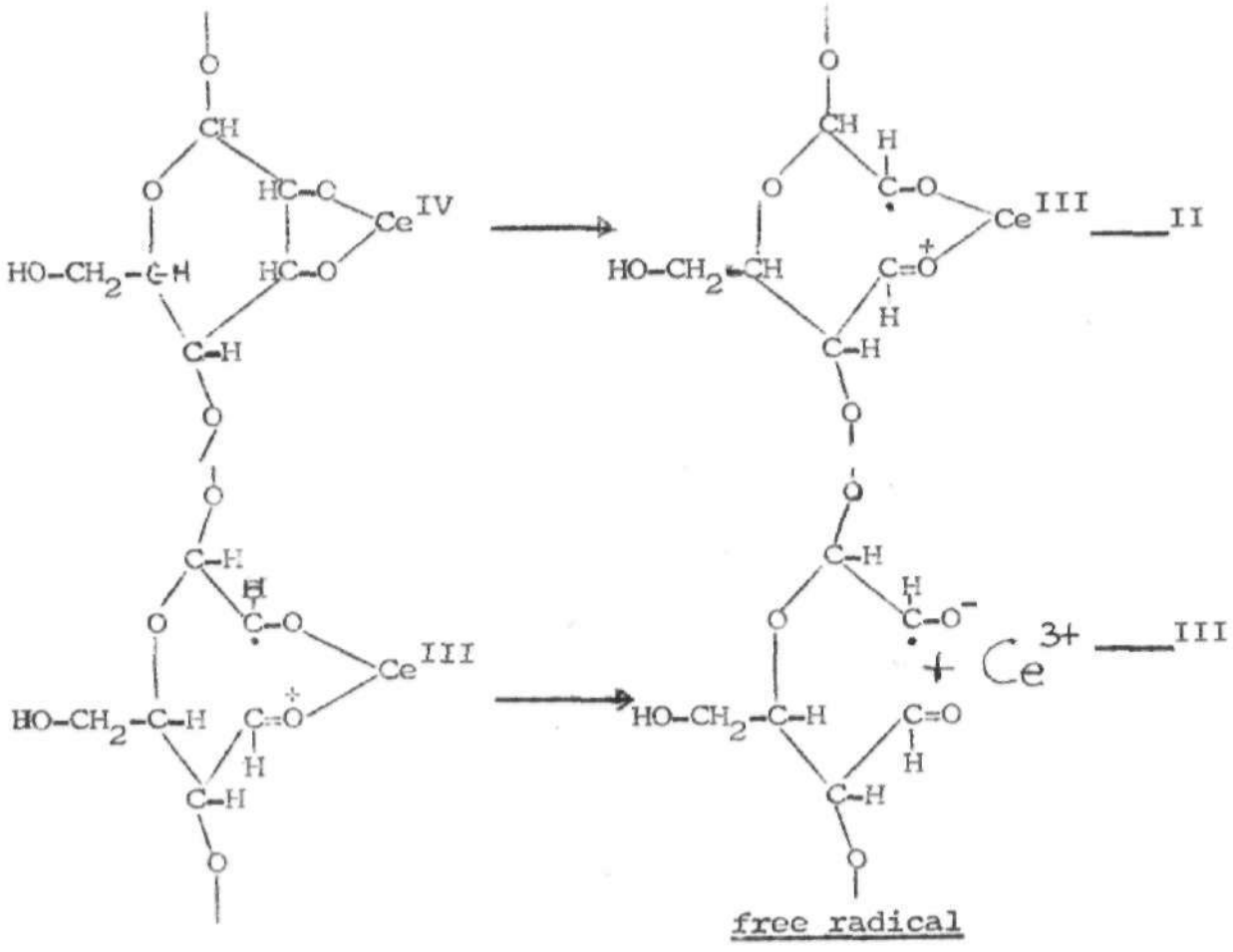
where Ce^{4+} represents the Ceric complexes as they exist in aqueous solution, B the Ceric-alcohol complex, and $\dot{R}CHOH$ a free radical. The important feature of the oxidation with Ce IV ion is that it proceeds via a single electron transfer with formation of a free radical on the reducing agent. If the reducing agent is cellulosic material and the oxidation is carried out in presence of a vinyl monomer the free radical produced on the polymeric cellulose backbone initiates graft polymerization (30).

Reports by Mino and co-workers (23, 24), and Katai (31) support free-radical mechanisms based on the oxidation of glycols for initiation of graft copolymerization reactions of cellulose by Ce IV ion.

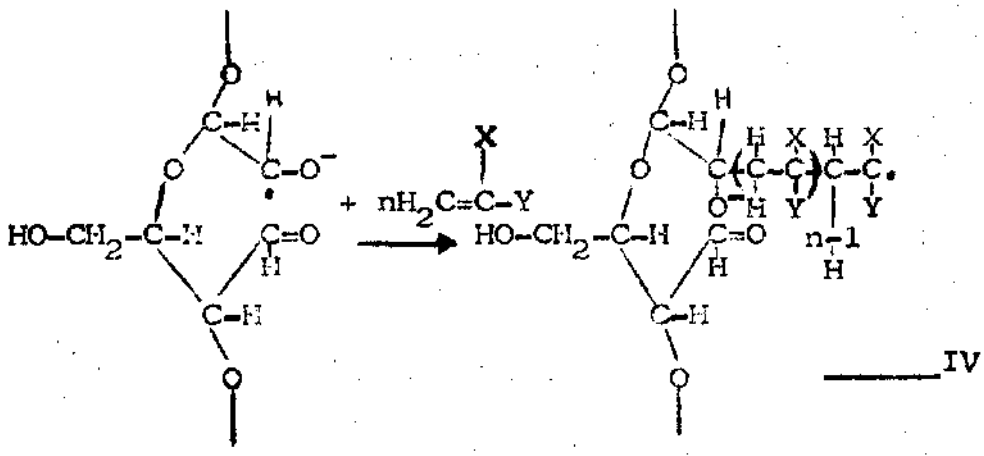
Arthur, Baugh and Hinojosa (27) have suggested that the Ceric ion would form a chelate with cellulose molecule, possibly through C_2 and C_3 hydroxyl groups as shown in reaction I



There would follow a transfer of electrons from the cellulose molecule to Ceric ion which would result in its reduction to Cerous ion, breakage of C_2-C_3 bond, and formation of a radical site as shown in reactions II and III.



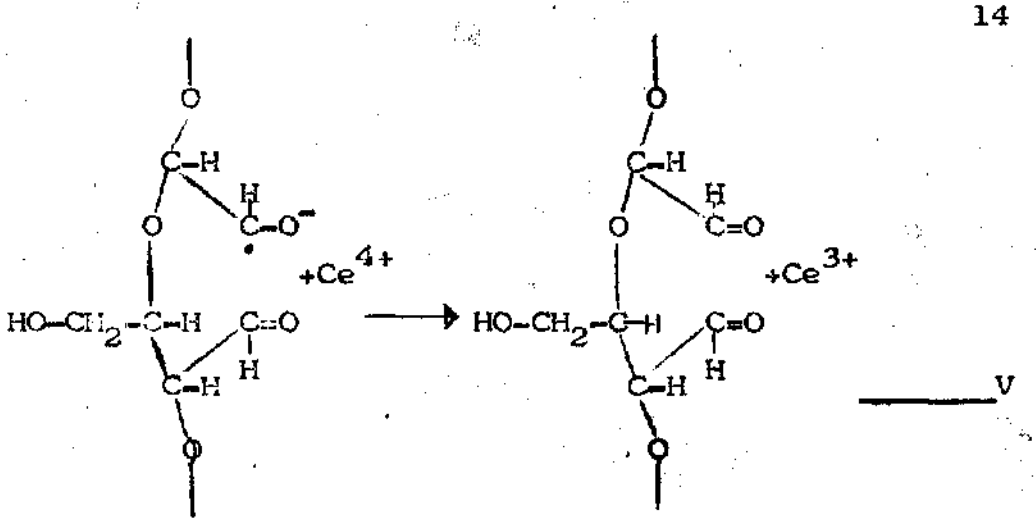
Grafting of the vinyl monomer onto cellulose chain involves addition of the monomer to the free radical sites along the chain length as shown in IV,



IV

where X may be hydrogen or methyl group, and y methyl carboxylate or cyanide group.

The decay of radical sites on cellulosic material has been suggested by Martel and Calvin (32). On initiation of graft copolymerization at this site, as shown in reaction IV, additional Ceric ion could chelate with cellulose forming additional free radical in the manner described. Then termination of radical sites could result in the subsequent reaction of Ceric ion with the radical as shown in V.



Termination of propagating vinyl polymer may be effected either by exhaustion of initiator, exhaustion of the monomer or by a chain transfer agent. Termination is diffusion - controlled, that is, it is governed by the rate at which the reactive sites in growing radicals can come together rather than by chemical factors.

1.6 Theories on dyeing

Dyes are surface-active agents. When dissolved in water dye molecules tend to concentrate more closely together at a surface than in the body of the solution. Direct dyes in particular are aromatic compounds with azo-linkages, of extended π-electron system, with polar substituents, and with water solubilizing groups (e.g. $-SO_3^-$, $-COO^-$).

In solution the forces which hold dyestuff to textile fibres are complex, and the process of dyeing consists of three stages:

i. migration of the dye from the solution to the fibre surface, and

ii. adsorption of the dye onto the surface of the fibre,

iii. diffusion of the dye from the surface towards the centre of the fibre.

The adsorption of dye molecules onto the fibre surface is governed by electro-potential forces, temperature and agitation.

Cellulose textile fibres carry a nett negative charge when immersed in aqueous solution (33, 34). Most dyes when in solution exist in molecular or partially ionized state. In the direct dyes, the chromophore-containing ions bear negative charges that are repelled by the zeta-potential of the cellulose fibres. Migration of dye molecules to the surface of the fibre is accelerated by increasing the temperature of the dye-bath to promote vibrational activity of the dye molecules.

Addition of electrolytes counteracts the effect of the negative zeta potential. The diffusion of dye molecules in isotropic medium towards the centre of the fibre is governed by Fick's law (35) which states that the rate of transfer of a diffusant through a section of a unit area is proportional to the concentration gradient measured normal to the section. Expressed mathematically the statement is,

$$F = -D \frac{\partial c}{\partial x}$$

where F = rate of transfer per unit area of section.

C = concentration of the diffusing substance.

X = space co-ordinate measured normal to the section.

D = diffusion coefficient (with the dimension of length^2 time^{-1})

D is therefore a measure of the ability of transfer in a steady state of flow across the section when the concentration gradient is constant.

In an anisotropic medium such as most fibres, the diffusion properties depend on the direction in which they are measured. Fick's second law which is of more fundamental consequence applies to non-steady state conditions. It describes the accumulation of dye C in a medium at a given point X, as a function of time t, and it is generally expressed as,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

In a non-steady state diffusion, concentration varies in a non-linear manner with the penetration distance. The total amount of dye adsorbed at any instance therefore may be represented by a concentration gradient which indicates the presence of strong or weak adsorption forces between the dye and cellulose fibres (36).

