III

RESULTS AND DISCUSSION

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III.1 ESTERIFIED COTTON

1 (a) Cellulose esters

Many cellulose esters including partial esters and mixed esters have been synthesized from cotton and other cellulosic materials. Of these, cellulose acetate and cellulose nitrate are widely used commercial resins.

Glucose unit of cellulose has three hydroxyl groups. Of these, the primary hydroxyl group is more reactive than secondary ones in esterification process. Cellulose reacts with acids, acid anhydrides, acid chlorides and acid salts to form esters. The reactivity of cellulose with organic acid or anhydride decreases with increasing carbon chain of the aliphatic acids. Esters with longer carbon chains are usually prepared by using acid chloride or acid and impellent. Use of dibasic or polybasic acids usually results in the formation of cross-linked esters.

Easter have been prepared by using (i) acids (26, 29, 179) (ii) acids with acid catalysts such as H_2SO_4, etc. (42, 180) (iii) acids and acid anhydrides (181-184) (iv) acid and ammonia (185) (v) Sodium or potassium salts of acids (27, 28, 180) (vi) acids with acetic anhydride or trifluoracetic anhydride impellent (15, 17, 19, 20, 22, 186, 187) (vii) acid anhydrides (31-34, 188-196) (vii) acid chloride with pyridine (20, 45, 187, 188, 197) (viii) acid chloride with pyridine (20, 45, 187, 188, 197) etc. Saponification of esters results in partial esters (198) and cross-linked esters are formed by the esterification with diabsic and polybasic acids and their derivatives (27, 199, 200).

The esters of the following organic acids have been synthesized : (i) acetic acid (19, 184, 190, 192, 198, 201, 202) (ii) propionic acid (190, 192) (iii) butyric acid (190, 192) (iv) adipic acid (22, 30) (v) benzoic acid (30) (vi) oleic acid (21, 188) (vii) palmitic and steric acids (20) (viii) lionlic and linolenic acids (188) (ix) acetylene carboxylic acid (26) (x) phenyl steric acid (21) (ix) β-alanino, ε-amino caproic acid (203) (xii) amic acids (185) (xiii) sorbic acid (204) (xiv) tosylate propiolic acid, pyruvic acid and α —methoxy acrylic acid (42) (xv) chloromethyl phosphonic acid (180) (xvi) 5-bromofuran carboxylic acid and 5-=bromothiophen carboxylic acid (57), etc. Cross-linked esters of the following acids have been obtained : (i) phthalic acid (32, 33) (ii) malonic and succinic acids (17, 30) (iii) citric acid (28, 29, 205) (iv) butane tetra carboxylic acid and diglycolic acid (205) (v) mellitic acid, pyromellitic acid, 1, 2, 3, benzene tricarboxylic acid, 1, 2, 3, 4 benzene tetra carboxylic acid, 3, 3', 4, 4' - benzophenone tetracarboxylic acid, 1, 2, 3, 4, cyclopentane tetracarboxylic acid, 1, 2, 3 propane tricarboxylic acid, etc. (27-29) (vi) cinnamic acid (199) (vii) crotonic acid (200) etc. The following mixed esters have been prepared (i) acetate maleate (40, 45, 179, 191, 195, 196) (ii) acetate acrylate and acetate methacrylate (43, 45, 206-210) (iii) acetate sorbate (39, 181-183, 201, 208, 210, 211) (iv) acetate succinate (44, 194) (v) acetate oleate (39, 193, 201, 208, 210, 211) (vi) sterate terphthalate (197) (vii) acetate trifluoracetate (186), etc. Half esters of succinic acid, maleic acid and phthalic acid have been obtained (189).

In the present studies, cotton fibres and fabrics were esterified by anhydride and chloride methods. A brief discussion of the esterifying reagents follows.

1 (b) Esterifying agents - acid anhydrides and acid chlorides

The acid anhydrides of sebacic, adipic and fumaric acids were prepared by treating the acids with acetic anhydride. These were also reported by Dhimar (177). The anhydrides were considered to be polymeric. Polymeric anhydrides reported in literature are polyadipic anhydride (212), poly suberic anhydride (213), polysebacic anhydride (214), polyazelaic anhydride (215), poly iso and terphthalic anhydrides (216, 217). Dhimar observed that the yield of poly anhydride increased in order

$$\text{fumaric} < \text{adipic} < \text{sebasic}$$

IR spectra of these products are presented in Fig. II.1 (a). For the purpose of comparison, IR spectra of adipic, sebacic and fumaric acids are presented in Fig. III.1. The spectra of acids and anhydrides are different and the spectra of anhydrides show the presence of anhydride band in $6\,\mu$ region.

Acid chlorides of sebacic, adipic and fumaric acids were prepared by treating the acids with thionyl chloride and those of acrylic and methacrylic acids were prepared by treating the acids with benzoyl chloride. These were reported by Narkhede (178).

These products and maleic anhydride were used for esterifying cotton fibres and fabrics.

1 (c) Esterification of cotton fabrics

Cotton fabrics used for studies were warp-40^{S} Guddag DCH 32 type and weft-36^{S}-H_4 type.

These fabrics were destarched before esterification. The extent of esterification was observed in terms of % add-on

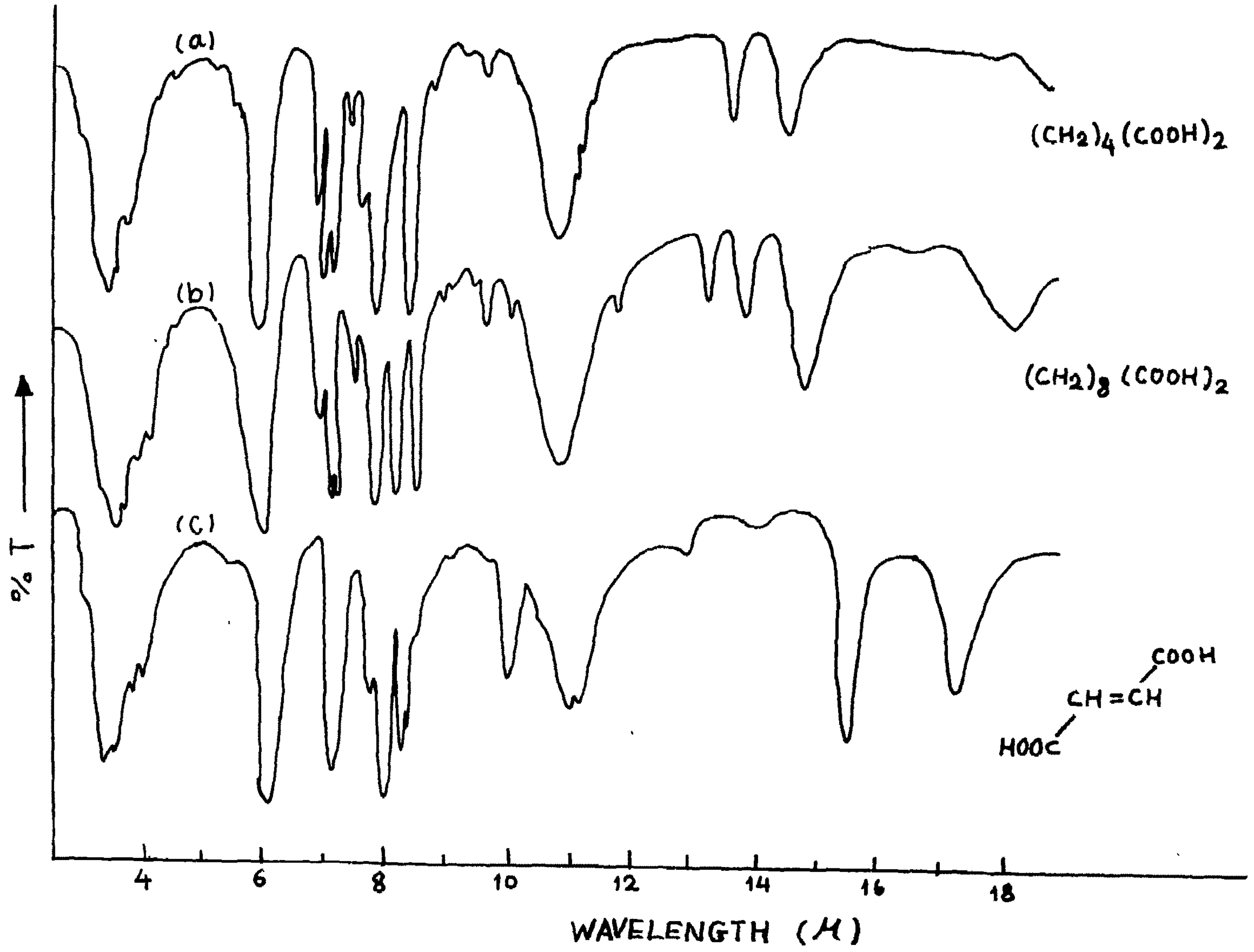


FIG. III.1 IR SPECTRA OF (a) Adipic Acid (b) Sebacic Acid (c) Fumaric Acid for each sample. The results (% add-on) are shown in table II-4. Hence the degree of monosubstution is calculated and presented in table III-1, and shown graphically in Fig. III.2. It is generalized from the results that (i) the degree of esterification is very low in case of esterification with adipic, fumaric and maleic acid derivatives, (ii) good degree of substitution is achieved with sebacic acid derivatives, (iii) increasing the time of reaction increases to a small extent the degree of substitution in case of sebacic acid derivatives (iv) increasing the temperature from RT to 90-105° C increases the degree of substitution, the variation being well marked in case of sebacic acid derivatives (v) the degree of substitution with reference to solvent/medium in chloride method increases as

Carbon tetrachloride < Dimethyl formamide < Chloroform

(vi) the degree of substitution with reference to fumaric and maleic acids is low and comparable and (vii) the degree of substitution increases with increase in the carbon chain of the acid.

1 (d) Polymerization of esterified fabrics

Since % add-on observed in case of samples esterified with fumaric and maleic acid derivatives (and also with acrylic and methacrylic chlorides) and washed was low. These samples

Table III.1

1 (a)

No	Product	Degree of mono-substitution (D.S.) per glucose unit
1	CSb-1	0.13
2	CSb-2	0.52
3	CSb-3	0.50
4	CAd-1	0.01
5	CAd-2	0.03
6	CFm-1	0.02
7	CFm-2	0.04
8	CMl-1	0.01
9	CMl-2	0.02

1 (b)

No.	Product	Degree of mono-substitution (D.S.) per glucose unit
1	CSbc(D)-1	0.38
2	CSbc(D)-2	0.41
3	CSbc(D)-3	0.15
4	CSbc(Ch)	0.04
5	CSbc(Ct)	0.19
6	CAdc(D)-1	0.01
7	CAdc(D)-2	0.01
8	CAdc(Ch)	0.02
9	CFmc(D)	0.01
10	CFmc(Ch)	0.03

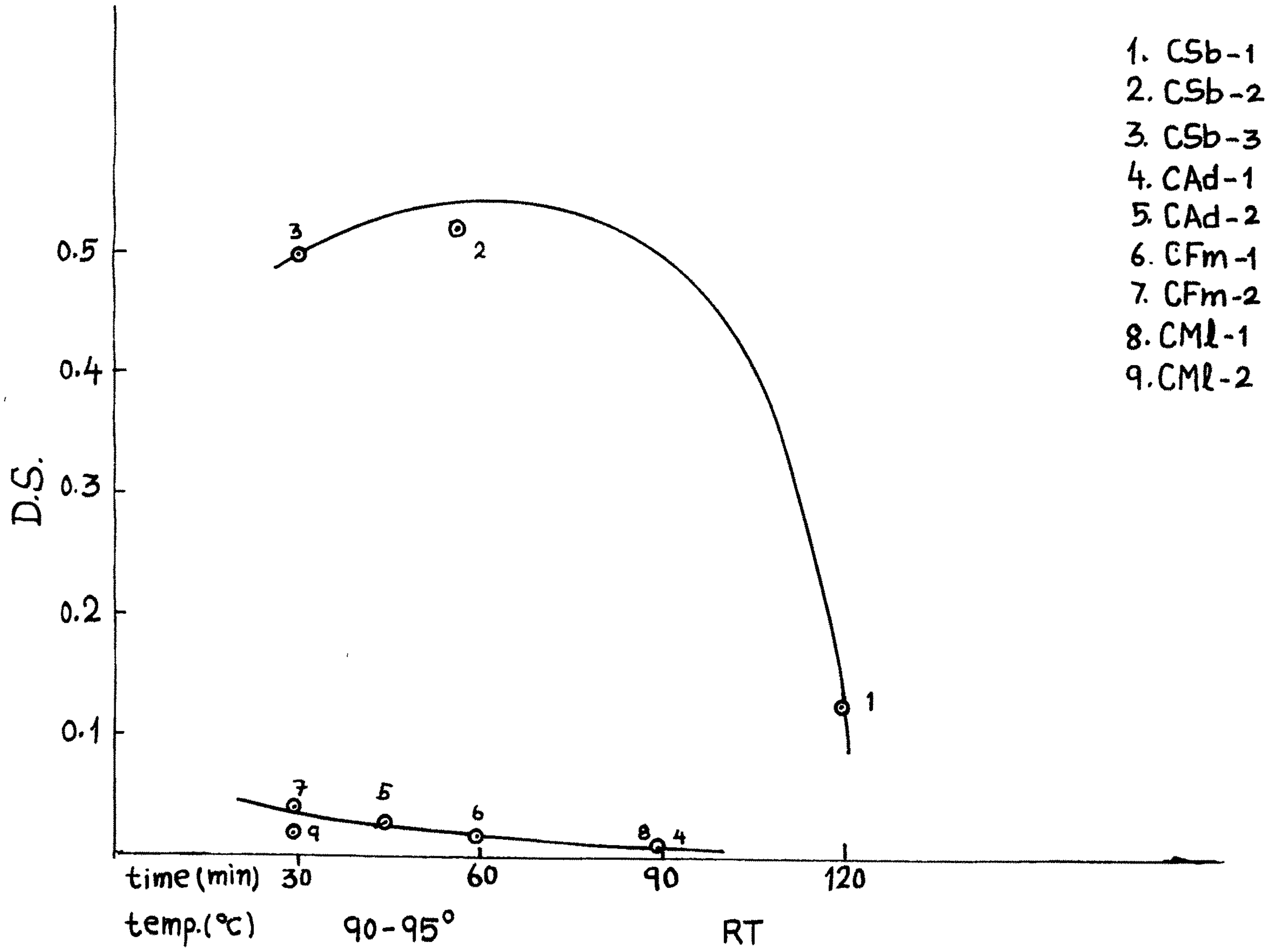


FIG.III.2(d) D.S. vs. time, temp OF ANHYDRIDE TREATED FABRICS

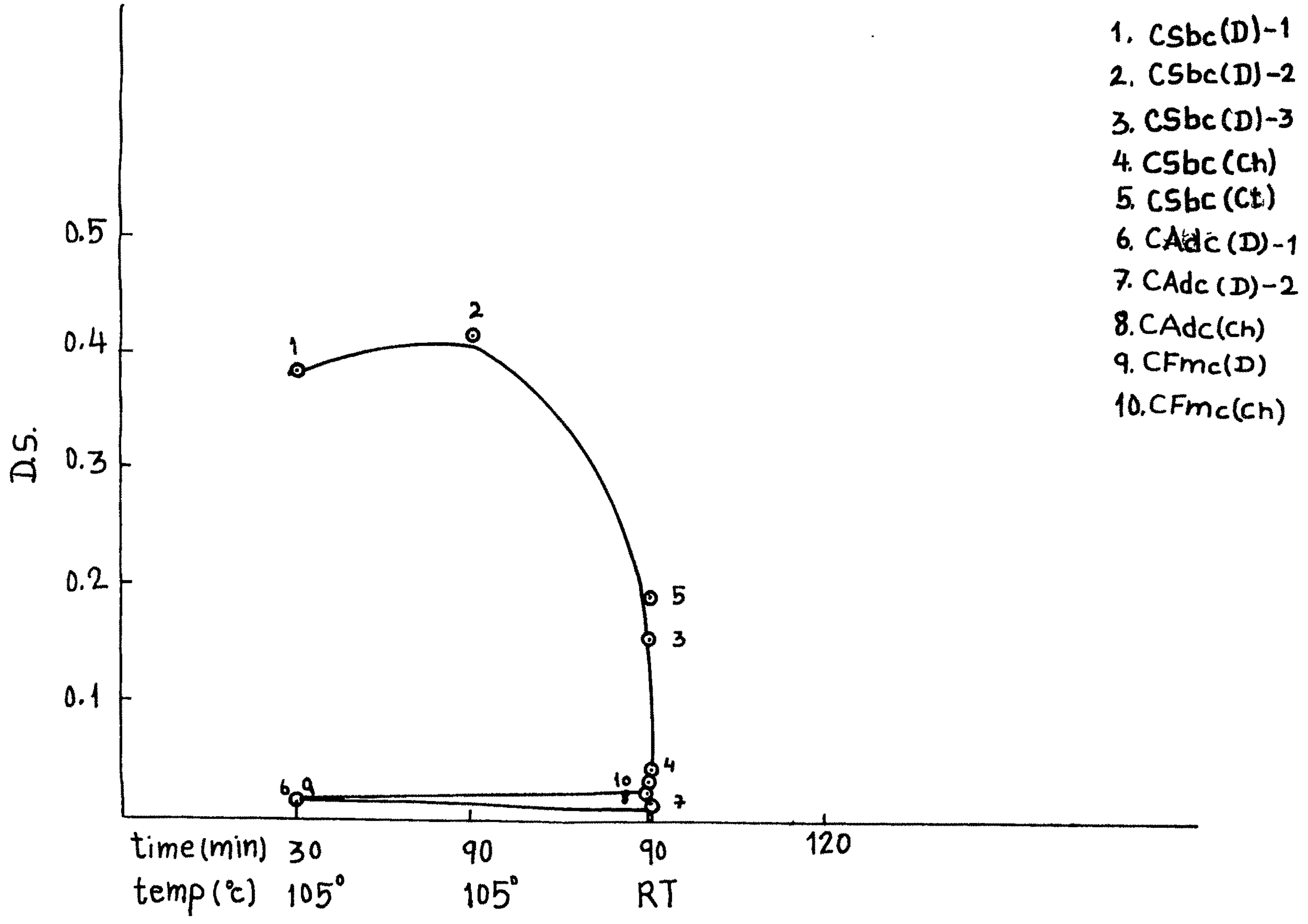


FIG.III.2(b) D.S. vs. time, temp OF ACID CHLORIDE TREATED FABRICS were first esterified, then polymerized with benzoyl peroxide, and thereafter water washed.

The results of % add-on for these polymerized samples are used to calculate their degree of substitution. The values are presented in table III.2. The results show that (i) the degree of substitution (D.S.) increases by polymerization, (ii) D.S. is higher with fumarate than with maleate (iii) D.S. is higher for acrylate than for methacrylate and (iv) washing of the samples lowered the degree of substitution in case of acrylate and methacrylate.

1 (e) Esterification of cotton fibres

Cotton linters have been esterified by anhydride and chloride methods. The products were extracted with alcohol. Alcohol-soluble products and alcohol insoluble products were obtained and have been studied separately. From the values of % add-on for alcohol insoluble products, the degree of monosubstitution has been calculated and presented in table III.3. It has been observed that all the products have been analysed for % C and % H and formulae have been suggested on the basis of the assumption that the degree of substitution is 0.2 (table II.5). Calculated percentages have fair agreement with observed ones.

Table III.2

2 (a)

No.	Product	Degree of mono-substitution (D.S.) per glucose unit
1	BCFm	0.17
2	BCMl	0.12

2 (b)

No.	Product	Degree of mono substitution (D.S.) per glucose unit	
		Polymerized	Water washed
1	BCAc	0.24	0.02
2	BCMac	0.14	0.03

Table III.3

No.	Product	Degree of mono-substitution (D.S.) per glucose unit
1	CfSb	0.13
2	CfAd	0.13
3	CfFm	0.12
4	CfMl	0.20

Alcohol-soluble products exhibit melting behaviour. Their analytical data have been used to suggest their formulae (tableII.5). It is observed that (i) fumaric and maleic anhydrides formed mono esters (ii) sebacic anhydride formed triester and (iii) degree of esterificatioon with adipic anhydride is 1.5. The degree of substitution is considered to increase in terms of acid in esters as

fumaric ~ maleic < adipic < sebacic

Aldrich Chemical Co. is marketing cellulose acetate and cellulose acetate butyrate having melting point of 240° C and 235° C respectively. Malm and coworkers (46) recorded the melting points of triesters of various aliphatic acids.

1 (f) Further characterization of esterified products

f (i) Diameter of the fibre and fabric

Diameter of the esterified fabric or fibre was measured using optical microscope with magnification X500. The results are presented in table II.4. In each case increase in diameter has been observed. These values are correlated to their degree of substitution as shown in Fig.III.3. It can be generalized that (i) for the same acid component in the esterified product, increase in the degree of substitution increases to a greater extent

