

## PHOTOLYSIS OF CELLULOSE\*

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**ABSTRACT**

The paper reviews in brief the salient features of the work under study at T.D.E.L., Kanpur. The requisite historical background is provided. The results are reported under two main heads—(i) Fundamental studies on the action of light on cellulose, and (ii) Barriers for the prevention of light attack on cellulose.

Under fundamental studies, the method of nitration of cellulose has been examined, and it is shown that the formulations reported in literature as not causing degradation of cellulose during nitration, do cause degradation. It is pointed out that the classical methods of the evaluation of degradation of cellulose by estimation of cuprammonium fluidity, methylene blue absorption, and degree of polymerisation by end-group assay have no value stoichiometrically, and, that it is better to base the evaluation on tensile strength data, reducing power, and degree of polymerisation as estimated through nitrocellulose viscosities. It has been possible to understand in outline the pattern of photolysis. The use of artificial source of light such as mercury arc has its disadvantages. The post-irradiation phenomenon has been studied in detail and some important findings are reported.

Extensive investigations, on barriers which will minimise the extent of photolysis have shown that urea-formaldehyde resin and hydrated manganese oxide are outstanding. The mechanism of protection has been investigated.

### Introduction

(a) Although the degradative influence of sunlight on cotton materials has been known for a long time, systematic investigations to ascertain the nature and mechanism of such degradation have been a matter of recent history. Witz<sup>1</sup> put forward the theory in 1883 that the action of light on cellulose is of a chemical nature. Harrison<sup>2</sup> reported in 1912 the formation of oxy-cellulose and certain simple organic substances of strong reducing power during the combined action of air and light on cellulose. Work on similar lines was carried out by Doree and Dyer<sup>3</sup> who could reduce cellulose in the form of a fine powder by prolonged exposure to a quartz mercury lamp. Aston<sup>4</sup> put forward the theory that the tendering of cellulose by sunlight is influenced by the ambient conditions. Barr<sup>5</sup> and later Vignon<sup>6</sup> noticed the great influence of moisture on the tendering of exposed samples of cellulose. Simola<sup>7</sup> observed degradation of cotton exposed to sunlight after the radiation had been filtered through glass windows and Sommer<sup>8</sup> observed 50 per cent. loss in tensile strength of cotton as a result of 940 hours of exposure to sunshine. In recent years the problem has been studied on more fundamental lines by Stillings and Van Nostrand<sup>9</sup> and other workers<sup>10,11,12,13</sup> with a view to elucidating the mechanism of degradation and ascertaining the nature of the products obtained.

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\* A review paper on the work carried out at the Technical Development Establishment, Laboratories, Kanpur.

(b) Work on this subject has been in progress at the Technical Development Establishment, Laboratories, Kanpur, for the last few years. The object of the work has been two fold, *viz.*, (1) to elucidate the mechanism of light attack on cellulose and (2) to evolve barriers for cellulosic textiles stores against attack by sunlight. The present paper describes in outline the results obtained to date. The paper is divided into two parts, the first dealing with fundamental studies on the action of (1) sunlight and (2) simulated sunlight on cellulosic materials and the second dealing with the evolution of suitable barrier treatments.

## FUNDAMENTAL STUDIES ON THE ACTION OF LIGHT ON CELLULOSE

### Source of Irradiation and Technique of Exposure

(a) **Introduction.**—It is now generally accepted that cellulose is degraded mainly by the ultra-violet region (below wave length  $4000 \text{ \AA}^\circ$ ) of the sun's spectrum<sup>14, 15, 16</sup>. The visible region (of wave length  $4000$  to  $7000 \text{ \AA}^\circ$ ) and the long wave length infra-red region (beyond  $7000 \text{ \AA}^\circ$ ) do not have any appreciable effect<sup>4, 17</sup>. Pech<sup>18</sup> has suggested that the presence of the visible and the infra-red regions actually oppose to a certain extent the action of ultra-violet rays. Kauffmann<sup>19</sup> considers the region about  $3500 \text{ \AA}^\circ$  as effective, while visible light is without action. A similar opinion has also been expressed by Frompton, Foley and Webber<sup>12</sup>. The function of the ultra-violet region in causing degradation has also been considered to be the possible production of ozone or ionised oxygen<sup>4</sup> or even oxides of nitrogen<sup>10</sup> which subsequently act on the cellulose. Montonna and Winding<sup>20</sup> consider the action as catalytic though this concept is disputed by Heuser and Chamberlain<sup>10</sup>.