Other parameters which influence the rates of dyeing at microscopic level have been summarized (37) as:

i variations in the nature and concentration of ionizable groups both in the dye and in the polymer substrate.

ii. interactions between all species in both phases,

iii. changes in physical structure of the substrate and the release and formation of stresses together with changes in amorphous regions,

iv. changes in structure and molecular orientation of the dye in both phases and in boundary layers.

In most dyeing processes in solution phase, the free energy of the dye solution is initially greater than that of the fibre phase. This difference in free energy accounts for transfer of the dye to the fibre until equilibrium is attained when the free energy in the liquid and solid phases are equal.

The effect of temperature on the activation of molecular vibrations of the solute until it exceeds the critical energy for it to migrate from solution to fibre has been summarized by this form of Arrhenius equation:

$$D_T = D_o e^{-E/RT}$$

where D_T = diffusion coefficient at temperature T,

D_o = a constant

E = Activation energy

R = Gas constant, and

T = thermodynamic temperature.

From the logarithmic form(i.e. $\log D_T = \log D_o - E/RT$), it is possible to determine the activation energy of dyeing E, by plotting $\log D_T$ against I/T

Heat of dyeing ΔH^o, is a measure of the strength of the bonds by which the dye is held to the fibre and it is generally expressed as:

$$\Delta H^o = \left(\frac{\Delta \mu_1^o}{T_1} - \frac{\Delta \mu_2^o}{T_2}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1}$$

where ΔH^o = heat of dyeing,

$\Delta \mu_1^o$ = difference in standard potential at T_1

$\Delta \mu_2^o$ = difference in standard potential at T_2

The concept of dye being dissolved in a solid is thought to be a confusion of solution with adsorption by some colourists. Adsorption isotherms are obtained by plotting values of concentration of dye per unit weight of the solid $D\phi$, against the values of concentration of dye in solution after dyeing $D\zeta$, at constant temperature. Dyeing processes are characterized by three categories of adsorption isotherms: Nernst, Langmuir and Freundlich.

The Freundlich isotherm best describes the adsorption of direct dyes on cellulose substrates. The classical work of Freundlich (38) on adsorption shows that the ratio of the amount of adsorbed dye on a given amount of solid to the concentration of dye in solution is not a constant at different concentrations of the dye-bath. The $D\phi/D\zeta$ curve therefore is not a straight line nor does it reach a point at which it becomes parallel to horizontal axis, as shown in Fig.2.

The more generalized form of Freundlich adsorption isotherm, $D\phi = K D\zeta^{x}$

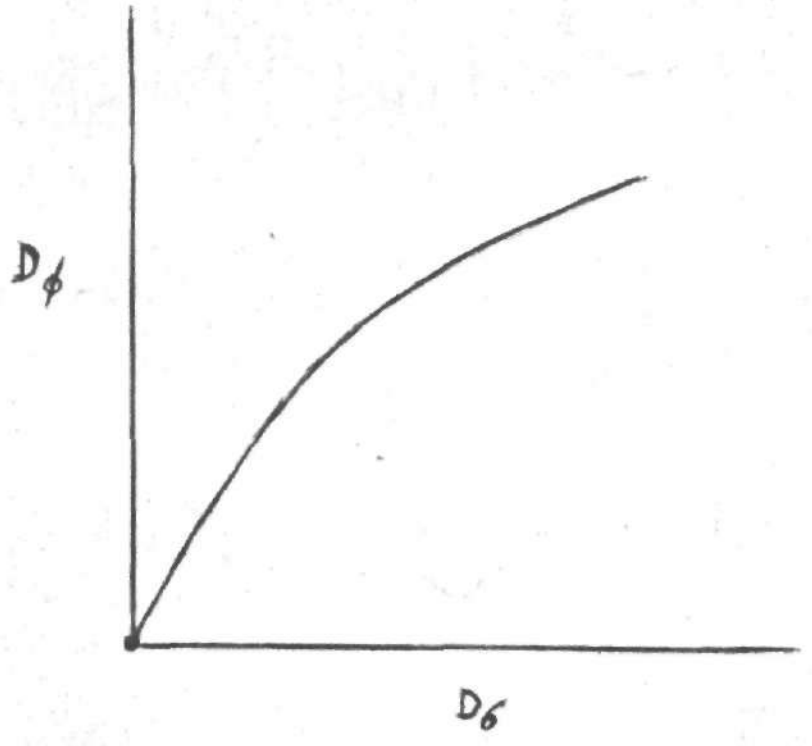


Fig 2: D_ϕ versus D_σ plot

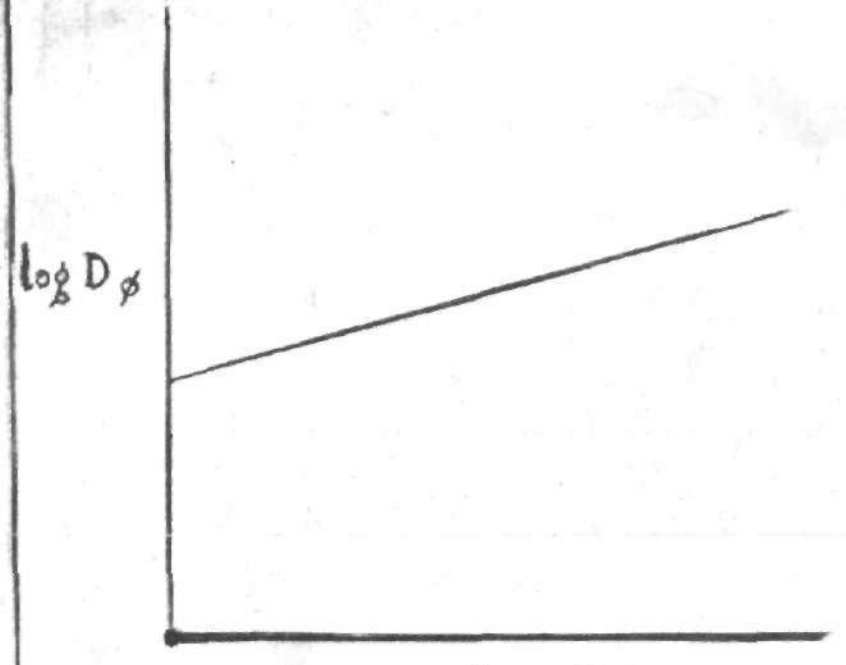


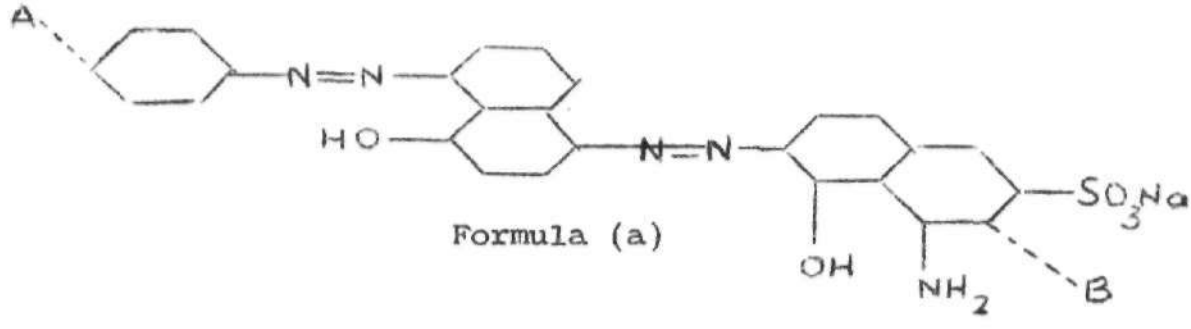
Fig 3: $\log D_\phi$ versus $\log D_\sigma$

states that if D_6 is raised to a power x(of the order 0.5), then $D\phi/D6^{x}$ is a constant at a given temperature (39). From the logarithmic form of Freundlich adsorption isotherm,

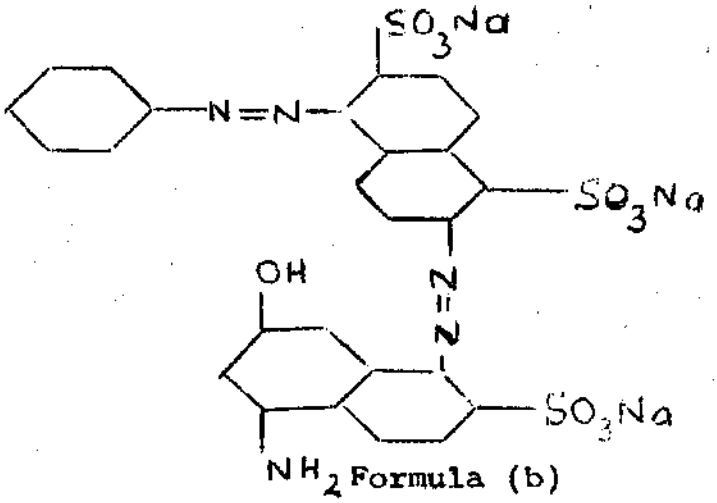
$$\log D\phi = \log K + X \log D6$$

a plot of log Dø against log D_6 is expected to be a straight line, of the form shown in Fig. 3.

The nature of affinity of cellulose substrates for direct dyes has only been explained recently. Since cellulose has no polar groups capable of forming salt linkages, it was assumed that the binding forces were purely physical. In 1928 Meyer (40) expressed the view that substantivity was associated with extended linear structure of the dye so that it could align itself on the fibre surface. In formula (a) for example, the dye molecule is linear in the direction of A.....B, whilst the bisazo compound, formula (b) has no such configuration and is non-substantive:



Formula (a)



Formula (b)

When this concept is applied to the molecules of azo dyes, it would appear that only the trans isomers are substantive, but commercial dyes are equilibrium mixtures of both trans and cis forms. It is believed that the cis form is transformed to the trans configuration as the later is adsorbed by the fibre.

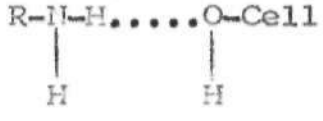
Further contributions to the theory of relationship between structure and substantivity were made by Hodgson (41) and Hodgson and Marsden (42). They postulated that not only must the dye molecule be linear but the benzene nuclei must be coplanar.

Schirm (43) attributed substantivity to a system of conjugated double bonds.

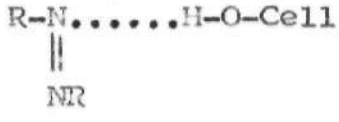
Preston (44) also suggested that molecules of substantive dye attached to cellulose chains should be

predominantly orientated parallel to the fibre and should exhibit dichroism.

Leed (45) suggested that affinity of direct dyes, to cellulose substrates might be due to the interaction between electrons in an extended conjugated system and the hydrogen atoms of the hydroxyl groups of the cellulose substrates. Groups like -OH, $-NH_2$, and -N=N- in the dyestuff molecules as in (c) and (d) respectively are capable of forming hydrogen bond with hydroxyl groups of cellulose fibres.