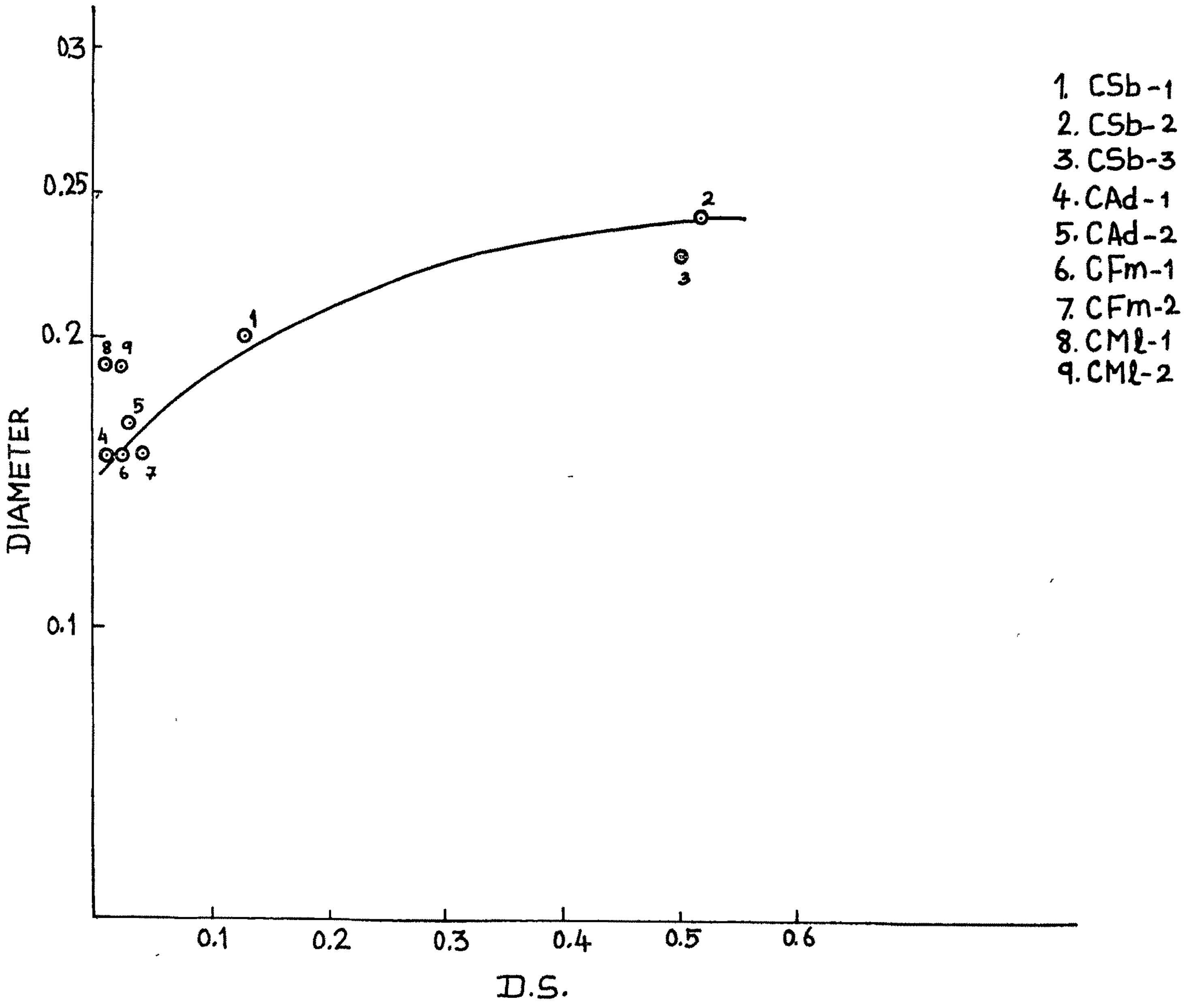


FIG. III.3 (d) DIAMETER VS. D.S. OF ESTERIFIED FABRICS

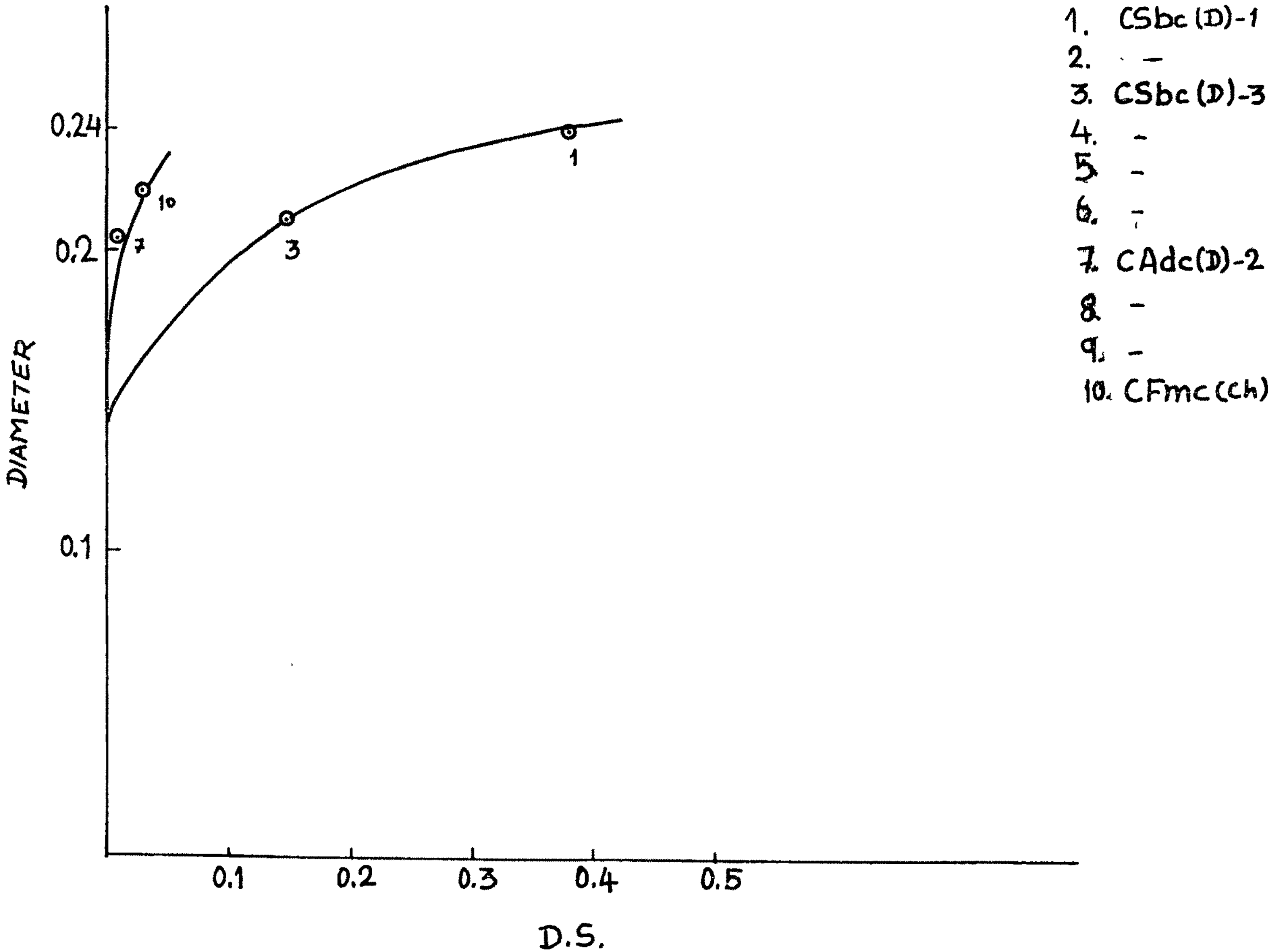


FIG III.3(b)DIAMETER VS. D.S. OF ACID CHLORIDE TREATED FABRICS

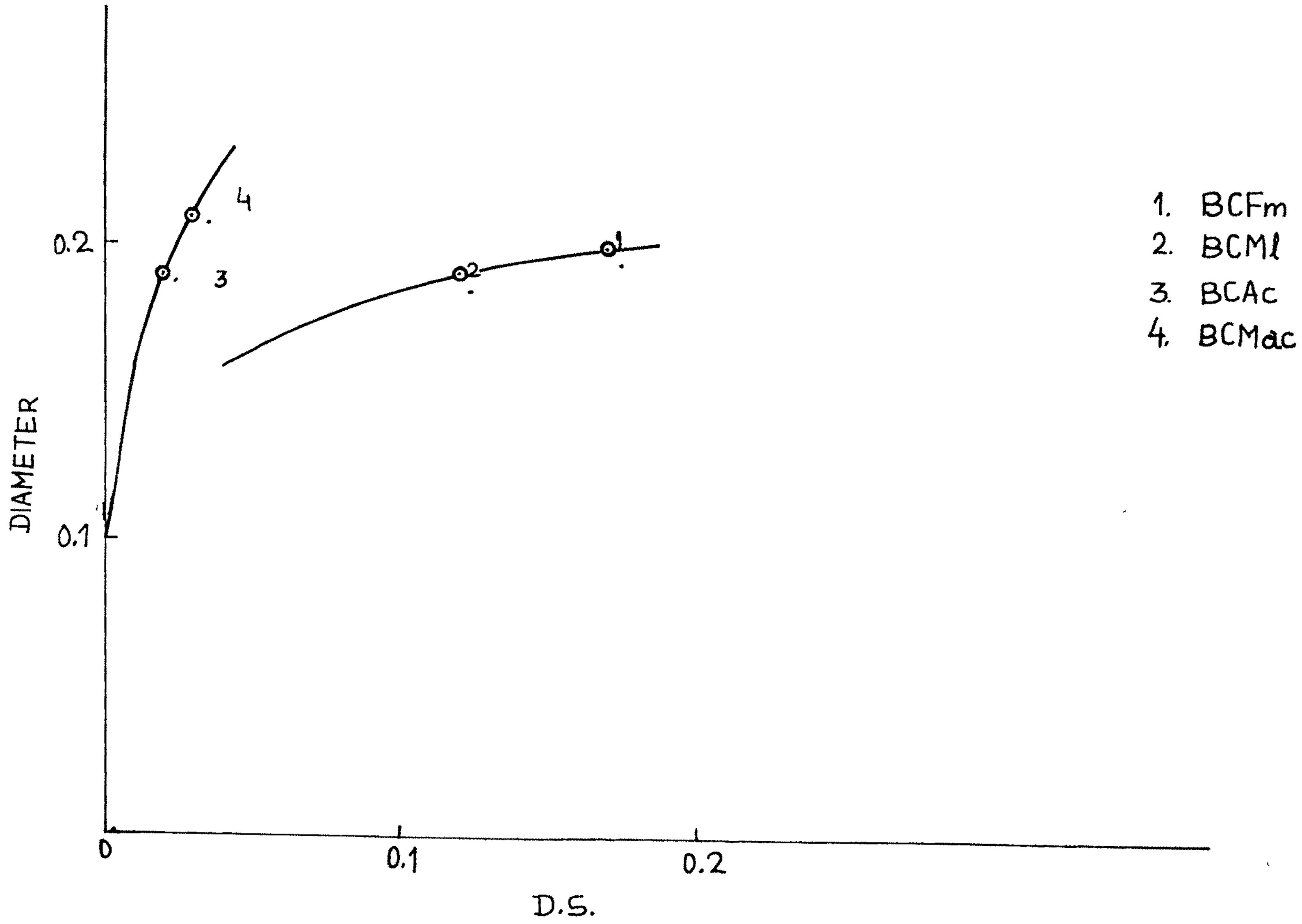


FIG. III.3.(c) DIAMETER VS. D.S. OF POLYMERIZED FABRICS

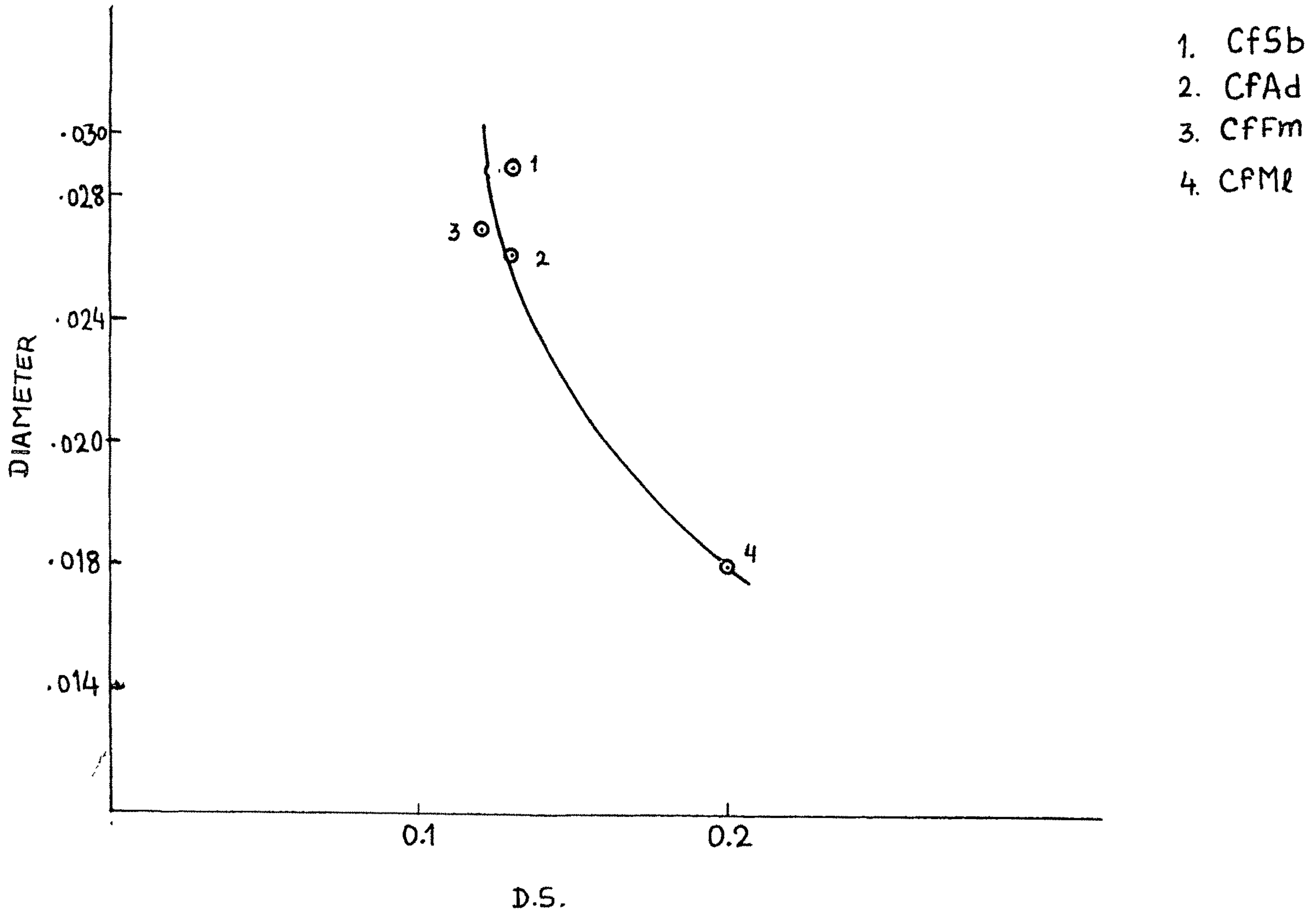


FIG. III.3 (d) DIAMETER VS. D.S. OF ESTERIFIED Γ FIBRES the diameter of the fabric, (ii) for the esterified fabrics containing different acid components, the increase in diameter is greater as

adipic acid $\leqslant$ fumaric acid $<$ maleic acid $<$ sebasic acid

whereas, for the fibres esterified with different acid anhydrides, the increase in diameter of the fibre is greater as

maleic $<$ adipic $<$ fumaric $<$ sebacic

(iii) the increase in diameter is greater for the fabrics esterified by acid chloride than that for the fabrics esterified by acid anhydride to a comparable degree of substitution.

e (ii) Crease recovery of esterified fabrics

Crease recovery angles (CRA) for the esterified fabrics have been measured (table II.4) and are correlated with the degree of substitution of the products as shown in Fig.III.4. It is generalized from the results that (i) in case of fabrics esterified with sebacoyl chloride, with the increase in the degree of substitution, CRA increases reaching a relatively high value of 247° at DS $\sim$ 0.4, (ii) in case of fabrics esterified with sebacic anhydride, increase in the degree

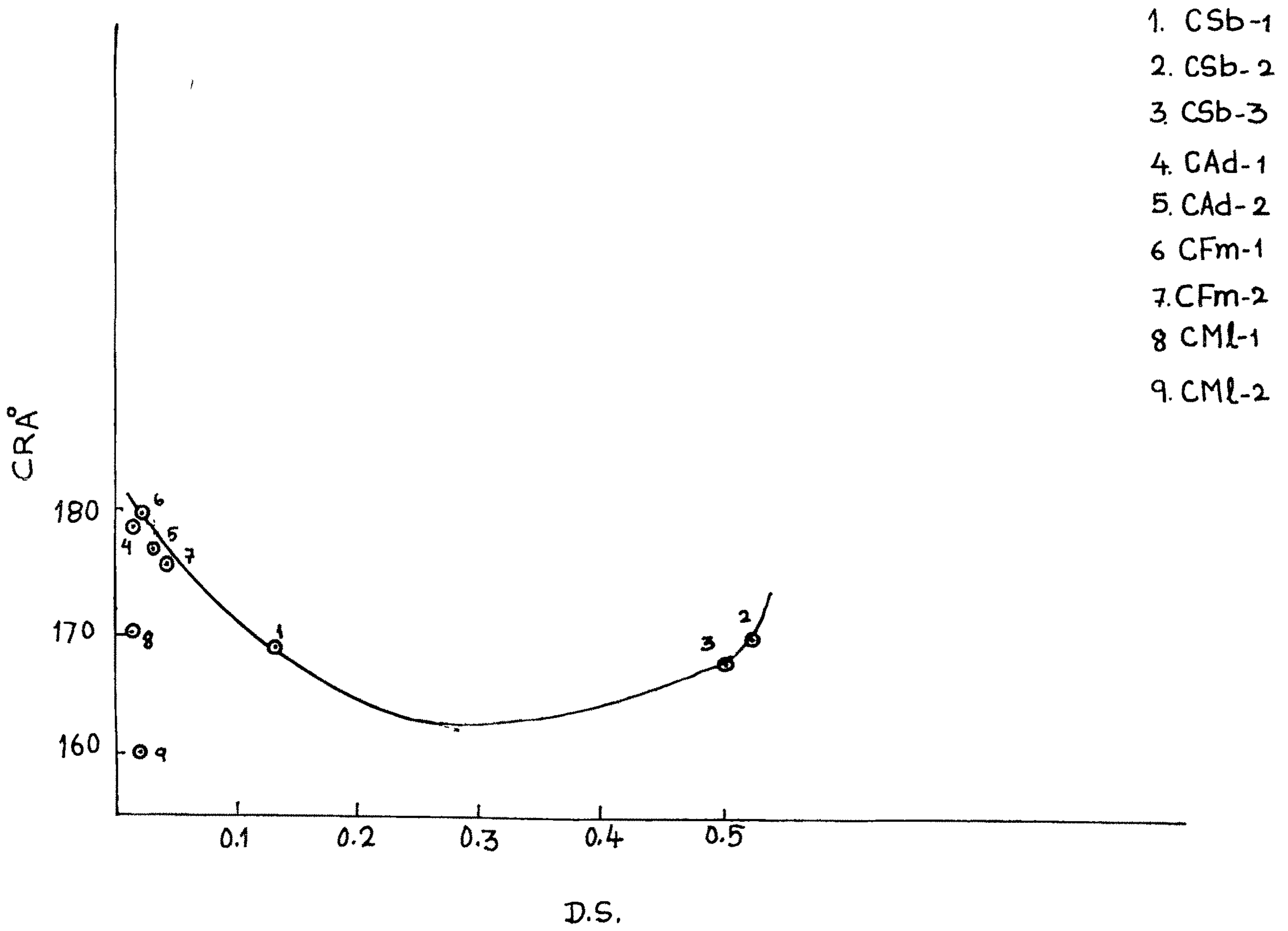


FIG. III. 4 (d) CRA° VS. D.S. OF ESTERIFIED FABRICS

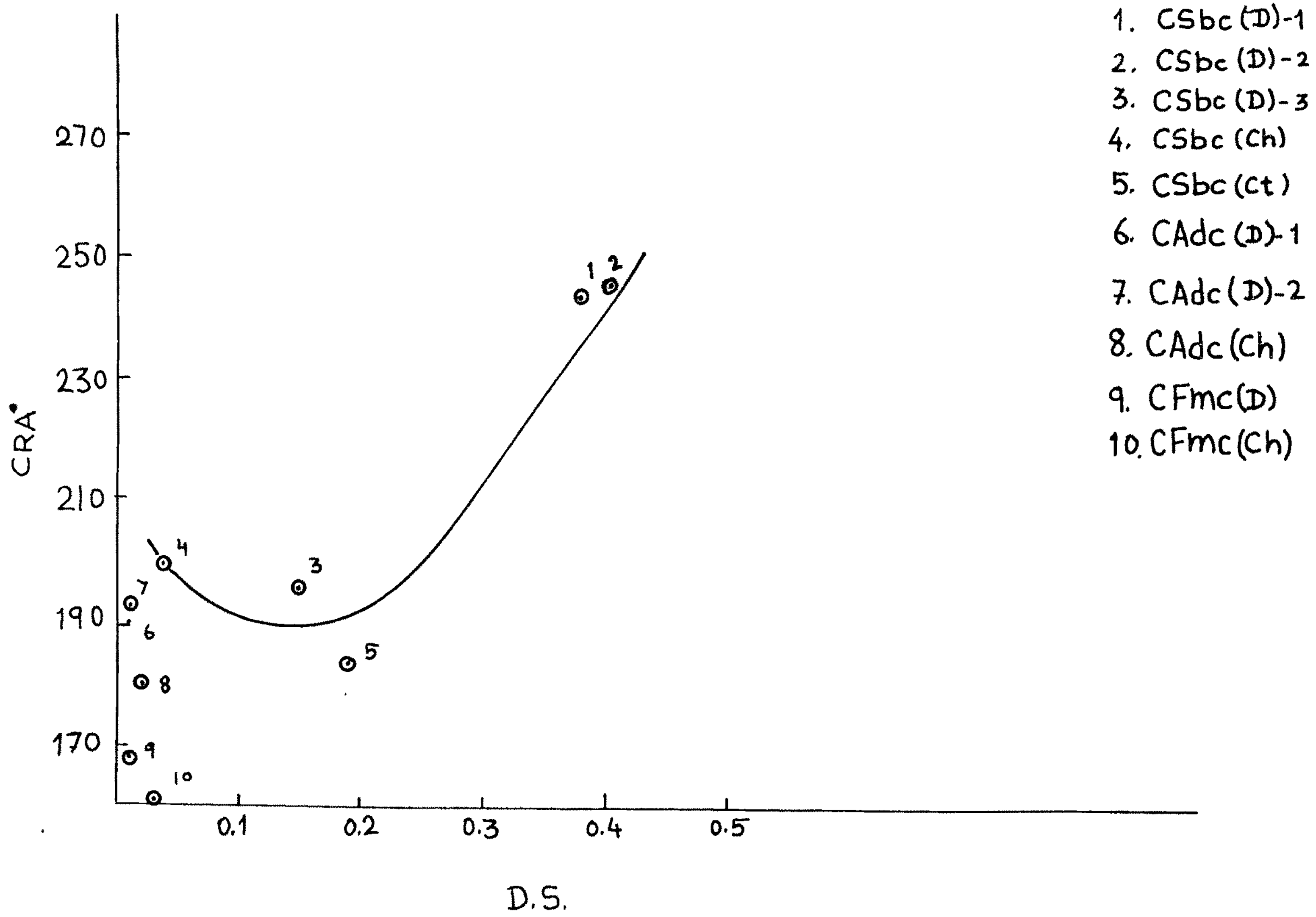


FIG III.4(b) CRA° VS D.S. OF ACID CHLORIDE TREATED FABRICS of substitution does not have any appreciable change in CRA° (iii) in case of fabrics esterified with adipic, fumaric or maleic acid derivatives, increase in the degree of substitution may decrease the CRA°.

f (iii) IR Spectra

IR Spectra of some of the esterified fabrics and fibres are presented in Fig.II.3. As generally observed, the IR spectra of soluble products have a fine structure which is absent in those of insoluble products. In all the spectra of soluble products the absorption bands in 6 μ region due to COO group are strong. In the insoluble products also the absorption band due to COO group is observed in 6 μ region but is generally weak. ATR spectra of some of the samples were taken (not presented) and they also showed the presence of ester group. IR spectra of some of the products in 6 μ region are presented in fig.III.5.. IR spectra of CSb and CfSb showed less fine structure. However when these products were repeatedly washed with alcohol or xylene, the IR spectra of the washed products had better fine structure and intense bands for ester group. Similarly CfFm and CfAd were studied before and after alcohol washing. IR spectra of these products before washing and after washing did not show corresponding

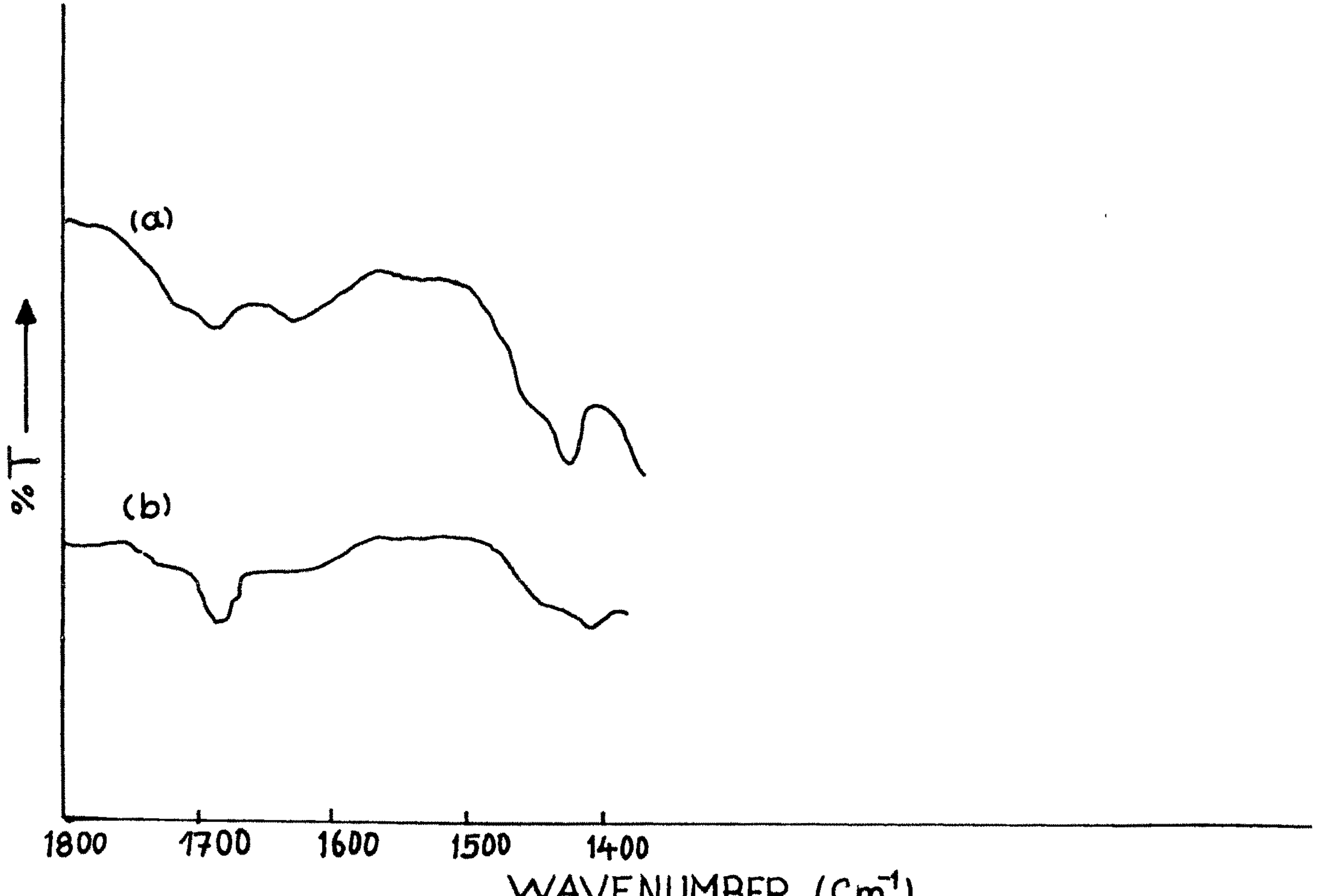


FIG. III.5 (A) IR SPECTRA OF (a) CSb (b) CfSb

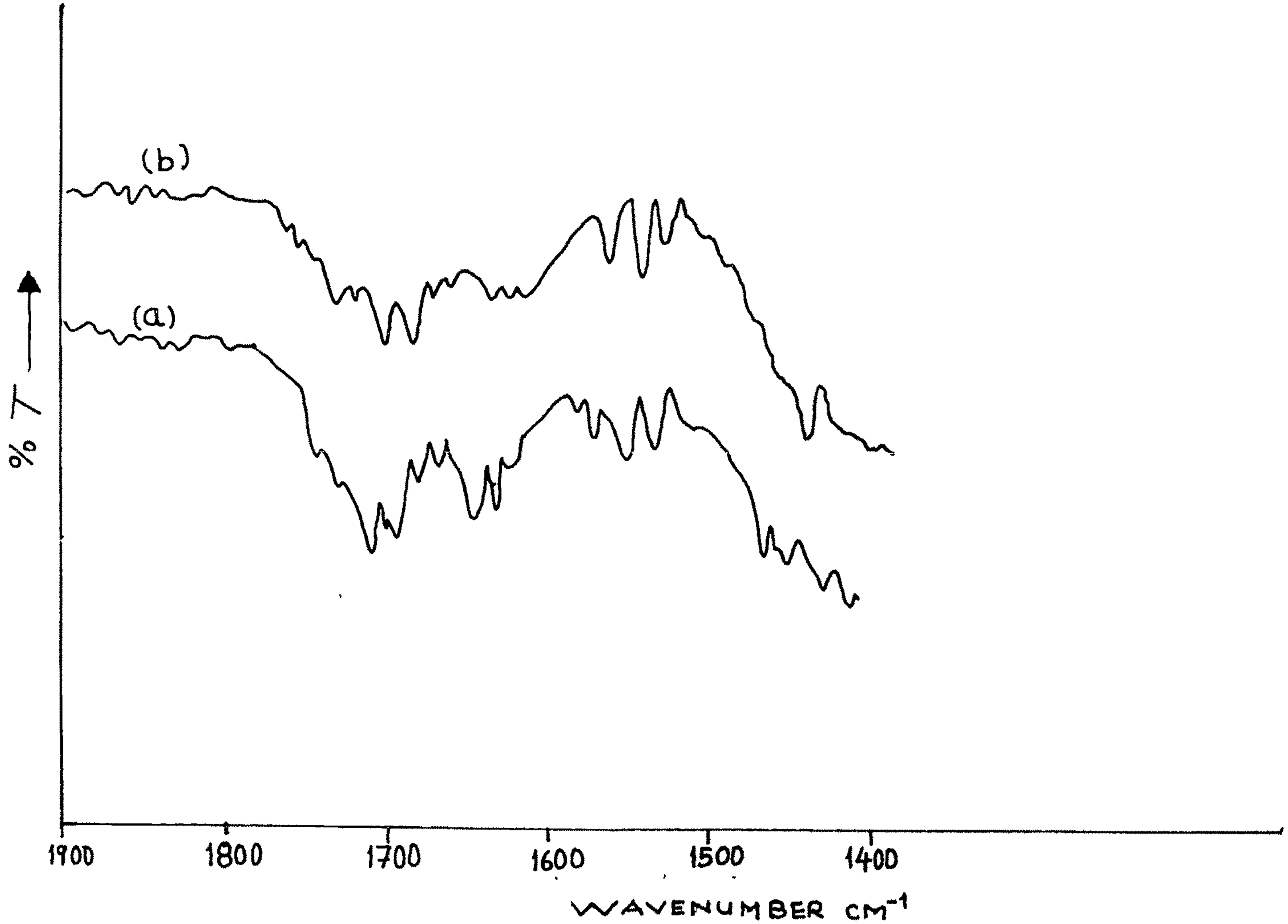


FIG. III.5 (B) IR SPECTRA OF (a) CfAd (b) CfFm (Alc. WASH)

FIG. III.5 (C) IR SPECTRA OF (a) CfAd (b) CFFm.

