

The deterioration of cellulose

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Abstract

This review covers the literature up to about 1969, which describes the deterioration of cellulosic materials through exposure to light, ultraviolet and high energy radiation.

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THE DETERIORATION OF CELLULOSE

A literature review

The effects of exposure to light, ultra-violet and high energy radiation

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Introduction.

Cellulose is the principal constituent and the source of strength of articles made from wood, paper, cotton, linen and other vegetable fibres. The deterioration of the cellulose becomes apparent as a progressive loss of strength and elasticity, sometimes but not always accompanied by discolouration. This deterioration is caused by subtle chemical changes which affect not only the physical properties of the object but also the rate and course of subsequent ageing processes.

Purified cellulose is much more stable than the impure or chemically altered material of its various commercial forms. The chemistry of cellulose degradation is therefore inseparable from the chemistry of its impurities. The number of substances that are commonly found in association with cellulose is very large and the nature of most of them is obscure. Many may have little effect on its permanence but some accelerate and others may inhibit decay. In no case has the detailed course of the reaction been elucidated.

I have not tried to collect all the data available ; there is too much and it has been reviewed already (3,67). My aims are to describe the causes of deterioration likely to affect museum objects, to give an idea of the magnitudes of their effects, to explain the current theories of their mechanisms, and to suggest what further information is needed and what processes or materials show promise of slowing the rate of deterioration.

Only inanimate agents of decay are described, a restriction which is extended to exclude the effects not only of micro-organisms but also of conservation methods.

High energy radiation.

Cellulose is seriously damaged by doses of about 10^6 rad (*) of ionizing radiation of almost any kind (11, 12, 17, 18, 59, 68, 75). The dose from background radiation seldom exceeds 0.12 rad per year (20, 47, 50). High energy radiation is therefore not yet a serious danger to cellulose.

Far ultraviolet radiation

(of wavelength less than about 3 400 Å).

Far ultraviolet radiation causes degradation of cellulose by direct breaking of chemical bonds. The photolysis of cellulose, as this phenomenon is called, has been thoroughly studied but such radiation is not, or need not be present in museums. Its only interest to conservation scientists is that photolysis commonly interferes with the interpretation of the results of experiments on the photosensitized degradation of cellulose in which mercury vapour lamps have been used (37, 43). The photolysis of cellulose has been reviewed recently (60).

Near ultra-violet and visible radiation 3 400 - 7 000 Å.

At wavelengths greater than 3 400 Å photolysis does not occur but degradation of cellulose continues through photosensitized reactions whose proposed mechanisms will be des-

(*) Rad : The quantity of radiation which deposits 100 ergs of energy per gram of material. I have assumed that cellulose has an absorbing power approximately equal to that of animal tissue.

cribed later. The result is loss of strength, chemical changes of great variety and, in some circumstances, discolouration.

The rate of deterioration depends on numerous factors but it is, in normal museum conditions, fast enough to deserve detailed investigation.

Experimental conditions vary greatly so I have derived rough estimates of the rate from several publications.

The most commonly used light sources for experiments are the carbon arc, the mercury vapour lamp and daylight. At first sight it might seem that the first two sources would be best for measuring the rate of reaction. But their spectral energy distribution is very different from that of daylight or any commonly used artificial light and it varies with the operating conditions and design of the lamp. The spectral sensitivity of cellulose is unknown (see below) and so daylight is the only source which allows even an appropriate calculation of the rate of deterioration of cellulose in a museum.

Egerton (24) exposed 180 denier (*) cotton yarn to daylight, behind glass. At 100 % relative humidity the yarn lost 17 % of its original strength, and in complete dryness 10 %, during an exposure of 4 000 microwatt hours per square centimetre per 10 Å at 4 600 Å. From this one can estimate a strength loss of 14 % during an exposure of about three million lux hours (Mlxh) at 60 % RH.

This is the fastest rate of deterioration that I have found in the literature. The data of Little (49) suggest a loss of strength of 14 % during about 50 Mlxh. From Jones (35) one can estimate that the cotton yarn lost 50 % of its original strength in 68 Mlxh. The cotton cloth exposed by Goldthwait & Robinson (32) lost 47 % of its tensile strength after an exposure of roughly 180 Mlxh. Richter (66) found that paper made from purified wood fibre lost about 30 % of its resistance to repeated folding during 100 hours of exposure (each side) behind glass to sunlight. This corresponds to about 10 Mlxh. The fold endurance of paper is acknowledged to deteriorate faster than other physical properties. Feller (29) has derived figures of similar magnitude for the rate of deterioration.

(*) Denier = the weight in grams of 9000 metres of yarn.

These figures are based on rough estimates of the exposure conditions and on the interconversion of physical units which have no fixed relationship (*). They must therefore be taken as only a very approximate guide to the rate of deterioration of cellulose and are presented here because much of the subsequent information on rates of deterioration in different circumstances is comparative.

Let us take 50 Mlxh of daylight as a light dose likely to cause serious physical deterioration of cellulosic materials and assume that the reciprocity principle (see below) is valid in this case.

Objects on permanent display in museums are seldom illuminated with less than 300 lux for about ten hours a day. A dose of 50 Mlxh would accumulate in about fifty years.

Daylight is therefore an important cause of damage to cellulose.

The effect of artificial light cannot yet be calculated but some results on the effects of fluorescent lamp light have recently been obtained by Leene (44).

The nature of the damage and the rates of the various reactions which occur depend on a large number of factors which themselves show an intricate interaction in their effects. The influences which have so far been recognized as important are these :

- Light intensity.
- Spectral energy distribution of the light.
- Temperature.
- Physical form of the material : thickness, density.
- Composition of the surrounding atmosphere : concentrations of oxygen, water vapour & pollutants.
- The state of chemical degradation of the cellulose.
- Natural impurities of cellulosic materials.
- Artificial impurities : dyes, pigments, acids, alkalis and metal salts.

(*) The exposure has been given in a variety of units, most of which are not interconvertible. The commonest are : sun-hours, exposure time, langleys and lux-hours. I have taken the langley as equal to 1.2 kilolux-hours (klxh) and the sunlight-hour as equivalent to 70 langleys. Exposures given in weeks are not an adequate measure of the radiant energy received. The usual measure of light energy in museums is the lux so I have converted all the experimental data into this unit. For details see Appendix A.

Light intensity.

It has been generally assumed in the conservation literature on fading and degradation of materials by light that the reciprocity principle holds. The rate of reaction is assumed to be proportional to the light intensity (other factors being equal). By the same principle the total quantity of light energy reaching the object, regardless of the rate at which it is received, governs the amount of damage done.

At present we have no other way of relating the results of experiment with the museum environment. There is no proof that reciprocity holds over the great differences of light intensity between the apparatus of impatient scientists and the dim galleries of a museum. There is certainly no theoretical justification for assuming it since the details of the reactions through which cellulose decays in light are almost completely unknown.

A small amount of experimental work provides circumstantial evidence for the reciprocity of cellulose photo-degradation over a narrow range of light intensities.

Aston (6) showed the relationship between the fraction of the original tensile strength retained by linen fabric (coated with cellulose acetate) and the energy of the daylight incident upon it throughout the year (fig. 1).

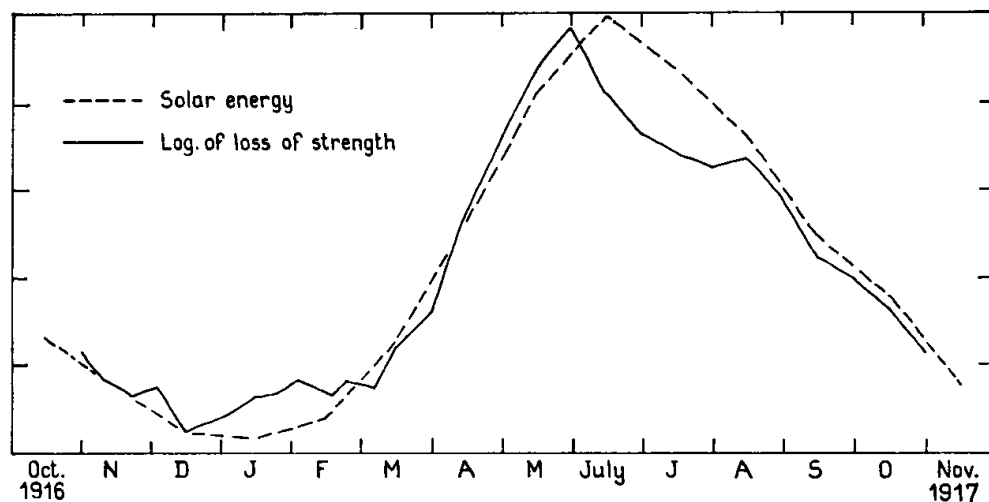


Fig. 1. — Relation between intensity of solar radiation and deterioration of linen cloth (coated with cellulose acetate). Exposed in the open. Each strength measurement was plotted at the middle of the three month exposure period to which the sample was subjected. From Aston (6).