(b) **Exposure to Sunlight.**—Studies on the effect of sunlight carried out in these laboratories involved the exposure of fresh fabrics to sunlight only at Kanpur (Lat.  $26^\circ 28' \text{N}$ , Long.  $80^\circ 21' \text{E}$  and height 416 feet above sea level). In actual practice, one yard lengths of the fabric of Indian tentage were mounted on wooden frames. These frames were exposed on racks (four feet above the ground) facing south and inclined at an angle of  $45^\circ$ . The exposure was maintained during hours of sunshine only, the frames being removed indoors at the end of the day and also during cloudy or rainy weather. Samples were cut from the fabrics according to a randomised plan, initially and at regular intervals and examined for the extent of degradation by means of the procedures outlined later in this paper. The chemical examination was always carried out on material obtained by dethreading the fabric, shredding the threads and finally averaging them. This was found necessary owing to the high degree of heterogeneity in respect of degree of polymerisation of the cellulose of the fabrics used. To illustrate, in one of the fabrics investigated, the chain length varied from 1750 to 2100 glucose residues over an area of one foot square. After averaging, the variation was only 50 residues (maximum).

(c) **Exposure to Artificial Source of Light.**—Since degradation by sunlight was found to be a slow process involving long periods of exposure, it was found necessary to supplement the study by exposure of fabrics to ultra-violet light in the laboratory. A suitable source of

'uviarc' for the purpose would have been the carbon arc<sup>21</sup>, but owing to the comparatively low intensity of this source, it was decided to use the 'Hanovia' High Alpine Sun Mercury Vapour Lamp which emits a powerful spectrum from 2200 Å° in the ultra-violet to about 20000 Å° in the infra-red with bright spectral lines at 2536 Å° and 4358 Å°. The intensity of the lamp in the ultra-violet region was measured by the method of Wagner, Webber and Siu<sup>21</sup>. At a distance of 30 cms., the intensity in the ultra-violet region was found to be 55 times as much as in sunlight at Shahjehanpur\* (Latitude 26°N, Longitude 80°E). The low frequency ranges (below 2900 Å°) in the far ultra-violet of this mercury arc lamp are, however, absent in sunlight. As suitable filters were not available for removing the low frequency ranges, the fabrics were irradiated directly by the lamp at a distance of 30 cms, the intensity being maintained uniform over the surface of irradiation by a suitable technique<sup>22</sup>. A blast of air maintained by a fan reduced the temperature of the fabric during irradiation from about 55°C to about 30°C. The chemical examination was carried out on averaged material, as in the case of exposures to sunlight but without any delay as post-irradiation effect<sup>9</sup> had to be avoided. In view of the differences in the intensities in the ultra-violet range of the sun's spectrum and the 'uviarc', a strict comparison between the degradations by the two sources could not be expected. Cunliffe and Farrow<sup>23</sup> have indicated that it is unsafe to predict the behaviour of textiles towards sunlight on the basis of observations under artificial light, particularly regarding their (textiles) chemical nature. In view of this, outdoor exposures were always planned and executed to confirm conclusions reached in the laboratory.