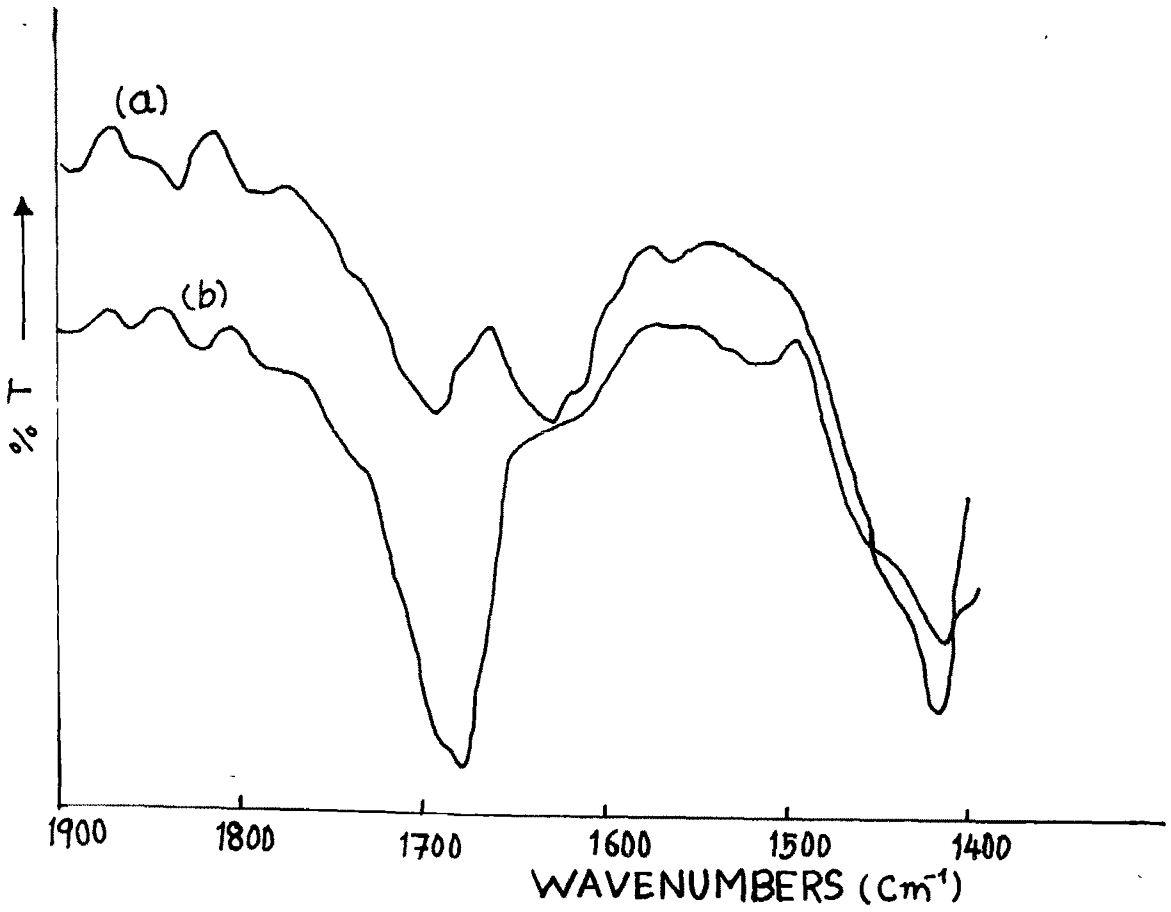


FIG. III.5 (D) IR SPECTRA OF (a) CSb (ALC. WASH) (b) CfSb (XYLENE REFLUX) large differences although differences in fine structure were observed.

f (iv) Thermogravimetric studies

Thermograms of some of the esterified products are presented in fig.II.2. If the thermal characteristics of soluble products (S-CfSb, S-CfAd, S-CfFm and S-CfMl) are compared it is observed that (i) thermogram of S-CfM1 differs from those of other products as regards the low temperature weight loss of the product on heating, (ii) the temperature of steep weight loss of the product increases in order as

$$\text{S-CfMl} < \text{S-CfAd} < \text{S-CfSb} < \text{S-CfFm}$$

(iii) thermal weight loss % increases with different products as

$$\text{S-CfSb} < \text{S-CfMl} < \text{S-CfAd} \sim \text{S-CfFm}$$

If the thermal characteristics of their insoluble residues (CfSb, CfAd, CfFm and CfMl) are compared, it is observed that (i) the temperature of steep weight-loss of the product increases in order as

$$\text{CfMl} < \text{CfAd} < \text{CfSb} \sim \text{CfFm}$$

which is the same order as for soluble products, (ii) thermal weight-loss % of the product at 700° C increases in order as

$$i\text{-CfAd} \sim i\text{-CfFm} < i\text{-CfMl} \sim i\text{-CfSb} .$$

although % variation is less than 8. When the thermal characteristics of CfAdc and CfFmc are compared amongst themselves and with those of other related products, it is observed that (i) the temperature of steep weight-looss of the product increases in order

$$\text{CfAdc} < \text{CfFmc}$$

(ii) temperature of steep weight-loss of the acid anhydride-treated product is lower than that of the acid chloride treated product for fumaric acid and reverse is true for adipic acid (iii) general pattern of thermal decomposition of these products (CfFmc, CfFm, etc.) is comparable to that of untreated cotton fibres.

f (v) SEM studies

Micrograph [Fig.II.4 (a)] shows typical cross-sections observed in untreated cotton fibres. As expected, the cross-sections are been-shaped (having a bilateral structure) and lumen can be seen at the centre of each cross-section.

In the micrograph of maleic anhydride treated cotton fibres

[Fig.II.4 (b)], the cross-sections look more round and the lumen portion appears to have filled up.

In figure II.4 (c), the fibre structure of fibres esterified with adipic anhydride appears to have suffered a damage induced by cross-linking. With regard to retention of properties, cotton fibres esterified with maleic anhydride would be better in performance than fibres esterified with adipic anhydride. Small weight gains and deposits on surfaces, indicate linear chain-coating of the esterified fibres.

f (vi) Polymerization of esterified fabrics

It is observed that (i) BCFm has higher % add-on and greater increase in diameter than BCMl (ii) BCMac has higher % add-on after washing and has greater increase in diameter than BCAc (iii) BCAc has higher % add-on than BCMac before washing.

1 (g) Attempted esterification with cinnamic anhydride

Cinnamic acid was treated with acetic anhydride to get cinnamic anhydride. The product melts at 115° C and its IR spectrum is presented in Fig.II.1(b). It shows the presence of absorption bands at 1710 and 1765 cm^{-1} indicating anhydride group.

When it was used to esterify the cotton fabrics and fibres, no appreciable amount of add-on was detected. However, when one sample of esterified fabric was tested for crease recovery, CRA of 218° was observed. It implies that even with very low degree of esterification relatively high value of CRA may be obtained. It may be noted here that although very low add-on was observed for the cellulose esterified with cinnamic anhydride, good % add-on (8-39) was observed when cellulose was esterified with trans cinnamoyl chloride (218).

1 (h) Attempted esterification with LAB acid chloride

Linear alkyl benzene sulphonic acid slurry (LAB acid) available commercially was treated with thionyl chloride to get LAB acid chloride and the product was used to esterify cotton fabrics and fibres. IR spectrum of LAB acid chloride is presented in Fig.II.1(c) and IR spectrum of chloride-treated fibres is presented in Fig.II.3(g).

1 (j) General consideration

IR spectra of anhydrides [fig.II.1 (a)] show some of the characteristic differences amongst themselves. Thus IR spectrum of Sbn has absorption bands at 1690, 1730 and 1795 cm^{-1} indicating multiple CO groups. Further, bands at 2820 and 2895 cm^{-1} indicate the presence of CH_2 and CH_3

groups. Hence it is suggested that terminal groups in Sbn would be acetate groups. Similarly, in case of Adn, absorption bands at 1680, 1715 and 1785 cm^{-1} indicate multiple CO groups and bands at 2820 and 2920 cm^{-1} indicate CH_3 and CH_2 groups. Hence in case of Adn also terminal acetate groups are suggested. However, in case of Fmn absorption bands for CO are at 1680 and 1790 cm^{-1} and for free and H - bonded hydroxyl at 2900 and 3100 cm^{-1}. These indicate carboxyl terminal groups in the anhydride chain with some H - bonding.

Natural cellulose in cotton is termed cellulose I and exists in chair form while cellulose in mercerized cotton is termed cellulose II and exists in boat form. Of the three hydroxyl groups at 2, 3 and 6 positions in cellulose unit the relative accessibility of hydroxyl grooup for reaction increases in order

$$\underline{3}\ \mathrm{OH} < \underline{6}\ \mathrm{OH} < \underline{2}\ \mathrm{OH}$$

Esterification of cotton fibres has led to the isolation of four cellulose esters soluble in alcohol and having relatively low melting point. Triester insoluble in acetone is isolated in case of esterification with sebacic anhydride, degree of esterification is 1.5 for the esterification with adipic anhydride and 1.0 for the esterification with maleic and fumaric anhydrides and the products are soluble in acetone. It appears that saturated anhydride can esterify the cellulose to a greater extent than unsaturated anhydrides. Thus, four new cellulose esters have been prepared and characterized by their analysis, melting point, solubility, IR spectra, TG analysis, etc. It is believed that they are formed by intramolecular or intrachain esterification reaction.

It is also observed that cotton fabrics esterified with maleic or fumaric anhydride and washed have much lower degree of esterification than the fabrics esterified with these anhydrides, polymerized and washed. It may be that soluble esterified products formed intially are insolublized by polymerization. It may also be that acid anhydride would decrease the degree of polymerization of cellulose by acid cleavage at loose points (18, 50, 53). SEM studies indicate that during acylation surface layer swells, becomes spongy and may become brittle or may lead to cleavage at loose points (219).

% add-on observed for fabrics esterified with adipic anhydride, and maleic anhydride were low, namely 0.3-0.9, 0.2-0.4 respectively whereas that observed for fibres esterified with these reagents was high, namely 4.5 and 5.0 respectively. This difference can be understood in terms of diffusion rate of reaction. It may be noted here that % add-on for cellulose esterified with adipic and maleic acid salts was reported to be 3.2 and 3.7 respectively (28), and % add-on for cellulose esterified with adipic acid in presence of trifluoracetic anhydride was reported to be 3.4 (17).

Crease recovery or wrinkle resistance of textile fabrics is related to hydrophilic groups present (220). Greater wrinkling would be observed when the apparel was more hydrophilic. Actually wrinkling would depend on the swelling and deswelling characteristics of the fibres and these will depend on the balance of hydrophilic and hydrophobic sites in the fibres. This aspect will be considered later.

III.2 FORMALIZED COTTON

2 (a) Formalization of cotton

Cotton and rayon have been formalized by various aldehydes, methylolated derivatives of amides, amines, phenols, etc. Usually these reagents are used as crosslinking agents. Cotton has been formalized by (i) formaldehyde (72, 80), (ii) formaldehyde with acid catalysts (71, 82, 85, 88, 89), (iii) formaldehyde in vapour phase (62, 71, 86, 87, 95), (v) diethyl formal (63, 221), (vi) urea and formaldehyde (74, 80), (vii) dimethylol urea (222), (viii) dimethylol ethylene urea (75, 84, 96, 97, 102, 103, 223), (ix) dimethylol thiourea (224), (x) methylolated melamine (96), (xi) methylolated acrylamide (100), (xii) methylolated dioxane (225), (xiii) dimethylol ethylene urea and polyvinyl alcohol (103), (xiv) oxidized polyvinyl alcohol (226, 227), (xv) phenol and formaldehyde (78), (xvi) wool keratin hydrolyzate and formaldehyde (228), (xvii) glyoxal (95), (xviii) glutraldehyde (68) etc.

The structural characteristics of formalized cotton have been studied by IR spectroscopy (229 - 231), thermal analysis (232), electron microscopy (72, 74), etc. in addition to the usual chemical techniques of analysis. Acids cause cleavage of cellulose macromolecule and hence decrease its degree of polymerization (87, 96). Oxymethylene bridges of different lengths are also formed (59, 65, 91). Degree of swelling and solubility are related to the number of crosslinks (87). Cross-links between the lamellae of cotton have been related to crease retention (73).

In the present studies cotton fabrics have been formalized in presence of polyvinyl alcohol under different conditions, followed by other treatments.

2 (b) Polyvinyl alcohol

Polyvinyl alcohol has been used as a reagent together with aldehyde in these investigations. It is available commercially in many different grades depending on its degree of polymerization and degree of hydrolysis. Some companies offer more than ten different major grades and more than hundred subgrades of polyvinyl alcohol. On the basis of % hydrolysis, they fall into (i) fully hydrolyzed group having about 98% hydrolysis, (ii) partly hydrolyzed group with 87-89% hydrolysis or 78-80% hydrolysis. In terms of degree of polymerization (DP) the major groups are of : (i) low viscosity group with DP of 600, (ii) medium viscosity group with DP of 1700, and (iii) high viscosity group with DP of 2400, with subgroups having DP of 1000, 2000, 2800 and 3200. Polyvinyl alcohol used in these investigations was of Koch-Light make (K-grade). It is 97% hydrolyzed and its degree of polymerization is 1640. In few experiments polyvinyl alcohol of SD chem make (S-grade) was used. Its degree of hydrolysis is 80 and its degree of polymerization is 2840. Polyvinyl alcohol is a linear polymer, its chain having pendant alcohol groups. This group can undergo etherification and formalization reactions.

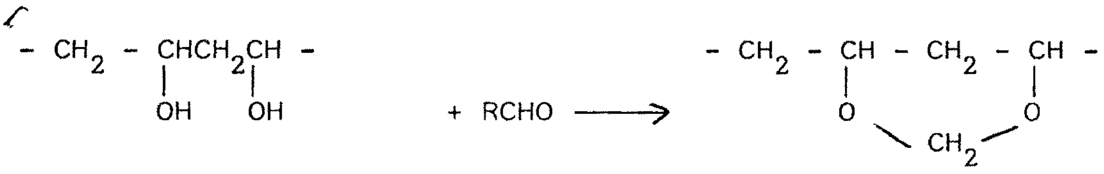
2 (c) Polyvinyl formals

Polyvinyl alcohol can be formalized with different aldehydes as shown in table III.4. Because of the difunctionality of formal reaction, it is assumed that reactions may take place by any one or all of the following three mechanisms : (i) intramolecular formalization of 1, 3 glycol group, (ii) intermolecular formalization, and (iii) intramolecular formalization of 1,2 glycol group (fig.III.6)

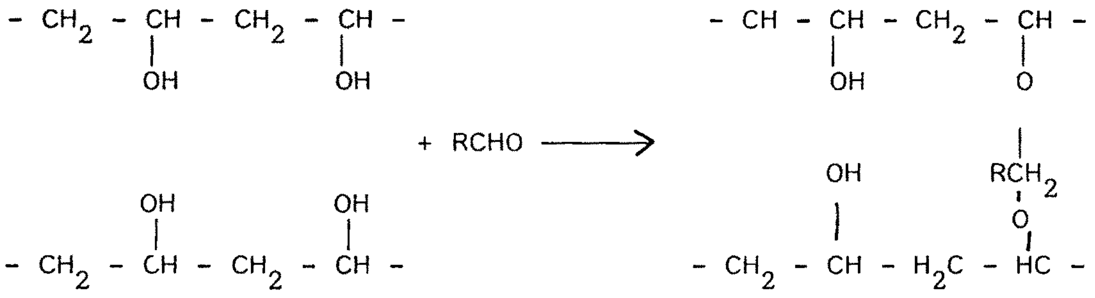
Table III.4

POLYVINYL FORMALS

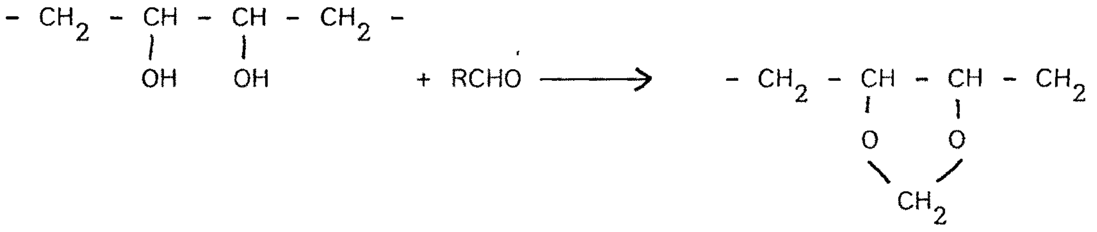
Some aldehydes used to form formals	Reference
HCHO	233
CH_3CHO	234
C_2H_5CHO	235-237, 238
$C_7H_{15}CHO$	239
CH_2CHCHO	240
CHO CHO	241
$2\text{-}C_{10}H_7CHO$	242
$O\text{-}HOC_6H_4CHO$	243
$P\text{-}HOC_6H_4CHO$	243
$P\text{-}HOCC_6H_4CHO$	244
$O\text{-}HSO_3C_6H_4CHO$	245
furfural	246



(i) intramolecular formalization (1,3 glycol)



(ii) intermolecular formalization



(iii) intramolecular formalizatioon (1,2 glycol)

Fig. III.6

Intermolecular reaction is likely to cause gelling due to the occurrence of cross linking.

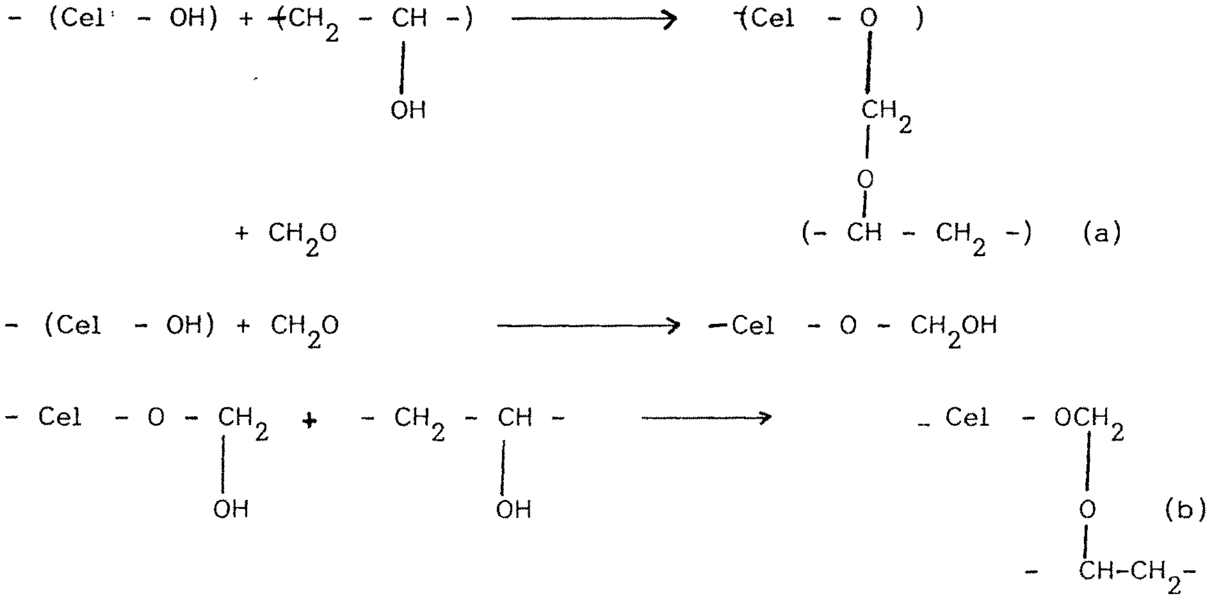
Polyvinyl alcohol of different grades has been widely used for warp sizing. PVA with DP of 1700 is suitable for spun yarns. Fully hydrolyzed PVA is applied to hydrophilic yarns such as cotton, linen etc. We have considered that polyvinyl formal reaction with cellulose can modify cellulose fabrics improving crease retention.

2 (d) Cotton fabrics modified with polyvinyl alcohol and formaldehyde

Cotton fabrics were formalized under different conditions. In the first case, fabrics having sorbed polyvinyl alcohol (S-grade) were formalized in presence of hydrochloric acid catalyst (CVF). In the second case, the fabrics were methylolated with formaldehyde in presence of excess acid and then treated with polyvinyl alcohol (S-grade) in presence of alkali to form formalized fabrics (CVFa).

The reactions taking place can be represented as shown in eq.III.1.

% add-on is used to calculate the degree of monosubstitution as indicated from eq.III.1. The values are presented in table III.5. The results show that (i) gelation of cellulose and polyvinyl alcohol by formaldehyde yields



$$-(\mathrm{Cel}-\mathrm{OH}) + (\mathrm{CH_2}-\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{CH}}}-) + \mathrm{CH_2O} \longrightarrow (\mathrm{Cel}-\underset{\displaystyle (-\mathrm{CH}-\mathrm{CH_2}-)}{\underset{|}{\mathrm{O}}}\!)\quad \text{(a)}$$

$$(\mathrm{Cel}-\mathrm{O}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH}-\mathrm{CH_2}-)\quad \text{(a)}$$

$$-(\mathrm{Cel}-\mathrm{OH}) + \mathrm{CH_2O} \longrightarrow -\mathrm{Cel}-\mathrm{O}-\mathrm{CH_2OH}$$

$$-\mathrm{Cel}-\mathrm{O}-\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{CH_2}}} + -\mathrm{CH_2}-\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{CH}}}- \longrightarrow -\mathrm{Cel}-\mathrm{OCH_2}-\mathrm{O}-\mathrm{CH}-\mathrm{CH_2}-\quad \text{(b)}$$

Eq. III.1

Table III. 5

No.	Product	Degree of mono substitution per glucose unit
1	CVF	0.029
2	CVFa-1	0.003
3	CVFa-2	0.011
4	CVFa-3 (i)	0.003
	CVFa-3 (ii)	0.006

a formalized cellulose with a low degree of substitution (ii) the products obtained from cellulose first methyloated with formaldehyde and then treated with polyvinyl alcohol have very low degree of substitution, probably because oxymethylene liks (formal links) have low stability and undergo cleavage by acids and alkalis.

2(e) Cotton fabrics modified with polyvinyl alcohol and Paraformaldehyde

Since low % add-on was observed with formaldehyde, paraformaldehyde was used for formalization so that greater concentration can be utilized for reaction.

In the first case cotton fabrics were treated with paraformaldehyde under acidic condition so that greater methylolation can be achieved. The methylolated product was then treated with polyvinyl alcohol under alkaline condition (CVP).

In the second case, cotton fabrics having sorbed polyvinyl alcohol from solution were reacted with paraformaldehyde under alkaline conditions (CVPn).

In the third experiment, cotton fabrics having sorbed polyvinyl alcohol from solution were treated with paraformaldehyde in presence of acetic acid and subsequently refluxed with acetic anhydride (CVPan).

% Add-on of these products is used to calculate the degree of formalization. The values are presented in table III.6. The results indicate that higher degree of substitution has been achieved by the use of paraformaldehyde in place of formaldehyde solution. However, hydrolytic and washing stability of the products was low. Hence, attempts were made to improve stability by resinification.