The temperature and relative humidity of the air and the spectral energy distribution of daylight change with the seasons so no significance can be attached to the slightly greater degradation per unit light energy observed in winter.

Launer & Wilson (42) irradiated newsprint with carbon arc light at various intensities for various times. Their results are shown graphically in figure 2. It is not possible to decide, from the information given, if the divergence of the tracks on the graph has any significance.

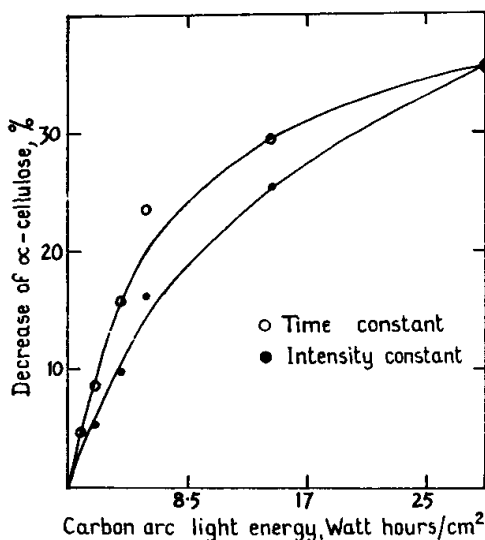


Fig. 2. — The rate of deterioration of newsprint irradiated for a constant time at various light intensities: ○ and at constant light intensity for various times: ● From data of Launer & Wilson (42).

In the same article there are examples of two other ways in which the reciprocity law may apparently fail even when the individual reactions obey it:

Irradiated paper yellowed faster in the dark than paper which had not been exposed to light. It is quite possible therefore that in a dim light paper may yellow by a reaction independent of light faster than it is bleached by photochemical reaction. The net result would be a progressive yellowing rather than the bleaching predicted by accelerated testing.

Samples of paper exposed to the carbon arc light without strict temperature control yellowed

but when the paper temperature was held at 30 ° C. bleaching occurred. Many experiments in which bright light sources have been used have allowed the samples under test to heat far above room temperature and the results cannot be extrapolated to predict the effect of dim light at normal temperature (fig. 19).

The high temperature generated at the face of the specimen by absorption of light reduces the relative humidity of the air surrounding the fibres. The photochemical deterioration of

cellulose has a temperature coefficient and is also dependent on the moisture content of the fibres.

The interplay of all these factors makes the evaluation of accelerated ageing tests difficult and it would be unwise to place too much reliance on the reciprocity principle in discussing the rate of decay of paper and cloth in museum conditions.

The spectral energy distribution of the light.

It is evident from the results of numerous experiments that cellulose is more rapidly damaged by u.v. and blue radiation than by light of equal energy but longer wavelength. The wavelength dependence has not been accurately measured. No source has been available with sufficient intensity to provide enough light in a narrow waveband. The mercury spectrum has been used but its action has usually been hastened by using low grade paper or by immersing the cellulose in a solution of an oxidising agent. Filtered daylight has also been used but it has a fluctuating spectral energy distribution and bandpass filters of sharp cut-off, high transmittance and permanence have only recently become available.

Aston (5) exposed linen threads in a row parallel to the lines of a mercury spectrum, each of which covered about 6 threads. The exposure lasted four weeks. The threads were removed and the number that broke at the irradiated part gave a rough measure of the damage done. The mercury lines

Effect of weathering on doped linen fabric under coloured glasses. April 1919 - Nov. 1921		
Approximate short wave limit of transmission of filter (A)	Colour	Relative Log. (Initial strength/final strength) (100 for exposure in the open)
3350	clear	73
3350	blue	83
3450	violet	66
3450	purple	56
3650	blue-green	23
4900	green	7
5100	orange red	5
5650	red	4

from 2570 to 3660 Å caused considerable damage but the visible spectral lines caused no damage. The statistical uncertainty was very large so no quantitative results could be deduced. A similar experiment using the spectrum of sunlight failed to work. In a later experiment (1, 62) coloured glasses were used over doped linen fabric exposed to daylight.

The lack of detailed spectral transmission data for the filters prevents accurate evaluation of the results.

A very similar experiment was made more recently by Fynn and co-workers (31). They also were hampered by poor filters. Their blue filter for example transmitted shorter wavelengths than the u.v. filter. The *Degradative Index* given by the authors is not very helpful as it compares the action of equal amounts of radiation of very different bandwidths.

It is possible to deduce from their data that about four-fifths of the loss of strength of cotton cloth irradiated by daylight through glass is caused by wavelengths between 3000 and 4000 Å (*). The authors also found considerable degradation in red and yellow light, which is not in agreement with the results of others.

Köhler (40) exposed papers of various constitutions to daylight filtered through coloured glasses. He measured the loss of resistance to folding and the copper number of the papers. He also gave the spectral transmission of the filters. Only two filters had sufficiently sharp cut-offs to give meaningful results :

(*) The rate of deterioration is first order. I have multiplied the gradient of the plot of deterioration against log (time) for each filter by a small factor to account for the differences in peak transmission of the filters.

<i>Filter</i>	<i>Corrected rate constant</i>
Corex (clear)	50
u.v.	41
blue	39
yellow	21
red	21

Both the blue and the corex filter transmit more u.v. than the u.v. filter. The fact that the blue filter causes about as much degradation as the u.v. suggests that it is the region between 3000 and 4000 Å which is causing most of the damage. The combined transmission of u.v. and red filters is very much exceeded by that of the clear glass in all spectral regions so the high rate reported for long wavelength light is difficult to understand.

	Copper number & % fold retention After 62 days exposure to daylight	
Clear glass	7.11	6
Antikglas (transmits wavelengths > 5000 Å)	2.17	74
Unexposed	1.56	100

Whittaker (83) exposed viscose rayon to daylight under coloured filters and obtained results qualitatively similar to those of Aston. His experimental data was much more meagre and the results will not be given here.

Lanigan (41) in an ingenious experiment exposed moist cellophane film to the mercury spectrum and revealed the formation of oxycellulose at the irradiated points through its power of reducing silver in complex solution to the metal, which stained the cellophane. A graph of the optical density of the film against the wavelength of the irradiating light showed no detectable damage in the visible region but appreciable blackening in the u.v. spectral region. The strong mercury line at 365 m μ caused considerable damage. The information is qualitative but impressively presented (fig. 3).

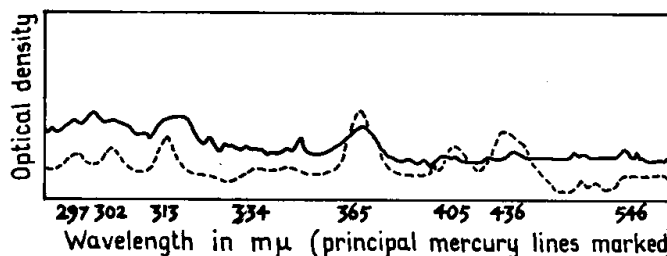


Fig. 3. — Optical density of viscose sheet and viscose dyed with Cibacron yellow R----- irradiated with mercury spectrum in moist air & developed by reduction of complex silver ion. From Lanigan (41).

Little (49) gives a table of the effect of radiation of varying minimum wavelength on the fluidity of cotton. The great potency of u.v. radiation is made clear.

Cotton exposed to daylight under high humidity		
Screened by	Short wave cut-off (m μ)	Fluidity increase
Quartz	280	14.8
Glass	310	5.9
OY 18	430	0.3

All the experimenters who used coloured filters observed greater degradation in blue than in white light (which included all the radiation passed by the blue filter). The phenomenon remains unexplained. It may possibly be due to the smaller heating effect of blue light and the consequent higher relative humidity at the surface of the cellulose.

The data given so far refer to fairly pure cellulose. The presence of other materials very much alters the effect of different spectral regions.