(c)

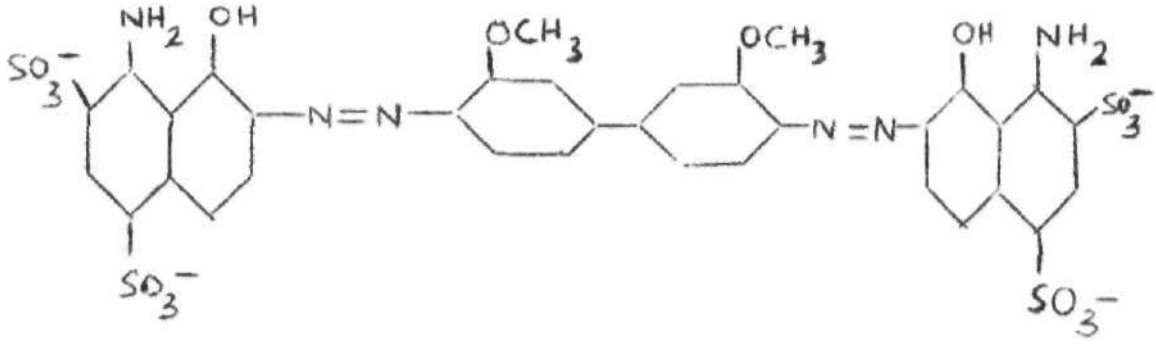


(d)

1.6.1 Effect of addition of electrolytes on dyeing of cellulose fibrics

Addition of electrolytes to dye liquor tends to promote exhaustion of direct dyes although the effect varies considerably with dyestuffs. Cellulose fibres which assume a negative charge when immersed in aqueous

solution, repel similarly charged ions of the direct dyes. Electrolytes reduce or extinguish the charge on the fibre, thus facilitating the approach of the dye ion to the range at which hydrogen bonding or Van der Waals' forces can be effective (46). It would therefore be expected that the effectiveness of electrolytes in promoting exhaustion vary directly with the molecule of the dye. Hence Chlorazol Sky Blue FF with four sulphonic acid groups in the molecule only stains cotton fabric until electrolyte is added after which it exhausts well.



Chlorazol Sky Blue FF (C.I. Direct I) anion

1.6.2 Effects of temperature, concentration, and pH of dye-bath on dyeing of cellulose fabrics.

Increase in temperature of the dyebath decreases the amount of dye molecules adsorbed at equilibrium. Increase in kinetic energy of the dye molecules by increase in temperature hastens the speed at which equilibrium is attained at that temperature.

A typical Freundlich isotherm for a direct dye indicates that percentage exhaustion increases as the concentration of the dye in the solution becomes greater. Dyeing in short-liquor ratio will enhance heavy shades for direct dyes.

Direct dyes are invariably applied to cotton fabric from neutral solution. No advantage seems to be gained by addition of acid; mild alkali has a retarding effect on the rate of adsorption.

1.6.3 Effect of agitation on dyeing of cellulose fabrics.

When the amount of dye in the solution is limited, the diffusion of the dye molecules into the fibre could be more rapid than the assembly on the surface, and agitation will then become a significant factor.

Alexander and Hudson (47) have shown that the rate of diffusion of dye molecules into fibre is dependent on the concentration of dye molecules in the interfacial layer, and is influenced by the degree of agitation which leads to much greater decrease in time of half-dyeing.

Stirring of dye-bath in dyeing process is essential in order to maintain high concentration of the dye in the interfacial layer, and to decrease the time of half-dyeing.

1.7 Scope of Present Investigation

Cellulose fabrics have been industrially treated with bifunctional reactants derived from formaldehyde to impart dimensional stability, wrinkle recovery and other desirable properties. However it is now recognized that as a result of cross-linking the cellulose chain, the fabric becomes difficult to dye with direct dyes. Grafting of vinyl polymers onto the cellulose structure is now being investigated as a means of improving the desirable characteristics but little has been reported.

This investigation deals with the study of the effect of grafting specific polyvinyl compounds onto standard and modified celluloses. The cellulose structures were modified by oxidation with various oxidizing agents, followed by cross-linking with dimethylol-urea and formaldehyde. The effect of grafting on the affinity of Chlorazol Sky Blue FF to these substrates has also been investigated.

It is hoped that this investigation will not only provide further insight into the grafting process but also that the physical and dyeing properties of cellulose will be improved by the various processes.

CHAPTER TWO

EXPERIMENTAL METHODS AND RESULTS

2.1 Standard Cellulose

The cotton fabric 22 picks/cm and 24 ends/cm in the weft and warp directions respectively (from Kaduna Textiles, Limited) was scoured, bleached and partially mercerized by standard method (48). The purified material was used as standard cellulose, and it has the following properties:

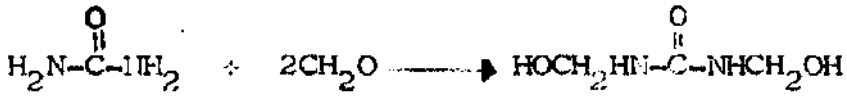
Copper number 0.08; carboxyl content 0.78 mEq COOH/100g of bone-dry cellulose; and moisture content 6.1% at 65% R.H. These properties were determined by the various standard methods described elsewhere (49, 50, 51).

2.2 Resins

The resin, dimethylol-urea (DMU) was prepared by mixing 60 parts of urea (1 mole) and 170.3 parts of 37% (ANALAR grade) aqueous formaldehyde (2 moles) and reacting for 15 hours at 28°C in constant temperature

water-bath. The pH range of 7-8 was maintained by addition of monosodium phosphate as buffer (52). The resulting dense precipitate of dimethylol-urea was filtered, washed with anhydrous alcohol and vacuum dried.

Equation for the reaction is as shown:



urea (1 mole) formaldehyde (2 moles) Dimethylol-urea

The formaldehyde resin was prepared by diluting 37% (ANALAR grade) aqueous formaldehyde to 14.8% aqueous solution with distilled water.

2.3 Preparation of Oxycelluloses

All oxycelluloses prepared in this investigation were limited to oxygen consumption of 5(53).

2.3.1 Chromic acid Oxycellulose (CrO_4^{2-} - Oxycell.)

10.2g of standard cellulose was treated with 0.1N potassium dichromate solution acidified with 0.2N

sulphuric acid, for 48 hours in a 2-litre quick-fit flask at 28°C. The material to liquor ratio was maintained at 1:50 (15). After oxidation, the fabric was washed liberally with distilled water, and dried in air. Oxygen consumption of the standard cellulose was determined volumetrically by measuring the fall in concentration of the acidified dichromate solution (54).

2.3.2 Metaperiodate Oxycellulose (IO_4^- - oxycell)

12.5g of standard cellulose was treated with 0.01M sodium metaperiodate solution for 24 hours in an amber-coloured bottle in darkness at room temperature, in material to liquor ratio of 1:50. At the end of the oxidation period, the oxycellulose was washed with distilled water and dried in the air (55). The fall in metaperiodate concentration, a measure of oxygen consumption, was determined by the method of Müller and Freidberger (56).

2.3.3 Hypochlorite oxycellulose (OCl^- — oxycell.)

8.6g of standard cellulose was treated with 0.04N sodium, hypochlorite at pH 7.4, at 28°C, with shaking

for 12 hours. Material to liquor ratio was maintained at 1:50. After oxidation period, the oxycellulose was steeped with 0.1N hydrochloric acid, washed free of the acid and then dried in air (16).

Oxygen consumption of the standard cellulose was determined by measuring the fall in hypochlorite concentration due to oxidation.

2.4 Cross-linking Cellulose Samples with Resins.

2.4.1 Cross-linking with Dimethylol-urea (DMU).

Standard and oxidized celluloses were treated with dimethylol-urea (DMU). In all cross-linking reactions with dimethylol-urea, the bath was made up of 3% dimethylol-urea on weight of fabric (Owf), 1% Teepol-X on weight of fabric (Owf), and was acidified with 12.5% hydrochloric acid (pH5.6). The materials were padded with the resin solution, centrifuged to maximum wet pick-up, dried in oven at 150°C for 3 minutes and conditioned at 65% Relative Humidity for 24 hours (57.)

2.4.2 Cross-linking with Formaldehyde (Pad-Wet Batch Process)

In all formaldehyde treatments, the cellulose materials were immersed in 14.8% aqueous formaldehyde in 50% phosphoric acid (pH 5.6). After thorough wetting out to a maximum wet pick-up, the samples were stored for 24 hours in polythene satchets after which they were neutralised with 2% sodium carbonate solution, washed thoroughly with distilled water and dried in air at room temperature (58).

Percentage add-on values of dimethylol-urea and formaldehyde to standard and oxidised celluloses are as shown in Tables 1 and 2 respectively.

2.5 Purification of Monomers

2.5.1 Methyl methacrylate (MMA)

Methyl methacrylate (BDH reagent grade) was vigorously shaken with 10% sodium hydroxide (for removal of hydroxy-quinol stabilizer) and washed with distilled water. The purified monomer was dried by storing over anhydrous calcium sulphate, at 28°C.

2.5.2 Acrylonitrile (AN)

Acrylonitrile was purified by distillation at reduced pressure (for separation of methoxy-quinol stabilizer). The freshly distilled monomer was stored in a 250cm^3 stoppered Erlenmeyer flask, at 28^{o}C.

2.6 Grafting of Cellulose samples with Monomers (Solution Technique)

The grafting reactions were carried out as follows: 0.01M Ceric ammonium nitrate (BDH reagent grade), in 0.1M nitric acid was introduced into 250 cm^3 Erlenmeyer flask and kept in a thermostat for 10-15 minutes. The material to liquor ratio of the sample to Ceric solution was maintained at 1:30. The required amount of monomer was added in the material to monomer ratio of 1:1 weight for weight (W/W); and 5 g of sample was immediately introduced. The flask was stoppered, and the contents stirred occasionally during the polymerization. After one hour, the sample was washed thoroughly with hot soap solution (to remove loosely adhering homopolymer) and then with distilled water

and dried.

For grafting with acrylonitrile (AN), it was observed that extraction of grafted samples with dimethyl formamide (DMF), caused negligible loss in weight. Removal of homopolymer was carried out with thorough soaping and washing; solvent extraction was not considered necessary. In the case of methyl methacrylate (MMA), the grafted samples were extracted repeatedly with dry acetone to a constant weight (58). Calculation of the graft yield values of poly (methyl methacrylate) and poly(acrylonitrile) on the cellulose samples are as shown in Tables 3 and 4 respectively.

2.7 Measurement of Crease Recovery and Tensile Properties

2.7.1 Crease Recovery Angle Measurement.

Rectangular fabric samples (5cm x 2.5 cm) were cut parallel to the warp and weft directions from pre-conditioned samples. For each sample, six specimens were cut with care to avoid selvedges, end pieces and creased places.

Each specimen was folded into two-halves so as to give a crease of 2.5 cm length, and was placed under 2 kg weight for 2 minutes after which it was transfered to the Shirley Crease Recovery Angle tester. The crease recovery angle was measured after the sample was hung freely for 2 minutes. Six measurements were taken for each fabric sample in the warp direction only, and the average crease recovery angle (W^{O}) was determined. All measurements were made at 28°C, at 65% Relative Humidity.