2(f) Cotton fabrics modified with polyvinyl alcohol, paraformaldehyde and resorcinol

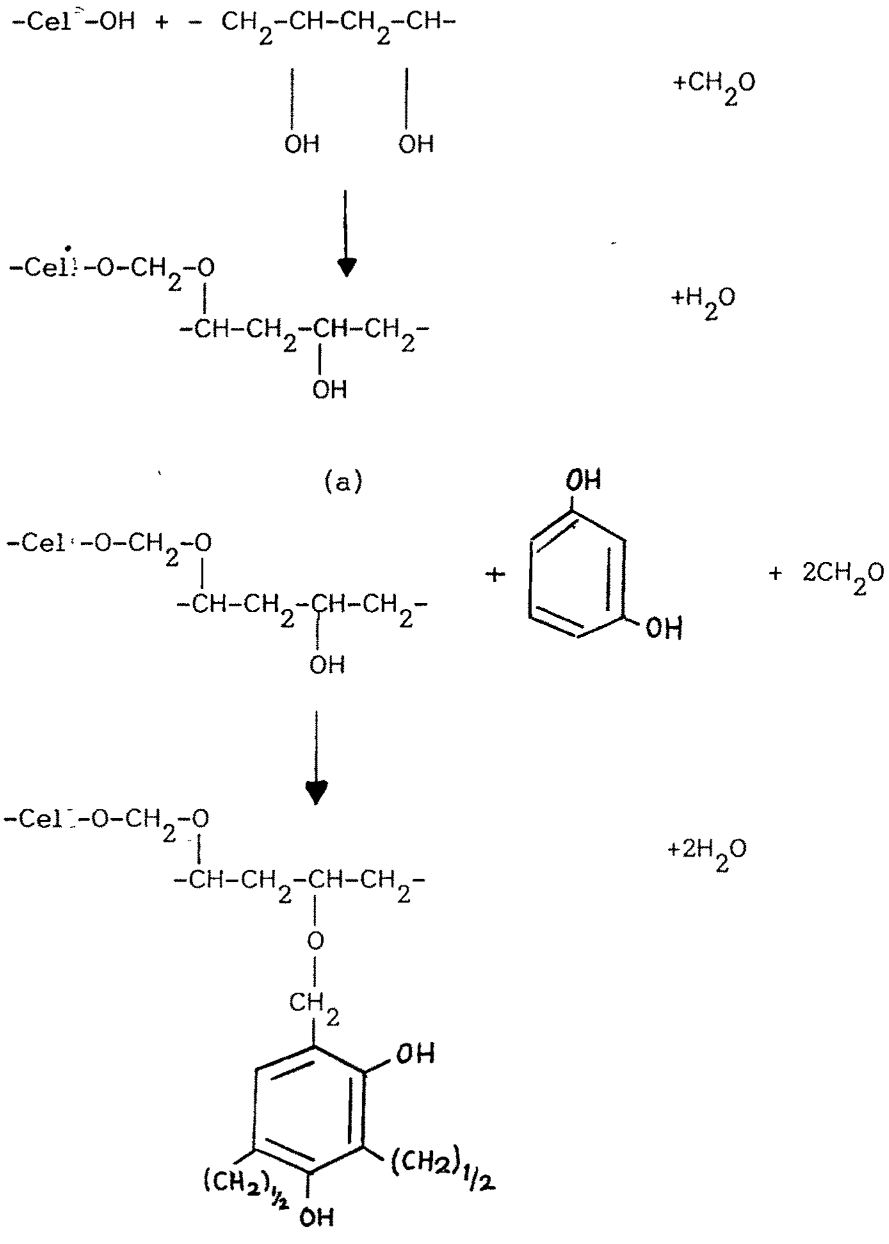
Cotton fabrics having sorbed polyvinyl alcohol were treated with paraformaldehyde in presence of acid or alkali and were subsequently treated with resorcinol in presence of alkali (CVPR). The probable reaction taking place in the reacting system is represented by eq.III.2. % Add-on of these products is used to calculate the degree of formalization including resinification as suggested in eq.III.2. The values are presented in table III.7. The results show that the degree of substitution decreases on resinification. This may be attributed to the unstability of methoxy linkage to alkali during resinification.

2(g) Cotton fabrics modified with polyvinyl alcohol, paraformaldehyde and melamine

Cotton fabrics having sorbed polyvinyl alcohol from solution were treated with paraformaldehyde in acetic acid and

Table III.6

No.	Product	Degree of mono substitution per glucose unit
1.	CVP	0.26
2.	CVPn (Wp)	0.32
	CVPn (Wf)	0.44
3.	CVPan	0.14



(a)

(b)

Eq.III.2

Table III.7

No.	Product	Degree of mono substitution per glucose unit
1.	(i) CVPR (Wp)	0.015
	(ii) CVPR (Wf)	0.024
2.	CVPR-1	-
3.	CVPR-2	0.013
4.	CVPR-3	0.022

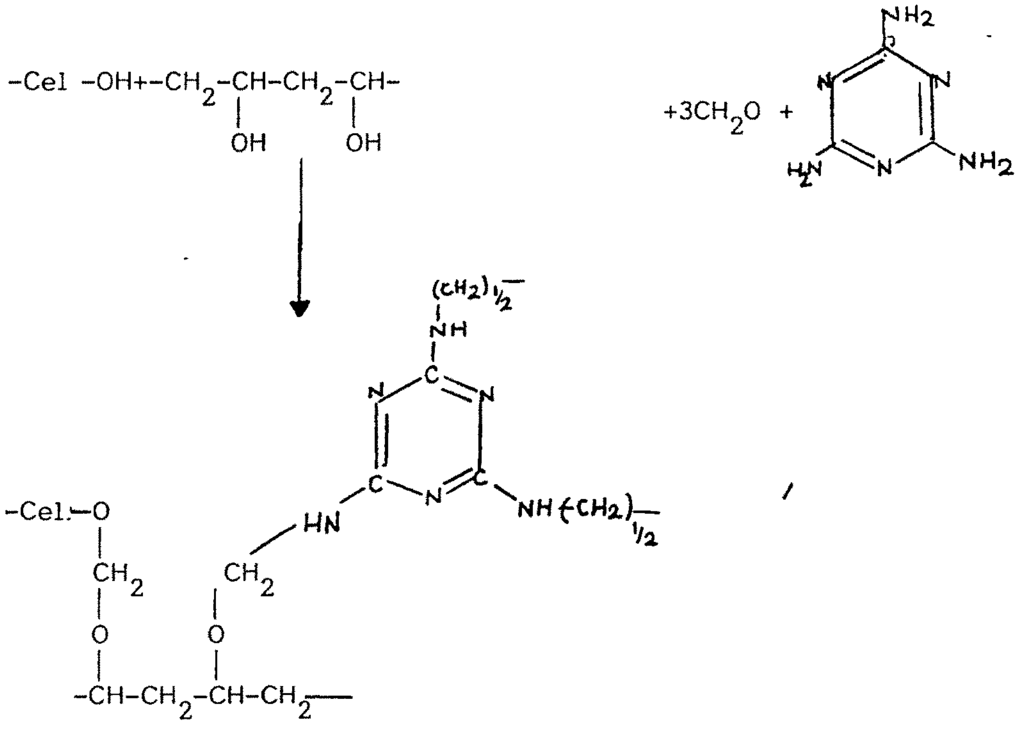
then resinified with melamine in presence of alkali. The reactom expected to take place is suggested in eq.III.3. % Add-on of these products is used to calculate the degree of formalization including resinification as suggested in eq.III.3. The values are presented in table III.8. The results show that the degree of substitution is higher for the product resinified with melamine than one resinified with resorcinol.

2(h) Cotton fabrics modified with polyvinyl alcohol, formaldehyde, butyraldehyde and melamine

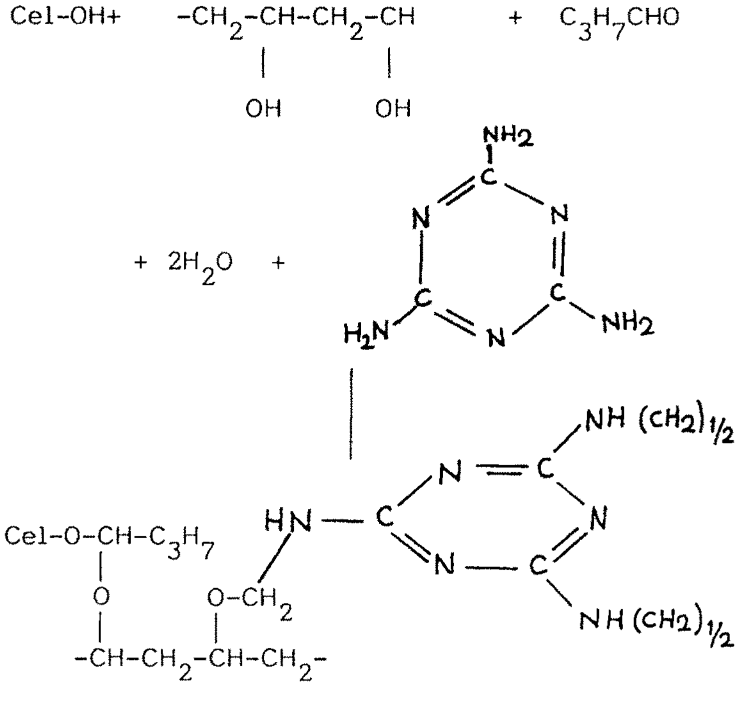
Cotton fabrics having sorbed polyvinyl alcohol from solution were formalized with butyraldehyde in presence of acetic acid and then resinified with melamine and formaldehyde. The reaction expected to take place is suggested in eq.III.4. % Add-on of the product is used to calculate the degree of formalization including resinfication as suggested in eq.III.4. The value is presented in table III.8. The result shows that the degree of substitution for the product formalized by butyraldehyde (and formaldehyde) is higher than that for the prdouct formalized by formaldehyde alone or by paraformaldehyde and resinified.

2(i) Formalized cotton

The scanning electron photomicrographs of unmodified cotton and formalized (and resinified) cotton, have been presented



Eq. III.3



Eq.III.4

Table III.8

No.	Product	Degree of substitution per glucose unit
1.	CVPM-1	0.020
2.	CVPM-2	0.024
3.	CVBFM	0.030

in fig.II.5. In fig.II.5(d), the yarn exhibit somewhat smooth surface rather than untreated yarn.

Fig.II.5(c) shows formalized cotton yarn with smooth surface with some coating on the surfaces indicative of polymer formation. In fig.II.5(d) & (e) the yarn exhibits similar smooth surface with less coating. These smooth surfaces (with coating) can be an indication of polymer cross-linking.

2(j) Break strength and % elongation at break

Break strength and % elongation of some of the treated fabrics have been shown in table II.10. There is a difference between untreated warp and weft fabric.

The treated fabric-CVF has low degree of substitution and has low break strength and % elongation compared to untreated fabric. The treated fabric-CVP has high degree of substitution and has improved break strength and % elnogation. The treated fabrics (CVPR-1) have much higher values of break strength and % elongation than untreated fabric. Warps of treated fabrics CVPM and CVBFM also show better break strength and % elongation than untreated fabrics.

The results show that (i) resinification improves elasticity and strength of formalized fabrics, and (ii) formalization by formaldehyde and butyraldehyde results in improved break strength and % elongation than that by formaldehyde alone in resinified products.

2(k) Crease recovery

Crease recovery angles of some of the treated fabrics have been presented in table II.11. When the fabrics are formalized and acetylated as in CVPan, the treated fabrics have improved crease recovery. The formalized and resinified fabrics do not show increase in crease recovery but if the fabrics are formalized with butyraldehyde and formaldehyde, the treated fabrics have much better crease recovery that the fabrics obtained by formalization with formaldehyde alone.

2(l) X-ray Diffractogram

Fig.II.6 shows the X-ray diffractograms of untreated cotton fabric and treated cotton fabric - CVBFM.

It is observed that (i) the diffractogram relates to cellulose-I form, indicating that use of alkali during the reaction has not modified the cellulose structure, (ii) intensity of the peaks have increased and become sharper in treated fabrics as compared to untreated fabrics indicating the modification of crystalline nature.

2(m) General considerations

Many reviews have appeared in the cross-linking of cellulose by formaldehyde and its derivatives (80, 100, 247, 248, 249, 250). Cross-linking may be intermolecular at 6,6' hydroxyls. Intramolecular linkage at 2,3 hydroxyl, may be observed (86). The cross-linking stabilizes cellulose-I form and reduces mercerization of cotton (223). Cross-linking increases disorder of cellulosic materials (224) as

rayon > cotton > cellulose diacetate

The degree of cross-linking is found to be nearly 0.02 for formalized cotton (99). Acid acts as a catalyst in the formalization reaction of cellulose at pH lower than 3 but at the same time it lowers its degree of polymerization (84, 96). If pick up of DMU by cellulose is more than 10%, it increases the brittleness and rigidity of the product (222). Thermal response of cotton finished with methylol amide agents indicated that thermal stability of finishes is different from its hydrolytic stability (251). Glyoxal-glycol processes have been developed for dry press finishes(252).

In the present studies, cross-linking of cellulose takes place with polyvinyl alcohol through methoxy linkages formed by reaction with formaldehyde. These linkages are unstable in presence of acid and hence pick-up by cellulose would be relatively low. Although both cellulose and polyvinyl alcohol are polymers yielding copolymer products on reaction, we have used monomeric units - glucose and vinyl alcohol in calculations and graphical presentations.

The studies of break strength, % elongation and crease recovery of some of the treated fabrics indicated that formalization by butyraldehyde and formaldehyde should be preferred to that by formaldehyde alone. Abhyanker and coworkers (253) observed that crease recovery was improved by resinification.

X-ray studies have shown that (i) formalization has not modified cellulose I structure and (ii) crystalline nature has been modified. Further considerations on cross-linking by esterification and formalization will be considered later.

III.3 GRAFTED COTTON

3(a) Grafting of cellulose

Cellulose in its different forms (natural, regenerated and synthetics) has been grafted with various monomers (particularly vinyl type) (or polymers) using different polymerization techniques. Thus cotton fabrics and linters, viscose, rayon, cellophane, cellulose esters etc have been grafted. The monomers used for grafting are (i) Styrene (254-266), (ii) methyl acrylate and methyl methacrylate (258, 259, 260, 263, 264, 267-273), (iii) acrylamide and methacrylamide (108, 109, 258, 267, 269, 273, 274, 275, 276-282), (iv) acrylic acid and methacrylic acid (263, 274, 283-289), (v) vinyl chloride (271), (vi) vinyl pyridine (275), (vii) acrylonitrile (260, 263, 264, 269, 273, 275, 276, 282, 292-307) (viii) acrolein (308), (ix) butadiene (271, 297), (x) chloroprene (309) etc. The grafting mechanism may be free radical or ionic and the initiation may be by the use of (i) Ce (IV) ions (256, 257, 258, 260, 265, 269, 272, 279, 281, 289, 293, 300, 302, 303, 310, 311), (ii) persulphates (259, 260), (iii) Fe (II) ions and hydrogen peroxide (261, 266, 285, 311, 312), (iv) Mn (III) (276), (v) U (VI) ions (314), (vii) benzoyl peroxide (260), (viii) periodic acid (291, 296), (ix) ozone (260), etc. The initiation can also be by (i) γ -radiation (267, 311), (ii) UV radiation (258, 285, 288, 314), (iii) γ or UV radiation (264, 274, 275, 280, 297, 298, 315) (iv) photoinitiation (270, 278, 294), etc. The polymerization may be (i) by freezing (287), (ii) by pad cure (277), etc., and may involve the formation of hydroperoxide intermediates (282, 292, 306, 316), etc. The grafted cellulosic materials have been studied by (i) X-rays spectrometer (261, 262, 317), (ii) optical Microscope (261, 317) (iii) electron microscope (261, 264, 294), (iv) IR spectrophotometer (254, 256, 263, 267, 288, 298, 301), etc. The studies also include (i) sorption and swelling (255, 309, 318) (ii) kinetics (255, 319) (iii) soil retardation (315) (iv) size change (302) (v) molecular wt & dispersity (265. 287, 311), (vi) synergism (320) (vii) antimicrobial characteristics (286), etc., in addition to the usual studies of crease retention, elongation, break strength, tear strength, abrasion resistance, etc.

3(b) Characterization of Grafted Copolymers

(i) Solubilization and Fractionation Techniques

The first step in characterization would appear to be extraction of homopolymer with solvent to leave the copolymer behind. The residual product is described as a "graft" copolymer.

The solubility behaviour is dependent upon the amount of homopolymer, and purification procedures have been developed.

The following procedure for the isolatin of cellulose-polyacrylonitrile graft copolymer has been reported (321). The crude product was Soxhlet extracted with dimethylformamide under anhydrous conditions until fresh extract contained no solute. The extract contained homopolymer and graft polymer in which the homopolymer content was very high and was precipitated from solution by ether and methanol. The undissolved material consisting of graft polymer and unreacted cellulose was given three charges of fresh cuprammonium solution each of 5 hr. duration to dissolve free cellulose. The residue, consisting of pure graft polymer only, was washed with water and methanol, and dried.

Similar procedures were adopted with other graft copolymers of cellulose: cellulose-poly (methyl methacrylate) product was first extracted with benzene and the cellulose-polymethacrylonitrile product was extracted with acetone to remove the respective homopolymers.

Cumberbirch and Holker (122) determined the carboxyl content of cotton copolymerized with acrylic acid using a tetravalent ceric ion initiator. The coplymer was dissolved in cuprammonium hydroxide and the solution acidified with dilute hydrochloric acid. The precipitates retained 80% of the original carboxyl content indicating that this portion of the poly (acrylic acid) was grafted to the cellulose.

(ii) Spectroscopy

Spectroscopic examination of the fractions obtained from a polymerizing system may yield further information on the nature of the polymerization mechanism.

Singh, Thampy, and Chipalkatti (322) measured the IR spectra of varius forms of cellulose copolymerized with methyl methacrylate or methyl acrylate using manganic sulfate and sulfuric acid initiator. The indication in the spectra that an ester group had been formed supported the claim that grafting of polymer had occured at the hydroxyl groups.

(iii) Chemical evaluation

The actual weight increase of polymer gives much information as to the nature of the chains if the initiation step is well controlled and the polymerization can be carried out under conditions of low homopolymer formation.

The alkylation and diazotization method (323) of obtaining

The number-average molecular weight obtained by experiment compared to the theoretical number-average molecular weight calculated from the number of initiating sites and the weight uptake of polymer, gave a measure of the efficiency of the free radicals in forming grafted polymer chains.

Livshits, Levites, and Rogovin (324) established that, for redox-initiated polymerization of cellulose, the molecular weight of grafted poly (methylacrylate) chains was virtually independent of reaction time. This is in contrast to the finding of Kulkarni and Mehta (125) that short reaction times formed chains of lower degree of polymerization. However, since Livshits et al. used polymer "add-ons" of 20% and Kulkarni and Mehta needed approximately 20% polymer to solubilize the graft, it appears that the degree of polymerization increases to a constant value and the total amount of polymer formed increases with reaction time because of the increased number of chains formed.

For free-radical-initiated polymerization in cellulose substrates the degree of polymerization of grafted polyacrylonitrile chains was much higher than the degree of polymerization of homopolymer formed simultaneously. This difference has been attributed to a gel effect in which the growing polymer chain is protected sterically from termination reactions. On the other hand, the anion in graft polymerization technique leads to the formation of homopolymer and graft polymer active centres to initiate polymerization has been used to enable characterization of polyacrylonitrile chains formed on cellulose.

An experimental determination of the total amount of grafted polymer and the estimate of the number of side chains enables calculation of the mean degree of polymerization. However, it is a useful means of comparing the degree of polymerization under different polymerization conditions and initiator concentrations. The grafted copolymers of cellulose are thus characterized according to the amount of polymer, the number of chains, and the mean degree of polymerization.

Kulkarni and Mehta (125) prepared cellulose-polyacrylonitrile grafts from a ceric ion-initiated polymerization, extracted with dimethylformamide after acetolysis to dissolve away ungrafted cellulose and to obtain only a fraction of low cellulose content which was precipitated from solution with ice cold water. This fraction, to be soluble in dimethylformamide, contained polymer chains of relatively high degree of polymerization and was only formed at low initiator concentrations or high reaction times. The size of the cellulose fragment being small compared to the polymer chain enabled the fraction to be characterized by normal techniques of polymer chemistry applicable to polyacrylonitrile.

of approximately the same molecular weight (325). The molecular weight of the polymer chains in this case is much less than that obtained by free-radical initiation techniques and for this lower degree of polymerization, termination occurs before a gel is formed. Consequently, there is little difference between homopolymer and graft polymer molecular weights.

(iv) Location of grafted polymer

The location of grafted polymer in natural macromolecular materials has been sought by electron and light microscopy, chemical analysis and physical methods.

The relationship between location of graft polymer and the variable parameters of polymerization have been investigated by electro-microscopic survey of copolymers formed from cotton and vinyl monomers (326). Microtomed sections were immersed in a solvent for cellulose, such as cupriethylene diamine, and a solvent for the particular homopolymer before being electron micrographed. Chemically initiated grafting using tetravalent ceric ion evenly distributed polymer throughout the cell walls of the fibres at all levels of polymer add-on. Grafting of methyl methacrylate by preirradiation formed graft polymer only in the outer layers of cotton fibres even for a polymer add-on of 50%, whereas poly (vinyl acetate) was grafted uniformly. It was concluded that uniform distribution of polymer throughout the fibre was obtained for a fibre left relatively unswollen by the polymerizing solution. However, the grafted polymer can be restricted to the outer layers with solvents which cause swelling, so that the fibre assumes a rounded shape with clear growth layers.

Vinyl acetate in methanol solution formed a network polymer throughout the fibres, including a complete opening up of the fine structure of the fibre.

3(c) Grafting of Cotton

In the present studies, various vinyl monomers were grafted on cotton fibres and fabrics under different conditions. % grafting and % efficiency of grafting were evaluated in in each case by using the following relations :

(i) $$\% \text{ grafting} = \frac{(W_2 - W_1)}{W_1} \times 100$$

and

(ii) $$\% \text{ efficiency of grafting} = \frac{(W_2 - W_1)}{W_3} \times 100$$

where W_1 = weight of the original sample,

W_2 = weight of the grafted sample, and

W_3 = weight of the monomer

(c) (i) Grafting of acrylonitrile or acrylamide on cotton farbics using potassium persulphate and sodium bisulphite

Cotton fabrics were treated with acrylonitrile or acrylamide in presence of the redox initiator - potassium persulphate and sodium bisulphite (KPS+SBS) under acidic condition. The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were evaluated.

(c) (ii) Grafting of acrylonitrile or acrylamide on cotton fabrics using iron (II) ammonium sulphate and hydrogen peroxide.

Cotton fabrics were treated with acrylonitrile or acrylamide in presence of iron (II) ammonium sulphate and hydrogen peroxide (FAS+HP). The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were evaluated. The values are presented in Table III.9.