The spectral sensitivity to discolouration of ground wood pulp (57) closely follows the ultra violet absorption of lignin. The paper is sensitive mainly to ultra violet radiation : in light of wavelength greater than about 480 m μ it bleaches slightly.

The bleaching effect of light of long wavelength is probably attributable to the bleaching of the coloured degradation products of cellulose rather than to any chemical change in the cellulose molecules.

The spectral sensitivity of low grade paper was given by Judd (33, 34, 36, 78, 79). There is no experimental detail, and no indication of what criterion of damage was used. In view of the

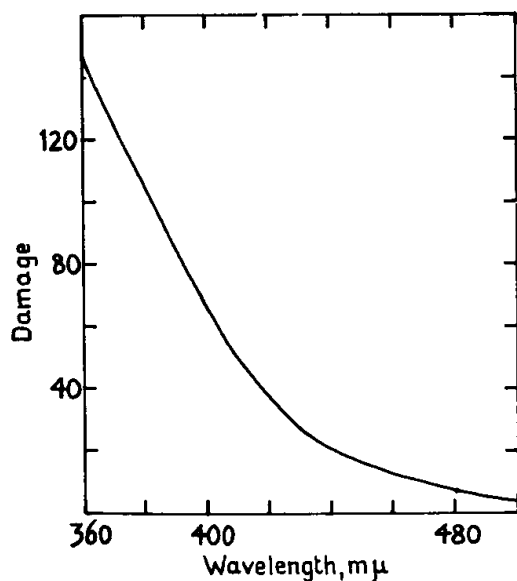


Fig. 4. — Dependence of damage to low grade paper on the wavelength of the incident light. From NBS (78).

work mentioned above which suggests that the behaviour of mechanical wood pulp is largely conditioned by the presence of lignin (which occurs in no other commonly used cellulosic material except Jute), too much reliance should not be placed on the calculations based on these figures (fig. 4).

Dyeing and pigmenting of cellulose materials may greatly increase not only the damaging effect of light but also the range of wavelength over which it is active. The work of Lanigan (41) showed this very

clearly in the case of certain vat dyes. The dyed cellophane showed reducing properties where it had been irradiated with lines of the mercury spectrum in the visible region (fig. 3). The damaging wavelengths depend on the individual dye and not on the cellulose.

Estimation of the damage done to cellulose by museum lighting demands a knowledge of the spectral energy distribution of the source used for the experiment, the s.e.d. of the museum light source, and the spectral sensitivity of the cellulosic material. The reciprocity principle, or some other relationship between light intensity and reaction rate, must be assumed. Such a calculation was published by L. S. Harrison (33). It is valid for estimating an unspecified sort of damage to low grade paper by the fluorescent lamps tested. Though obviously qualitatively correct it must not be allowed to obscure the fact that the spectral sensitivity of cellulose is unknown and is worth finding out.

Temperature.

The temperature coefficient of photochemical reactions is difficult to measure because the light energy is mostly turned to heat at the surface of the sample and so a thermocouple must be embedded in the sample, or alternatively the sample must be very well ventilated with a rapid stream of air at constant temperature. Another complication is that unless precautions are taken a rise in sample temperature above the ambient conditions will cause a drop in the relative humidity around the fibres of the sample. This generally causes a fall in the rate of reaction which masks the acceleration of the reaction by heat. At the high temperature unavoidable in accelerated ageing apparatus the nature of the deterioration may change if the cellulose when damaged by light becomes susceptible to thermally controlled reactions. In any case it becomes difficult to distinguish between the temperature dependence of the photochemical reaction and thermal acceleration of non-photochemical reactions.

Probably because of these experimental difficulties there is not much information on the temperature coefficient of cellulose degradation by light.

Egerton & Shah (27) irradiated viscose with a high pressure mercury vapour lamp (maximum intensity at about 365 m μ) and showed that at normal temperatures the reaction has a small

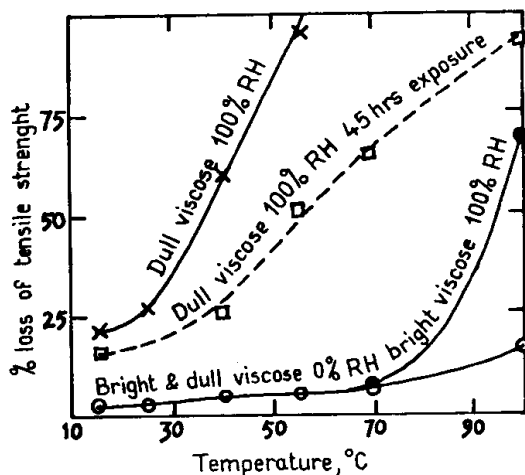


Fig. 5. — Viscose yarn, with & without TiO₂ delustrant, exposed for 95 hours to a high pressure mercury vapour lamp. From Egerton & Shah (27).

positive temperature coefficient (fig. 5). The graph also shows that the decomposition of viscose sensitized by titanium dioxide has a very large temperature coefficient.

Some vat dyes show the same behaviour. Here again we see how the degradation of cellulose is conditioned by the nature of its impurities.

The yellowing of ground wood pulp in light increases with temperature much more than can be accounted for by the non-photo-chemical darkening process (80, 84). All

other papers bleach in light so this is probably a reaction of the lignin-cellulose mixture and not characteristic of other cellulosic materials.

The physical form of the material.

The light flux reaching the inside of a piece of cloth or paper is less than that at the surface because of reflection from the fibre surfaces. In fact the fibres at the very back of the paper will receive a light flux equal to the transmittance of the paper. For a thick paper this may be less than 5 % of the incident light. The rate of deterioration therefore is probably proportionately lower. In the case of dyed or delustred (pigmented) fibres the light flux on the shaded side may be much lower. This has two effects : firstly it means that a thick cloth or paper will retain a greater percentage of its original strength on exposure than a thin cloth, and secondly, it means that tests for degradation that involve taking an average over the whole test piece may give misleading results.

In fact all tests except reflectance and fibre strength take an average over many fibres of which a large number have not received the same light dose as the light measuring instrument (if used).

A theoretical treatment of the effect of this on the evaluation of DP is given by Flynn (30).

Cunliffe & Midgley (19) found that the average strength (per unit cross sectional area) of the fibres of an exposed cotton yarn was about the same as that of the yarn itself but the strength of the fibres exposed singly was about half this value.

Little (49) showed an interesting graph (fig. 6) of the effect of yarn thickness and twist on photodegradation.

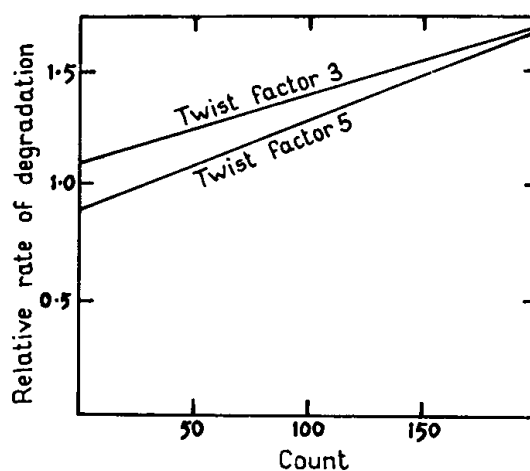


Fig. 6. — The effect of density & thickness on the rate of degradation of grey cotton yarn exposed to daylight for 4 months. From Little (49).

Kleinert and Mössmer (39) showed the relationship between % fall in tensile strength and yarn thickness of viscose :

Denier	% fall in strength
1.5	37.4
2.7	27.5
3.75	21.7
4.5	14.1

The two graphs (fig. 7) taken from Barr & Hadfield (8) show clearly the different effects of tests which measure total damage (tensile strength) and those which average the damage through the thickness of the specimen (fluidity). The rate of loss of strength is about the same for both coarse and fine fabrics. The loss of strength calculated as a percentage of the original strength is very different.

