Studies of Kinetics and Electrical Properties of Cellulose Fiber by Cynoethylation

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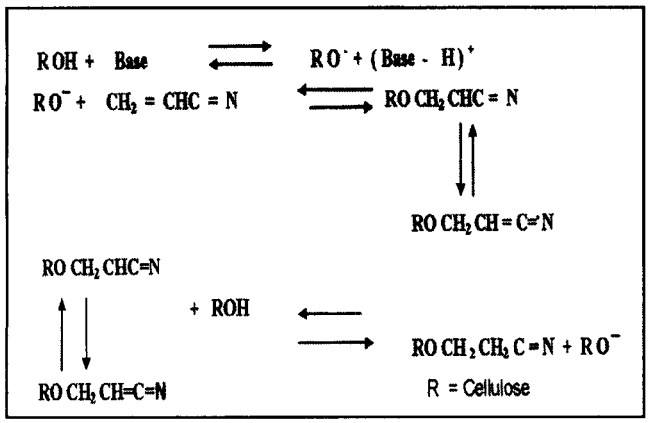
The aim of the research is to study the chenical modification of different samples like Brown wood pulp, White wood pulp, Bagasse pulp, with respect to Cynoethylation in presence of Acrylonitrile solution. The improvement of the properties such as Physical strength, Electrical Properties like Electrical resistance, Heat resistance, Insulation, and changes in paper characteristics with chemical modification have been investigated, and represented as bar charts. Kinetic study process that acrylonitrile was the limiting reactant for the product Cynoethylcellulose. The first order kinetics expression based on calculation of fractional conversion, cynoethylation as a function of time and has been presented by graph. The plot was linear and passing through the origin confirming that first order Kinetics Model for synthesis of Cynoethylation. The first Order Cynoethylation rate constant for Brown wood pulp and White wood pulp are 0.1995 and 0.3659 respectively. The chemical structure and composition of the product obtained by reaction of cellulose with acrylonitrile is supported by different characteristics IR absorption band and spectroscopic characterization of cynoethylated sample are investigated and presented by table and graph.

Keywords : Cynoethylation, Bursting Strength, Degree of Substitution, Heat Resistance and first order kinetics model

INTRODUCTION

Cynoethylation of cellulose pulp is the reaction between active hydrogen of hydroxyl group of cellulose and the double of acrylonitrile. Frequently performed with a basic catalyst. The reaction is exothermic and requires control. Because of the strong electron-withdrawing character of the nitrile group, the 13 carbon of acrylonitrile is rendered relatively positive and is attached by nucleophilic alkoxide anions. The generally accepted mechanism is as follows:



Useful Catalyst includes the Hydroxides, Oxides, alkoxides, Cyanides Hydrides and amides of the alkali metals themselves. In general 1.5% of catalyst based on the weight of acrylonitrile is staisfactory. (1,-5)) The cynoethylation of cellulose materials has been the subject of continuing research. It is conducted when heat resistance and electrical resistance are important requirement. The data of Harp ham et al (1) show that cynoethylation of inters produces increasing the bursting, tearing and folding strength at a lower level of substitution (DS-0.06) Spadaro and co- worker (6) obtained increases in strength at a DS value of about 0.2 with decreases as the substitution increased further but these were considered to be insignificant. Morton and Bikales (7) used a Kraft pulp at a higher substitution (DS-0.2-0.6). They found a slight increases in a tensile strength at a DS of about 0.19 with a regular decreases at a higher substitution. They are doubtful about the significance of the maximum for plotting Tearing strength vs. Degree of Substitution, (Fig no. 2) in the case of bursting strength there was no such maximum. They pointed out, however that spadaro found optimum properties. Especially folding endurance, for cynoethylated linters