Measured crease recovery angles for the samples are shown in Table 5.

2.7.2 Measurement of Tensile Properties

Tensile properties of the fabric samples were measured with Instron tensile machine, model 1026. Measurements were performed on 1.0 cm strip of samples at cross-head speed of 50 mm/min, and at chart proportional drive of 1:5.

A guage length of 5.0 cm test samples was used on a 1026 CM load cell of 0-50 kg range. Six

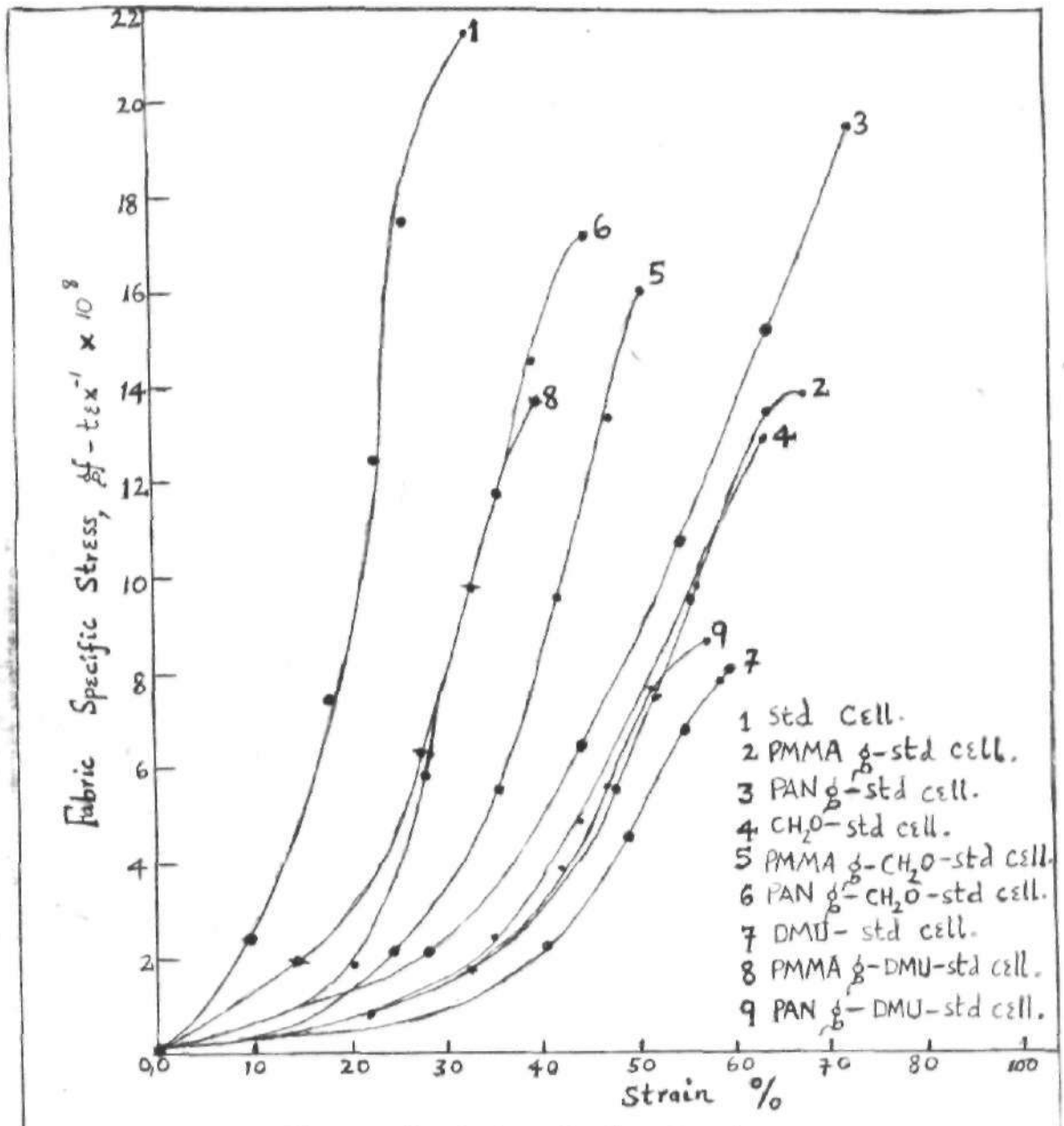


Fig. 4a: Plot of Specific Stress against Strain for various samples

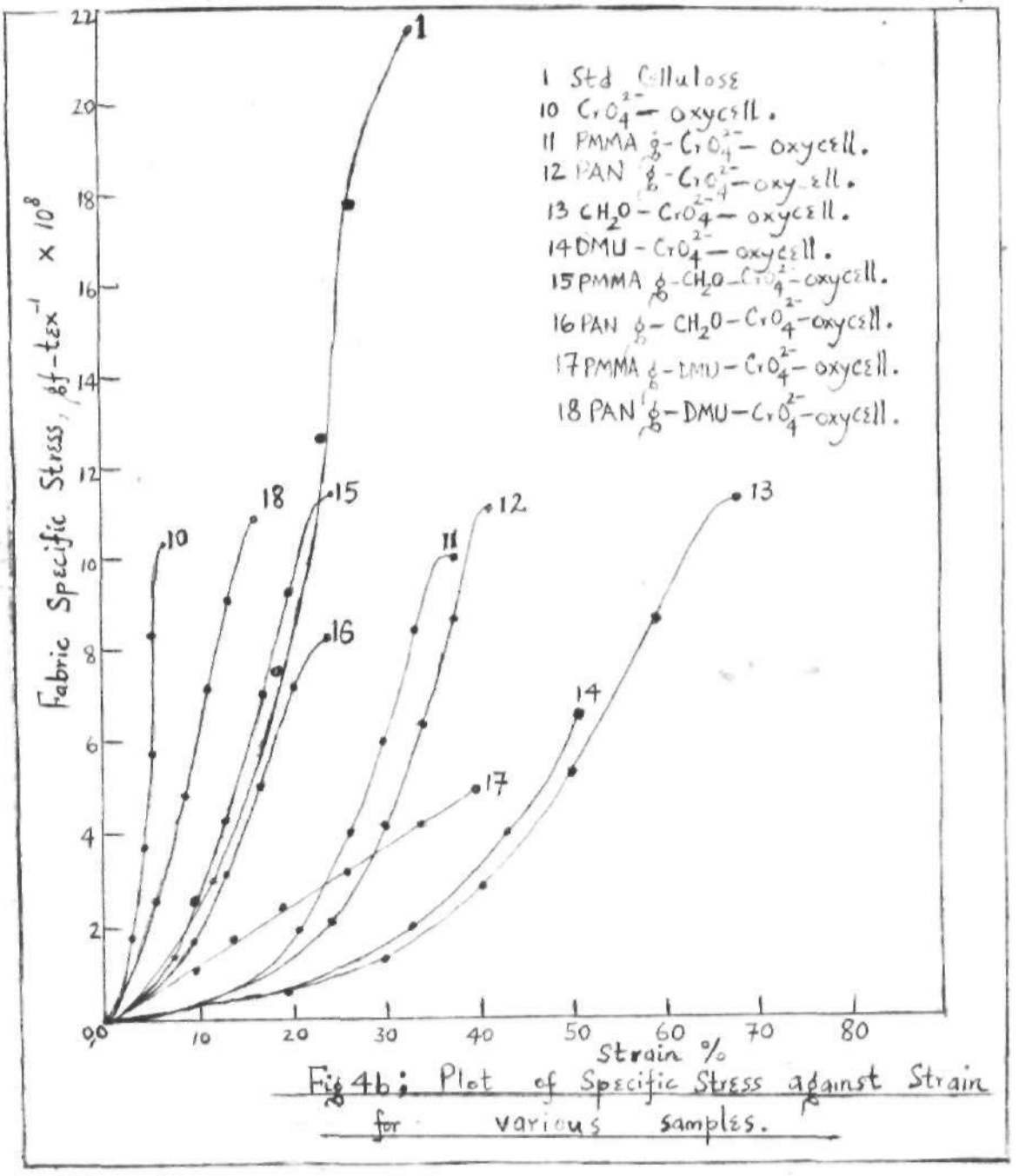


Fig 4b: Plot of Specific Stress against Strain for various samples.