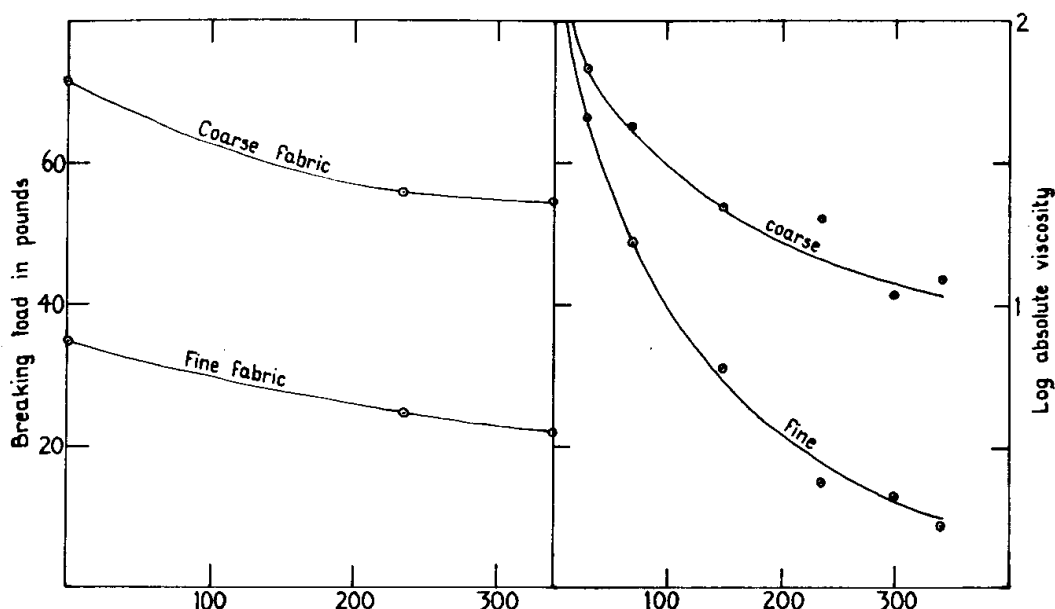


Fig. 7. — Exposure to daylight of cotton fabrics of different thickness. From Barr & Hadfield (8).

MacClaren and co-workers (51) measured the viscosity of each of the layers of a pile of thin papers irradiated by a mercury vapour lamp and observed a very rapid drop in degradation with depth. Damage was limited to the top six thousandth of an inch.

To the effect of attenuation of the light with increasing specimen thickness must be added a possible shielding of the interior by degraded cellulose on the surface (10). This may absorb u.v. radiation and possibly slow the rate of diffusion of oxygen to the centre.

Discolouration is usually measured with the test sample laid on a white plate or on a pile of unexposed pieces of the same material. It is therefore independent of thickness (except for very thin material).

The influence of the atmosphere.

1) Effect of atmospheric water vapour.

The moisture content of cellulosic fibres depends mainly on the relative humidity of the atmosphere. Nearly all investigators have therefore used the RH rather than the moisture

content of air as a parameter in their experiments. Irradiation of cellulose lowers the RH of the air close to the fibres because they are at a higher temperature than the ambient air. The temperature difference varies with the colour of the object, the light intensity and the ventilation of the fibres.

The RH among the fibres is more or less unmeasurable. It is always lower than that of the ambient air.

The degradation of cotton cellulose by light increases with a rise in relative humidity of the surrounding air. Egerton showed the effect of light on cotton at 0% and 100% RH (4,48) (fig. 13).

Viscose rayon on the other hand is quite insensitive to changes of RH but when delustred with titanium dioxide it becomes extremely sensitive to RH (fig. 5) (24).

The photochemical tendering of vat dyed cotton shows, in many cases, a dependence on RH with an intermediate maximum at about 40 % RH and a yet higher rate at 100 % RH (4,48) (fig. 13).

There is little information on the effect of intermediate values of RH on the photodegradation of undyed cotton. Ashton & Probert (4) gave intermediate values but the degradation was small because they were mainly concerned with sensitizing vat dyes.

Launer & Wilson (42 43) compared the degradation of papers by carbon arc light at 0 % and 58 % RH.

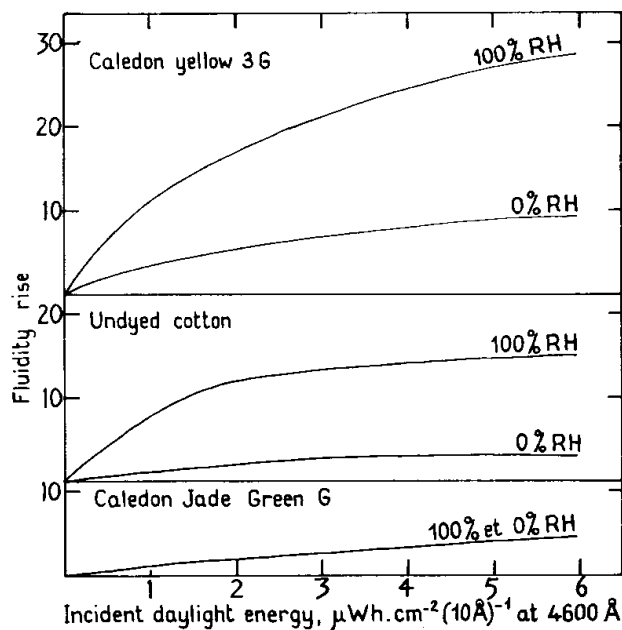


Fig. 8. — Effect of relative humidity on the rate of degradation of dyed & undyed cotton. From Egerton (22).

Effect of moisture on the degradation of paper irradiated by carbon arc light						
	Decrease in α cellulose		Fluidity increase		Fall in pH	
	0 %	58 %	0 %	58 %	0 %	58 %
Relative humidity :						
Type of paper.						
Soda-sulfite :	2.7	5.6	1.2	2.9
(3 papers)	4.8	7.0	1.2	4.0	0.55	0.4
	6.2	6.2	1.4	2.8	0.55	0.45
Newsprint :	20.0	31.3	1.6	1.7
New rag :	5.2	4.2	0.9	1.3	0.45	0.3
	5.3	3.0	1.7	1.7	0.35	0.1
Old rag :	5.2	3.5	1.0	1.4	1.15	0.85
	6.8	4.0	1.3	1.4	0.8	0.3
From Launer & Wilson (43).						

	Decrease in α cellulose		Decrease in DP		Original DP
	0 % RH	58 %	0 % RH	58 %	
New cotton rag	1.1	0.4	230	445	1660
New rag with clay & alum.	3.3	1.2	20	65	695
Old rag, clay & alum.	9.6	6.1	75	75	575
From Launer & Wilson (42).					

Notice that low RH causes greater damage to cotton cellulose if α cellulose content is the criterion of decay but less if damage is assessed on fluidity measurements.

Absence of water vapour inhibits the rate of bleaching of paper in light.

Water vapour reduces damage to cellulose by far u.v. radiation (43) so experiments in which mercury vapour lamps have been used as a source must be interpreted carefully unless exposure has been made through ordinary glass.

2) Oxygen.

Many workers have observed a great decrease in light damage to cellulose in the absence of oxygen. The relationship

between loss of strength of cotton and oxygen pressure has been given by Egerton (22) (fig. 9).

In the far u.v. region oxygen is not necessary for cellulose degradation (43) and for this reason the results of experiments made with mercury vapour lamps may be misleading. Nevertheless the results of Stilling & Van Nostrand (73) in mixed near and far u.v. are of interest :

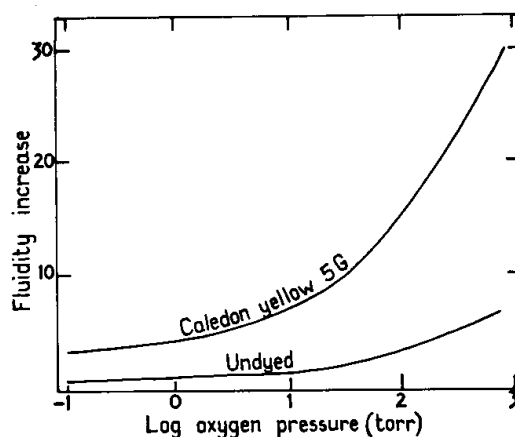


Fig. 9. — The effect of oxygen on the rate of degradation in daylight of dyed & undyed cotton. From Egerton (22).