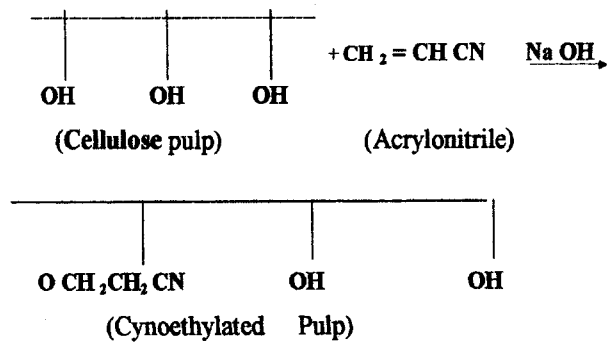
at about this substitution. McKay and Bikales (8) later found a similar effect. This maximum is reasonable cellulose etherified with others hydrophobic constituents (like methyl or Acetyl groups) shows just this type of behavior: increased effinity for water at low DS value and a subsequent decrease. This increased moisture adsorption result in swelling during the beating and higher strength in the sheet. Mizutant et al (9) obtained increased folding strength and elogation with a cynoethylated Kraft pulp of some what higher DS (0.4). They found however slight decrease in tearing and tensile strength. Morton and Bikales (7) found a decrease in bursting strength that is a linear with nitrogen content. With blend as well of untreated Kraft pulp cynoethylated pulps, they found a decrease; the plots are concave (Bursting Strength vs. Cynoethylated Pulp) indicating that the blends are weaker then unblended Cynoethylated Pulp at the same nitrogen level. Such blend has been patented (7) for making extensible paper. The bulk of furnish is untreated wood pulp, but 1-10% of cynoethylated, hydroxyethylated or Carboxyethylated pulp is also used. Specially regenerated Cynoethylated cellulose may replace the cynoethylated pulp Jayne (10) has shown that the strength of the cynoethylated fiber can be enhanced by heat bonding while it still contains at least 10% moisture. Wink *et al* (14) found a similar effect on the dry sheet to play a part in the improvement of thermal stability. Cellulose plastics are the polymers, which have the cellulose as their major constituents. These are prepared by reacting cellulose from natural sources with various chemicals, cellulose is the main constituent of the cell walls of plants. (11-13)

Experimental Methodology

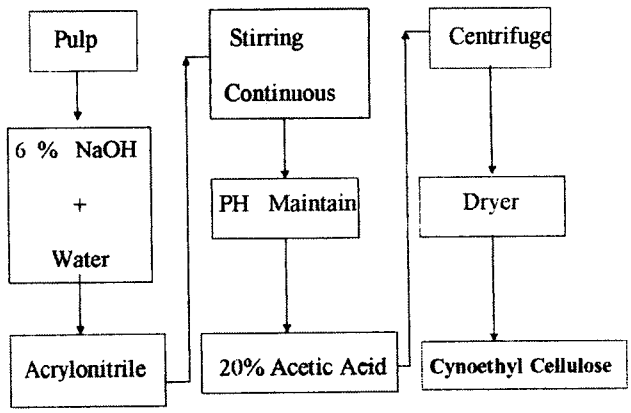
Cynoethylation Upgradation Technique

Acrylonitrile (144 gram) was added over a 5 min period to a mixture of 500 gram (dry basis) of pulp is 9200 gram of 6% aqueous sodium Hydroxide (1840 gram) in a aluminum pot, The slurry was maintained at 19 to 20°C for two hours with continuous stirring. Acidification to 4 to 5 with 20% aqueous acetic acid served to stop the reaction after one hour pH 4 to 5 Maintained in 1 hours. The product was washed thoroughly with water, centrifuged and dried in an air blower at 55 to 65 °C. The cynoethyl cellulose contain 0.56% N which in equal to degree of Substitution (D.S.) of 0.06.

Chemical Reaction: Cynoethylation Technique



Detailed Process Flow Chart is as follows:



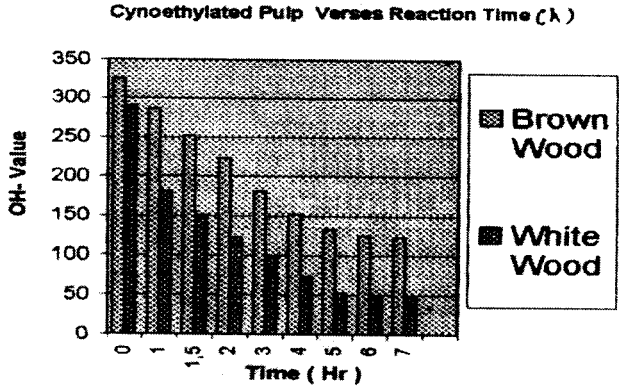
Hydroxyl value Determination

Hydroxyl value of cynoethylated pulp with respect to specific time should be investigated during the synthesis and recorded in a tabulated forms for Brown wood pulp and White wood pulp.