(c) (iii) % Grafting

Plots of % grafting vs temperature for specific period of time of reaction for grafting are presented in fig.III.7. It has been observed that (i) with KPS+SBS initiator system, one hr reaction curve shows maximum % grafting of acrylonitrile on cotton at 60°C and three hr reaction curve for acrylamide grafting on cotton at 60°C and one hr reaction curve for acrylonitrile grafting and three hr reaction curve for acrylamide

Table - III.9

9 (a)

No	Sample	Temperature °C	Time (hr)	% Grafting	% Efficiency of grafting
1	KAn-g-C-1	(i) 50	1.0	2.0	0.3
		(ii) 60	1.0	10.8	1.9
		(iii) 80	1.0	8.7	1.7
2	KAn-g-C-2	(i) 50	3.0	7.0	1.1
		(ii) 60	3.0	7.8	1.5
		(iii) 80	3.0	7.2	1.3
3	FAn-g-C-1	(i) 50	1.0	27.5	4.2
		(ii) 60	1.0	39.8	5.9
		(iii) 80	1.0	33.5	5.3
4	FAn-g-C-2	(i) 50	3.0	31.4	4.6
		(ii) 60	3.0	29.7	4.8
		(iii) 80	3.0	19.9	3.3

9 (b)

No.	Sample	Temperature °C	Time (hr)	% Grafting	% Efficiency of grafting
1	KAa-g-C-1	(i) 50	1.0	3.4	0.5
		(ii) 60	1.0	3.7	0.6
		(iii) 80	1.0	1.7	0.3
2	KAa-g-C-2	(i) 50	3.0	6.1	1.0
		(ii) 60	3.0	14.9	2.9
		(iii) 80	3.0	5.7	0.9
3	FAa-g-C-1	(i) 50	1.0	23.1	3.5
		(ii) 60	1.0	20.3	3.2
		(iii) 80	1.0	18.2	2.9
4	FAa-g-C-2	(i) 50	3.0	27.3	4.8
		(ii) 60	3.0	17.7	3.1
		(iii) 80	3.0	15.2	2.7

9 (c)

No	Sample	Temperature °C	Time (hr)	% Grafting	% Efficiency of grafting
1	BAn-g-C-1	60	3.0	-	-
2	-2	73	3.0	3.1	0.5
3	-3	80	3.0	3.2	0.7
4	BAa-g-C-1	50	1.0	-	-
5	-2	60	1.0	-	-
6	-3	80	1.0	6.8	1.2
7	BAa-g-C-4	60	1.0	-	-
8	-5	65	1.0	1.5	0.2
9	-6	80	1.0	2.5	0.4
10	-7	75	1.0	15.1	2.5

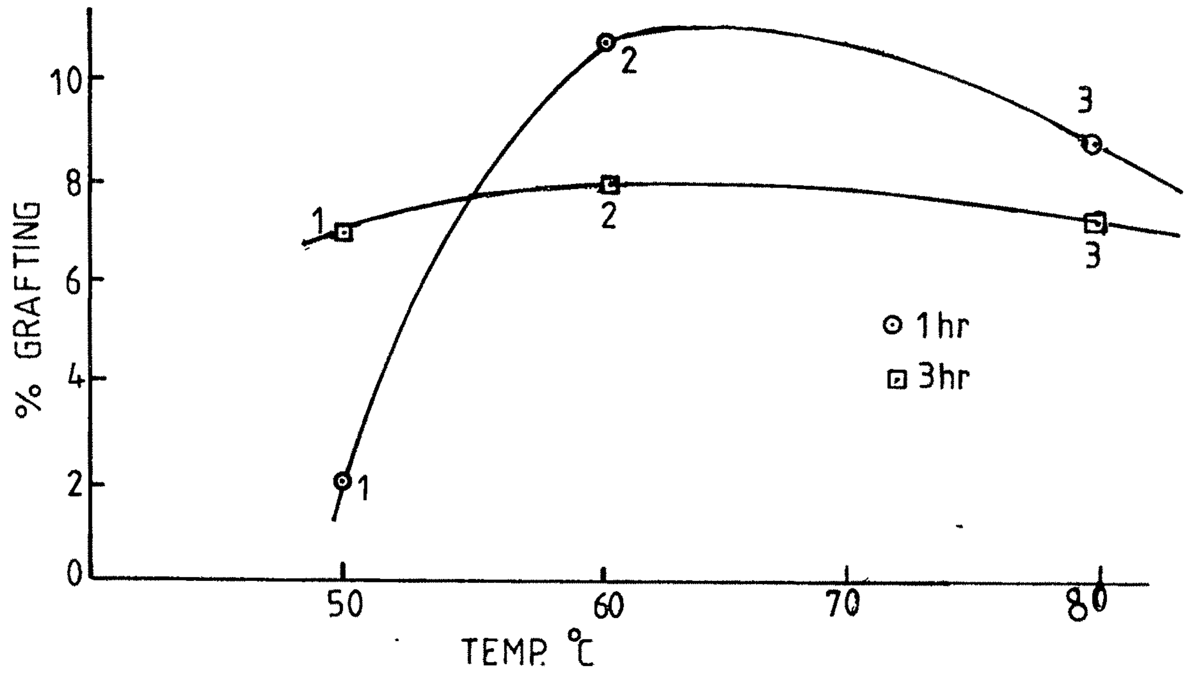


FIG.III 7(a). % GRAFTING Vs. TEMP. OF ACRYLONITRILE-GRAFTS (KPS + SBS) INITIATOR

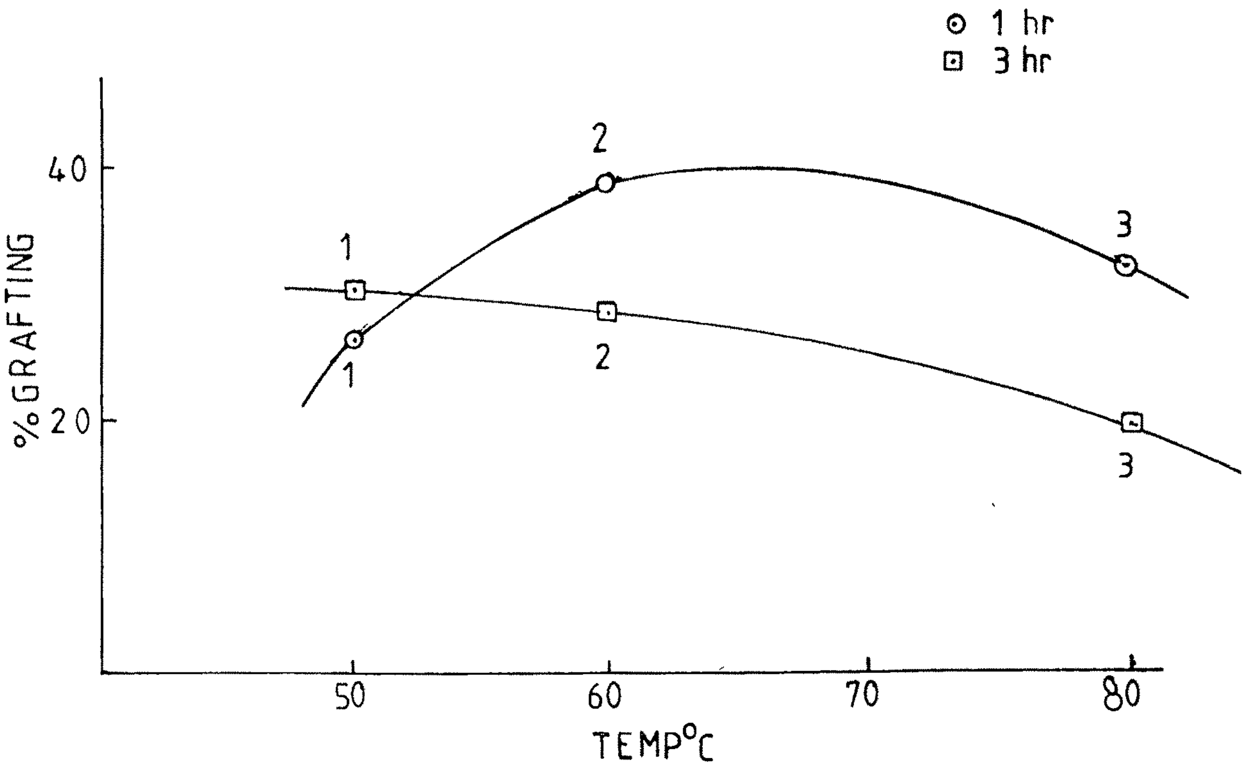


FIG. III. 7(b) % GRAFTING Vs TEMP. OF ACRYLONITRILE-GRAFTS (FAS+HP) INITIATOR

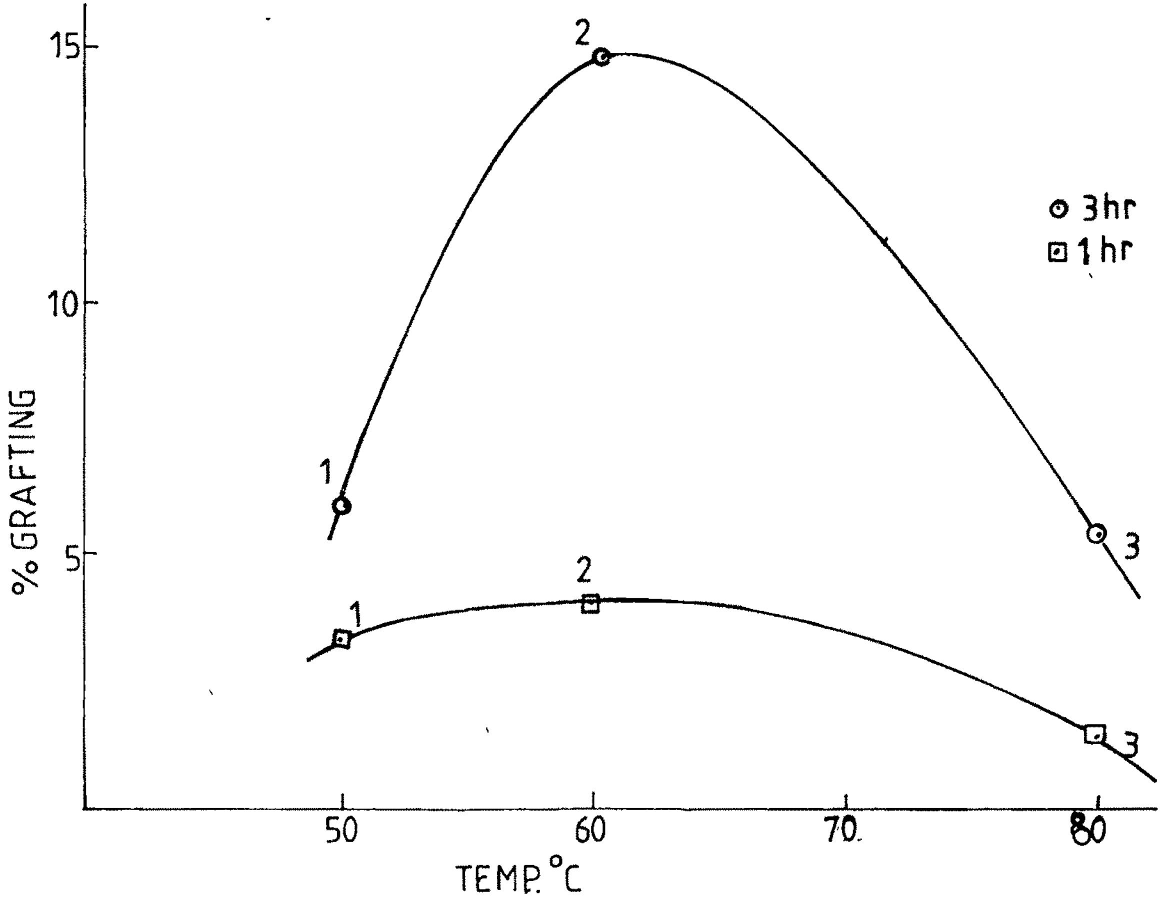


FIG. III. 7(c). % GRAFTING Vs. TEMP. OF ACRYLAMIDE GRAFTS
(KPS + SBS) INITIATORS.

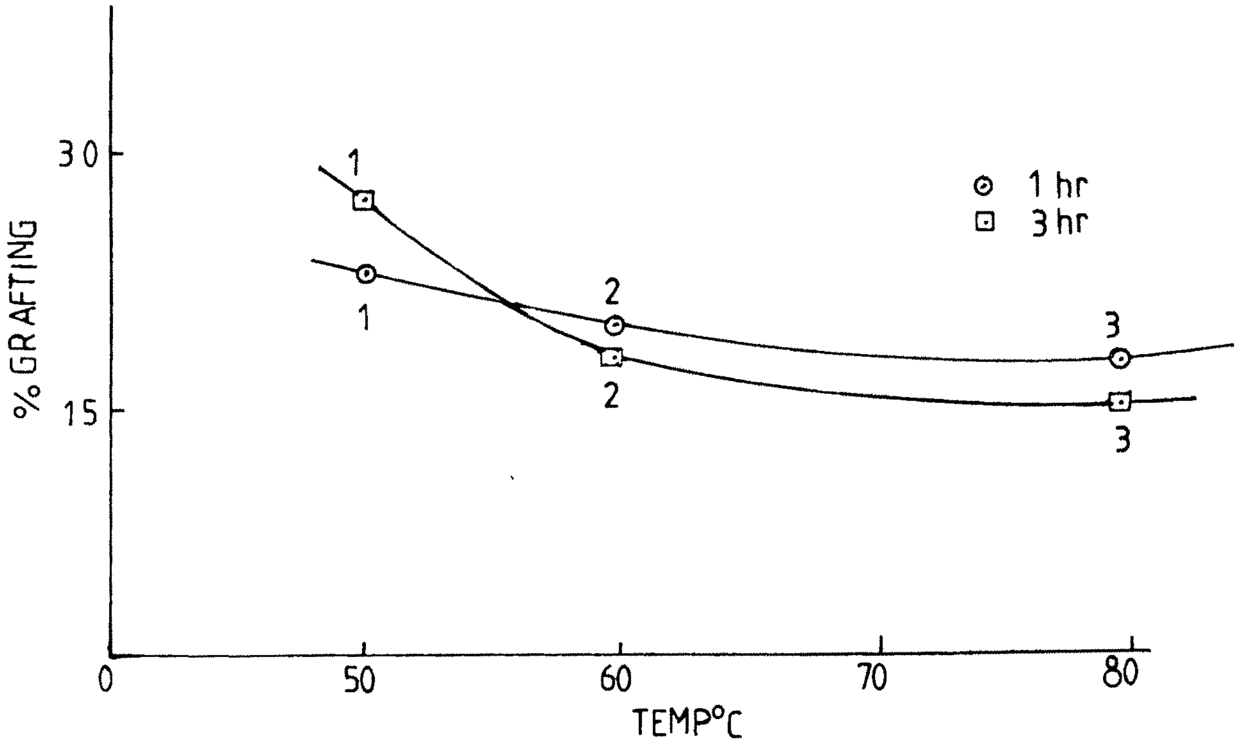


FIG III 7(d) % GRAFTING Vs TEMP OF ACRYLAMIDE-GRAFTS (FAS+HP) INITIATOR

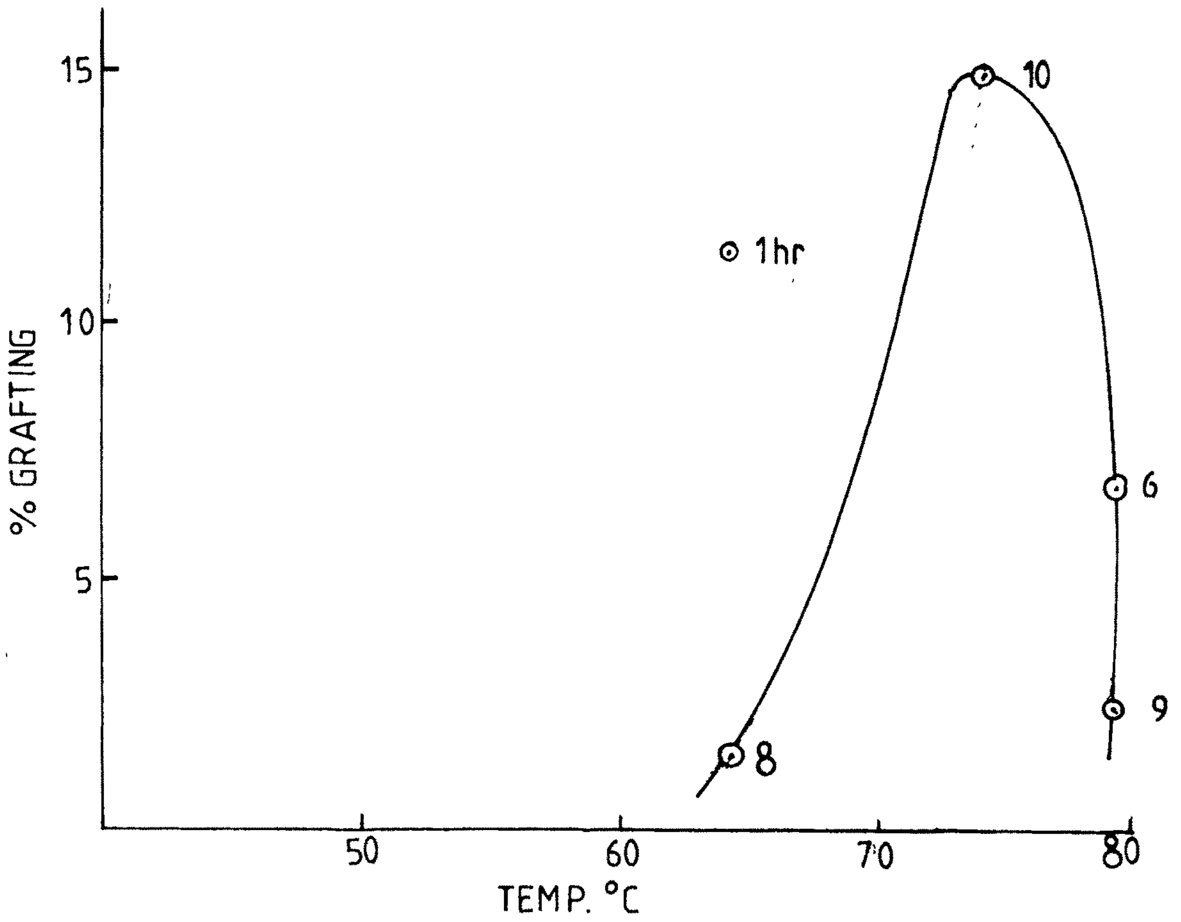


FIG.III. 7(e) % GRAFTING Vs. TEMP. OF ACRYLAMIDE GRAFTS (BP) INITIATOR grafting indicate small change in % grafting with increase in temperature of reaction from 50°C to 80°C, (ii) with FAS+HP initiator system, one-hr reaction shows maximum % grafting of acrylonitrile on cotton at 60°C and three hr curve for grafting of acrylonitrile on cotton and one and three hr reaction curves for grafting of acrylamide on cotton show decrease in % grafting with increase in temperature of reaction from 50° to 80°C, (iii) with BP initiator system, no grafting may be observed below 60°C and maximum % grafting of acrylamide on cotton is observed at 75°C.

Plots of % grafting vs % efficiency of grafting are presented in fig.III.8. These plots show linear relationship between % grafting and % efficiency of grafting. Hence

$$\%\ \text{grafting} = K_g \times \%\ \text{efficiency of grafting}$$

where K_g is a constant. Values of K_g are presented in Table III.10. The values are close to 5.5 for (KPS+SBS) initiator system and to 6.1 for (FAS+HP) or (BP) initiator system, indicating the effect of initiator system on the constancy of the ratio % grafting ÷ % efficiency of grafting for grafting of acrylonitrile or acrylamide on cotton.

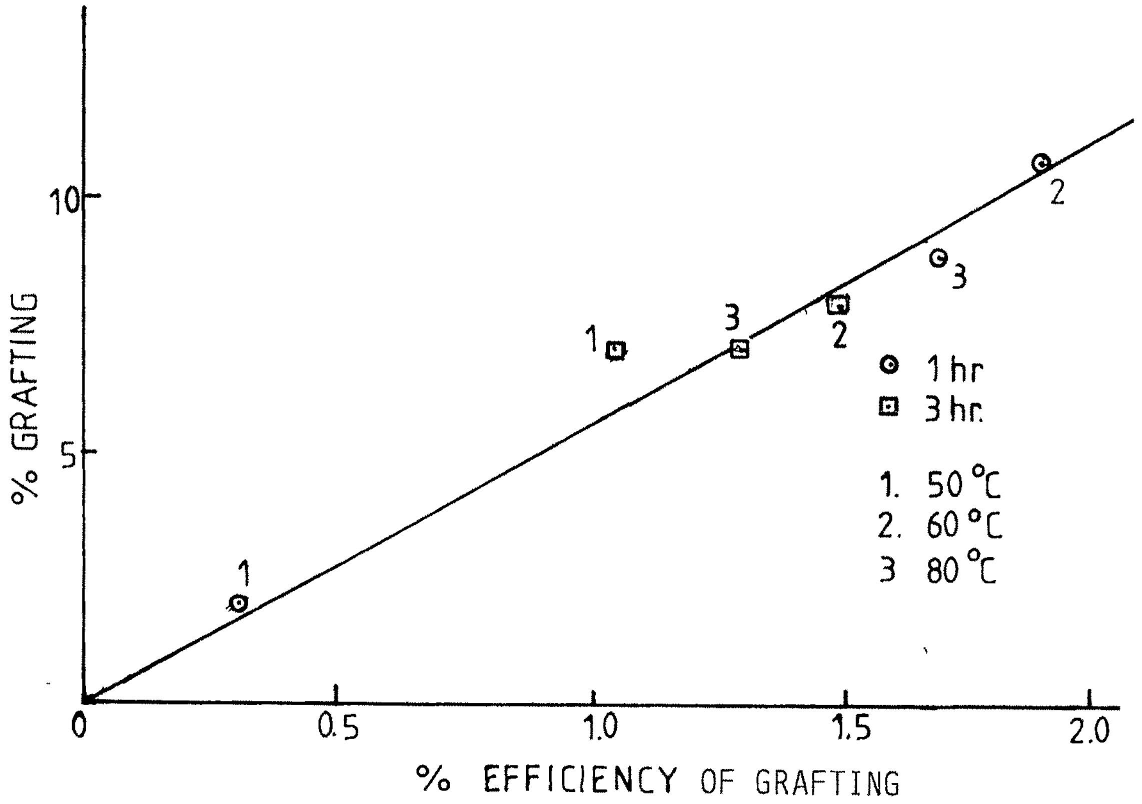


FIG. III 8(a). % G Vs %E OF ACRYLONITRILE-GRAFTS (KPS+SBS) INITIATOR.

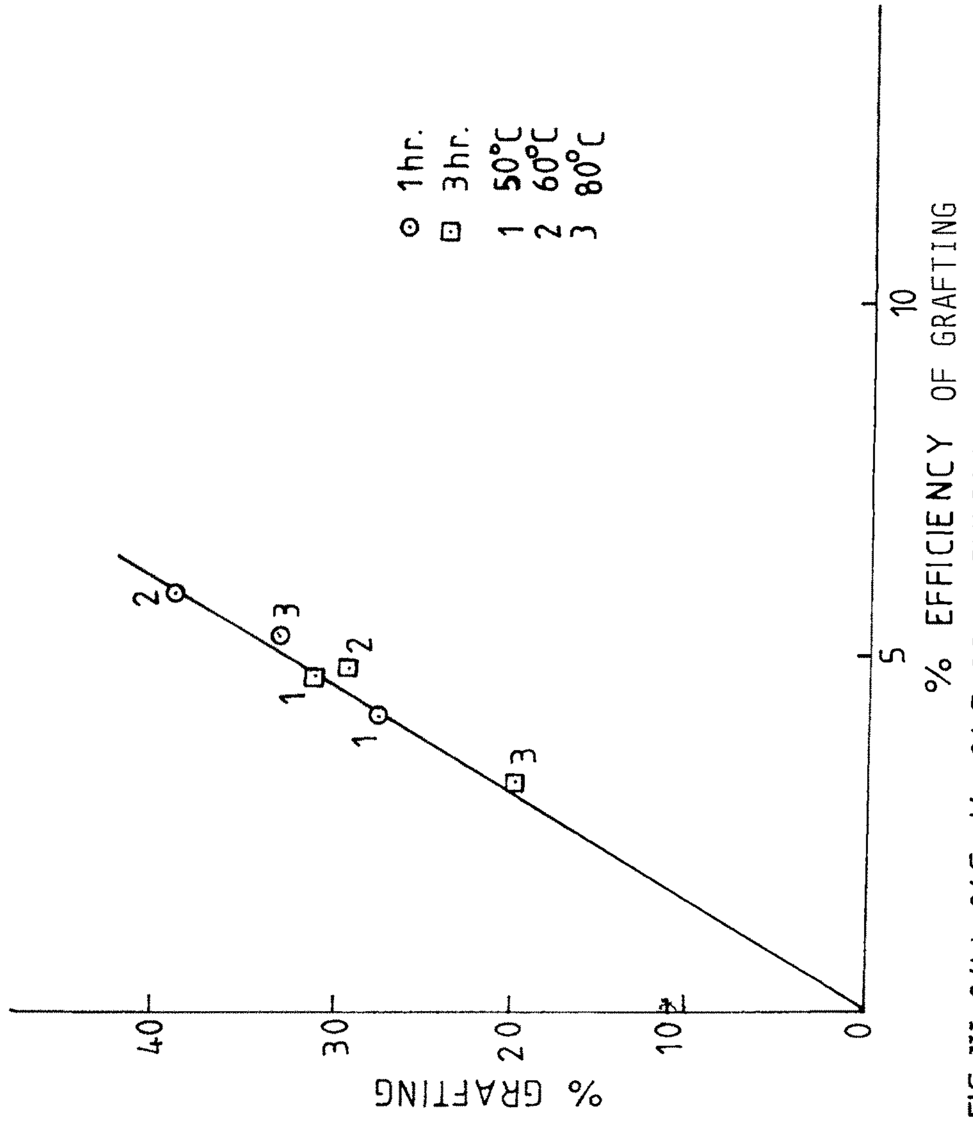


FIG.III 8(b) %G Vs %E OF ACRYLONITRILE-GRAFTS (FAS+HP) INITATOR

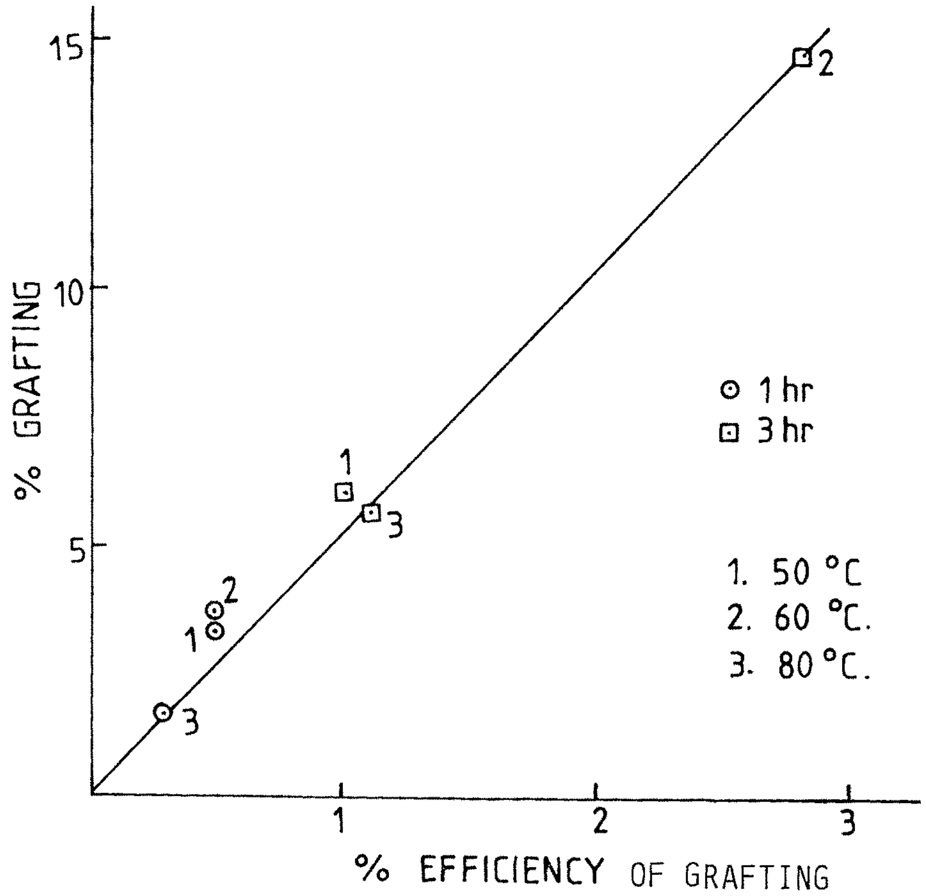


FIG III 8 (c). % G Vs. %E OF ACRYLAMIDE GRAFTS
(KPS + SBS) INITIATOR.