Oxygen concentration %	Copper number	% α cellulose	DP
Unexposed	0.28	96.8	1400
0	0.42	95.1	1290
10	0.58	92.2	950
20	0.78	90.0	870
100	1.49	82.9	740

Launer & Wilson (42) exposed newsprint to carbon arc light in various atmospheres :

% oxygen concentration	% decrease in α cellulose	Increase in Copper number	Lowering of pH
21	31.3	15.7	1.7
1.1	17.1	—	1.3
0.21	13.7	—	1.1
0.11	12.2	4.6	1.0
0.03	6.5	2.2	0.75

Yellowing decreased as the oxygen concentration diminished. The bleaching of most papers is inhibited by exposure in an inert gas. Ground wood pulp however is bleached by exposure in nitrogen (43). Bleaching is of course as much a symptom

of chemical change as yellowing and there is no doubt that much less chemical change of cellulose occurs on exposure in an inert gas. Launer & Wilson pointed out that paper exposed to light in absence of oxygen does not suffer the accelerated discolouration on subsequent storage which they noticed with paper irradiated in air.

3) Air pollutants.

There is evidence that sulphur dioxide and perhaps other pollutants accelerate the photochemical decomposition of cellulose. Jones (35) described the effect of exposing dyed cotton and viscose rayon to light in an atmosphere of damp air and sulphur dioxide with and without nitrogen dioxide. The acceleration by light of the loss of strength and rise in fluidity is very marked.

Viscose Rayon dyed and exposed to daylight for 2 months in various atmospheres						
	Dry air	Dry air + SO ₂ ** unexposed	Dry air + SO ₂ exposed	Moist air*	Moist air* + SO ₂ unexposed	Moist air* + SO ₂ exposed
3 % Caledon Blue RC :						
Hrs. sunshine	210	0	213	210	0	210
% loss of strength	0	2	5	3	11	53
Fluidity rise	7.1	— 1.1	1.4	2.4	6.3	17.1
Acidity (% H ₂ SO ₄)	—	—	—	—	0.05	0.07
4 % Caledon brown G :						
% loss of strength	4	10	8	1	20	50
Fluidity rise	0	1.4	1.8	1.3	5.4	16.5
Acidity	—	—	—	—	0.04	0.04
** 0.3 % SO ₂ .						
* Bubbled through distilled water.						
Based on data of Jones (35).						

Little (49) described some experiments which showed that light greatly accelerates the damage caused by sulphur dioxide :

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Effect of Sulphur Dioxide and Light on Cotton		
	Fluidity increase	
	Clean air at 90 % RH	Air with SO ₂
Unexposed	0	0.2
Exposed 4 days	1.8	11.8
Exposed 10 days	3.5	18.4

The damage caused by light to cotton yarn in moist air with sulphur dioxide was measured by Cunliffe & Midgley (19). The damage was considerably greater than that in moist air alone but it is impossible to deduce how much was caused by photochemical action (also far u.v. radiation was present).

The oxidising smog of western American cities causes photochemical damage (55).

State of degradation of the paper.

Launer & Wilson (42) showed that paper made from old rag was less stable than that from new rag (fig. 15).

Effect of pre-degradation on the light damage of cellulose.		
	Decrease in α cellulose % during 40 hrs irradiation by carbon arc.	Lowering of pH
Papers		
New rag with 10-13 % clay	2.0	0.0
& a small amount of rosin	4.0	0.0
in some cases	2.6	0.2
	5.5	0.3
	3.4	0.5
	3.7	0.1
Old rag 12 % clay	5.3	0.4
Some with rosin	6.2	—
	6.2	0.8
	7.1	0.3

Natural impurities.

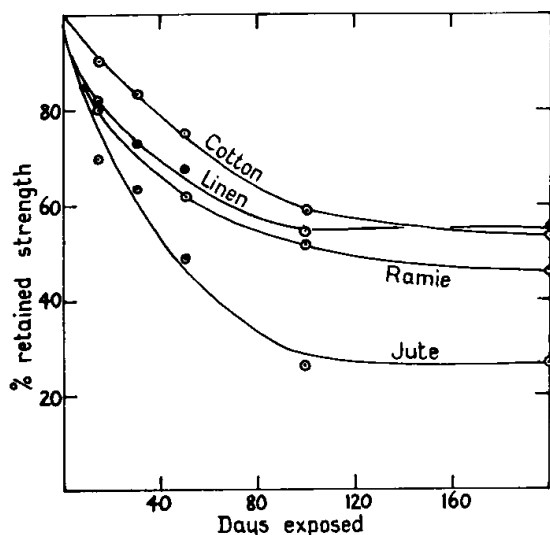


Fig. 10. — Resistance to light degradation of various cellulosic fibres. From Turner (76).

Some natural impurities of cellulose have an important influence on the rate of photochemical decay. Lignin almost certainly accelerates degradation.

The relative rates of deterioration of cotton, linen, ramie and jute were given by Turner (76) (fig. 10). The data were obtained in the open however and the relative endurance of the different fibres may be different when exposed behind glass (49) (fig. 11).

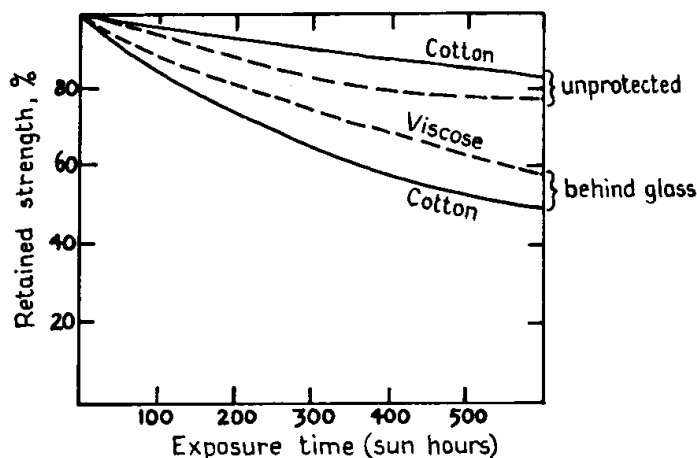


Fig. 11. — Effect of glass on the relative light stabilities of cotton & viscose. From Little (49).

Jute is very sensitive to damage by light (14) :

% strength loss of yarn exposed to north daylight behind window glass		
Fibre	7 months	12 months
Jute	40	50
Hemp	30	50
Cotton	20	32
Linen	18	20
From Bot & v. Vreeswijk (14).		

Launer & Wilson compared paper made from pulps of different origin. The nature of the purification treatment and residual chemicals probably have as much influence as the degree of purification achieved so it is difficult to interpret this data (fig. 15). There is no doubt that the process of preparing pulp for paper-making has a profound effect on the lightfastness of the product.

Groundwood, which receives almost no purification treatment is notably sensitive to light, suffering both discolouration and loss of strength (42). The discolouration has been attributed to decomposition of lignin with some accompanying damage to the cellulose (80). Many experiments on mechanical wood pulp have involved rather short exposures and the initial yellowing is followed by slow bleaching (21).

The effect of light on groundwood paper has been reviewed and studied by Lewis, Nolan and co-workers (45).

The rates of deterioration of bleached and unbleached cotton have been compared. Cunliffe & Midgley (19) found that to begin with bleached cotton degraded more than raw cotton but the loss of strength became nearly equal after long exposure. Bayley & co-workers (10) found an exactly opposite effect.

Dyes and pigments.

Most dyes and pigments have no appreciable effect on the rate of degradation of cellulose. Some have a protective effect. This may in some cases be a genuine inhibition of the reaction or in others simply a filtering and absorption of the light rays. Certain dyes have a powerful accelerating effect on photo-degradation (see fig. 8, 9 & 12) notably some orange and yellow vat dyes and a few basic and sulphur dyes (4, 22, 23, 24, 48, 77). Zinc oxide and some forms of titanium dioxide, which are used as delustrants for fibres, also cause photochemical damage (fig. 5).

Vat dyes not only accelerate the action of light but also change the wavelength at which its action is greatest (fig. 3).

In general the rate of reaction increases with relative humidity with an intermediate maximum at about 40 % RH (4,48) (fig. 13).

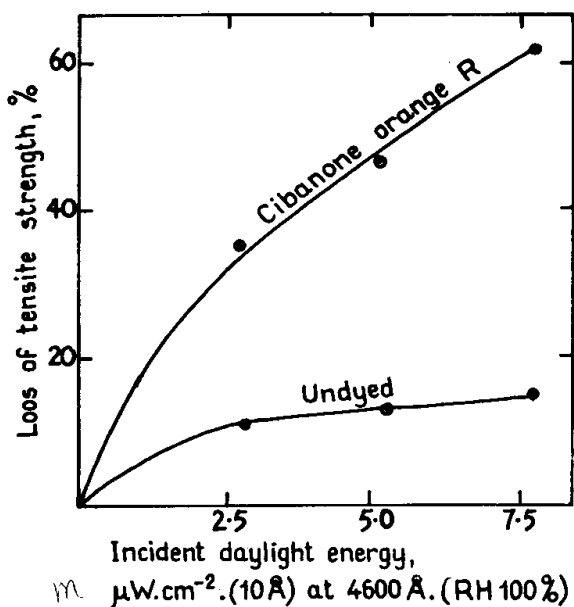


Fig. 12. — Acceleration of photochemical damage to cotton by a vat dye. From Egerton (22).