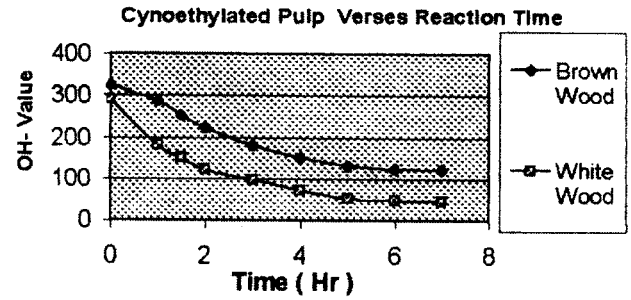
Table. 1 : Hydroxyl value of Cynoethylated Pulp vs. Reaction Time

Time (Hrs)	Brown wood (OH-Value)	White wood (OH-Value)
0.0	324.80	290.07
1.0	286.20	181.00
1.5	251.60	151.00
2.0	223.15	123.00
3.0	180.58	98.00
4.0	151.58	73.00
5.0	132.45	53.00
6.0	125.00	49.00
7.0	123.00	46.50

Bar Chart No. 1



Graph Chart No. 2

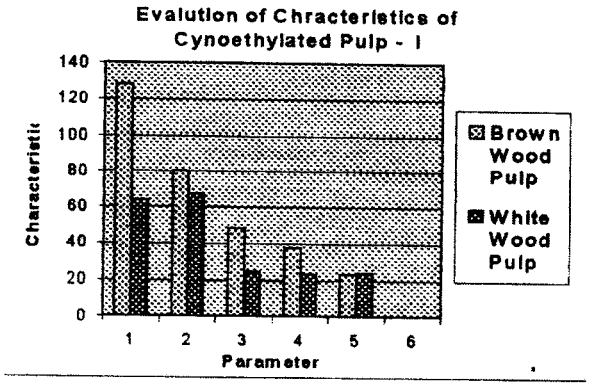


Characterization of Cynoethylated pulp by TAPPI Standard Method and recorded in with and without Chemical Reaction in a tabulated form Table 2

Property	Unit	White wood Pulp		Brown wood Pulp		Bagasse Pulp	
		with	without	with	without	with	without
GSM (10x10)	g/m^2	280	292	344	233	380	392
Burst Strength	gm/cm^2	6.7	6.7	8.0	.8.0	6.0	6.0
Bursting Factor	----	23.92	22.94	23.25	34.33	15.78	15.31
Tearing Strength	gm/cm of width	24	24	48.0	48.0	58.11	58.11
Tear Force	gm/cm^2	64	64	128	128	154.96	154.96
Tear Factor	---	22.85	21.19	37.20	45.33	40.78	39.53
Folding Endurance	MIT	1.0	1.5	2.5	3.0	1.5	2.0
Consistency	%	2.2	2.5	2.5	2.5	2.5	2.5
Freeness		67	67	80	80	60	60
Thickness	mm	0.36	0.63	0.53	0.50	0.58	0.53

Heat Resistance by Calibrated Oven : It can be determined with the help of oven. Samples which are initially weighted are placed in a oven, Maintain the temperature at 60 °C and record the observation for different span of time in minutes (15, 30, 45, 60) for their respective weight and tabulate the data, heat Resistance can be calculated by the following relations and represented as per following tables :

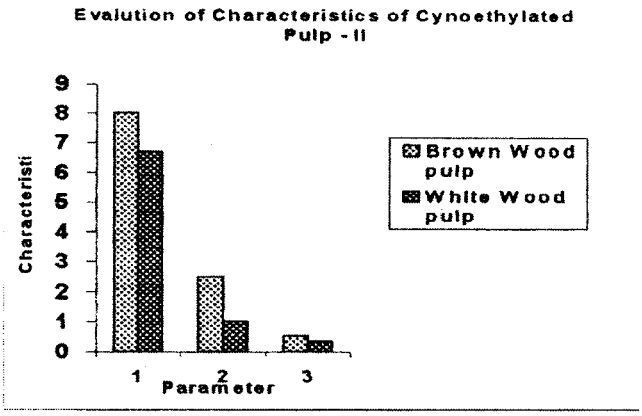
Bar Chart No. 2



Parameters

1=Tear force, 2 = Freeness, 3 = Tear Strength, 4= Tear factor 5= Bursting factor

Bar Chart No. 3



Parameters

1=Bursting Strength, 2= Consistency, 3 ,Thickness

Determination of Surface Resistivity and Heat Resistance

i. Surface Resistivity by Sigma Milton Megohm Meter

Voltage : 500. Rx Factor: (10 * Scale Reading):