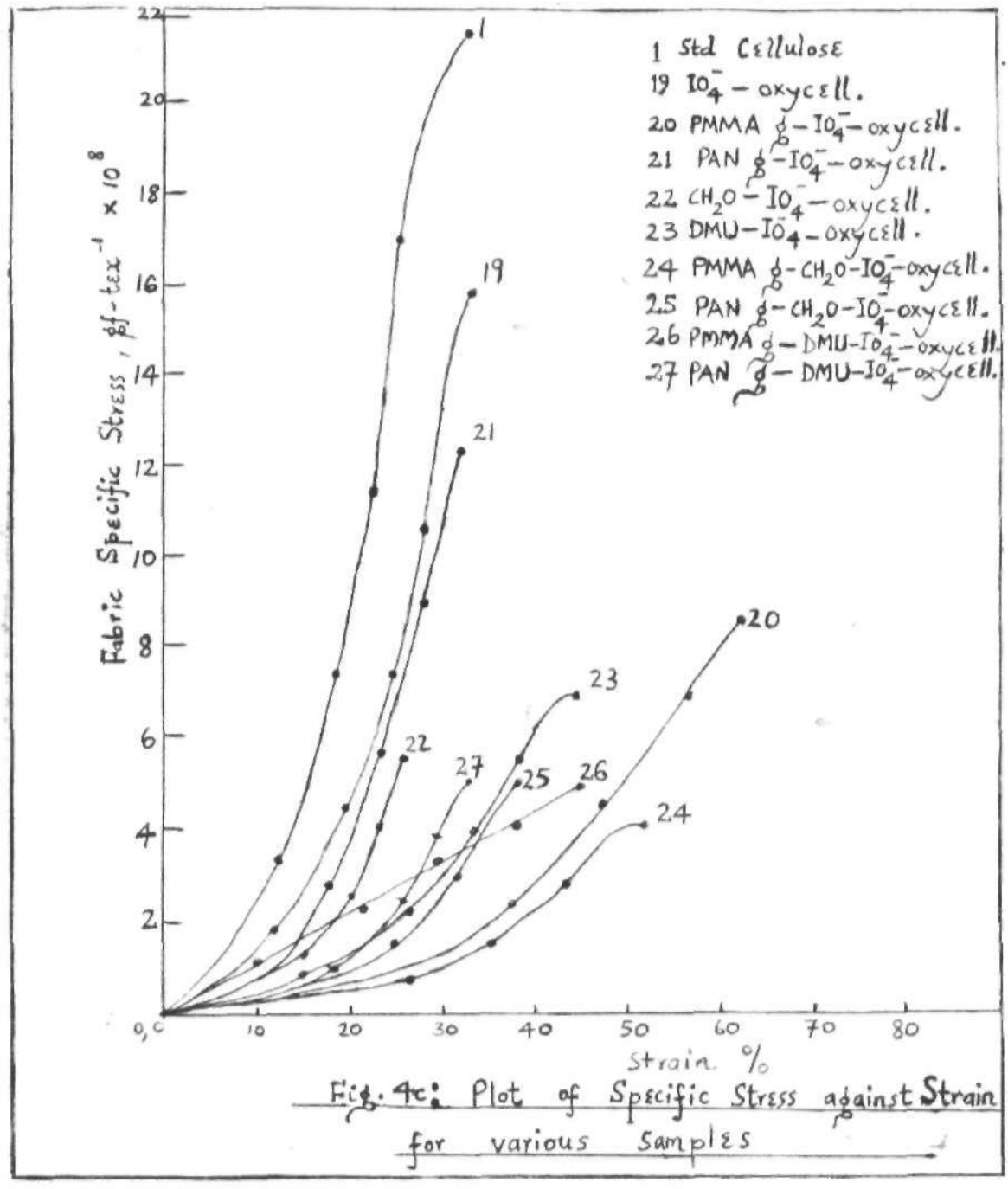


Fig. 4c: Plot of Specific Stress against Strain for various samples

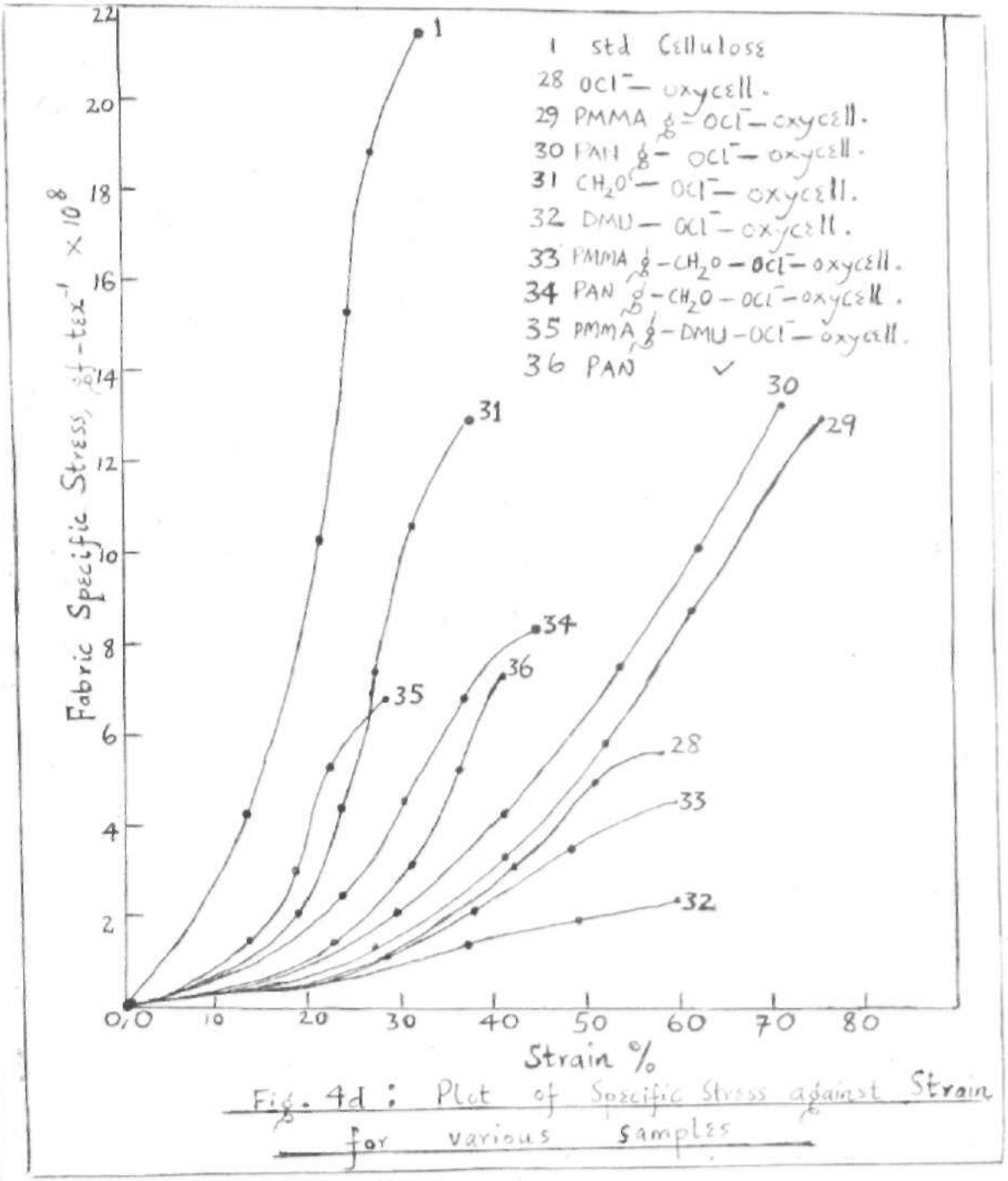


Fig. 4d : Plot of Specific Stress against Strain for various samples

measurements were taken for each sample, and average breaking load was determined.

Specific stress-strain chart profiles for the fabric samples are as shown in the series of comparative plots for standard cellulose, modified and grafted cellulose substrates in Figs 4a to 4d.

Values of measured tensile properties like initial modulus, breaking stress, and extension at break are shown in Table 5.

2.8 Dyeing Process

2.8.1 Purification of Dye

Chlorazol Sky Blue FF was purified by the method of Robinson and Mills (59). Fairly concentrated solution of the dye was prepared in distilled water, and pure crystals of sodium acetate were added to salt out the dye, followed by filtration. The filtered dye was again dissolved in distilled water and salted out with sodium acetate crystals. The sequence was repeated five times. The final filtered dye containing sodium acetate was extracted with absolute alcohol in a Soxhlet extractor to remove sodium acetate. The dye was filtered and

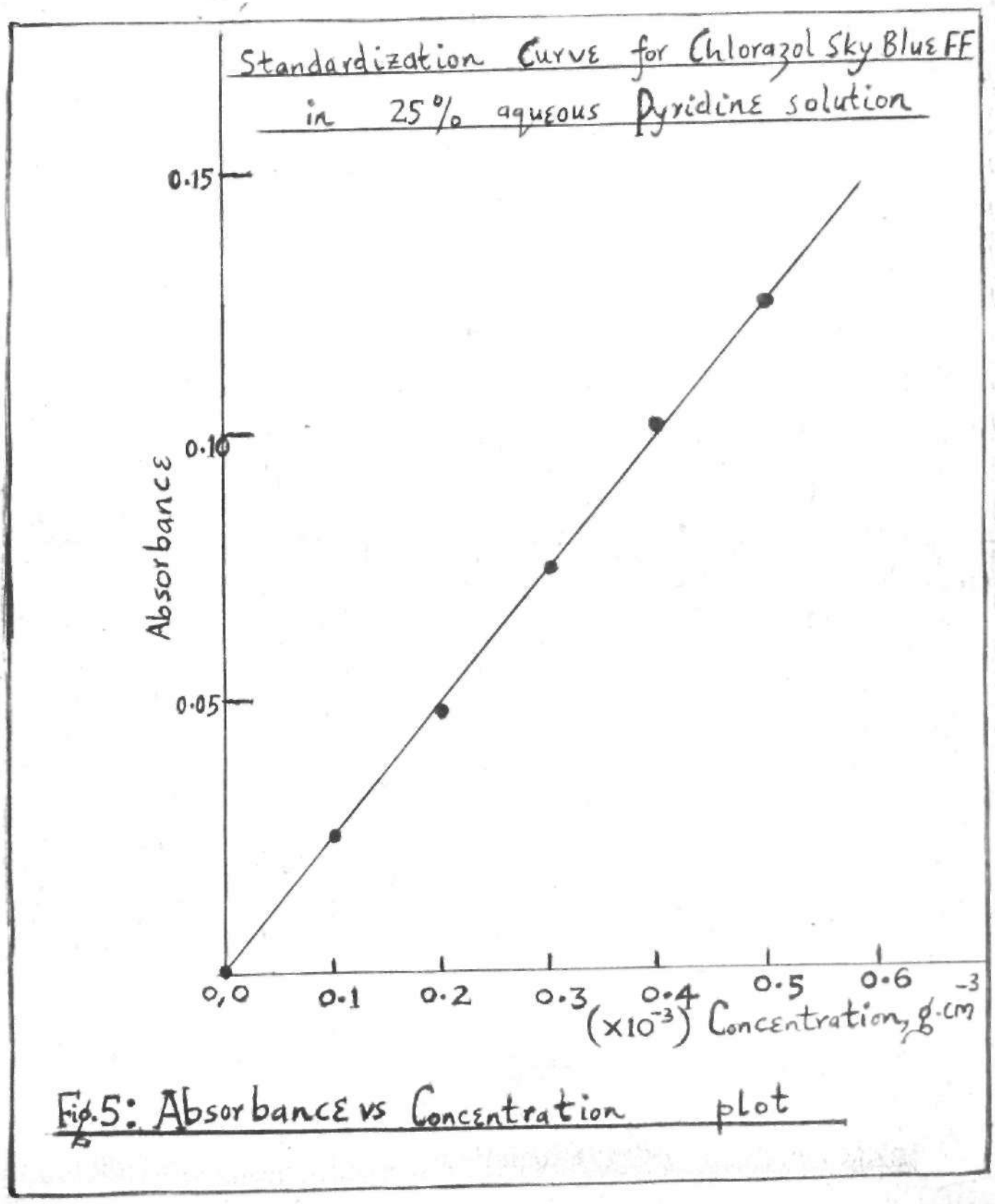


Fig.5: Absorbance vs Concentration plot

then crystallized from 50/50 ethanol/water mixture.

The purified dye was stored in a dessicator over phosphorus pentoxide. The melting point was found to be in the range of 62°- 64°C.

2.8.2 Standardization of Chlorazol Sky Blue FF

Absorbances of known concentrations of Chlorazol Sky Blue FF in 25% aqueous pyridine solution (concentration range of 100 to 500 mg cm^{-3}($\times 10^{-3}$) were measured at wavelength of 630 nm with Beckman KD-2A spectrophotometer, with 25% aqueous pyridine solution as reference. A plot of absorbance against concentration showed compliance with Beer's Law, as shown in Fig. 5.

2.9 Dyeing of Samples

The samples were dyed by the method of Ibe and Valko (60). The samples to be dyed were exposed for 6 hours in the stirred dye-bath. The initial dye concentration in the dye-bath was varied in the range of 100-500 mg($\times 10^{-3}$ cm^{-3}), and the dyeing was carried out in the presence of sodium chloride (5.0g $\times 10^{-3}$ cm^{-3}),

at 95°C, keeping a liquor ratio of 1:50 (61). After 6 hours of continuous dyeing, the dyed samples were removed, plunged in ice-cold water, blotted between filter paper and dried.

2.10 Determination of $D\phi$ and $D\varsigma$

The dye adsorbed by samples of known weight was extracted with 25% aqueous pyridine solution. A complete extraction was accomplished at room temperature by leaving the samples in aqueous pyridine solution for 24 hours. Concentrations of the dye extracts $D\phi$, were determined with Beckman KD-2A spectrophotometer at 630 nm wavelength, and interpolating the value of $D\phi$ from the calibration curve for Chlorazol Sky Blue FF in 25% aqueous pyridine solution.