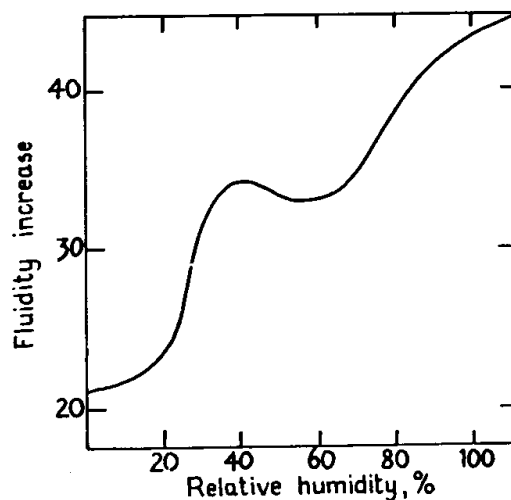


Fig. 13. — Effect of RH on the sunlight degradation of cotton dyed with Caledon yellow 5 G. From Little (49).

Egerton (27) believe that different reaction mechanisms operate at high and low RH (fig. 5). This is supported by the observation of Little (48) that the relation between degradation of cellulose and dye fading, noticeable at high RH, does not hold at low RH.

The temperature coefficient of these reactions is high (fig. 5).

There is no information on the effect of natural dyes on the photo-degradation of cellulose.

Acids alkalis and salts.

Cellulose is most stable in a neutral condition. Both acid and alkali cause damage independent of light so it is important to separate the processes. This can be done if the temperature of the test specimens is kept low.

Agster (2) measured the change in DP with exposure to daylight of viscose impregnated with sulphuric acid or sodium hydroxide (fig. 14). A similar experiment was made with wood

pulp by Lewis & co-workers (46) who found increased darkening of the paper at high and low pH. However their experiment may have reached a rather high temperature.

The presence of ammonia increases the rate of degradation of cotton in light (19).

Egerton (26) observed an increase in degradation with alkali content of cotton.

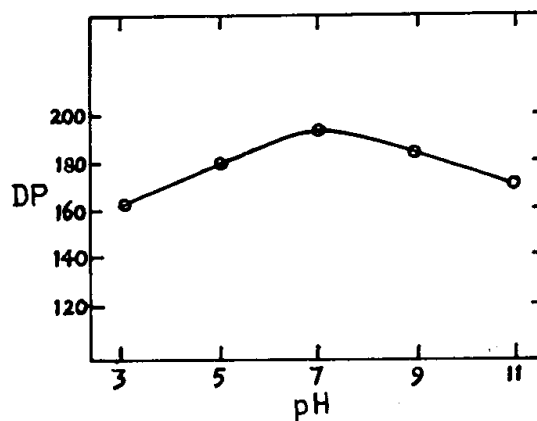


Fig. 14. — Viscose rayon exposed to daylight behind glass for 16 weeks. pH adjusted by impregnation with NaOH or H₂SO₄. From Agster (2).

Cotton treated with sodium carbonate solution and exposed to mercury vapour lamp (high pressure) at 100 % RH	
% Conc. of solution	Fluidity rise
0	7.9
1	15.0
3	26.8
8	32.0

Little (49) showed that the acceleration of tendering by residual alkali is greater at high RH.

Effect of residual alkali on the degradation of cotton by light		
	Fluidity increase	
	Neutral	Alkaline
10 % RH	1.5	2.9
30 % RH	3.8	17.7

Richter (66) treated purified wood pulp paper with borax or alum and found considerably increased degradation of the acid paper on exposure to Florida sunlight. The temperature must have been high because the papers yellowed. Paper trea-

ted with magnesium hydroxide solution, which raised its pH from 4.4 to 6.0 (after exposure), was very well preserved (see table on page 143).

Launer & Wilson produced considerable stabilization of newsprint by adding sodium bicarbonate to bring the pH from 5.0 to 7.2.

During the last 60 or so years a good many different substances have been tested for their effect on the light fastness of cellulose and the performance of some of them has been patented. There is no evidence that any real success has been achieved. Iron compounds are frequently cited as both accelerating and reducing damage. According to Sippel (71) all iron salts except rust (hydrated ferric oxide) cause damage in light. Little (49) quoted an experiment by Cunliffe who found that ferric hydroxide had a protective effect. Barr & Hadfield (9) found that ferric hydroxide increased the rate of degradation and that demineralisation of cotton with dilute hydrochloric acid improved its light resistance.

According to Agster (2) the ferric ion is responsible for the damage. In covalent compounds it is ineffective and complexing agents will therefore inactivate iron :

Effect of iron & copper salts on the photosensitized degradation of rayon. (Original DP 258)				
<i>Treatment</i>	% DP retained after :			
	2	4	8	16 weeks exposure
Untreated	92.2	89.1	83.7	72.1
N/1000 Ferric ammonium sulphate	85.6	81.4	74.4	57.8
As above but treated with Calgon (sodium hexametaphosphate)	91.5	88.4	80.6	70.2
N/1000 Copper sulphate	88.4	85.6	77.5	65.5
N/1000 Copper sulphate plus Calgon	91.1	88.3	81.8	68.6

Richter (66) tested the effect of various iron compounds on the light fastness of paper :

Sunlight exposure (in the open) of waterleaf paper Impregnated with solution of various reagents	
<i>Chemical</i>	% fold retention
Nothing	58
0.001 % Ferric nitrate	52
0.001 % Ferric oxalate	48
0.001 % Ferrous oxalate	49
0.001-0.5 % Ferric oxalate followed by ammonia	53
0.2 % Sodium molybdate	27
Satd. Magnesium hydroxide soln.	64

I have included Richter's experiment with sodium molybdate to show not that anything is worth trying (*) but that *anything* used to impregnate cotton must be tested for its effect on the light resistance of the fibre (10).

Michie & Neale (52) showed that iron has a protective effect on degradation by light but that copper accelerates degradation. Little stated that copper reduces damage by sensitising vat dyes but increases damage to cotton dyed with inactive dyes (48). Since iron is believed to accelerate damage by sulphur dioxide and copper accelerates the alkaline oxidation of cellulose (52) they must be regarded as dangerous impurities.

The reaction order.

The rate of photochemical decomposition of cellulosic material diminishes as the reaction proceeds (fig. 2, 7, 8, 11, 15).

Some results (31, 76) show a logarithmic relationship between decay and irradiation ; that is, the rate of deterioration is proportional to the amount of material left undamaged.

(*) A good example of this approach can be found in (65).

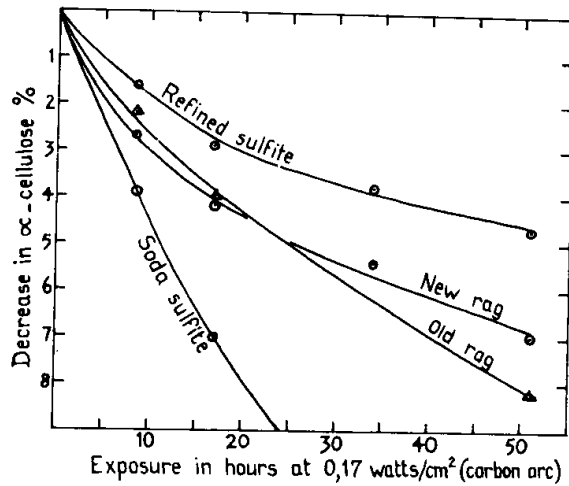


Fig. 15. — The rate of degradation of papers made by different processes. From data of Launer & Wilson (42).