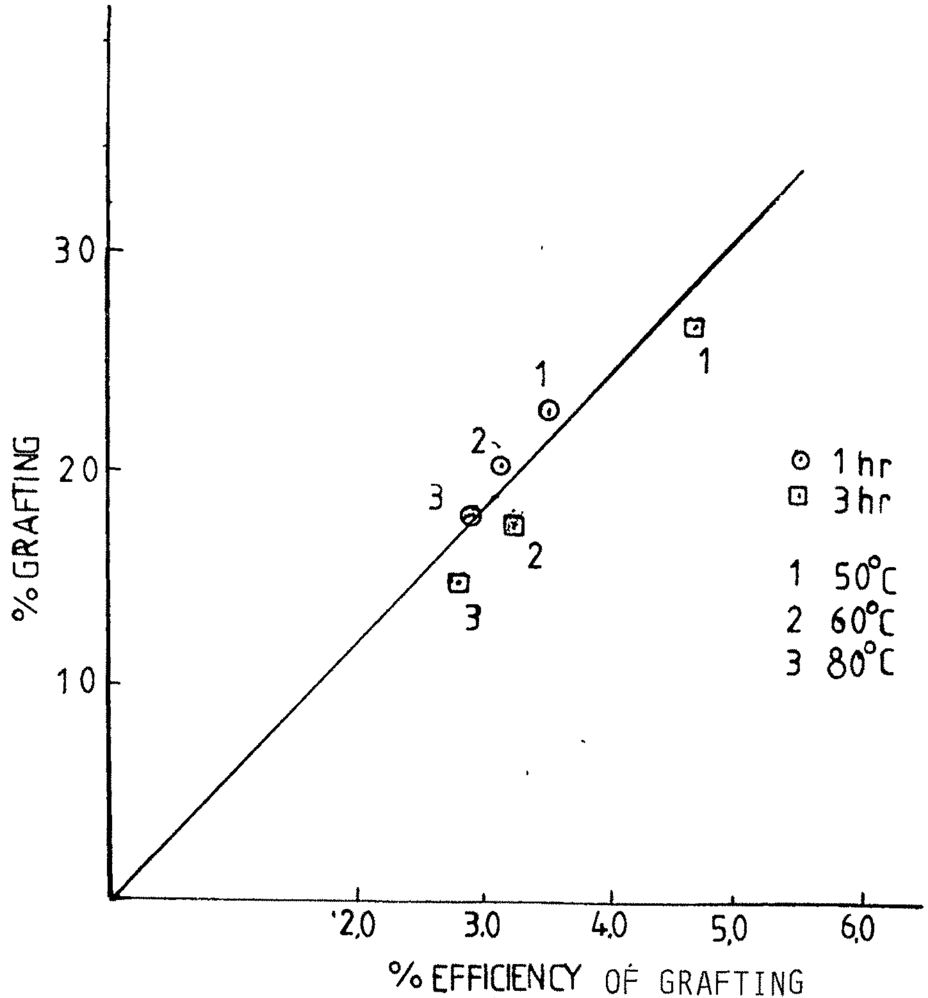


FIG.III.8(d) %G Vs %E OF ACRYLAMIDE-GRAFTS (FAS+HP) INITIATOR

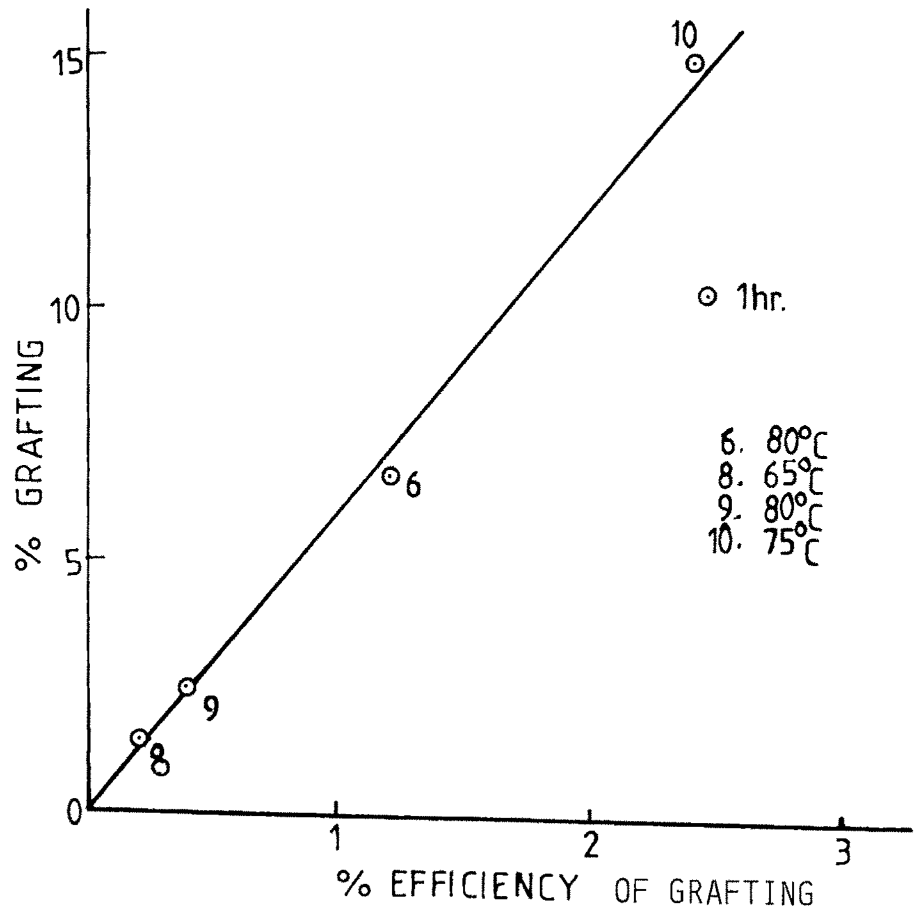


FIG III 8(e) % G Vs % E OF ACRYLAMIDE-GRAFTS (BP) INITIATOR.

Table III.10

% grafting = $K_g \times$ % efficiency of grafting

No	Grafting monomer	Initiator	K_g
1	Acrylonitrile	KPS+SBS	5.6
2	Acrylonitrile	FAS+HP	6.7
3	Acrylamide	KPS+SBS	5.4
4	Acrylamide	FAS+HP	6.1
5	Acrylamide	BP	6.1

Plots of % efficiency of grafting vs time of reaction are presented in fig.III.9. The plots indicate the following : (i) in case of (KPS+SBS) initiator system and efficiency of grafting acrylonitrile on cotton, rate of efficiency change increases upto 50°C and decreases at higher temperatures (60-80°C) after one hr and upto one hr, the rate increases with temperature as

$$50^\circ < 80^\circ < 60^\circ$$

(ii) with (FAS+HP) initiator system and efficiency of grafting of acrylonitrile on cotton, the rate of efficiency change upto one-hr increases with temperature as

$$50^\circ < 80^\circ < 60^\circ$$

(same as observed in (i) above), and decreases after one hr, (iii) in case of (KPS+SBS) initiator system and efficiency of grafting of acrylamide on cotton, rate of efficiency change upto one hr increases with temperature as

$$80^\circ < 50^\circ < 60^\circ$$

and above one-hr as

$$50^\circ < 80^\circ < 60^\circ$$

and (iv) with (FAS+HP) initiator system and efficiency of grafting of acrylamide on cotton, the rate of efficiency change upto one-hr increases with temperature as

$$80^\circ < 60^\circ < 50^\circ$$

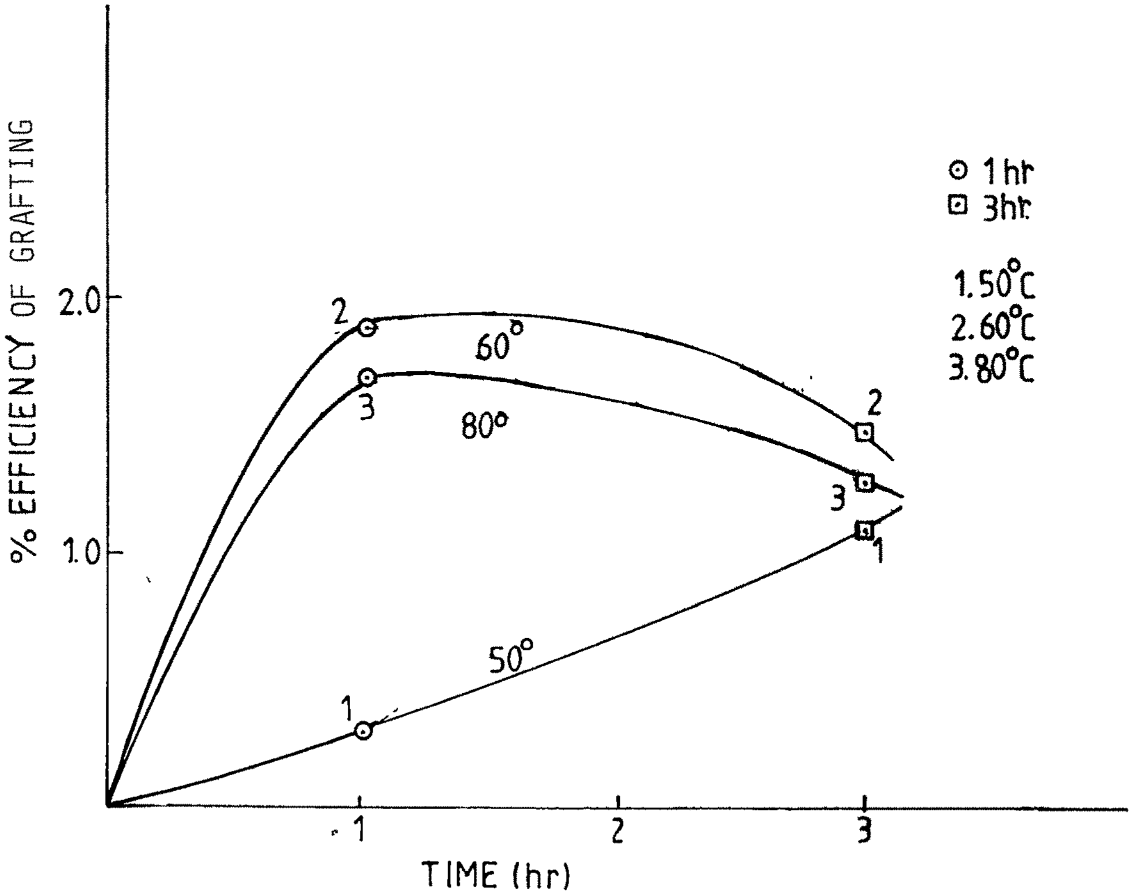


FIG. III. 9(a). % EFFICIENCY Vs TIME OF K-An-g-C (KPS + SBS)

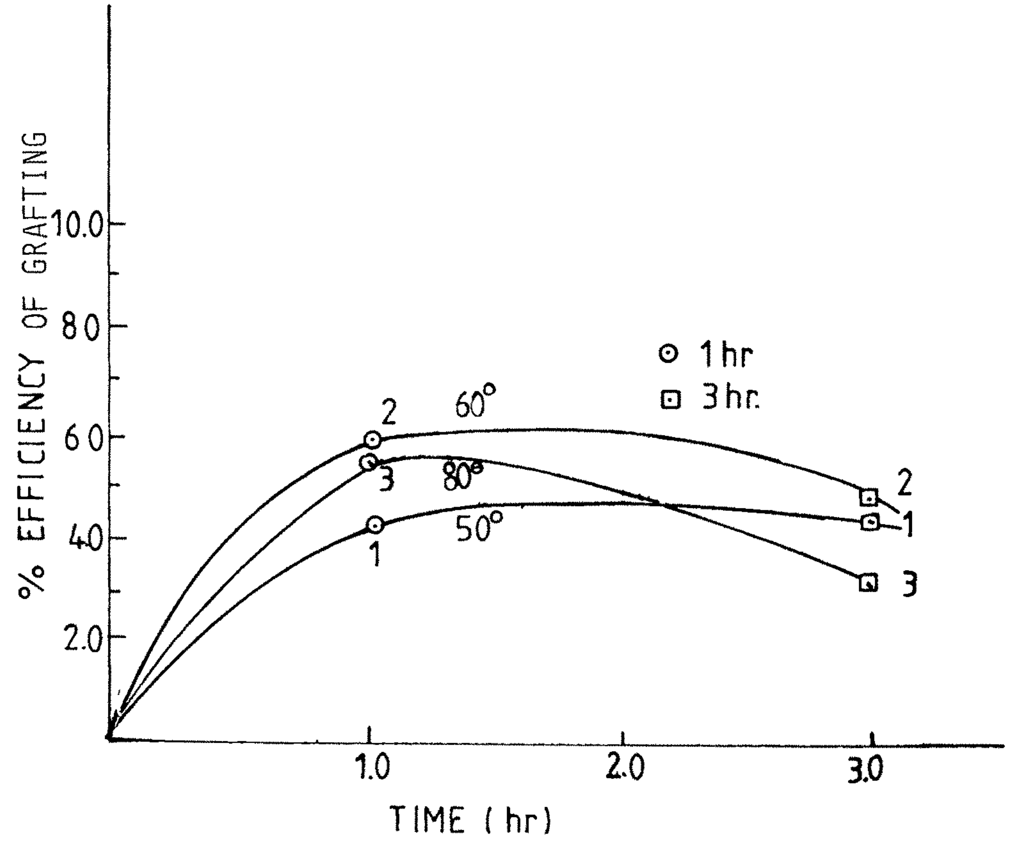


FIG III 9(b). % EFFICIENCY Vs. TIME OF F-An-g-C
(FAS + HP).

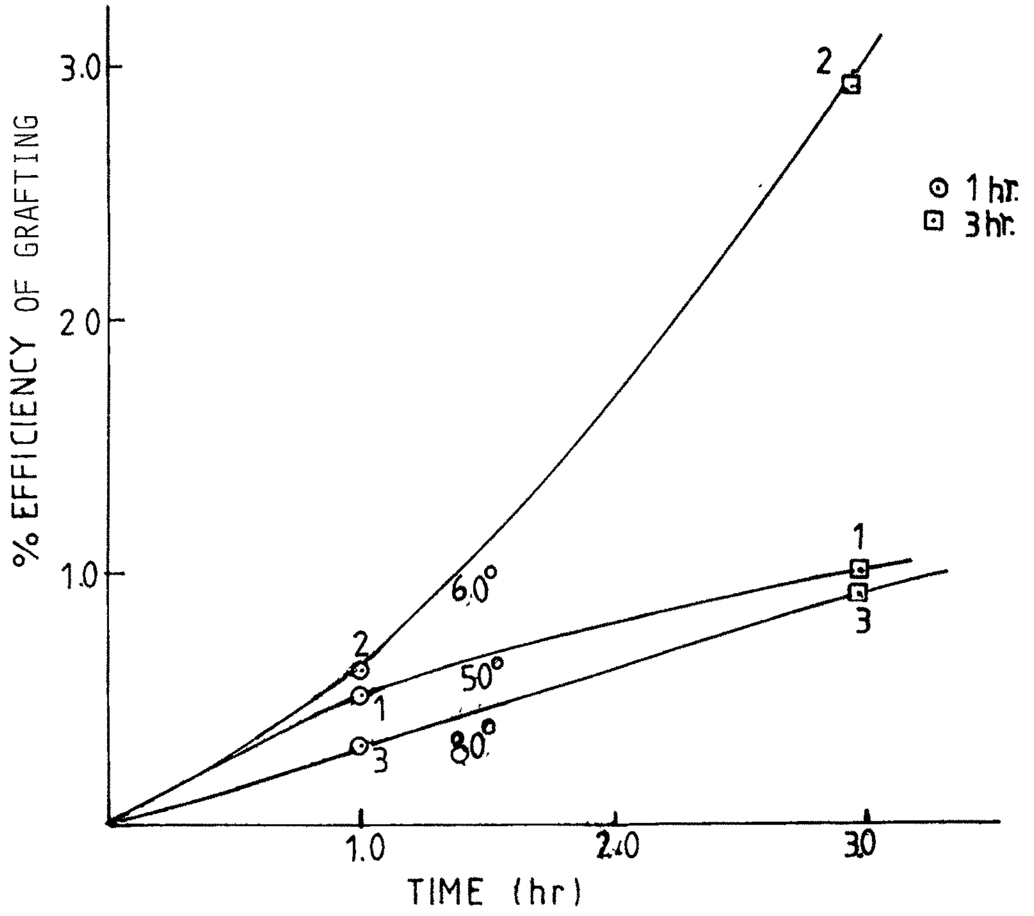


FIG. III. 9(c) % EFFICIENCY Vs. TIME OF K-Aa-g-C (KPS + SBS).

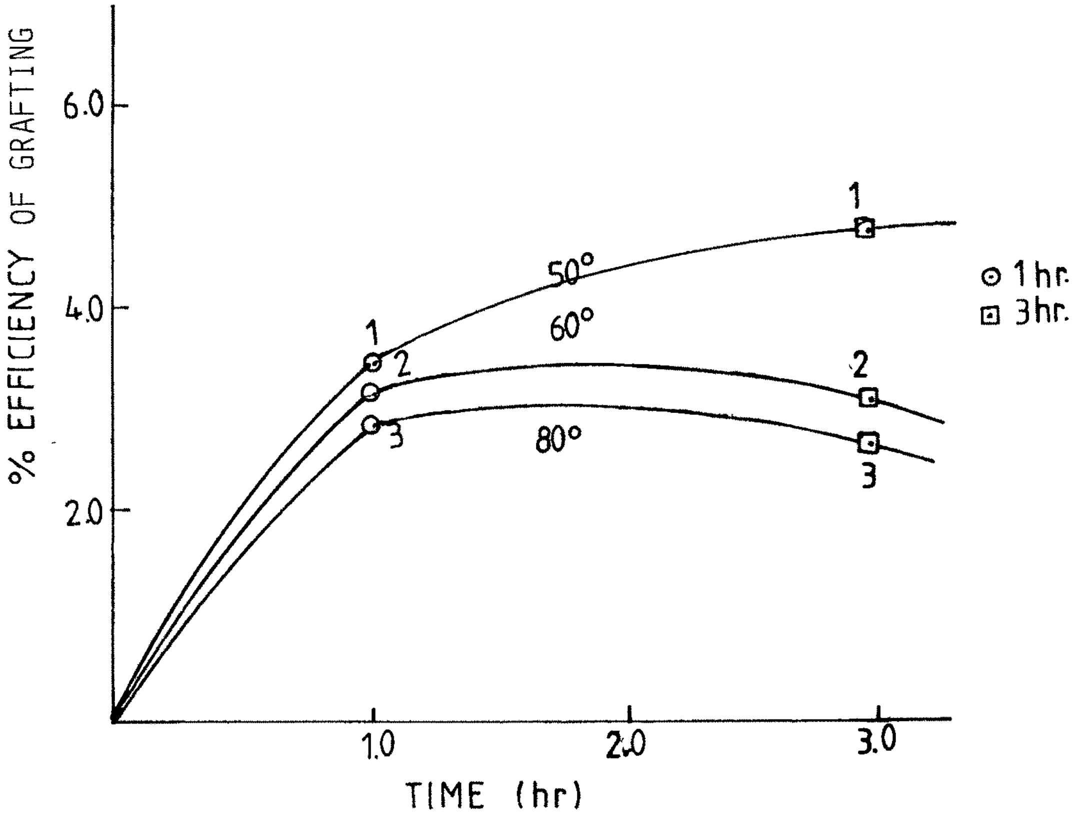


FIG.III. 9(d). % EFFICIENCY Vs. TIME OF F-Aa-g-C (FAS + HP).

and (iv) with (FAS+HP) initiator system and efficiency of grafting of acrylamide on cotton, the rate of efficiency change upto one-hr increases with temperature as

$$80° < 60° < 50°$$

and above one hr, the rate increases much slowly upto 50°C and decreases at higher temperature (60°-80°C).

3(d) Grafting of cotton after pretreatment

Cotton fabrics and fibres were treated with alcohol and sodium hydroxide. The neutralized fabrics were used for the studies.

(d) (i) Grafting of acrylonitrile on pretreated cotton fabrics and fibres using potassium persulphate and sodium bisulphite.

Pretreated cotton fabrics (or fibres) were reacted with acrylonitrile in presence of potassium persulphate and sodium bisulphite (KPA+SBS) as initiator. The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were evaluated.

(d) (ii) Grafting of methacrylic acid on pretreated cotton fabrics using iron (II) ammonium sulphate and hydrogen peroxide

Pretreated cotton fabrics were reacted with methyacrylic acid in presence of iron (II) ammonium sulphate and hydrogen peroxide (FAS+HP). The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were calculated.

(d) (iii) Grafting of acrylamide or vinyl acetate on pretreated cotton fabrics using benzoyl peroxide

Pretreated fabrics were reacted with acrylamide or vinyl acetate in presence of benzoyl peroxide (BP). The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were evaluated.

(d) (iv) Grafting of methyl methacrylate on pretreated cotton fibres using iron (II) ammonium sulphate and hydrogen peroxide

Pretreated cotton fibres were reacted with purified methyl methacrylate using iron (II) ammonium sulphate and hydrogen peroxide (FAS+HP) as initiator. The homopolymer was removed from the product and % grafting and % efficiency of grafting for the grafted fabrics were evaluated.

The values of % grafting and % efficiency of grafting of the pretreated fabrics and fibres are presented in table III.11. The comparison of the values leads to the following considerations :

(i) in case of grafting of acrylonitrile, % grafting and % efficiency of grafting increases as KAn-g-c $<$ KAn-g-Ctf $<$ KAn-g-Ct

(ii) in case of methyl methacrylate grafting on pretreated cotton fibres and fabrics using (BP) initiator system, the values of % grafting efficiency of grafting are higher for fibres and than for fabrics,

(iii) in case of grafting of methyl acrylic acid on pretreated cotton fibres and fabrics using (FAS+HP) initiator system, the values of % grafting and % efficiency of grafting are higher for fibres than for fabrics. This can be attributed to the greater availability of surface for reaction in case of fibres than in case of fabrics.

3(e) IR Spectra

IR spectra of some grafted cotton fabrics and fibres are presented in fig.II.7. In spectra (a) and (b), the absorption band at 2230 cm^{-1}, characteristic of $C \equiv N$ group in acrylonitrile is observed (327). The absorption band at 1645 cm^{-1} in these spectra may be attributed to water present

Table III.11

11 (a)

No	Sample	% Grafting	% Efficiency of grafting
1	KAn-g-Ct	21.2	5.9
2	FMa-g-Ct	1.3	1.6
3	BMM-g-Ct	12.5	8.1
4	BAa-g-Ct	10.5	2.1
5	BV -g-Ct	7.2	1.6

11 (b)

No	Sample	% Grafting	% Efficiency of grafting
1	KAn-g-Ct[illegible]f	14.4	3.6
2	FMa-g-Ct[illegible]f	21.7	6.3
3	BMM-g-Ct[illegible]f	12.8	9.0

in these grafted products (327). In spectrum (c), the absorption band at 1715 cm^{-1}, characteristic of the ester group in methyl methacrylate is observed (328). Similarly, absorption band at 1710 cm^{-1} characteristic of the carboxyl group is observed in the spectrum of methyl methacrylic-grafted cellulose. Thus IR spectra provide definite evidence of grafting on cellulose.

3 (f) SEM Photographs

The scanning electron microphotographs (figure II.8) of both unmodified and grafted cotton fabrics exhibit smooth surface for grafted fabrics as compared to unmodified fabrics (8 a,b,c,f)

In figure 8(d), the grafted fabrics show little evidence of polymer build-up at low magnification. Here, the interyarn spacing decreases, because of increase in yarn diameter due to grafting.

Figures 8(e) and (h) present the yarn cross-sections of grafted fabrics. The cross-sections appear to be swollen and their characteristic appearence is different from untreated yarn. Polymer has deposited towards the centre of yarn.

3 (g) General

Cellulosic graft polymers have been reviewed by Hebeish and Guthrie (329).

In chemical grafting, cellulose, monomer, initiator and medium are present. Swelling is an important prerequisite to render the system accessible to the monomer. Other factors are concentration of monomer and initiator, time and temperature of reaction, diffusion of monomer to the fibre and adsorption of monomer on the fibre.

Initiation by free redicals has been generally employed to produce grafting, though grafting can also be achieved by anionic reaction. Grafting of acrylonitrile, methyl methacrylate, etc on cellulose has been investigaged by various workers using redox systems such as Fe^{2+} + H_2O_2, $K_2S_2O_8$ + Fe^{2+}, etc as initiators (328, 330-334). The mechanism of grafting of vinyl monomer (M) on cellulose (Cel-OH), by free radical initiation can be expressed as shown in fig.III.10.

Recent studies on grafting of cellulose with acrylonitrile (An), methyl methacrylate (Mm) and acrylamide (Aa) with Mn^{3+} initiation showed that % conversion for Aa was low (8-10%) (335).

Nishioka and Kokai (336) observed that when grafting of cellulose was carried out in a homogeneous system using ammonium persulphate initiator, optimum temperature for grafting was found to be characteristic of each monomer and % grafting of acrylonitrile was higher than that of methyl methacrylate. Efficiency of grafting decreased with temperature in case of acrylonitrile and increased in case of methyl methacrylate.

Initiation $\text{Cel-OH} \longrightarrow \text{Cel-O}^{\bullet}$

Grafting $\text{Cel-O}^{\bullet} + \text{M} \longrightarrow \text{Cel-OM}^{\bullet}$

Propogation $\text{Cel-OM}^{\bullet} + n\text{M} \longrightarrow \text{Cel-O}\ (\text{M})_n\ \text{M}^{\bullet}$

Termination $\text{Cel-O}\ (\text{M})_n\ \text{M}^{\bullet} \longrightarrow \text{Cel-O}\ (\text{M})_n\ \text{M}$

Homopolymerization $\text{M} \longrightarrow \text{M}^{\bullet}$

$\text{M}^{\bullet} + n\text{M} \longrightarrow (\text{M})_n\text{M}^{\bullet}$

$(\text{M})_n\text{M}^{\bullet} \longrightarrow (\text{M})_n\text{M}$

Fig.III.10 Grafting by free radicals

Hebeish and coworkers (337) observed that the rate of grafting decreases with temperature as

$$50^\circ > 60^\circ > 70^\circ$$

and rise in temperature (i) increases concentration of free radicals, (ii) accentuates swelling, (iii) improves solubility of methyl methacrylate (MMA), (iv) accelerates diffusion of MMA and (v) enhances the rate of propagation.