Measured dye concentrations in the fabric samples $D\phi$ and dye concentrations in the bath after dyeing $D\varsigma$ at various initial dye-bath concentrations are shown in Table 6. A series of plots of log $D\phi$ against log $D\varsigma$ (Fig.6) for some cellulose substrates showed compliance with the expression,

$$\log D\phi = \log K + x \log D\varsigma \quad .$$

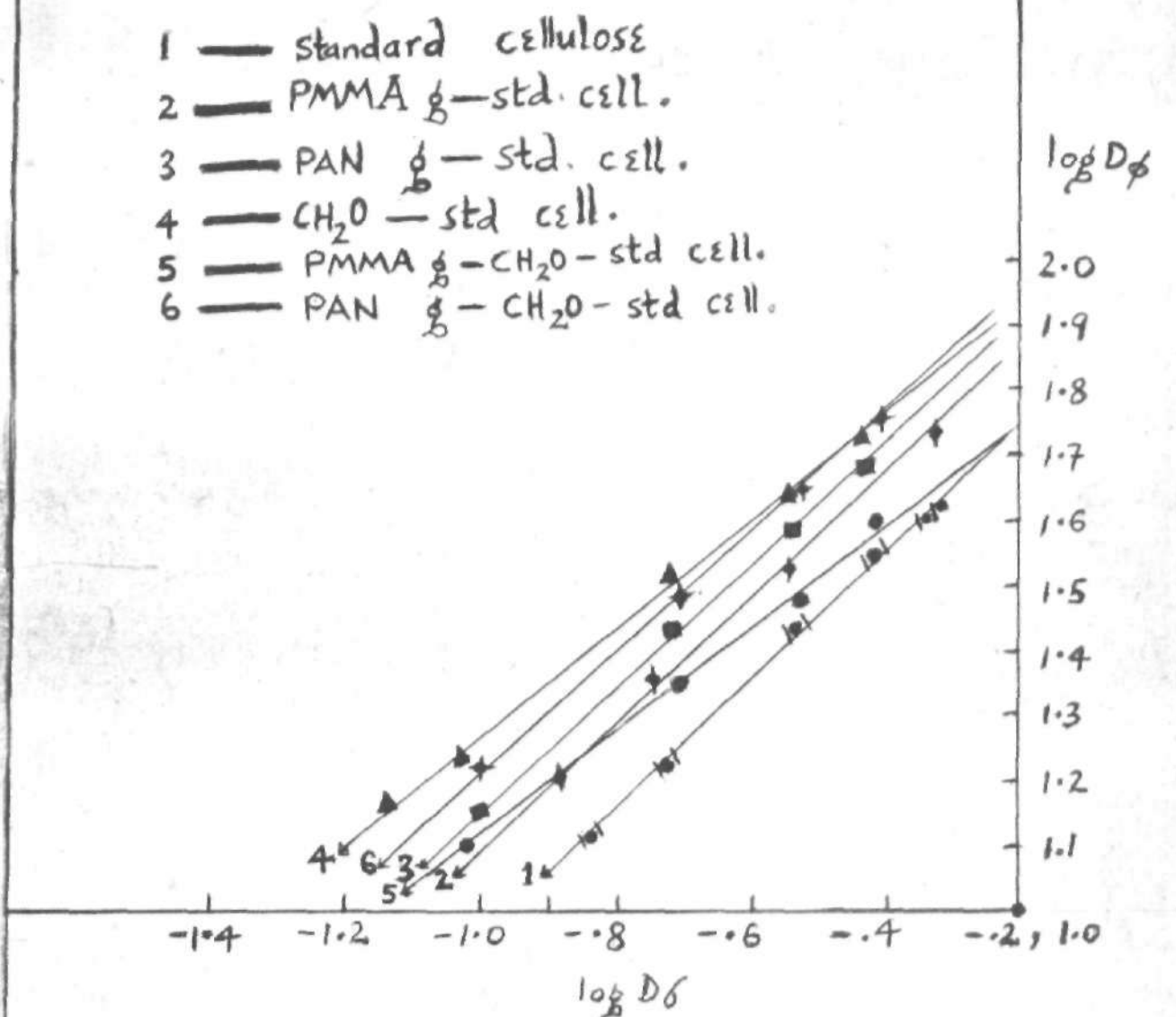


Fig 6: Plot of log Dφ against log D6 for various samples

Table 1: Cross-linking Standard Cellulose and Oxycelluloses with Dimethylol-urea (DMU)

Bath Composition: 3% DMU Owf
1% Teepol - X Owf
12.5% HCl (pH5.6)

Substrate	% DMU Add-on
Standard Cellulose	2.72
CrO_4^{2-} - oxycellulose	3.14
IO_4^- - oxycellulose	3.14
OCl^- - oxycellulose	5.32

TABLE 2: Cross-linking Standard Cellulose and Oxycelluloses with Formaldehyde

Bath Composition: 14.3% Formaldehyde Owf
50% Phosphoric acid (pH 5.6)

Substrate	% CH_2O Add-on
Standard Cellulose	9.61
CrO_4^{2-} - oxycellulose	4.32
IO_4^- - oxycellulose	4.31
OCl^- - oxycellulose	6.69

TABLE 3: Graft Yield of Poly(acrylonitrile) (PAN) on Cellulose Samples

Substrate	% PAN graft yield
Standard Cellulose	33.6
CH_2O - std. cellulose	30.5
DMU - std. cellulose	31.6
CrO_4^{2-} - oxycellulose	25.2
CH_2O - CrO_4^{2-} - oxycell.	11.1
DMU - CrO_4^{2-} - oxycell.	8.9
IO_4^- - oxycell.	30.5
CH_2O - IO_4^- - oxycell.	18.8
DMU - IO_4^- - oxycell.	14.6
OCl^--oxycell.	36.1
CH_2O-OCl^--oxycell	24.0
DMU-OCl^--oxycell.	19.5

TABLE 4: Graft Yield of Poly(methyl methacrylate) (PMMA) on Cellulose Samples

Substrate	% PMMA graft yield
Standard Cellulose	37.2
CH_2O-std. cellulose	31.6
DMU - std. cellulose	23.2
CrO_4^{2-} - oxycellulose	30.7
CH_2O-CrO_4^{2-}-oxycell.	22.9
DMU - CrO_4^{2-}- oxycell.	22.9
IO_4^- - oxycell.	35.9
CH_2O-IO_4^- - oxycell.	28.1
DMU-IO_4^--oxycell.	26.3
OCl^--oxycell.	32.3
CH_2O-OCl^--oxycell.	30.3
DMU-OCl^--oxycell.	28.3

TABLE 5

	Substrate	Initial Modulus gf-tex^{-1} x 10^8	Breaking Stress gf-tex^{-1} x 10^8	Extension at Break (%)	CRA (W^o) in Warp Direction only
1.	Standard Cellulose	0.213	21.53	33	63
2.	PMMA g-std Cellulose	0.027	13.87	68	87
3.	PAN g-std Cellulose	0.052	19.19	72	66
4.	CH_2O-std Cellulose	0.040	12.79	63	64
5.	PMMA g-CH_2O-std Cell	0.058	16.14	51	81
6.	PAN g-CH_2O-std Cell.	0.128	17.26	45	58
7.	DMU-std cellulose	0.020	8.20	60	71
8.	PMMA g-DMU-std.Cell.	0.067	13.72	40	75
9.	PAN g-DMU-std Cell.	0.040	8.69	58	69
10.	CrO_4^{2-}-oxycell.	0.500	10.33	6	54
11.	PMMA g-CrO_4^{2-}-oxycell.	0.060	9.98	37	82
12.	PAN g-CrO_4^{2-}-oxycell.	0.043	11.09	41	78
13.	CH_2O-CrO_4^{2-}-oxycell.	0.153	10.31	68	64
14.	DMU-CrO_4^{2-}-oxycell.	0.024	6.46	50	75
15.	PMMA g-CH_2O-CrO_4^{2-}-oxycell.	0.172	10.45	22	75
16.	PAN g-CH_2O-CrO_4^{2-}-oxycell.	0.135	9.37	24	68

TABLE 5 (CONTD.)

	Substrate	Initial Modulus $gf\text{-}tex^{-1} \times 10^8$	Breaking Stress $gf\text{-}tex^{-1} \times 10^8$	Extension at Break (%)	CRA(W^o) in Warp Direction only
17.	PMMA g-DMU-CrO_4^{2-}-oxycell.	0.122	6.75	28	72
18.	PAN g-DMU-CrO_4^{2-}-oxycell.	0.400	11.35	18	58
19.	IO_4^--oxycell.	0.022	15.83	33	97
20.	PMMA g-IO_4^--oxycell.	0.027	8.55	62	67
21.	PAN g-IO_4^--oxycell.	0.067	12.23	32	52
22.	CH_2O-IO_4^--oxycell.	0.054	5.54	26	82
23.	DMU-IO_4^--oxycell.	0.044	6.89	44	90
24.	PMMA g-CH_2O-IO_4^--oxycell.	0.025	4.09	52	58
25.	PANg-CH_2O-IO_4^--oxycell.	0.045	4.9	38	55
26.	PMMA g-DMU-IO_4^--oxycell.	0.088	4.13	38	79
27.	PAN g-DMU-IO_4^--oxycell.	0.042	4.38	31	58
28.	OCl^--oxycell.	0.034	5.65	59	43
29.	PMMA g-OCl^--oxycell.	0.029	13.00	76	68
30.	PAN g-OCl^--oxycell.	0.041	13.36	71	61
31.	CH_2O-OCl^--oxycell.	0.060	12.97	38	60
32.	DMU-OCl^--oxycell.	0.020	2.26	58	71

TABLE 5 (CONTD.)