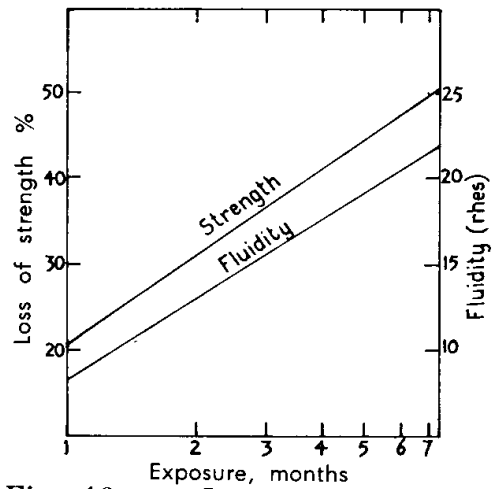


Fig. 16. — Loss of strength & increase of fluidity of cotton exposed behind a blue filter to sunlight. From Fynn, Sands & Campbell (31).

The rate of deterioration and its rate of change both depend on the criterion of damage chosen (61, 63, 66) (fig. 17 & 18).

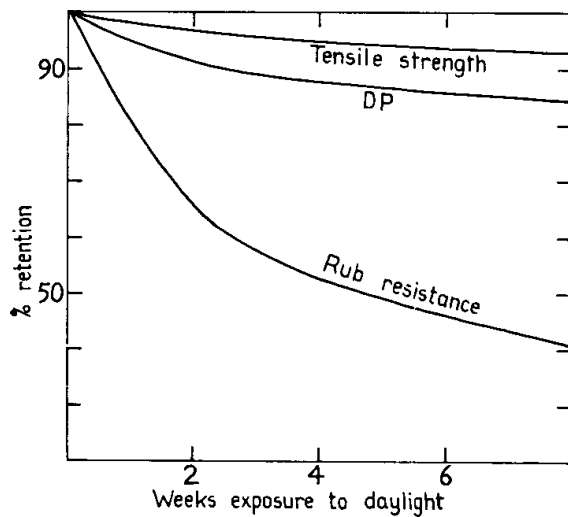


Fig. 17. — The degradation of viscose rayon according to various criteria. From Agster (2).

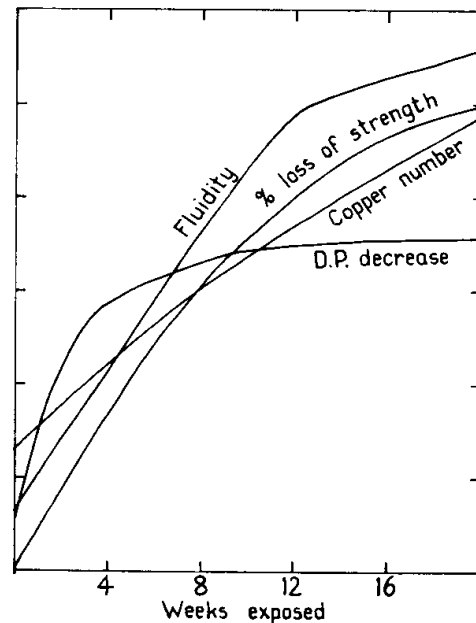


Fig. 18. — The degradation of cotton yarn according to various criteria. The loss of strength reached 50 % after 20 weeks. From Race (61).

Discolouration, being the product of at least two competing reactions, follows a particularly complicated course (21, 42, 46, 80) and initial yellowing may be followed by bleaching. In most circumstances paper bleaches in light (fig. 19).

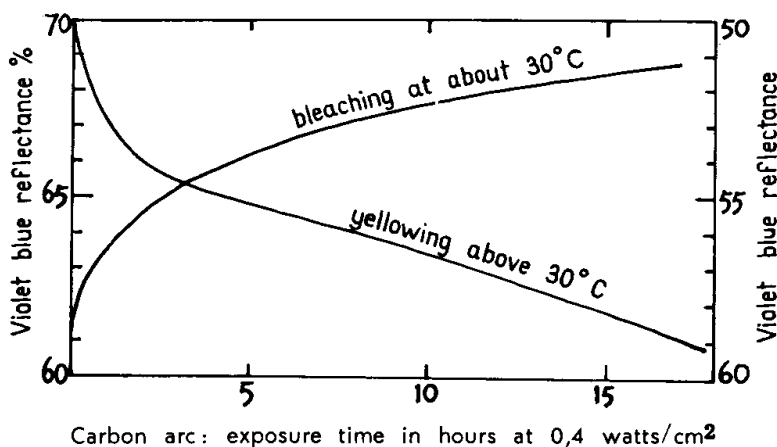


Fig. 19. — Soda-Sulphite paper yellows or bleaches in light according to the temperature (initial reflectance 60 %). From Launer & Wilson (42).

The relationship between the various criteria of degradation.

Light damage can be detected by most of the common analytical procedures for evaluating damage to cellulose. When *comparing* the damage to materials treated in different ways however, one finds that different tests for damage often place the materials in a different order of merit. There is only room here to cite a few cautionary examples.

Launer & Wilson (43) found that cotton paper suffered a greater fall in α cellulose content in dry than in moist air but the fall in DP (derived from fluidity measurements) was smaller in dry than in moist air. Paper derived from wood cellulose did not exhibit this contradictory behaviour (see table p. 134).

Goldthwait & Robinson (32) showed that mercerised cotton (cotton swollen by treatment with sodium hydroxide solution) lost less strength than cotton when exposed but suffered a greater rise in fluidity of its cuprammonium solution.

Obviously it is important to test for deterioration of the quality thought important in the object. But tests for chemical as well as physical damage are essential because the chemical state of cellulose affects the rate of ageing in the dark.

Discolouration.

The factors that cause change of colour of cellulosic materials are reassembled here. Ground wood pulp behaves differently from other commercial forms of cellulose. It darkens in light and is only very slightly bleached by long wavelength light. The darkening is not very much accelerated by heat. Cellulose free from lignin is bleached by light at normal temperature. It is yellowed by far ultra-violet light, not normally encountered in museums. Exposure to light causes chemical changes in the cellulose which accelerate the non-photochemical yellowing with age. In a dim light this yellowing may overcome the concurrent bleaching by light.

It should be emphasized that yellowing of additives to paper may overshadow yellowing due to decomposition of cellulose (38).

The discolouration of cellulose has been reviewed by Spinner (72) and by Stübchen-Kirchner (74).

Prevention of light degradation of cellulose.

A collection of data on the various factors influencing the photodegradation of cellulose should end with a note on chemical and environmental ways of protecting cellulose. But apart from the removal of harmful influences no method of improving the light fastness has proved to be both effective and without effect on the appearance of the material.

Enclosing art objects in an inert atmosphere has been used to protect them from light damage (78). This method must be used with caution because oxygen is essential to the *stability* of some materials. Prussian Blue, for instance fades by reduction in an inert atmosphere.

Latent damage by light.

It is important to realise that photo-oxidation of cellulose not only causes immediate physical weakening but also renders cellulose more susceptible to damage by reagents to which unoxidised cellulose is immune.

Alkalis attack oxidised cellulose (18 a). Most soap solutions and many detergents are alkaline and one wash in such a solution can cause serious damage to oxidised cellulose (83). It is even possible that de-acidification treatment may provoke this kind of degradation (I must stress that this is merely a speculation).

Oxidised cellulose generally discolours more rapidly in the dark. Much research has been done on the causes of yellowing of paper during storage. It has been reviewed recently by Spinner (72) and Stübchen-Kirchner (74).

The importance of cellulose degradation in museums.

It is of interest to compare the permanence of cellulose with that of dyes and pigments used in drawing, watercolour painting and textile dyeing.

The 50 Mlxh. estimated to cause serious damage to cellulose will cause slight fading of dyes of light fastness 7 (BS rating). Natural dyes and their corresponding lake pigments have an average light fastness of about 4 (58) but will still retain some colour after this exposure (64). Many inorganic pigments have a light fastness greater than 7 and some of these, such as Prussian Blue and ferric oxide, have also been used as textile dyes. The carbon ink of prints is absolutely light fast and so is pencil and silverpoint.

Although cellulose is one of the more permanent organic materials it may yet decompose faster than the dyes & pigments it is used to support.

Summary of the data on the light damage of cellulose.

Light and near ultra-violet radiation causes loss of strength and the symptoms of oxidation of cellulose. Discolouration only occurs with materials such as jute and low grade paper which contain lignin. The rate of deterioration is, from the point of view of a museum curator, fast.

The effect of light is aggravated by high temperature and high relative humidity and by the presence of oxygen and air pollutants. Some iron and copper salts and certain dyes and pigments accelerate the deterioration of cellulose.