### Test Methods

(a) **General.**—The degree of tendering of the fabrics exposed to sunlight was assessed by the classical test methods. It should be pointed out, however, that most of these have no value stoichiometrically. For example, the methylene blue test<sup>24</sup> may show the presence of carboxyl groups but is of no importance in defining the structural arrangement or position of the carboxyl. The copper number<sup>25</sup> does not delineate structure. It does not distinguish between the aldehyde groups arising out of the oxidation of the hydroxyls and those produced by the hydrolysis of the  $\beta$ -glucosidic linkages. The use of alkaline solution in the copper number method may lead to the rupture of the alkali-sensitive linkages leading to formation of additional reducing groups. This would affect the value of the copper number method as a measure of the initial reducing groups present. The use of cuprammonium viscosity<sup>26</sup> data for obtaining an estimate of chain length is also open to serious doubt owing to the strong alkalinity of this reagent. The assay of end reducing groups by the method of Hiller and Pacsu<sup>27</sup> has been found at Kanpur<sup>28</sup> to fail in respect of oxycelluloses. This method has also been found to be unsatisfactory by other workers<sup>29, 30, 31</sup>. It appears that permanganate oxidises reducing groups present in the body of the molecule in addition to the end aldehyde group. At Kanpur, degradation has been generally assessed by the determination of (1) tensile strength, (2) chain length by nitrocellulose viscosity<sup>32</sup> and (3) copper number. Cuprammonium fluidity was also estimated in a few cases. During early stages, carboxyl contents were estimated by the method of Neale and

\* The value for intensity of solar radiation at Kanpur is not available.

Stringfellow<sup>33</sup> but in view of the finding that the fabrics exposed either to sunlight or to the mercury arc did not at any stage have appreciable carboxyl contents, the determination of carboxyl content and methylene blue absorption was discontinued.

(b) **Nitration and Nitrocellulose Viscosity.**—(i) Staudinger<sup>34</sup> drew attention to the relationship between the viscosities of solutions of polymers and their molecular weights. For low concentrations of the solute, he considered that the function specific viscosity/concentration is linearly related to concentration and he proposed the empirical equation—

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = K_m \times M \text{ where}$$

$c$  is the concentration,  $\eta_{sp}$  is the specific viscosity,  $M$  the molecular weight and  $K_m$  is a constant for a given series of polymers. The

function  $\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$  has been known as the intrinsic viscosity  $[\eta]$  of the polymer. Batista<sup>35</sup> observed that the logarithm of specific viscosity/concentration had linear relationship with concentration over a wide range. This altered the Staudinger equation to

$$\lim_{c \rightarrow 0} \log \frac{\eta_{sp}}{c} = K_m \times M. \text{ The Staudinger equation has not been}$$

universally accepted and has been modified by other workers<sup>36,37</sup>. Kraemer<sup>38,39,40</sup> by comparing the intrinsic viscosities of high polymers with the molecular weights obtained by ultra-centrifugal measurements, has come to the conclusion that the intrinsic viscosity is a linear function of the molecular weight over a wide range of values. Recent workers<sup>41,42</sup> consider that a one constant equation is inadequate and have suggested a more general equation  $[\eta] = K \times M^a$  where 'a' is an additional constant. Mosimann<sup>43</sup> has suggested the values 3.8 for 'K' and 0.93 for 'a' for cellulose nitrate solutions. These values have been in use in these laboratories for the evaluation of molecular weights from intrinsic viscosity measurements. References exist in literature on the theoretical aspects of the above calculations<sup>44,45,46</sup>.

(ii) In the initial stages of the work at Kanpur, nitrations were carried out by the method described by Davidson<sup>47</sup>. The high figure of 13.7 per cent. for the nitrogen content of the nitration products reported by Davidson could not, however, be confirmed in these laboratories (see Table I). In the case of samples of high degree of polymerisation (D.P.), Davidson's formulation often failed to give soluble samples for viscosity determination. A change was, therefore, made in the nitration mixture by using 95 per cent. phosphoric acid instead of 89 per cent. acid used by Davidson<sup>47</sup>. The nitrogen contents obtained in the case of four different cellulose samples nitrated by both these formulations are given in Table I. Along with these, the method of nitration described by Mitchell<sup>48</sup> was also investigated and the values obtained for nitrogen contents by this method are also shown in Table I.