	Substrate	Initial Modulus $gf\text{-}tex^{-1} \times 10^{8}$	Breaking Stress $gf\text{-}tex^{-1} \times 10^{8}$	Extension at Break (%)	CRA (W^{o}) in Warp Direction only
33.	PMMA g-CH_2O-OCl^--oxycell.	0.036	4.55	60	85
34	PAN g-CH_2O-OCl^--oxycell.	0.070	8.34	45	82
35.	PMMA g-DMU-OCl^--oxycell.	0.073	6.62	28	72
36.	PAN g-DMU-OCl^--oxycell.	0.020	7.12	42	58

TABLE 6

$D\phi$ and $D\epsilon$ VALUES

	Substrate	Initial Dye-bath Conc. gcm^{-3} $(\times 10^{-3})$	$D\phi$ $g.kg^{-1}$	log $D\phi$	D_ϵ $g.cm^{-3}$ $(\times 10^{-3})$	log D_ϵ
1.	Standard Cellulose	0.1	14.5	1.161	0.095	-1.022
		0.2	27.0	1.431	0.193	-0.716
		0.3	38.0	1.580	0.295	-0.532
		0.4	47.3	1.675	0.398	-0.401
		0.5	55.7	1.804	0.495	-0.305

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	$D\phi$ $g.kg^{-1}$	log $D\phi$	$D\sigma$ $g.cm^{-3}$ ($\times 10^{-3}$)	log $D\sigma$
2.	PMMA g-std Cell.	0.1	8.0	0.903	0.085	-1.071
		0.2	18.0	1.225	0.190	-0.721
		0.3	27.0	1.432	0.290	-0.538
		0.4	35.0	1.544	0.390	-0.415
		0.5	42.6	1.629	0.495	-0.305
3.	PAN g-std Cell.	0.1	11.0	1.041	0.088	-1.058
		0.2	22.7	1.356	0.188	-0.727
		0.3	33.0	1.520	0.290	-0.538
		0.4	42.0	1.623	0.390	-0.409
		0.5	49.8	1.679	0.494	-0.306
4.	CH_2O-std Cell.	0.1	17.2	1.236	0.096	-.018
		0.2	33.0	1.519	0.193	-0.715
		0.3	44.3	1.626	0.295	-0.530
		0.4	54.0	1.732	0.398	-0.400
		0.5	63.7	1.804	0.495	-0.305
5.	PMMA g-CH_2O- std cell	0.1	12.5	1.097	0.093	-1.034
		0.2	22.5	1.352	0.192	-0.716
		0.3	29.2	1.465	0.294	-0.532
		0.4	34.5	1.538	0.395	-0.403
		0.5	38.9	1.590	0.497	-0.304

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	D_ϕ $g.kg^{-1}$	log D_ϕ	D_σ $g.cm^{-3}$ ($\times 10^{-3}$)	log D_σ
6.	PAN g-CH_2O-std cell.	0.1	16.0	1.204	0.095	-1.022
		0.2	30.0	1.477	0.198	-0.704
		0.3	42.0	1.623	0.298	-0.527
		0.4	51.0	1.714	0.395	-0.403
		0.5	60.0	1.780	0.494	-0.306
7.	DMU-std cell.	0.1	14.8	1.170	0.093	-1.034
		0.2	28.2	1.450	0.193	-0.710
		0.3	39.2	1.593	0.293	-0.534
		0.4	49.0	1.690	0.391	-0.406
		0.5	57.9	1.763	0.495	-0.305
8.	PMMA g-DMU-std cell.	0.1	9.4	0.973	0.092	-1.036
		0.2	17.0	1.230	0.193	-0.716
		0.3	23.4	1.369	0.293	-0.534
		0.4	28.8	1.459	0.393	-0.406
		0.5	33.4	1.524	0.49	-0.305
9.	PAN g-DMU-std cell.	0.1	9.8	0.991	0.090	-1.046
		0.2	19.0	1.279	0.180	-0.745
		0.3	29.0	1.462	0.293	-0.534
		0.4	37.0	1.549	0.385	-0.415
		0.5	45.5	1.658	0.495	-0.305

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	D_ϕ $g.kg^{-1}$	log D_ϕ	D_σ $g.cm^{-3}$ ($\times 10^{-3}$)	log D_σ
10.	CrO_4^{2-}-oxycell.	0.1	13.5	1.130	0.093	-1.034
		0.2	26.5	1.423	0.193	-0.716
		0.3	37.5	1.574	0.295	-0.530
		0.4	47.0	1.672	0.380	-0.420
		0.5	58.8	1.770	0.497	-0.497
11.	PMMA g-CrO_4^{2-}-oxycell.	0.1	11.5	1.061	0.098	-1.011
		0.2	22.0	1.342	0.195	-0.710
		0.3	31.0	1.491	0.295	-0.530
		0.4	40.0	1.602	0.383	-0.417
		0.5	48.3	1.684	0.495	-0.305
12.	PAN g-CrO_4^{2-}-oxycell.	0.1	8.5	0.929	0.095	-1.022
		0.2	17.0	1.230	0.185	-0.733
		0.3	26.5	1.423	0.295	-0.530
		0.4	34.5	1.538	0.395	-0.403
		0.5	42.2	1.625	0.495	-0.305
13.	CH_2O-CrO_4^{2-}-oxycell.	0.1	9.4	0.973	0.093	-1.034
		0.2	17.8	1.250	0.195	-0.716
		0.3	24.5	1.389	0.293	-0.534
		0.4	30.4	1.483	0.385	-0.415
		0.5	35.8	1.554	0.497	-0.304

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	$D\phi$ $g.kg^{-1}$	log $D\phi$	D_σ $g.cm^{-3}$ ($\times 10^{-3}$)	log D_σ
14.	DMU-CrO_4^{2-}-oxycell.	0.1	8.0	0.903	0.090	-1.034
		0.2	16.0	1.204	0.190	-0.721
		0.3	23.0	1.362	0.290	-0.538
		0.4	29.0	1.474	0.395	-0.403
		0.5	35.2	1.547	0.496	-0.305
15.	PMMA g-CH_2O-CrO_4^{2-}-oxycell.	0.1	13.5	1.113	0.093	-1.034
		0.2	26.8	1.428	0.193	-0.716
		0.3	37.5	1.574	0.293	-0.534
		0.4	47.0	1.672	0.385	-0.415
		0.5	57.3	1.758	0.495	-0.305
16.	PAN g-CH_2O-CrO_4^{2-}-oxycell.	0.1	11.6	1.064	0.083	-1.064
		0.2	21.5	1.334	0.185	-0.732
		0.3	31.0	1.574	0.293	-0.534
		0.4	40.5	1.607	0.393	-0.406
		0.5	47.7	1.679	0.496	-0.305
17.	PMMA g-DMU-CrO_4^{2-}-oxycell.	0.1	12.8	1.107	0.095	-1.022
		0.2	23.2	1.365	0.193	-0.716
		0.3	33.0	1.519	0.290	-0.538
		0.4	42.0	1.623	0.390	-0.409
		0.5	50.4	1.702	0.496	-0.305

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ $(\times 10^{-3})$	$D\phi$ $g.kg^{-1}$	log $D\phi$	$D\sigma$ $g.cm^{-3}$ $(\times 10^{-3})$	log $D\sigma$
18.	PAN g-DMU-CrO_4^{2-}-oxycell.	0.1	17.3	1.238	0.090	-1.046
		0.2	32.0	1.505	0.188	-0.727
		0.3	45.0	1.653	0.285	-0.545
		0.4	57.0	1.756	0.390	-0.409
		0.5	68.1	1.833	0.492	-0.308
19.	IO_4^- -oxycell	0.1	10.5	1.021	0.088	-1.058
		0.2	21.0	1.322	0.190	-0.721
		0.3	30.0	1.477	0.290	-0.538
		0.4	38.5	1.590	0.390	-0.412
		0.5	47.5	1.677	0.497	-0.304
20.	PMMA g-IO_4^- -oxycell.	0.1	7.5	0.875	0.095	-1.022
		0.2	15.0	1.176	0.195	-0.710
		0.3	22.0	1.342	0.295	-0.530
		0.4	28.0	1.447	0.390	-0.409
		0.5	33.1	1.519	0.496	-0.305
21.	PAN g-IO_4^--oxycell.	0.1	14.5	1.161	0.095	-1.022
		0.2	26.0	1.415	0.195	-0.710
		0.3	35.0	1.544	0.295	-0.530
		0.4	42.0	1.623	0.385	-0.414
		0.5	47.4	1.676	0.499	-0.302

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	$D\phi$ $g.kg^{-1}$	log $D\phi$	$D\sigma$ $g.cm^{-3}$ ($\times 10^{-3}$)	log $D\sigma$
22.	CH_2O-IO_4^- - oxycell.	0.1	12.0	1.079	0.095	-1.022
		0.2	22.0	1.342	0.190	-0.721
		0.3	30.0	1.477	0.285	-0.545
		0.4	37.0	1.568	0.390	-0.409
		0.5	43.6	1.640	0.497	-0.304
23.	DMU-IO_4^--oxycell.	0.1	13.0	1.114	0.090	-1.046
		0.2	24.7	1.393	0.185	-0.732
		0.3	33.0	1.519	0.280	-0.553
		0.4	41.0	1.613	0.395	-0.403
		0.5	47.2	1.672	0.497	-0.304
24.	PMMA g-CH_2O-IO_4^- - oxycell.	0.1	18.8	1.274	0.090	-1.046
		0.2	31.0	1.491	0.185	-0.732
		0.3	42.0	1.623	0.285	-0.545
		0.4	52.0	1.716	0.390	-0.409
		0.5	59.5	1.774	0.493	-0.307
25.	PAN g-CH_2O-IO_4^-- oxycell.	0.1	17.5	1.243	0.095	-1.022
		0.2	30.0	1.478	0.190	-0.721
		0.3	40.0	1.602	0.290	-0.538
		0.4	48.0	1.681	0.383	-0.406
		0.5	56.9	1.755	0.297	-0.304

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	D_ϕ $g.kg^{-1}$	log D_ϕ	D_σ $g.cm^{-3}$ ($\times 10^{-3}$)	log D_σ
26.	PMMA g-DMU-IO_4^- - oxycell	0.1	9.5	0.978	0.090	-1.046
		0.2	18.0	1.255	0.180	-0.745
		0.3	27.0	1.431	0.295	-0.530
		0.4	38.6	1.587	0.385	-0.415
		0.5	49.0	1.690	0.496	-0.305
27.	PAN g-DMU-IO_4^- - oxycell.	0.1	16.0	1.204	0.090	-1.046
		0.2	28.0	1.477	0.185	-0.732
		0.3	38.0	1.579	0.290	-0.538
		0.4	47.0	1.679	0.393	-0.406
		0.5	56.0	1.749	0.496	-0.305
28.	OCl^--oxycell.	0.1	8.0	0.903	0.085	-1.071
		0.2	17.0	1.230	0.190	-0.721
		0.3	25.0	1.398	0.393	-0.534
		0.4	31.0	1.491	0.380	-0.420
		0.5	38.3	1.582	0.498	-0.303
29.	PMMA g-OCl^--oxycell.	0.1	10.0	1.000	0.095	-1.022
		0.2	18.8	1.274	0.195	-0.710
		0.3	23.6	1.373	0.295	-0.530
		0.4	29.0	1.462	0.395	-0.403
		0.5	32.3	1.508	0.496	-0.305

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	$D\phi$ $g.kg^{-1}$	log $D\phi$	$D_{\mathcal{C}}$ $g.cm^{-3}$ ($\times 10^{-3}$)	log $D_{\mathcal{C}}$
30.	PAN g-OCl^--oxycell.	0.1	10.0	1.000	0.085	-1.071
		0.2	19.0	1.279	0.185	-0.732
		0.3	26.0	1.415	0.285	-0.545
		0.4	30.0	1.477	0.385	-0.415
		0.5	33.2	1.521	0.496	-0.305
31.	CH_2O-OCl^--oxycell.	0.1	13.6	1.134	0.095	-1.022
		0.2	24.0	1.280	0.190	-0.721
		0.3	31.0	1.491	0.285	-0.525
		0.4	37.0	1.568	0.380	-0.420
		0.5	41.7	1.620	0.497	-0.304
32.	DMU-OCl^--oxycell.	0.1	12.2	1.086	0.090	-1.046
		0.2	22.0	1.342	0.180	-0.745
		0.3	29.0	1.462	0.280	-0.553
		0.4	35.0	1.544	0.390	-0.409
		0.5	38.9	1.591	0.497	-0.304
33.	PMMA g-CH_2O-OCl^--oxycell.	0.1	12.0	1.097	0.080	-1.097
		0.2	16.5	1.204	0.190	-0.721
		0.3	21.0	1.322	0.275	-0.561
		0.4	25.0	1.398	0.380	-0.420
		0.5	28.3	1.452	0.497	-0.304

TABLE 6 (CONTD.)