The reaction of acrylonitrile with cotton is largely limited to the surfaces of the fibres having core hydroxyls largely unaffected (338).

III 4 Modified Cotton Cellulose

4 (a) Structural parameters of native cotton

Structural paramteters of Shanker-4 cotton at various stages of growth are presented in table III.12. The values are consistent for a model of cellulosic fibres having spiral arrangement of component fibrils.

In terms of a two-phase model of microcrystallites embedded in an amorphous matrix of cellulose chain molecules, X-ray diffractogram can be analysed and degree of crystallinity can be calculated. The crystalline index (CI) is calculated as

$$CI = 1 - \frac{h_{am}}{h_{am} + h_{cr}}$$

Table III.12

12 (a)

Structural parameters

Age of cotton fibres (days of growth after flowering)	Mature fibres (%)	Degree of Polymerization	50% azimuthal intensity X ray angle (degree)	Refrective Index		Birefringence Δn
				n_{11}	$n_{\perp}$	
a	b	c				
30	-	-	40.5	1.568	1.529	0.039
50	16	1970	33.5	1.579	1.534	0.045
70	74	2065	20.4	1.588	1.532	0.056

12 (b)

Physical properties

Age of cotton fibres (days of growth after flowring)	Mature fibres (%)	Degree of Polymerization	Effective length (mm)	Single fibre data		
				strength (g)	elongation (%)	elastic recovery (%)
a	b	c				
50	16	1970	27.8	2.6	7.8	79.7
70	74	2065	29.0	5.02	8.0	85.2

where $h_{am} + h_{cr} = h_{tot}$, as shown in fig.III.11. The values of CI calculated for the untreated cotton fabrics (fig.II.6) is 76% and that for modified cotton fabrics (CVPM) is 77.6%. Crystallinity of raw cotton has been observed as ~ 76% in general (339).

The physical properties of Shanker-4 cotton such as single fibre strength, % elongation, elastic recovery, etc show an increase with the age of fibres upto 70 days of growth (table III.12).

4 (b) Swelling of cellulose

Swelling of cellulose in water and sodium hydroxide solution may be intrafibrillar or interfibrillar. A temperature rise would provide interfibrillar swelling and reduce intrafibrillar swelling. Swelling of cellulose fibres is accompanied by a lengthwise contraction and a lateral expansion. This phenomenon of anisotropic swelling is characteristic of uniaxially oriented gels. It may be suggested that swelling causes reduction in crystallite dimensions and leads to a corresponding increase in the volume of the disordered regions. Thus swelling causes decrystallization of cotton without affecting the number of crystallite sites. A marked similarity in intensity distribution between raw cotton and cotton having different swelling history was observed from X-ray diffactograms of these cottons.

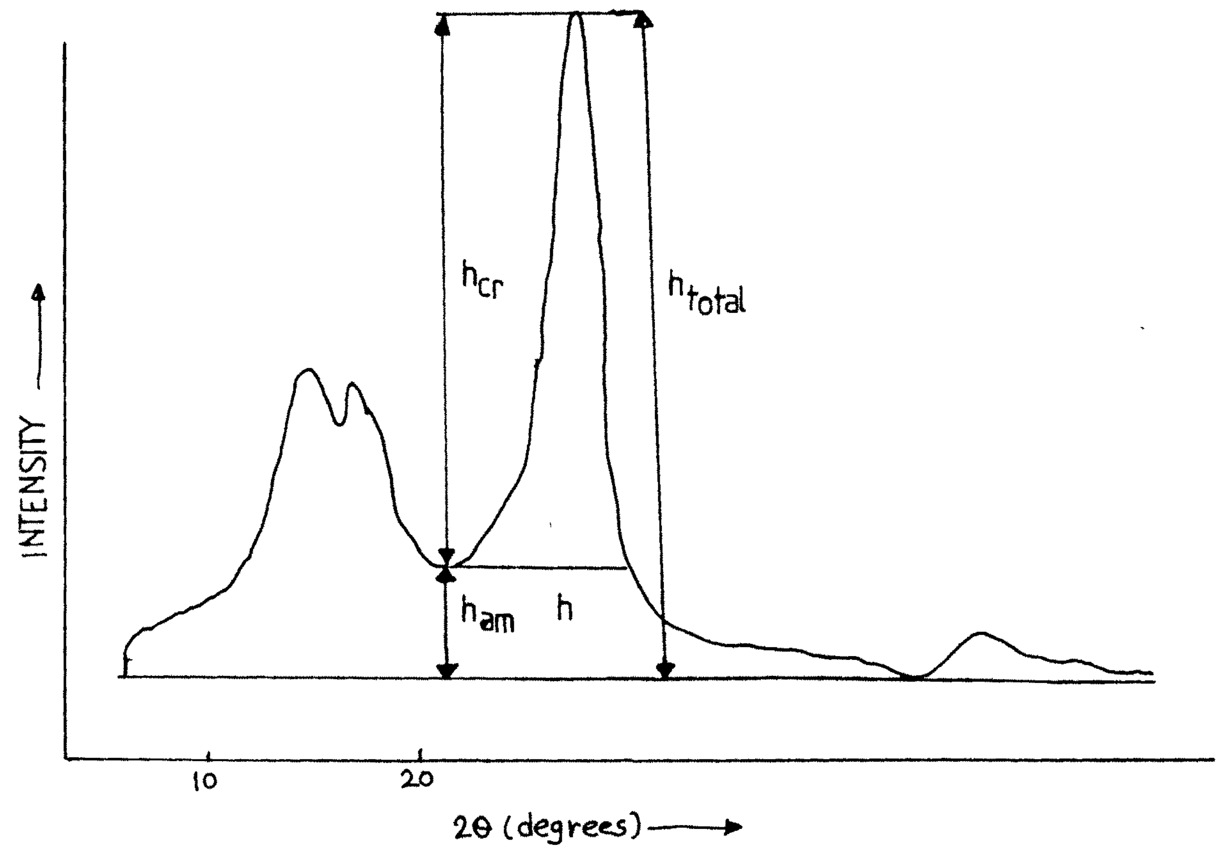


FIG. III. 11

From [illegible] earlier studies of rates of desorption of water at different water contents, it was concluded that the rates of drying decrease as the water content of cotton becomes less.

Swelling of cellulose by water can be related to the presence of hydrophilic groups such as OH. The reduction in the number of hydroxylic groups in a molecular unit by esterification, formalization, etc. may reduce the swelling by water.

4 (c) Polymer deposition

The effect of the deposition, by internal polymerization of polysterene, polymethyl methacrylate, polyacrylonitrile, etc inside cotton fabrics on the properties of the resulting fabrics was studied by Chitale and Kulkarni (340). It was found that tensile strength and crease recovery properties remain uneffected. Fabrics containing polymer deposits became stiff and glossy on calendering. Only fabrics treated with polyacrylonitrile were stable to repeated laundering, as they retained most of the stiffness and some of the gloss, probably due to better penetration and distribution of polyacrylonitrile in fabrics.

4 (d) Esterification

Formylation of cellulose revealed that there are two concurrent processes during the first 16 hr period of formylation :

(i) a fast reaction of easily accessible fraction of cellulose, governed by diffusion mechanism and (ii) a slow reaction of less accessible fraction of cellulose, governed by erosion mechanism. The esterification reactions carried out in the present studies were for much shorter duration than 16 hr and are considered (i) to be governed by diffusion mechanism and (ii) to involve largely the easily accessible fraction of cellulose.

4 (e) Crease recovery

Crease recovery bears a direct relationship to crystallinity. When a bending stress is applied to a cotton fibre, extension and contraction of its fibril structure occur. Strain developes in valence bond angles. Slippage on fibril interfaces and within fibrils occurs, and it leads to the break-down of existing H-bonds and formation of new ones. Recovery is primarily due to energy stored in the strained bonds and is acted by thermal motion of molecules. Return to the prestressed stage is incomplete and new bonds formed try to stabilize the stressed structure. It is, therefore, necessary to increase crystallinity or stabilize H-bond structure irreversibly.

Wet crease recovery in cotton

Marsh (341) and others (342) postulated that the cause of improved wet crease recovery is the cross-linking of the cellulose in the swollen state. On purification and drying, a collapse of the structure occurs. On reswelling, the cross-linked cotton is again filled out by water, causing the fibre to become firm and rigid. Steele (343) believed that wet crease recovery was due to intrachain linking on C_2 and C_3 hydroxyls of the same anhydro glucose unit (AGU). Reeves (344,345) reported that wet and dry crease recovery differ from each other because of the location of cross-links in cotton, that interlamellar links produce dry crease recovery and intermicrofibrillar links wet crease recovery.

Formalin solution imparts wet crease recovery to cotton fibres; but if water is largely removed or reduced by reaction with acetic anhydride, dry crease recovery then occurs (346).

Cross-linking (345) may be attributed to surface interchain links between some of the gross morphological units in cellulose such as microfibrils or lamellae. This idea is also useful in explaining why in case of formaldehyde a very small weight gain produces a large change in physical properties and formalin solution must be reduced to 20% water content to obtain good dry crease recovery.

4 (f) Cross-linked cotton

Resin finishing treatments on cotton textiles impart easy-care and durable press properties to the cotton fabrics but reduce their tensile strength and abrasion resistance. CRA of cotton (e.g.Laxmi cotton) cross-linked in the fibre form by formaldehyde D-process increased with increase in the bound formaldehyde from 0 to 1%. The lowering of tensile strength on corsslinking of cotton by formaldehyde may be attributed to the creation of cross-links in the fibre. However, the location of cross-links at interlamellar or intralamellar sites has no bearing on the extent of loss in rupture strain. Decrystalization prior to cross-linking improves CRA. Chemisorption of resins on cotton produces the cross-linking of cotton cellulose with resin. It was found that chemisorbed cotton has higher % extension at break and lower CRA than cross-linked cotton. Increase in CRA (DCRA) is related to % resin padded (R) as

$$\mathrm{DCRA} = \mathrm{B}e^{-A/R}$$

where A and B are constants. The values of A and B for poplin are 3.24 and 162.5 respectively. DCRA is also related to % abrasion loss (x) as

$$\mathrm{DCRA} = B' (X)^{A'}$$

where A' and B' are another set of constants.

From the earlier studies on equilibrium absorption of cross-linking agents such as DMEU, DMDHEU, etc on cotton cellulose at different equilibrium concentrations of cross-linking agent, it was concluded that (i) there was initial gradual increase in desorption, which can be related to Langmuir adsorption expression and (ii) there was a sudden decrease in adsorption beyond this region, which may be attributed to the formation of aggregated cross-linking molecules in solution. The amount of cross-linking agent absorbed on cotton fibres decreased on the addition of 1M sodium chloride. It may be attributed to the lowering of negative potential of cellulose by the addition of NaCl.

Cross-linking of the fibres in the dry collapsed state fixes cellulose chains in close proximity and leads to a high increase in dry crease recovery, significant improvement in wet crease recovery, decrease in moisture regain, etc. Cross-linking of the fibres in a swollen state fixes cellulose chains at a greater distance apart and leads to a poor increase in dry crease recovery, high moisture regain, etc. Cross-linking reduces elongation, toughness, swelling capacity in water, etc.

Cross-linking treatments to impart easy care properties are usually accompanied by serious losses in strength properties of cotton fabrics (347). This has been attributed to the fibre embrittlement by cross-links together with decrement in the degree of polymerization of cotton cellulose (348, 349).

In the present studies cellulose molecular units have been cross-linked by esterification with di- or polybasic acids and by formalization in presence of polyvinyl alcohol. On the basis of the assumption that cross-linking by esterification and formalization has taken place as suggested in their formula, calculations have been made to evaluate the number of cross-links per 100 anhydro glucose units of cellulose and the results are presented in table III.13. It has been observed that (i) high degree of cross-linking was obtained, when cellulose was esterified with sebacic acid derivatives, (ii) fibres had higher degree of cross-linking than fabrics when they were esterified with adipic, fumaric and maleic acid derivatives, (iii) degree of cross-linking observed by formalizing cellulose with paraldehyde was much higher than that when cellulose was formalized with formalin and (iv) resinification by resorcinol, melamine, etc lowered the degree of cross-linking of formalized cellulose.

CRA of the fabrics vs number of cross-links per 100 AGU of esterified cotton fabrics and formalized cotton fabrics is plotted in fig.III.12. The plots show that (i) CRA decreases with increasing number of cross-links upto 2.5 cross-links, per 100 AGU of esterified and formalized cotton fabrics (ii) comparisons of slopes of different lines indicate the increasing order CAd < CFm < CMl, (iii) increase in CRA is small as the number of cross-links per 100 AGU of CSb

Table III.13

Cross-links

13 (a)

No	Product	$\frac{\text{No of Cross-links}}{\text{100 anhydroglucose units}}$
1	CSb-1	6.5
2	CSb-2	26.0
3	CSb-3	25.0
4	CAd-1	0.5
5	CAd-2	1.5
6	CFm-1	1.0
7	CFm-2	2.0
8	CMl-1	0.5
9	CMl-2	1.0

13 (b)

No	Product	No of Cross-links / 100 anhydroglucose units
1	CSbc(D)-1	19.0
2	CSbc(D)-2	20.5
3	CSbc(D)-3	7.5
4	CSbc(Ct)	2.0
5	CSbc(Ch)	9.5
6	CAdc(D)-1	0.5
7	CAdc(D)-2	0.5
8	CAdc (Ch)	1.0
9	CFmc(D)	0.5
10	CFmc(Ch)	1.5

13 (c)

No	Product	$\frac{\text{No of Cross-links}}{\text{100 anhydroglucose units}}$
1	BCFm	8.5
2	BCM1	6.0
3	BCAc	1.0
4	BCMac	1.5

13 (d)

No	Product	$\frac{\text{No of Cross-links}}{100 \text{ anhydroglucose units}}$
1	CfSb	6.5
2	CfAd	6.5
3	CfFm	6.0
4	CfMl	10.0

13 (e)

No	Product	No of Cross-links / 100 anhydroglucose units
1	CVF	2.9
2	CVFa-1	0.3
3	CVFa-2	1.1
4	CVfa-3 (i)	0.3
	CVfa-3 (ii)	0.6

13 (f)

No		Product	$\frac{\text{No of Cross-links}}{100\ \text{anhydroglucose units}}$
1		CVP	26
2	(a)	CVPn (Wp)	32
	(b)	CVPn (Wf)	44
3		CVPan	19

13 (g)

No		Product	$\frac{\text{No of Cross-links}}{\text{100 anhydroglucose units}}$
1	(a)	CVPR (Wp)	1.5
	(b)	CVPR (Wf)	2.4
2		CVPR-1	-
3		CVPR-2	1.3
4		CVPR-3	2.2

13 (h)

No	Product	$\frac{\text{No of Cross-links}}{100\ \text{anhydroglucose units}}$
1	CVPM-1	2.0
2	CVPM-2	2.4
3	CVBFM	3.0

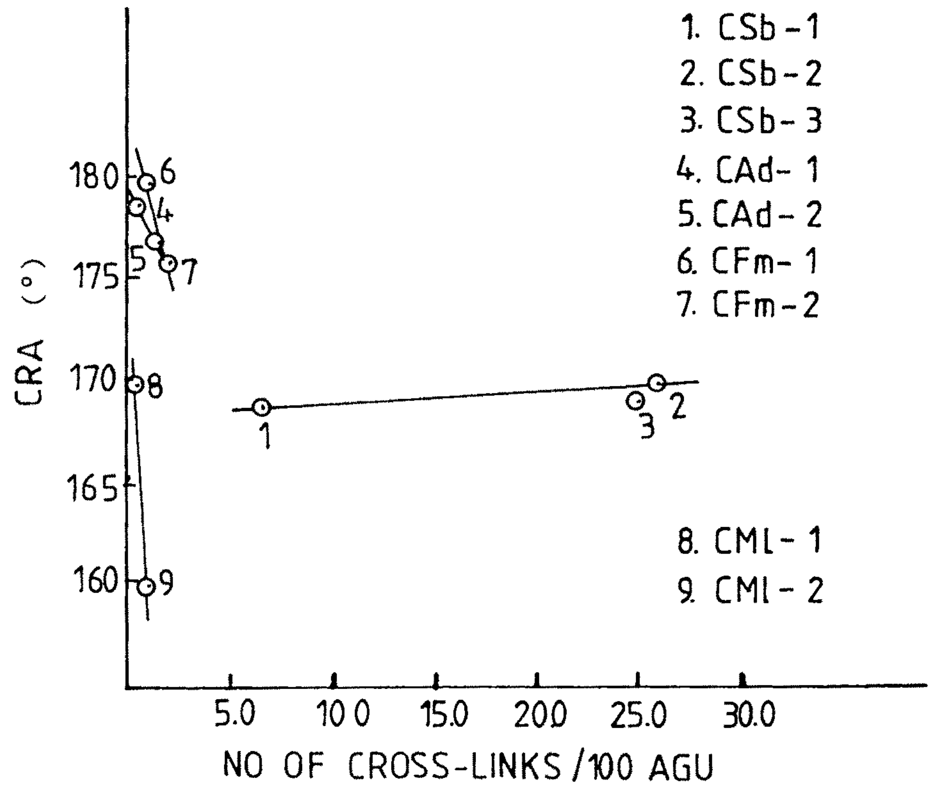


FIG.III. 12 (a) CRA Vs. NO OF CROSS-LINKS/100 AGU OF ESTERIFIED COTTON FABRICS.

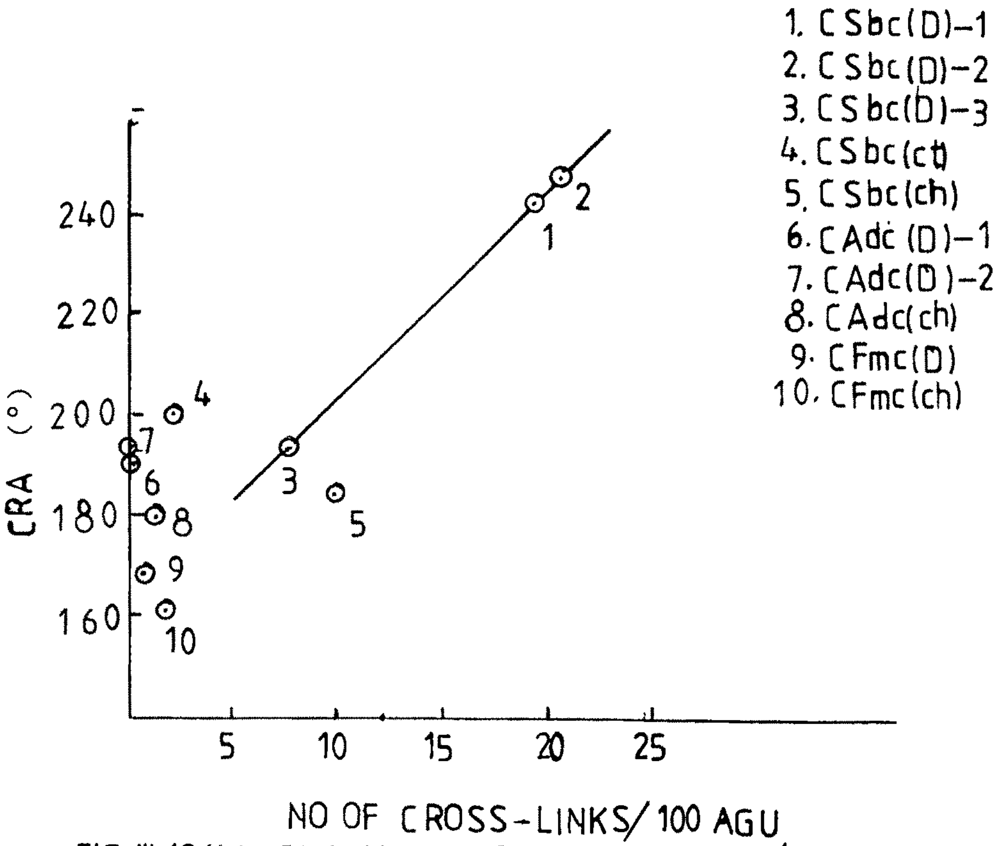


FIG III 12 (b) CRA Vs NO OF CROSS-LINKS/100 AGU OF ESTERIFIED COTTON FABRICS

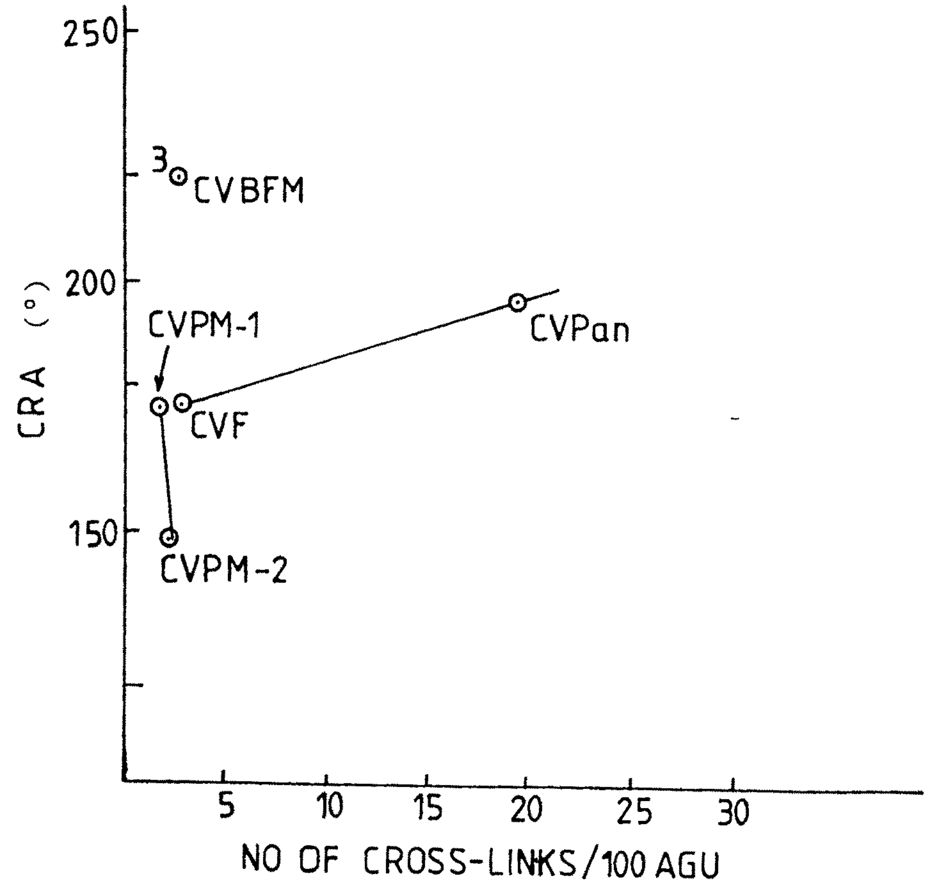


FIG.III.12 (c). CRA Vs. NO OF CROSS-LINKS/100 AGU OF FORMALIZED COTTON FABRICS.

or CVPan is increased from 5 to 30, (iv) CRA for CFm is greater than that for CMl for the same number of cross-links per 100 AGU of CFm and CMl, (v) relatively high value of CRA is observed for very low value of the number of cross-links per 100 AGU of the esterified cotton fabrics, (vi) CRA for CSbc is higher than that for CSb, (vii) CRA for CSbc prepared from different solvents show the increasing value of CRA with reference to solvents as Ch $<$ D $<$ Ct, (viii) relatively high value of CRA is observed for low number of cross-links per 100 AGU of CVBFM.

Diameter of the fabrics vs number of cross-links per 100 AGU of esterified fabrics is plotted in figure.III.13. The plots show that (i) in case of CFm and CMl, no change in diameter is observed with increase in the number of cross-links upto 2.5 cross-links per 100 AGU, (ii) in case of CAd, large change in diameter is observed with increase in the number of cross-links upto 2.5 cross-links per 100 AGU, (iii) in case of CSb and CSbc, increase in diameter is relatively small as the number of cross-links increases from 5 to 30, (iv) diameter for CfFm is larger than that for CfMl, and diameter of BCFm is larger than that of BCMl.

4 (h) Thermograms

Thermograms of cotton (natural and modified-grafted) are shown in fig.III.14. For natural cotton [fig.14(a)] after

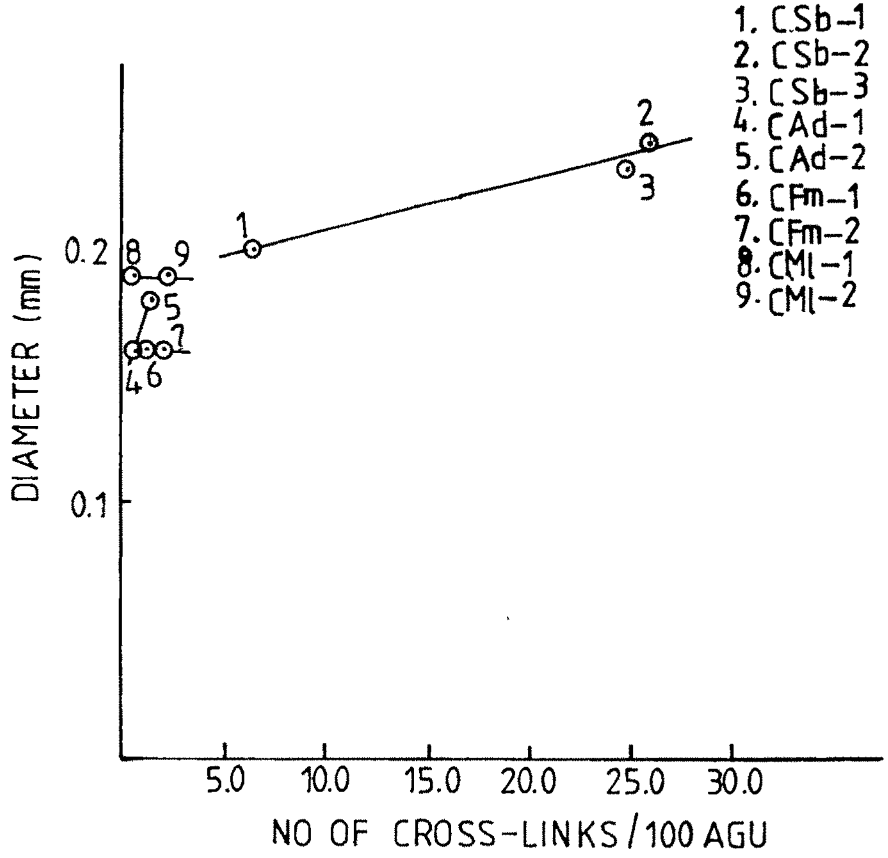


FIG. III. 13(a). DIAMETER Vs. NO OF CROSS-LINKS/100 AGU OF ESTERIFIED COTTON FABRICS.