TABLE I  
 Nitrogen Contents of Nitrocelluloses obtained by different  
 Methods of Nitration

No.	Basic cellulose sample used for nitration	Nitrogen content %		
		Method of Mitchell	Method of Davidson	Modified method using 95% phosphoric acid
1	Degreased cotton slivers .. ..	13.5	11.7	12.6
2	Surgical cotton .. ..	13.7	11.9	12.6
3	Fabric of Indian tentage .. ..	13.3	11.8	12.5
4	Satin drill (cellulosic) .. ..	13.5	11.7	12.6

It will be noticed that the highest value for nitrogen content is obtained when nitration has been carried out by the method of Mitchell<sup>48</sup>. The value recorded agrees closely with that reported by Mitchell<sup>48</sup> and by Hessler *et al*<sup>49</sup> who have used the same formulation. Davidson's formula has given the lowest values (about 11.7 per cent.) for nitrogen content.

(iii) Values of D.P. estimated through nitrocellulose viscosity data showed similar differences for the three methods of nitration. This may be observed from the results shown in Table II. Mitchell's method gives figures which are invariably higher than those obtained by the other two methods, the lowest figures being given by Davidson's method. This would imply that the degradation of cellulose takes place during nitration by certain formulations involving the use of phosphoric acid. This finding is of considerable importance in the light of different views expressed by workers in the field<sup>49,50,51,52,53</sup>. Notwithstanding this limitation, it has been observed in these laboratories that the D.P. figure for any material can be reproduced if nitration is carried out using the same formula for the nitration mixture. Figures obtained in any comparative assessment are, therefore, valid.

TABLE II  
 Degree of Polymerisation estimated through Nitrocellulose  
 Viscosities

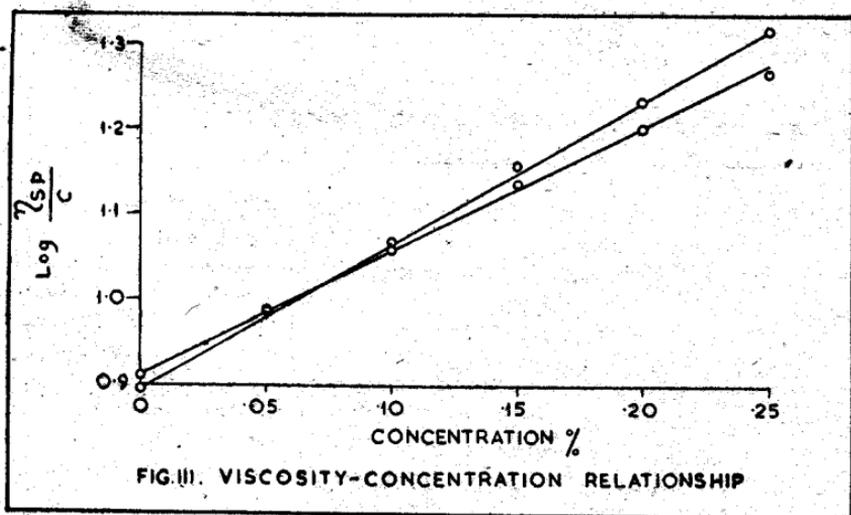
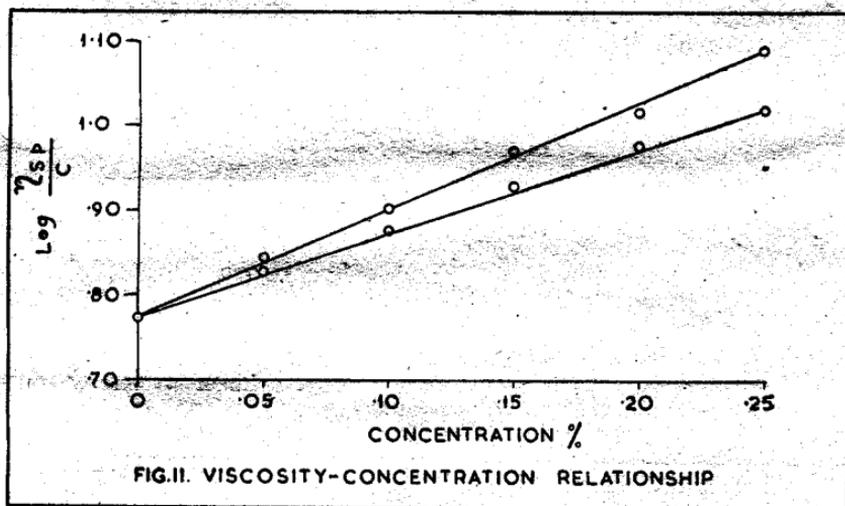
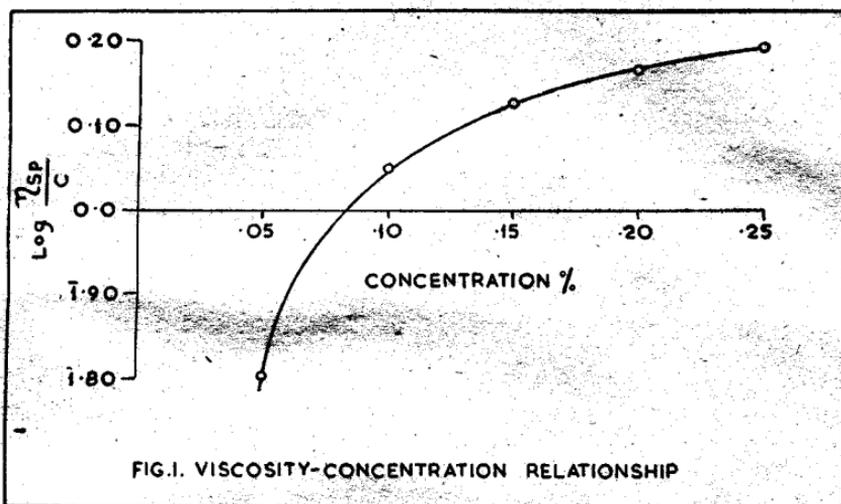
No.	Cellulose sample used	Degree of polymerisation				
		Nitration by Mitchell's method. D.P.	Nitration by Davidson's method.		Nitration by modified method.	
			D.P. figure	% departure from Mitchell's method	D.P. figure	% departure from Mitchell's method
1	Fabric No. 1 .. ..	3377	2400	28.9	2523	25.3
2	Fabric No. 2 .. ..	3652	2632	27.9	..	..
3	Fabric No. 3 .. ..	2697	1671	38.1	1872	30.6
4	Fabric No. 4 .. ..	2619	..	..	1910	27.1
5	Surgical cotton .. ..	1461	..	..	1070	26.8
6	Degreased silvers .. ..	3826	2673	30.1	2819	26.3
7	Degreased cotton .. ..	529	353	33.3	373	29.5