	Substrate	Initial Dye-bath Conc. $g.cm^{-3}$ ($\times 10^{-3}$)	$D\phi$ $g.kg^{-1}$	log $D\phi$	$D\sigma$ $g.cm^{-3}$ ($\times 10^{-3}$)	log $D\sigma$
34.	PAN g-CH_2O-OCl^--oxycell	0.1	14.5	1.164	0.090	-1.046
		0.2	26.5	1.423	0.195	-0.721
		0.3	35.0	1.544	0.295	-0.530
		0.4	38.0	1.580	0.395	-0.403
		0.5	40.6	1.608	0.495	-0.305
35.	PMMA g-DMU-OCl^--oxycell.	0.1	13.5	1.130	0.090	-1.046
		0.2	16.0	1.204	0.175	-0.757
		0.3	23.0	1.362	0.290	-0.538
		0.4	26.0	1.415	0.390	-0.409
		0.5	29.9	1.475	0.497	-0.304
36.	PAN g-DMU-OCl^--oxycell.	0.1	12.0	1.079	0.095	-1.022
		0.2	21.2	1.326	0.195	-0.710
		0.3	24.4	1.330	0.295	-0.530
		0.4	32.0	1.505	0.395	-0.403
		0.5	34.4	1.537	0.497	-0.304

CHAPTER THREE

DISCUSSION

3.1 Cross-linking.

Cross-linking of cellulose substrates in the swollen state has been observed to decrease with decreasing amount of secondary hydroxyl group or increase in the number of carboxyl groups but is independent of the number of primary hydroxyl groups in the cellulose. As a result of this observation it has been proposed that most cross-linking occur in the amorphous regions between secondary hydroxyl groups and the cross-linking agents (62).

In Table 1, percentage add-on of formaldehyde decreases for all modified celluloses when compared with the standard cellulose. The decreases observed in the add-on value of formaldehyde to oxycelluloses support the proposition that presence of secondary hydroxyl groups influence cross-linking since oxidation of cellulose decreases the available hydroxyl groups by conversion to aldehyde and carboxyl groups.

In Table 2, the add-on of dimethylol-urea to modified celluloses is also shown to be less that for standard cellulose. This is in line with the above proposal. Again, losses in hydroxyl groups of the oxycelluloses account for low add-on values of the resin to oxycelluloses. From Tables 1 and 2, it appears that hypochlorite oxycellulose retained more hydroxyl groups than chromic acid and metaperiodate oxycelluloses after oxidation since add-on values of the cross-linking agents to hypochlorite oxycellulose are higher than the add-on values of the other oxycelluloses.

3.2 Grafting

Generation of free radicals by reaction between secondary hydroxyl groups of the cellulose and Ceric IV ions initiates grafting. The presence of hydroxyl groups along the cellulose chain is therefore a major factor in determining the graft yield of poly(acrylonitrile) and poly(methyl methacrylate) onto cellulose. Table 3 shows that grafting of poly(acrylonitrile) onto oxidized celluloses was less than grafting onto standard cellulose. This is consistent with theory. Table 4 also

shows that grafting of poly(methyl methacrylate) onto oxidized celluloses was less than grafting onto standard cellulose. Cross-linking of standard and oxidized celluloses further decreased graft yield of the polymers on the substrates due to disappearance of more hydroxyl groups by cross-linking.

3.3 Effects of Grafting of Poly(acrylonitrile) and Poly (methyl methacrylate) onto Modified Celluloses on the Crease and Tensile Properties of the Substrates.

3.3.1 Effect of Oxidation.

Oxidation of cellulose by various oxidants leeds to general losses in tensile strength as shown in Table 5. The observed loss in tensile properties is due to the fabric degradation during oxidation. Apart from penetration and reaction of the oxidants with the crystalline and amorphous portions of the fabric resulting in cleavage of the 2,3 C-C bond of the anhydro-D-glucose unit, the ether linkage in the pyranose ring easily cleaves by hydrolysis. During this process the

degree of polymerization of the cellulose is reduced.

Comparism of crease recovery angles of oxycelluloses indicates that oxidation of fabric with various oxidants did not improve fabric crease resistance, except metaperiodate oxycellulose. The higher crease recovery angle values observed in metaperiodate oxycellulose have been attributed to structural changes that occurred as a result of the oxidation. In metaperiodate oxycellulose, the anhydro-D-glucose of the cellulose chain is oxidized and a dialdehyde is produced at the 2 and 3 positions. The aldehyde groups from one chain could react with hydroxyl groups from another chain leading to hemiacetal cross-linking that increases the ability of the fabric to resist creasing (63).

3.3.2 Effect of Cross-linking

Losses in tensile strength of cross-linked celluloses may arise as a result of hydrolytic degradation by the acid used as a catalyst.

Table 5 indicates that reduction in tensile strength for dimethylol-urea cross-linked substrates is greater than losses in formaldehyde cross-linked substrates.

It has been shown that dimethylol-urea cross-links both intramolecularly and intermolecularly to form a rather rigid three-dimensional network within the fibre. Such rigid network makes the fabric brittle and hence the greater loss in tensile strength. This also explains why dimethylol-urea seems to improve crease resistance of cellulose fabric more than formaldehyde.

3.3.3 Effect of Grafting on the Mechanical Properties of Cellulose fabrics.

Grafting polymers with polar groups onto cellulose is expected to modify the mechanical properties of the substrates by increasing interchain polar bonds in the accessible region of cellulose substrates. The tensile properties will be affected as a result of these cross-links. The observed increase in breaking stress of modified celluloses (Table 5) derives from the abundance of hydrogen bonding between polar groups in the grafted

polymers and the hydroxyl groups in the cellulose substrates.

Grafting of poly(acrylonitrile) and poly(methyl methacrylate) onto standard cellulose, metaperiodate oxycellulose, formaldehyde cross-linked metaperiodate oxycellulose, and dimethylol-urea cross-linked hypochlorite oxycellulose appears to decrease the tensile strength of the substrates. It is believed that these losses in tensile strength resulted from oxidative ring fission of glucose units by free radical mechanism during generation of free radical sites for grafting (31, 64). From Table 5, it does not appear that grafted poly(acrylonitrile) and poly(methyl methacrylate) altered the tensile properties of chromic acid - and formaldehyde cross-linked chromic acid oxycelluloses.

Grafting onto formaldehyde cross-linked standard cellulose, dimethylol-urea cross-linked chromic acid oxycellulose and hypochlorite oxycellulose is observed to improve the crease resistance of the substrates. Increases in crease recovery angles of the grafted substrates (Table 5), may have resulted from hinderance

of relative movements of cellulose chains during deformation by bending due to size of pendant groups in the grafted polymers.

Higher crease recovery observed in poly(methyl methacrylate) grafting than in poly(acrylonitrile) grafting of the cellulose substrates may have occurred because of the molecular size of poly (methyl methacrylate) which contains methyl and methyl carboxylate groups. The smaller size of poly (acrylonitrile) accounts for lower crease resistance that was shown by poly(acrylonitrile) grafted substrates.

3.4 Effect of Grafting Poly(acrylonitrile) and Poly(methyl methacrylate) onto Modified Celluloses on Dyeing.

It has been established that dye exhaustion on celluloses depends on the nature of the substrates (65, 66). From Table 6, it is observed that affinity of cross-linked celluloses for Chlorazol Sky Blue FF is low, while oxycelluloses show lower dye affinity than standard cellulose. These results indicate that conversion

of hydroxyl groups to aldehydes and carboxyl groups, and loss of hydroxyl groups by cross-linking led to reduction of dye affinity of substrates (67, 68, 69). Negatively charged carboxyl groups on the fabric repel similarly charged dye molecules, which decreases dye affinity of the fabric. Dye affinity which depends on availability of hydroxyl groups for hydrogen bonding with dye molecules is greatly affected by chemical changes in structure of cellulose due to oxidation, cross-linking and grafting. From Table 6, grafting of poly (acrylonitrile) and poly(methyl methacrylate)onto formaldehyde cross-linked hypochlorite oxycellulose, dimethylol-urea cross-linked standard cellulose and formaldehyde cross-linked metaperiodate oxycellulose appears to increase the dye affinity of the substrates. The polarity of the cyanide and methyl carboxylate groups in the grafted polymers greatly reduced the negative surface potential of the cellulose chain so that similarly charged dye molecules are within the range at which dye-fibre bonding may be formed. Grafting of poly(acrylonitrile) and poly(methyl methacrylate)

onto standard cellulose, formaldehyde cross-linked standard cellulose, dimethylol-urea cross-linked standard cellulose, chromic acid oxycellulose, metaperiodate oxycellulose, hypochlorite oxycellulose and dimethylol-urea cross-linked hypochlorite oxycellulose is observed to decrease the dye affinity of the substrates from Table 6.

Higher dye affinity values that are observed in poly(acrylonitrile) grafted substrates than in poly(methyl methacrylate) indicate that the more polar cyanide group in the grafted polymer is more effective in stabilizing dye-fibre bond than the methyl carboxylate group in the poly(methyl methacrylate). Steric hinderance to migration of dye molecules towards the fibre surface due to over-crowding by pendant groups in the grafted polymer appears greater in poly(methyl methacrylate) than in poly(acrylonitrile).

These variations in the physical and dyeing properties of grafted modified celluloses have been explained by considering the polarity of the substituted groups in the grafted polymer (70), molecular

weight and molecular weight distribution of the graft as well as the frequency of the grafted chain.

4. CONCLUSSION

The following conclussion may be drawn from this work:

i Oxidation and cross-linking decreased the tensile strength of the fabric.

ii. Metaperiodate oxidation improved fabric crease resistance whereas other forms of oxidation tended to decrease the same property.

iii. Cross-linking and grafting increased fabric crease resistance of all the cellulose substrates.

iv. Grafting increased the tensile strength of formaldehyde cross-linked standard cellulose, dimethylol-urea cross-linked chromic acid oxycellulose, and hypochlorite oxycellulose but it decreased the tensile strength of standard cellulose, metaperiodate oxycellulose formaldehyde cross-linked metaperiodate oxycellulose and

dimethylol-urea cross-linked hypochlorite oxycellulose.

v. Grafting increased dye affinity of formaldehyde cross-linked metaperiodate oxycellulose, dimethylol-urea cross-linked standard cellulose, and hypochlorite oxycellulose but it decreased the dye affinity of standard cellulose, chromic acid oxycellulose, metaperiodate oxycellulose, hypochlorite oxycellulose and formaldehyde cross-linked hypochlorite oxycellulose.

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