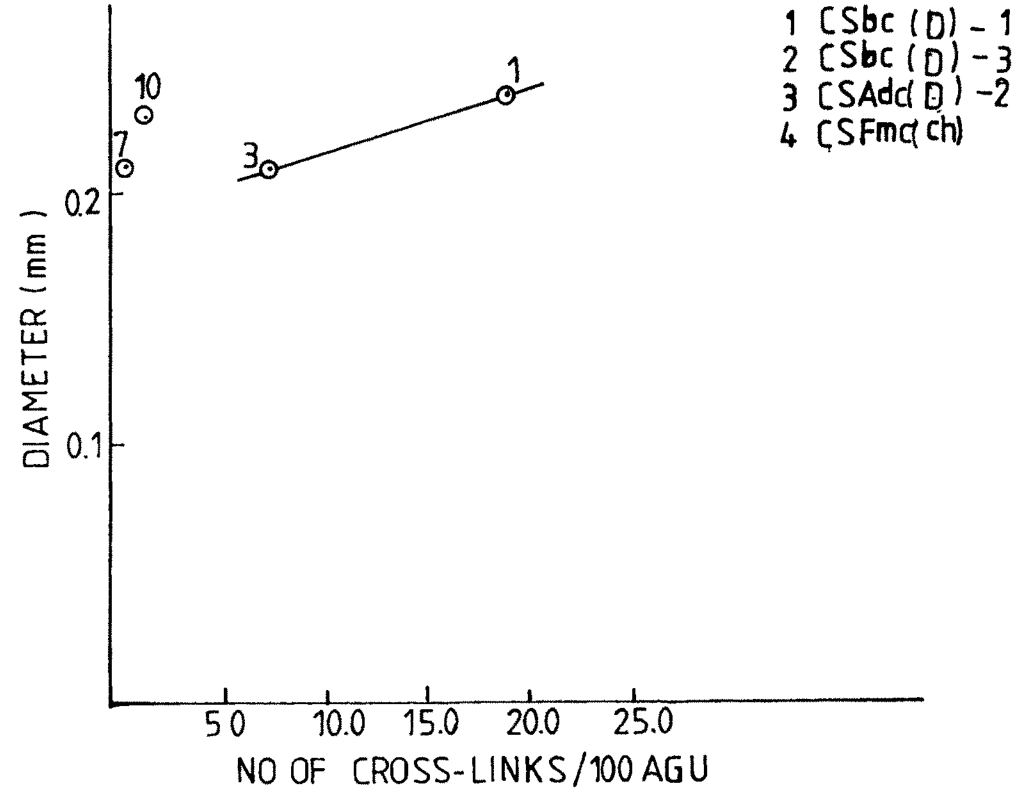


FIG. III. 13 (b) DIAMETER Vs. NO OF CROSS-LINKS/100 AGU OF ESTERIFIED COTTON FABRICS

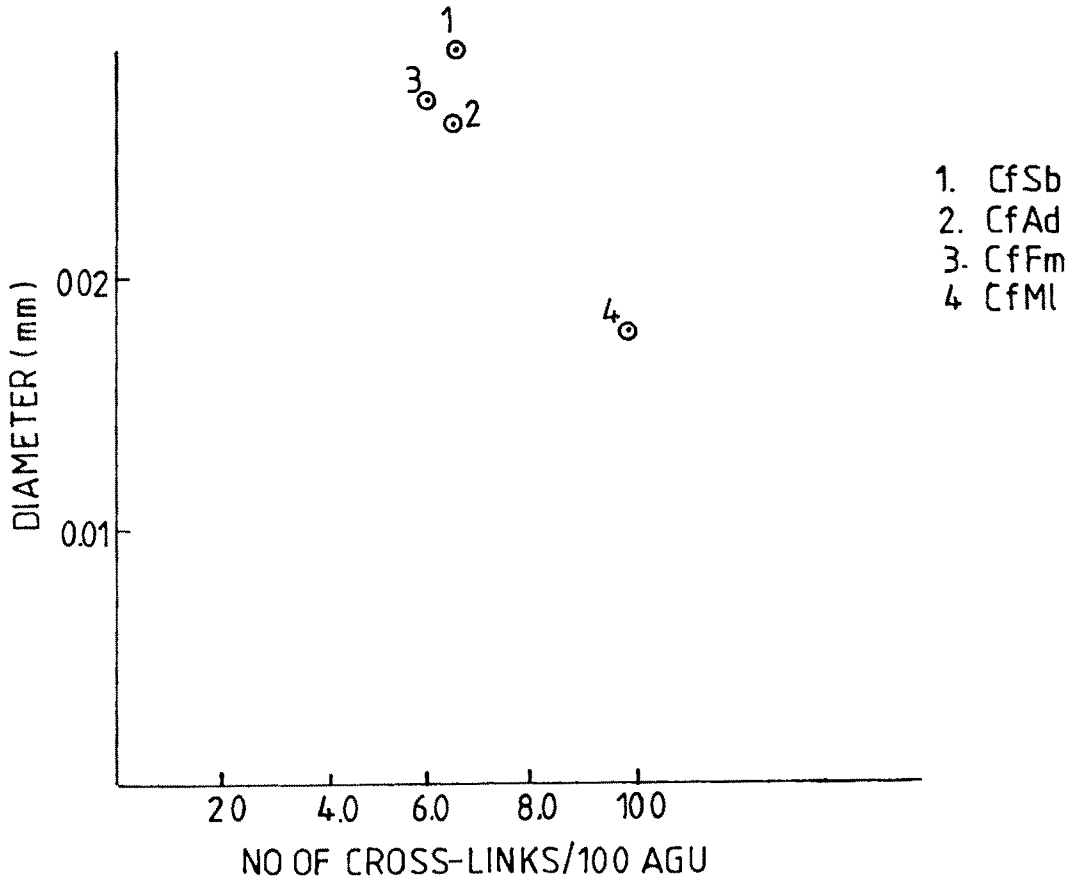


FIG.III 13 (c) DIAMETER Vs. CROSS-LINKS/100 AGU OF ESTERIFIED COTTON FIBRES

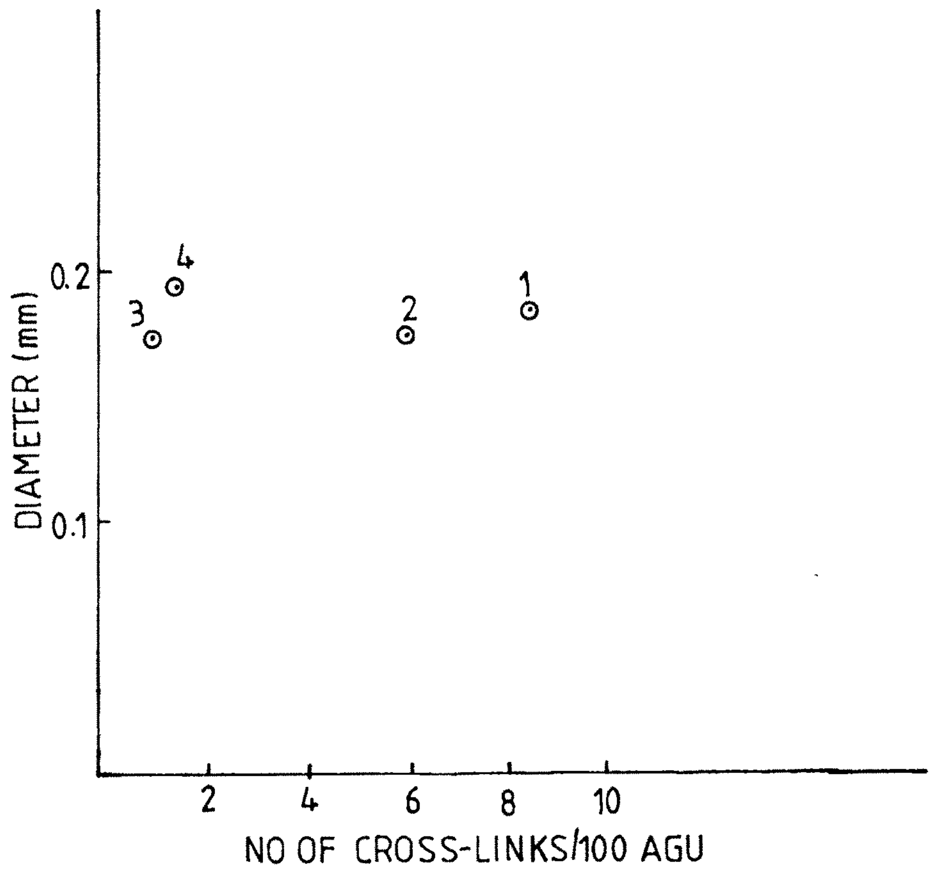


FIG. III.13 (d) DIAMETER Vs. CROSS-LINKS /100 AGU OF (1) BCFm (2) BCMl (3) BCAc (4) BCMac.

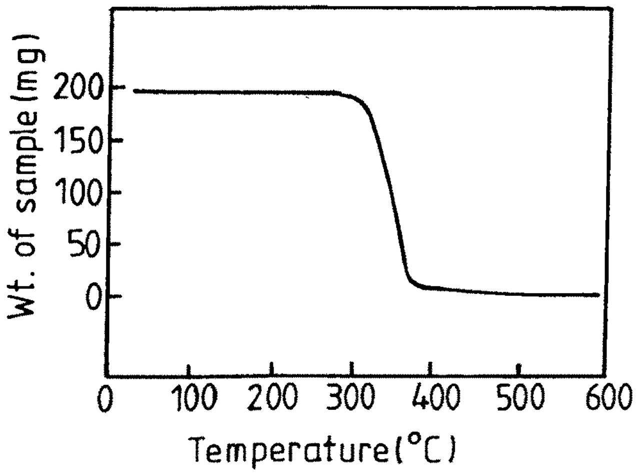


FIG. III. 14(a). TGA CURVE OF CELLULOSE

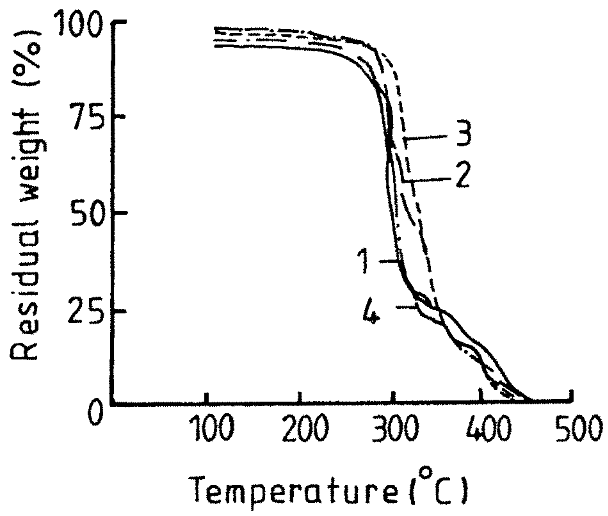


FIG.III.14(b) TGA CURVE OF NATURAL COTTON AND COTTON GRAFTED WITH METHYL ACRYLATE (1) NATURAL COTTON;(2) 15 % GRAFT COPOLYMERIZED, (3) 62 % GRAFT COPOLYMERIZED; (4) 74 % GRAFT COPOLYMERIZED.

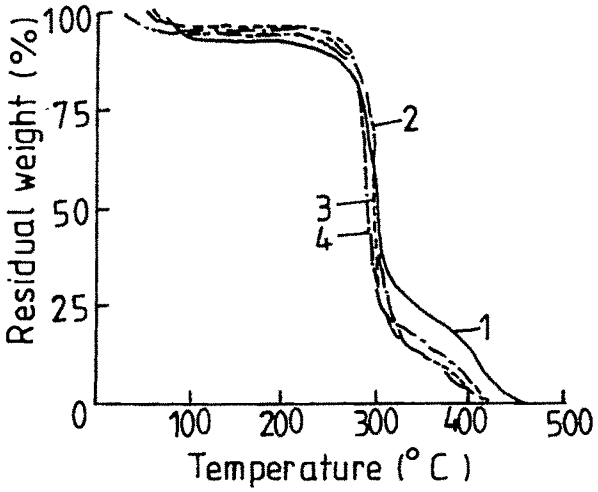


FIG. III.14(c). TGA CURVES OF NATURAL COTTON AND COTTON GRAFTED WIT METHYL METHACRYLATE :
(1) NATURAL COTTON;(2) 13.5 % GRAFT COPOLYMERISED;(3) 38% GRAFT COPOLYMERIZED;
(4) 55 % GRAFT COPOLYMERIZED

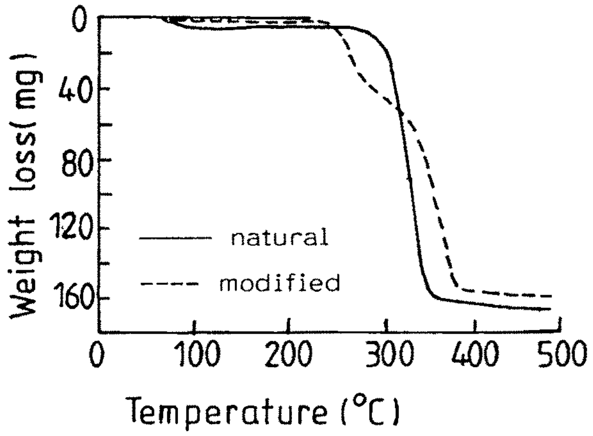


FIG.III 14(d) TGA CURVES OF MODIFIED COTTON FABRIC the initial loss of observed water, the decomposition starts at about 290°C and is completed at about 400°C, it corrosponds to the thermal depolymerization of cellulose.

Thermograms in fig.14(b) and (c)(350) shown that thermal stability increases with increase in % grafting of cellulose by acrylates. Cellulose grafted with acrylonitrile gives a DTA curve showing exothermic region from 260° to 335° with peak at 307°C, characteristic of homopolymerization of acrylonitrile. A second broad exotherm is shown for 340° to 400°C which may correspond to the interaction of polyacrylonitrile degradation products with those from cellulose. First TG loss is attributed to loss of polyacrylonitrile and second one involves cellulose depolymerization [fig.14(d)] (351).

III 5 Sorption

Cellulosic materials contain hydrophobic and hydrophilic groups. Hence these materials would sorb various substances like water, etc and may swell. Decrease in hydrophilicity may decrease the degree of sorption of substances like water.

The swellability and water repellency of (i) partially esterified cotton fabrics, (ii) formalized cotton fibres and (iii) grafted cotton fibres were studied by Benerito and coworkers (48), Baird (51), Molikuzieva and Tashpulatov (87), Rowland (158), Yul'chibaeva and coworkers (162), etc.

The sorption of NaCl and $CaCl_2$ was studied from aqueous and aqueous ethanolic solutions (168).

Recently reports have appeared in literature on (i) the determination of water retention value by the textiles (352), (ii) the combined diffusion of water vapour and heat through clothing (353), (iii) the relation of sweat to skin wettedness (170), (iv) clothing comfort in relation to the fabrics transmission rate of sweat (354), etc.

Sweat is a saline solution with about 5 % salt concentration under normal conditions. Hence, we considered to investigate the water and salt sorption by cotton and modified cotton fabrics from water and salt solutions (1 and 10% concentration). From the results presented in table II.15, the values of salt uptake and water sorption per g of dried fabrics have been obtained by using the relations

(i) salt uptake $= \dfrac{W_{DS} - W_{WD}}{W_{WD}}$

(ii) water sorption $= \dfrac{W_{AS} - W_{DS}}{W_{WD}}$ (from salt solution)

$= \dfrac{W_{AS} - W_{DS}}{W_{DS}}$ (from water) and are presented in table III.14. It has been observed that in case of untreated cotton fabrics, (i) the moisture content is about 6.8%, (ii) water sorption increases with increase in salt content of solution and appears to remain constant above 10% concentration and (iii) salt uptake by fabrics increases with increase in salt concentration of the solution.

In case of CVPn fabrics, (i) moisture content of CVPn fabrics has increased to 7.6%, (ii) water sorption by the fabrics increases with increase in salt concentration of the solution and (iii) salt uptake by the fabrics increases with increase in salt concentration.

Plots of (i) salt uptake (g/g) vs % NaCl in solution and (ii) water sorption (g/g) vs % NaCl in solution for the untreated and CVPn fabrics are presented in fig. III. 15. It is observed that (i) salt uptake for CVPn fabrics is lower than that for untreated fabrics for the same salt concentration and (ii) water sorption for CVPn fabrics is lower upto 2% NaCl concentration and higher above 2% NaCl concentration than that for untreated fabrics. The results generally indicate the effect of increase in hydrophobicity of the fabrics due to formalization reaction

In case of esterified fabrics (CSb-2 and CSbc), (i) moisutre content of the fabrics has decreased to 4.5 and 5.0%,

Table III. 14

Sorption

No	Product		Moisture content (%)	NaCl in solution (%)	Salt uptake/ g dried fabric (g/g)	Water-sorption/ g dried fabric (g/g)
1	Untreated fabrics	(a)	6.6	0	-	1.462
		(b)	7.0	1	0.070	1.716
		(c)	6.7	10	0.221	1.810
2	CVPn	(a)	7.7	0	-	1.410
		(b)	7.4	1	0.025	1.690
		(c)	7.6	10	0.197	2.812
3	CSb-2		4.4	10	0.186	1.259
4	CSbc		5.0	10	0.210	1.445
5	K-An-g-C-1		7.9	10	0.179	1.764
6	F-An-g-C-1		7.3	10	0.171	1.451
7	K-Aa-g-C-2		9.1	10	0.170	1.561
8	F-Aa-g-C-2		10.5	10	0.190	1.629

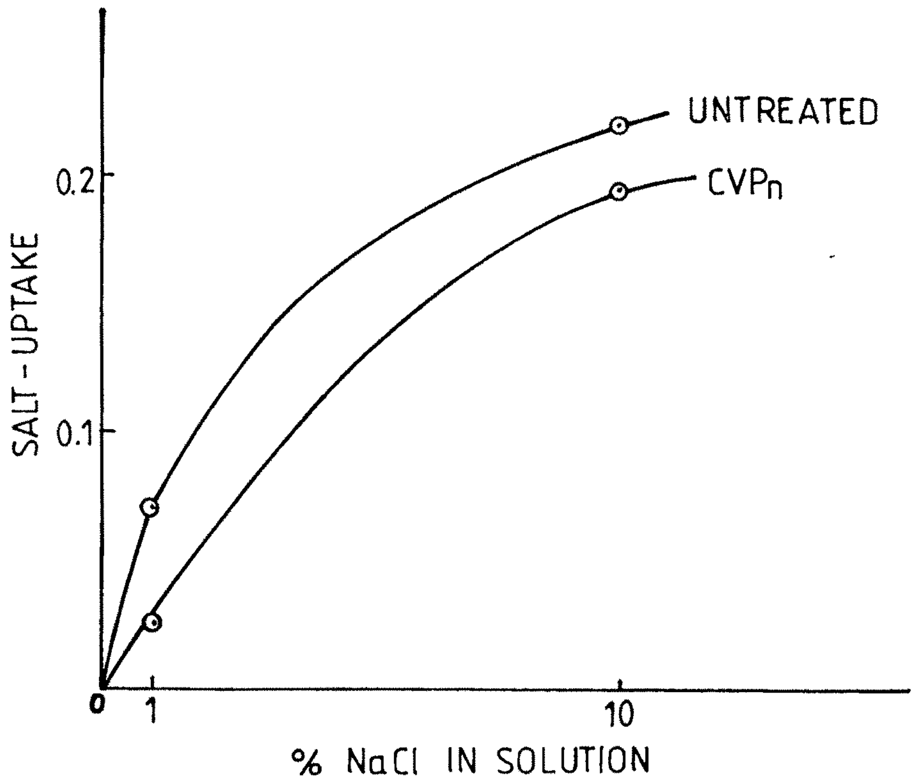


FIG.III.15(a) SALT UPTAKE Vs. % NaCl IN SOLUTION

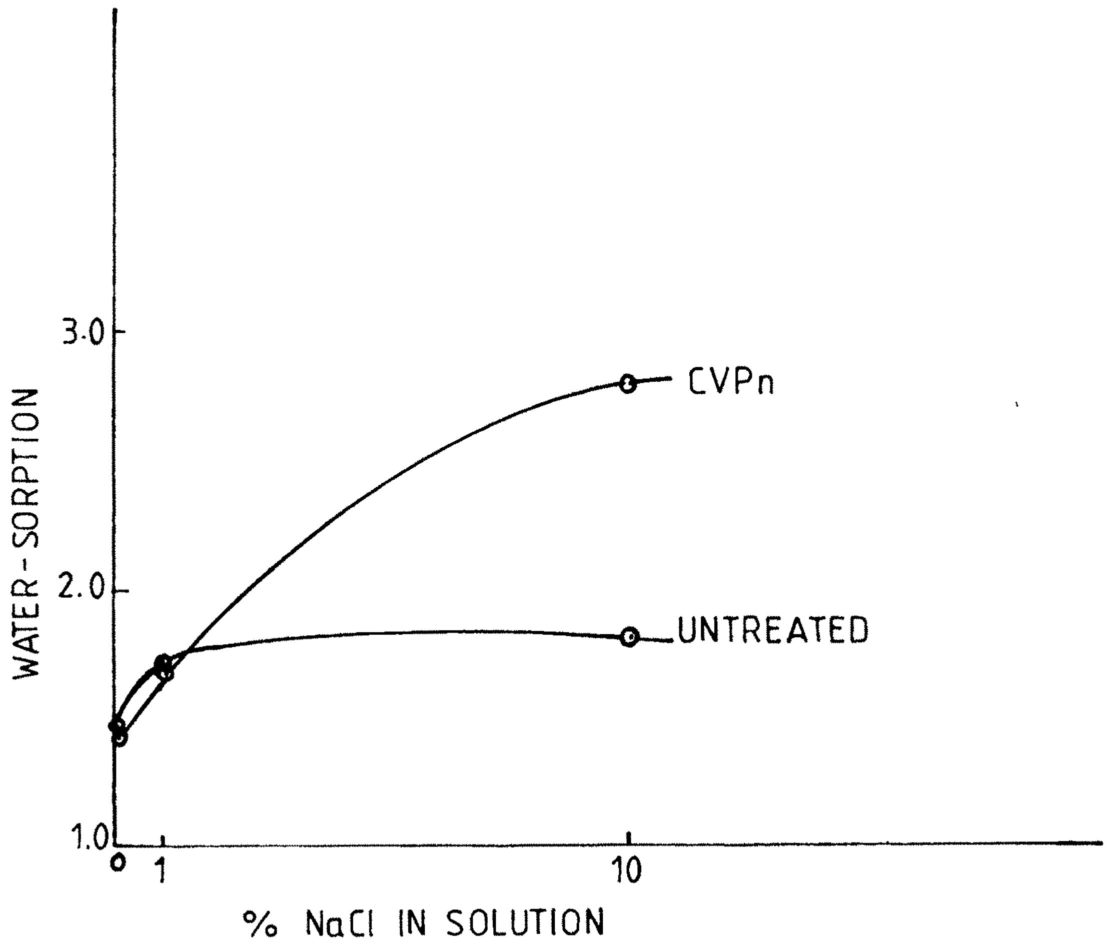


FIG. III.15(b). WATER-SORPTION Vs. NaCl IN SOLUTION respectively (ii) water sorption and salt uptake by CSb-2 and CSbc fabrics are lower than those for untreated fabrics from 10% NaCl solution. The results indicate the effect of decreasing the hydrophilicity of cellulose by esterification.

In case of grafted fabrics (K-An-g-C-1, F-An-g-C-1, K-Aa-g-C2 and K-Aa-g-C-2), (i) moisture content of the grafted fabrics has increased, varying from 7.3 to 10.5% and (ii) water sorption and salt uptake by the grafted fabrics are lower than those for the untreated fabrics from 10% NaCl solution. The results indicate the effect of increase in hydrophobicity of the fabrics due to grafting.

If the values of salt uptake and water sorption by modified fabrics from 10% NaCl solution are compared, it is observed that (i) the values of salt uptake increase in order

K-Aa-g-C-2 ~ F-An-g-C-1 < K-An-g-C-1 < CSb-2 <
F-Aa-g-C-2 < CVPn < CSbc < untreated

and (ii) the values for water sorption increase in order

CSb-2 < CSbc ~ F-An-g-C-1 < K-Aa-g-C-2 < F-Aa-g-C-2
K-An-g-C-1 < untreated < CVPn

The results can be generalized in terms of modification of fabrics as

(i) salt uptake : grafting < formalization < esterification
< untreated, and

(ii) water sorption : esterification < grafting < untreated
< formalization

Water sorption is generally considered a property of the less ordered region of cotton fibres, as crystallite regions are relatively less accessible. Esterification, formalization and grafting, in general, are expected to lower hydrophilic centres and by cross-linking may make such sites less available for sorption (332). Hence generally for both water sorption and salt uptake (for low concentrations in solutions) one may expect modified cotton to sorb less than natural cotton.