(c) **Certain Observations on Viscosity Graphs.**—(i) During the course of study of several samples of nitrocelluloses varying widely in D.P., it has been observed<sup>22</sup> that samples of very low D.P. of the order of 150 and below do not give a straight line graph on plotting  $\log$  [specific viscosity/concentration] against concentration. This is illustrated in Figure I for a sample whose D.P. is of the order of 130. It may be noticed that the graph actually shows a tendency to curve downwards, some of the values for  $\log \left[ \frac{\eta_{sp}}{c} \right]$  being negative. In such cases it has been possible to evaluate the intrinsic viscosity by the equation suggested by Howlett *et al.*<sup>46</sup>

(ii) Some insight into the heterogeneity of cellulose samples has also been possible by the determination of nitrocellulose viscosities. It has been noticed<sup>28</sup> that different samples having the same D.P. can have different specific viscosities at the same concentration. This would mean that their viscosity graphs would diverge from a common point on the  $\log \left[ \frac{\eta_{sp}}{c} \right]$  axis. One case of such divergence is shown in Figure II. A similar observation has been recorded by Brownsett and Davidson<sup>54</sup>. Ott<sup>55</sup> has explained this phenomenon on the basis of the assumption that the longer the molecular chain the greater the molecular interference and hence the viscosity of a non-uniform polymer will be greater at a given concentration than that of a uniform polymer of the same weight average chain length. It would, therefore, appear that the phenomenon must be traced to the heterogeneity of the basic cellulose material. Similar observations have been made in the case of cellulose acetate by Howlett *et al.*<sup>45</sup> who consider that the heterogeneity confers on the viscosity line a slope appreciably greater than that of a more homogeneous material of identical intrinsic viscosity. There have also been cases where viscosity graphs intersect each other (Fig. III) indicating that a sample with a lower D.P. can have a higher degree of heterogeneity than the one with a higher D.P.