D_1 = Diameter of Inner Electrode (Small Reading) = 53 mm

D_2 = Internal diameter of the ring Electrode (Big ring) = 73 mm

Table 3:

Sr. No.	White Wood Pulp		Brown Wood Pulp		Bagasse Pulp	
Parameter	Reacted	Un-Reacted	Reacted	Un-Reacted	Reacted	Un-Reacted
(Rx)	6.0*10	5.2*10	10.0*10	6.5*10	8.0*10	5.0*10
Reading	60.00	52.00	100.00	65.00	80.00	50.00
(Rs)	2710.79	2349.35	4517.98	2936.69	3614.38	2258.99

Surface Resistivity Rs. $= \frac{2 * 3.14 * \text{Reading}}{\text{Log}(D_2/D_1)}$

Rs.= 45.79856 * Rx, Rs = Surface Resistivity of test piece (ohm)

D_1 = Diameter of top inner element (mm)

D_2 = Internal diameter of ring top outer element (mm)

Development of Kinetics Model for Cynoethylation

Kinetic of Cynoethylation

Cellulose + Acrolonitrile = Cynoethylated Cellulose

Feed : 25 gm (12.5ml) of pulp + 7.2 gram (7.2 ml) of Acrolonitrile + 460 gram of Water

Total Volume of Reactant = 492.2 ml. (0.5 liter).

Product : Cynoethyl Cellulose

As per Stiochilometry Calculation Excess Reactant (492.3 ml, 0.5 liter) Limiting Reactant (Acrylonitrile): 7.2 gram: or 0.13584 gram mole

CAO=NAO/V=0.13584/500=0.27168Gram Mole/ Liter

Amount of Acrylonitrile reacted as per run :

$$\frac{\text{Difference Delta - OH) * 53}}{56100}$$

$$= (CAO - CA)$$

$$\text{Conversion (XA)} = \frac{(CAO - CA)}{CAO}$$

Equilibrium Constant (K) = 1/t (- In CA / CAO)

K can be calculated and represented the following tables

Table 4 : After 15 minute

Sample	Initial Weight (gram)		After 15 minute (gram)	
	Reacted	Un-Reacted	Reacted	Un-Reacted
White wood	0.3409	0.3577	0.3315	0.3463
Brown wood	0.5094	0.1691	0.4945	0.1651
Bagasse	0.4661	0.2034	0.4547	0.1997

Table 5 : After 30 minute

Sample	Initial Weight (gram)		After 30 minute (gram)	
	Reacted	Un-Reacted	Reacted	Un-Reacted
White wood	0.3409	0.3577	0.3483	0.3314
Brown wood	0.5094	0.1691	0.4966	0.1648
Bagasse	0.4661	0.2034	0.4552	0.2012

Table 6 : After 45 minute

Sample	Initial Weight (gram)		After 45 minute (gram)	
	Reacted	Un-Reacted	Reacted	Un-Reacted
White wood	0.3409	0.3577	0.3482	0.3475
Brown wood	0.5094	0.1691	0.4974	0.1647
Bagasse	0.4661	0.2034	0.4554	0.2011

Table 7 : After 60 minute

Sample	Initial Weight (gram)		After 60 minute (gram)	
	Reacted	Un-Reacted	Reacted	Un-Reacted
White wood	0.3409	0.3577	0.3408	0.3475
Brown wood	0.5094	0.1691	0.5094	0.1647
Bagasse	0.4661	0.2034	0.4661	0.2011

Table 8 : Estimation of Cynoethylation Reaction Parameter sample : Brown Wood

Time (t)	CAO-CA	XA	-In(1-XA)	K(1/hr)
0.0	0.0	0.0	0.0	0.0
1.0	0.03647	0.1343	0.1442	0.1442
1.5	0.06896	0.2538	0.2928	0.1952
2.0	0.09603	0.3545	0.4377	0.2188
3.0	0.1368	0.5035	0.7002	0.2334
4.0	0.1637	0.6024	0.9223	0.2305
5.0	0.1817	0.6689	1.1053	0.2211
6.0	0.1887	0.6958	1.1900	0.1983
7.0	0.1906	0.7017	1.2097	0.17728