### Mechanism of Degradation by Sunlight and by Artificial Light

(a) **Degradation by Sunlight.**—(i) As already pointed out, the degradation of cellulose by sunlight has some points of difference from degradation by the mercury arc. In sunlight, the reaction is slow and steady and a plentiful supply of oxygen is always available. The results obtained in these laboratories on exposure of certain fabrics to sunlight have already been described<sup>28</sup>. The nature of changes taking place include the slow oxidation of the functional hydroxyl groups of the glucose units into carboxyl groups through the intermediate formation of aldehydes and/or ketones. The carboxyl groups ultimately eliminate carbon dioxide. There is a gradual increase in copper number with increasing period of exposure marking the continuous formation of reducing groups and the essentially slower rate at which they are further oxidised to carboxyl groups. The carboxyls do not at any stage accumulate in the chains but show a tendency to rise and fall alternately. These changes are attended by a concomitant fall in D.P. which is due to the rupture of glucosidic linkages. With the progress of exposure, the tensile strength also decreases. In a typical case, the D.P. decreased from 2563 to 739 in the course of 2400 hours of exposure while the copper number rose from 0.06 to 3.63. At the same time, the tensile strength decreased by about 65 per cent.



(ii) The course of degradation of cellulose in the case of fabrics treated with metallic hydroxides/oxides<sup>24</sup> was the same as the control (untreated) samples, subject, of course, to any acceleration or retardation of degradation displayed by the metallic hydroxides/oxides. This will be obvious from the results summarised in Table III for certain treated and untreated samples before and after exposure to sunlight for 2400 hours. The fabric containing copper hydroxide/oxide has degraded much more rapidly than the control (untreated) fabric. Where manganese is present it has retarded degradation. A remarkable feature in the manganese-treated sample is the negligible increase in its copper number at the end of the exposure. Copper number represents the total reducing power of the cellulose molecule and is comprised of the contributions by (a) end aldehyde groups in the individual chains and (b) reducing groups resulting from oxidation of the hydroxyl groups in the glucose units. On theoretical grounds, the contribution by (a) will be small compared to contribution by (b). In the case of the fabric containing manganese it would appear that the functional groups of the glucose units have not been affected indicating the possible inhibiting effect of manganese. The mechanism of this inhibition is, however, not clear.

TABLE III

*Properties of Exposed Fabrics treated with Metallic Hydroxides/Oxides*

No.	Tests.	Untreated Fabric.		Fabric containing 0.56% Mn as hydroxide/oxide.		Fabric containing 0.53% Cu as hydroxide/oxide.	
		Before exposure.	After 2400 hrs. of exposure to sun.	Before exposure.	After 2400 hrs of exposure to sun.	Before exposure.	After 2400 hrs. of exposure to sun.
1	Bursting strength in lbs.	130	45	142	115	142	0
2	D. P. . . . .	2563	739	2210	1100	2475	Below 350
3	Cuprammonium fluidity.	3	35	6	18	8	Over 45
4	Copper number . .	0.06	3.63	0.02	0.18	0.12	Over 10

(b) **Degradation by Simulated Sunlight (Mercury Arc).**—(i) While as has been mentioned earlier there are points of difference between degradation by sunlight and by mercury arc, it should be noted that there are also points of resemblance<sup>22</sup>. Thus during irradiation of a fabric by the mercury arc, there is a gradual fall in tensile strength and D.P. and increase in copper number. A part of the reducing groups formed during irradiation gets further oxidised to carboxyls which, however, do not accumulate. Again, fabrics treated with manganese hydroxide/oxide degrade much more slowly than untreated controls during irradiation, even as in outdoor exposure, to which reference has been already made.

(ii) Though irradiation by the mercury arc causes more rapid degradation of cellulose than sunlight, the actual degradation observed is much less than what may be expected from intensity measurements. This fact is evident from the data for degradation by sunlight and by the mercury arc given in Table IV.

TABLE IV

*Comparison of Natural Sunlight against simulated Sunlight in respect of Degradation of Cellulose*

Sample	Source of light causing degradation	Test results.			
		Condition of sample before test	Breaking strength (warpwise)	D.P.	Copper number
Fabric No. 1.	Sunlight	Before exposure	163	2588	0.06
		After exposure to sun for 1500 hours.	69	815	4.28
	Mercury arc	Before exposure	161	2606	0.06
		After exposure to mercury arc for 48 hours equivalent to 2640 hours of sunlight.	130	1615	1.23
Fabric No. 2.	Sunlight	Before exposure	..	2145	0.35
		After exposure to sun for 2500 hours.	..	659	6.69
	Mercury arc	Before exposure	..	2642	0.27
		After exposure for 72 hours (equivalent to 3960 hours of sunlight).	..	1892	1.55

(iii) The variation in the extents of degradation by the two sources may be traced to the difference in radiation intensities and their ultra-violet ranges. The characteristics of the mercury arc leave the fabric in an unstable state at the end of the irradiation resulting in chemical changes being set up which are carried to completion subsequently, as observed by Stillings and Van Nostrand<sup>5</sup>. According to these workers, some of the glucosidic linkages in the chains get sensitised during the irradiation resulting in the rupture of these linkages during the post irradiation period. Precise information on the mode of this sensitisation is, however, lacking. It is perhaps analogous to the well known photo-sensitisation observed with certain synthetic polymers like polystyrene, methyl methacrylate etc. subsequently leading to depolymerisation<sup>56</sup>.

(c) **Alkali-sensitive Linkages in Irradiated Cellulose.**—(i) An important finding in the Kanpur laboratories is that the glucosidic linkages which had been sensitised during irradiation and which subsequently take part in post-irradiation effect, are sensitive to alkali<sup>57</sup>. In fact the boiling of the irradiated material in alkali brings about the same fall in D.P., as would result if the material is stored

in air or oxygen for the completion of the post-irradiation effect. Some recent work has indicated that if the irradiation was extended over a long period, e.g., 48 hours the fall in the D.P. by boiling with alkali is greater than what would result by the normal post-irradiation effect. This is being further investigated.

(ii) It may, however, be noted that these linkages that are sensitive to alkali are different from the alkali-sensitive linkages formed during chemical modification in celluloses on which subject considerable work has been reported by Davidson<sup>47</sup>. Chemically produced alkali-sensitive linkages are comparatively stable and can be detected even after months of storage. It is evident that the mechanism of formation of alkali-sensitive linkages is different in the two cases.

(d) **Reducing power of Irradiated Cellulose.**—It has been noticed in these laboratories<sup>28</sup> that the reducing power as estimated by copper number attained by cellulose during irradiation remains practically unaltered during post-irradiation storage. This observation is at variance with that of earlier workers<sup>9,10</sup> who have reported an increase in reducing power after post-irradiation storage. Since the finding in these laboratories has been confirmed on a number of occasions, it is obviously true. An observation of this type has profound importance in the delineation of the mechanism of degradation. Further work is in progress.

## BARRIERS

### Different Types of Barriers and the Mechanism of Barrier Effect

(a) **Introduction.**—The problem of evolving suitable barrier treatments on cellulosic materials for the prevention of actinic degradation is admittedly difficult. Cotton fibres of different origin exhibit specific differences in their susceptibility to tendering by light<sup>58</sup> and it cannot be assumed that a barrier treatment evolved for one particular sample of cellulose will be suitable for another. Various workers<sup>23,59,60,61,62</sup> have reported on the barrier properties of different compounds for cellulose. The available evidence is mostly a record of observations made and does not furnish information on either the theoretical background regarding the choice of the barriers or about the mechanism of protective effect. Experiments have been carried out in these laboratories to study the protection afforded by a wide variety of compounds, both of organic and inorganic origin.