Graph No. 3
Kinetics of Cynoethylation using Brown Wood Sample

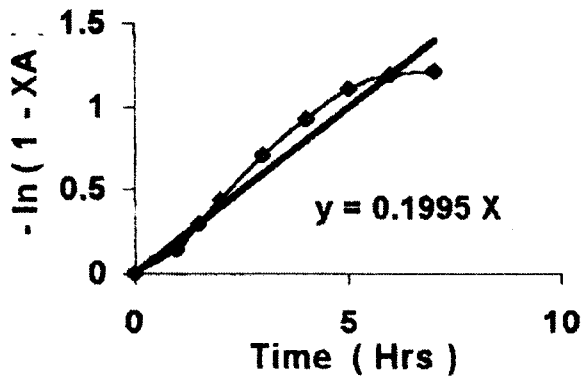


Table 9 : Estimation of Cynoethylation Reaction Parameter sample : White Wood

Time (t)	CAO-CA	XA	-In(1-XA)	K(1/hr)
0.0	0.0	0.0	0.0	0.0
1.0	0.10363	0.3815	0.4804	0.3202
1.5	0.13198	0.4858	0.6651	0.3325
2.0	0.15843	0.5832	0.8750	0.3500
3.0	0.18205	0.6701	1.1090	0.3696
4.0	0.20567	0.7570	1.4148	0.3912
5.0	0.22456	0.8266	1.7520	0.3893
6.0	0.22834	0.8405	1.8356	0.3671
7.0	0.23071	0.8492	1.8917	0.3439

Graph No. 4

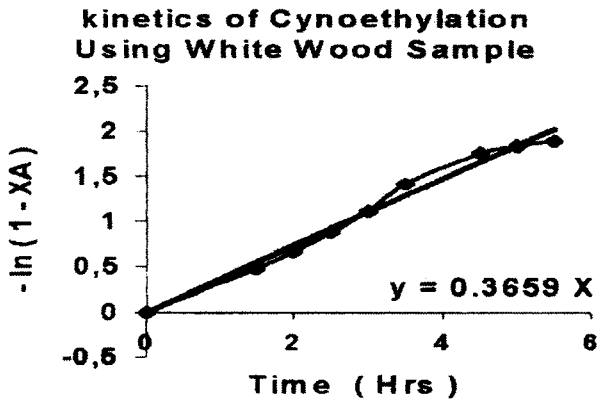


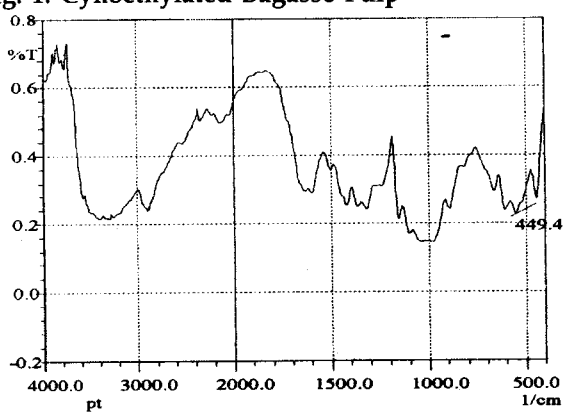
Table 10 : Spectroscopic Characterization

The Spectroscopic Characterization of Cynoethylated Sample is as follows

S.No.	Gourps/Vibrations (cm^{-1})	IR absorption
1.	*O - - H stretching of alcoholic - - OH groups	3605 - 3150
	* O - H deformation and C - O stretching	1400, 1360, 1305 1160, 1100, 1050
2.	*C - - H stretching of CH_3 > CH_2 > C - H groups	2970-2840
	* C - H deformation of > CH_2 > C - H groups	1460, 1360 1325
3.	* C - O stretching of alcoholic groups	1345, 1302 1102
	* C- O ether linkage and cyclic Ether linkage	1048 1102, 1048
4.	* C = H group	2260-2240
5.	* Modified structure Change in a Position of Substituent during the Process and Chemical Reaction and also Excess of CH_2 = CH OH	1670 - 1600