(b) **Investigation of certain Barrier Treatments.**—(i) **Organic Barriers.**—The effect of incorporating small quantities of salol (phenyl salicylate) in cellulose esters on their resistance to actinic degradation has been studied by Meyer and Gearhart<sup>63</sup>. They have reported that this chemical is effective even at a concentration of 1 per cent. This effect is manifest possibly owing to the fact that salol absorbs ultra-violet radiations and emits the resultant energy in some form not harmful to the material to which it has been added. It was thought desirable to investigate salol in relation to cellulose. Additionally, in view of the importance of urea-formaldehyde (U/F) resin in textile finishing it was considered of interest to investigate the barrier properties, if any, of this resin<sup>28</sup>. Treatment with salol was carried out in two concentrations of 1 and 4 per cent. in alcohol solution, giving a hold-up of about 80 per cent. on the weight of the fabric. Treatments with urea-formaldehyde (U.F) were carried out

in two concentrations, 4°Tw and 8°Tw. The U.F treated fabrics were cured at 150°C for three minutes. The treated pieces along with controls were exposed to the mercury arc and the breaking strength determined on samples drawn at suitable intervals. The results<sup>28</sup> have shown that while treatment with 1 per cent. salol accelerates degradation, some protection is afforded when the concentration is increased to 4 per cent. In the case of treatment with urea-formaldehyde (UF), protection is obtained in both the concentrations investigated, the extent of protection being greater with the higher concentration.

(ii) **Inorganic Barriers.**—A planned exposure trial was carried out at Kanpur<sup>28, 64</sup> for investigating the protection afforded to cellulose fabrics by various metallic hydroxides/oxides in different concentrations. The metals investigated were chromium, copper, iron, manganese, tin, titanium and aluminium. The metals were deposited as their oxides on the fabric by a double bath process involving initial treatment in a soluble salt solution and subsequent decomposition with aqueous solution of alkali. The treated fabrics and untreated control pieces were exposed during hours of sunshine for a total period of 2400 hours. The results showed that manganese (0.56 and 1.3 per cent) on fabrics retards in a remarkable manner the course of actinic degradation (*vide* results in Table III). Iron and aluminium in higher concentrations showed some protective effect in the early stages of exposure but were not suitable for long periods of exposure. Chromium did not have any effect on degradation while copper, tin and titanium were found to accelerate degradation, copper being the most degrading of the three.

(c) **Mechanism of Barrier Effect.**—Some attempts have also been made<sup>22</sup> to study the mechanism by which manganese hydroxide/oxide or any other agent could offer protection against actinic attack. As in the case of salol it was felt that manganese hydroxide/oxide should have a high absorption in the ultra-violet region of radiant energy while a compound like copper hydroxide/oxide which accelerates degradation should have low absorption. The ultra-violet absorption characteristics of these two compounds were determined by using uniform films of the bases prepared on quartz plates. The thickness of these films and their ultra-violet absorption coefficients are given in Table V. It will be observed that weight for weight copper hydroxide/oxide has a much-higher ultra-violet absorption coefficient than manganese hydroxide/oxide.

TABLE V.

*Ultra-violet Absorption of Copper and Manganese as Hydroxide/Oxide*

No.	Nature of film.	Density of film.	% absorption in U—V. region.	Region of absorption
1	Manganese hydroxide/oxide	182 mgs/ sq. ft.	46	Uniform over U—V region.
2	Copper hydroxide/oxide	50 mgs/sq. ft.	58	300—400 m $\mu$ .

This would indicate that the mechanism of protection cannot be explained on the basis of absorption of ultra-violet rays by the protective agent. The possibility that the protective action is catalytic is supported by the fact that manganese in 0.56 per cent. concentration on cellulosic fabric is found to be more effective<sup>28</sup> against actinic degradation than manganese in 1.3 per cent. concentration. At the same time it should be noted that fabrics containing manganese hydroxide/oxidé show very little increase in copper number on exposure to solar radiation (Table III) while the fall in D.P. is appreciable. This would indicate that the treatment has afforded higher 'protection' to the hydroxyls of individual glucose units than to the glucosidic linkages. Such an influence may be exerted through chemical or some other type of combination with the hydroxyl groups. A combination of this nature should be weak since it has been observed that the manganese may be leached out completely by very weak acids (pH 6.4) in the cold. Consequently, fabrics containing manganese hydroxide/oxide formed *in situ* lose their metal content rapidly during exposure to weathering<sup>22</sup>.

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