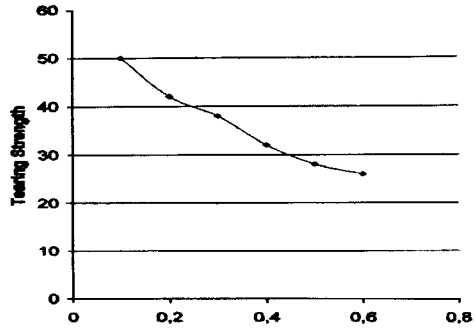
The IR Spectroscopic Characterization of Cynoethylated Bagasse Pulp Samples are represented as follows

Fig. 1. Cynoethylated Bagasse Pulp



X = axis (Wave number)
Y = axis (% T)

Tensile Strength of Cynoethylation Handsheet as a Function of the Degree of Substitution Fig . 2



RESULTS AND DISCUSSION

Kinetics study Process that Acrylonitrile was the Limiting Reactant for the Product Cynoethylated Pulp and Conversion data - In (1-XA) with respect to time (T) represent Straightline relation ship with empirical equation Brown wood pulp : Y = 0.1995 X. White Wood Pulp: Y = 0.3659 X Equilibrium constant was calculated for different span of time, it is indicated that Cynoethylation by using Brown Wood Pulp, and White Wood Pulp was gives first Order Kinetics Model and follows a equation :

Equilibrium Constant (K) = 1/t (- In CA / CAO)

Cynoethylation of Brown wood and White Wood Pulp was carried out with the help of acrylonitrile. The Wood pulp were characterized by very high initial hydroxyl value (325 and 290) While all the pulp used in a pervious experimentation (Acetylation and Carboxymethylation) were of low initial hydroxyl value in spite of lower initial hydroxyl value of white wood pulp, it has exhibited a very rapid drop in hydroxyl value and with seven the hydroxyl value was reduced to a one sixth of original value unlike white wood pulp brown wood pulp retained just 40% of initial hydroxyl groups. The basic reason of superior response of a white wood pulp over that of brown wood

Pulp. For Cynoethylation may be the presence of miner amounts of inhibiting factors in brown wood Pulp. The result of cynoethylation have been reported in a table 2. The first order Cynoethylation plot have been presented in graph No. 3 & 4. As seen from the graph, the plot was linear and passing through the Origin. The first order Cynoethylation rate constants for brown wood Pulp and White Wood Pulp. Were 0.20 and 0.36 hr^{-1} respectively. Thus the rate of constant of white wood Pulp was almost double of that of Brown Wood Pulp in other words the volume of Cynoethylation reactors for white wood Pulp will be almost half of that required for Cynoethylation of brown wood pulp.

Cynoethylation of Cellulose Pulp was carried out to enhance certain special Characteristics. Such as Heat resistance and electrical resistance. Although there was marginal improvement in mechanical properties after cynoethylation, the real factors were as above characteristics. The pulp selected for cynoethylation were characteristics by high initial hydroxyl value (325 and 290). As per Hydroxyl value table 1 Pulp Cynoethylation Equilibrium established after 7 hours and observed low hydroxyl value in case of Pulp highest initial hydroxyl value, Equilibrium established after 4 hours. This offer for more opportunity of degree of Cynoethylation for improvement in mechanical properties, chemical modification was required to be controlled at lower conversion. This limitation/restriction were not at all essential for upgradation heat resistance and electrical resistance of cellulose papers. The procedure for determination of heat resistance and electrical resistance of paper has already been described. The increase in electrical resistance as a measured by surface resistivity of cynoethylated Pulp, which is directly proportional to extent of Cynoethylation. The degree of cynoethylation was highest with brown wood pulp hence the rise in electrical resistance was higher (100-35/35* 100 = 50%) Bagasse Pulp also exhibited remarkable enhancement (60%) in electrical resistance. The heat resistance of paper was measured in terms of ability to withstand higher temperature without loss in weight All cynoethylated papers are able to withstand 70°C for the total duration of (0 to 60 minutes in a 15 minutes span of time). Without developing any darkening of colour and without any loss in weight. The result of electrical resistance and heat resistance measurements have been presented in a table 3 & 4 to 7.

As the electroscopic characterization the data indicated that Cynoethylation of Cellulose has been achieved through a reaction of cellulose with Acrylonitrile. The proposed chamical Structure and Composition of Product is supported by IR absorption bands. Data in a table 10

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