Other forms of radiant energy have a negligible effect.

The reaction mechanism.

The most important advance in studies of the reaction mechanism of the photo-degradation of cellulose was the realisation that two completely different processes occur during exposure.

At wavelengths less than about 3400 Å radiation causes direct rupture of interatomic bonds. This process is known as photolysis and has been studied in some detail.

At longer wavelengths the energy of each quantum of radiation is insufficient to break any of the bonds between the atoms of the cellulose molecule. Indirect destruction may still occur by processes described as photosensitized degradation.

In the experiments on cellulose deterioration published before about 1949 the results are often vitiated by use of a light source, such as the medium pressure mercury vapour lamp, which caused both photolysis and photosensitized reactions to proceed at the same time.

Some environmental factors such as oxygen pressure, humidity and the presence of certain vat dyes have different, or even opposite effects on the two kinds of degradation. The symptoms of degradation also are different: yellowing in the far u.v. and bleaching in the near u.v. for example.

Only the photosensitized reaction is likely to occur in museums because glass cuts off the short wave u.v. of daylight fairly efficiently.

The analytical tests for evaluating the degradation of cellulose show that the damage consists of chain scission (loss of tensile strength, rise in fluidity) and oxidation to give carbonyl groups along the polymer chain (rise in Copper Number). A small rise in Methylene Blue absorption indicates the formation of carboxyl groups.

Very little fundamental work has been done on the mechanism of the photosensitized degradation of undyed cellulose, probably because it is rather slow. Some vat dyes increase the rate of degradation very much. Since the dyes are light fast and valuable the process has been intensively studied. Many interesting publications have appeared on this subject. They have been reviewed recently (60, 69) and will be only briefly described here because it is by no means certain that the proposed mechanisms are applicable to the degradation of cellulose under other circumstances.

The most striking experimental observations which must be accounted for by any theory of the mechanism of the effect of vat dyes are these : The need for oxygen, the acceleration and apparent change in the nature of the reaction at high relative humidity, the degradation of undyed cotton at a small distance from the sensitizing dye or pigment and the effect of traces of copper & other metal salts (26, 27, 48).

Much of the work has been done on solutions of the dye with simple alcohols and sugars (model compounds for cellulose). Such systems can of course give no explanation for the effect of relative humidity and the « action at a distance » phenomenon.

There is at present a difference of opinion between some of those who have studied the heterogeneous system of the dyed fibre in air and those who have confined their studies to substances in solution.

Work on the photochemistry of solutions of alcohols and sugars with sensitising anthraquinone dyes suggests that the degradation process may begin with the direct extraction of

$$\begin{array}{l} \text{D} \xrightarrow{\text{light}} \text{D}^* \text{ (electronically excited dye)} \\ \text{D}^* \longrightarrow \text{D} \text{ (deactivation without reaction)} \\ \text{D}^* + \text{RCHOH} \longrightarrow \text{DH}\cdot + \text{RCOH} \\ \text{DH}\cdot + \text{O}_2 \longrightarrow \text{D} + \text{HO}_2\cdot, \quad \text{RCOH} + \text{O}_2 \longrightarrow \underset{\text{O}}{\underset{\text{O}}{\text{RCOH}}} \end{array}$$

This does not explain how chain scission occurs. Mere oxidation does not necessarily cause loss of strength. Schurz & Windisch (70), working on the photosensitizing effect of titanium dioxide, concluded that the next reaction is formation of carbonyl groups on the cellulose molecule. This is followed by a β -elimination reaction which is known to be the cause of the degradation of oxidised cellulose by alkalis (18 a). Lock (2 a) believes that this may occur when exposed material is washed but he also postulated an immediate scission of the glycoside bond following decomposition of the cellulose peroxy radical.

These experiments have mostly been conducted with homogeneous solutions of the reactants. Egerton has shown differences in the behaviour of homogeneous and heterogeneous systems which in other respects were similar (28). He has also shown that different reactions may predominate at different relative humidities (27).

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Egerton's theory is that the activated dye molecule transfers its energy to oxygen. The activated oxygen attacks the fibre and also reacts with water vapour to form hydrogen peroxide which is sufficiently stable to migrate through a few millimetres of air and damage undyed cellulose.

The factors that encourage photo activity in the dye have been discussed recently by Nitzl and Dörr (56). They relate the photo-degrading properties of some anthraquinone vat dyes to the nature of the electronic state of the excited molecule. Other workers have tried to relate photo-tendering action to the lifetime of the excited state (15, 16).

The problem of the photo degradation of cellulose is evidently a difficult one and much more fundamental research has yet to be done before a rational approach to the prevention of these reactions can be attempted.

The theories of the mechanism of the photosensitised degradation of cellulose have recently been reviewed by Phillips and Arthur (60).

Conclusions.

The experimental work on the deterioration of undyed cellulose in light has so far revealed almost nothing about the reactions that occur. The basic facts were adequately expounded by Witz (85) in 1883. Since then the study of the photochemistry of cellulose has languished in inconclusive experiments. The recent outstanding work on the effect of vat dyes may change this gloomy picture.

Suggestions for further study.

What work could usefully be done in conservation laboratories ?

Some missing data needs to be supplied :

The spectral sensitivity of cellulose should be discovered. It may turn out that a very small sacrifice of blue light in museum illumination will greatly favour the permanence of

cellulosic material. (It is even possible that intense illumination by yellow light may prove to be a safe way of bleaching paper or cloth unmixed with sensitive materials such as dyes).

The effect of RH on the rate of deterioration of cellulose does not seem to have been investigated in great detail. Research might reveal that a humidity lower than that recommended at present (50-65 % RH) is safer for those cellulosic materials in which a slight loss of flexibility is unimportant.

Iron compounds are present in paper and cloth as impurities and also as constituents of inks and mordant dyes. Their photochemical behaviour is not well understood.

The effect of alkalinity in increasing the rate of photo-degradation and post exposure degradation of cellulose should be investigated because some de-acidification techniques used in conservation to prevent degradation in the dark can raise the pH of paper to over 10 (*) (9 a).

The effect of air pollutants on the photochemical degradation of cellulose has not yet been thoroughly investigated but it would probably be simpler to prevent pollutants from reaching the material.

The light fastness of modern papers depends on all the variable factors provided by methods of preparation of the pulp and by coating and sizing products. The range of chemicals incorporated into modern papers is vast. Much research on the particular manufacturing methods that lead to low permanence is now being done in the industry and in independent laboratories. The subject needs a review to itself.

Papers which are free from mechanical wood pulp do not generally yellow during exposure. On the other hand the yellowing and degradation of paper in the dark as a result of damage by light is a problem. Much research is being done on the subject of *colour reversion* of paper and it is therefore doubtful if conservation scientists would be justified in tackling this subject.

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(*) The pH (cold extraction) of a filter paper impregnated with magnesium carbonate is about 10.4.

Appendix A

The lux is the unit of illumination. It can only be derived from units of radiation such as the langley (1 calorie of solar energy per square centimetre) or the sun hour if the spectral energy distribution is known.

$$\begin{aligned}\text{Solar radiation } G &= \int_{\lambda=0}^{\lambda=\infty} G_{\lambda} d\lambda \\ &= 2.4 \times 10^{-5} \int_{\lambda=0}^{\lambda=\infty} G_{\lambda} d\lambda \text{ langley sec}^{-1}\end{aligned}$$

where G is in watt. m^2 . The area under the heavy line in figure 20. gives the value of the integral for $\lambda = 3\,000$ to $7\,000 \text{ \AA}$, modified to take account of the absorption of radiation by window glass. For longer wavelengths I have used the data for air mass 2 given by P. Moon, Proposed standard solar radiation curves for engineering use, *J. Franklin Inst.* 230, 583-617 (1940).

$$\begin{aligned}\text{Solar illumination } E &= \int_{\lambda=0}^{\lambda=\infty} V_{\lambda} G_{\lambda} d\lambda \text{ lightwatt.} \\ &= 680 \int_{\lambda=0}^{\lambda=\infty} V_{\lambda} G_{\lambda} d\lambda \text{ lux}\end{aligned}$$

V_{λ} is the luminous efficiency at wavelength λ . This integral corresponds to the area under the dotted line in figure 20.

$$1 \text{ Langley} = \frac{8 \int_{\lambda=0}^{\lambda=\infty} V_{\lambda} G_{\lambda} d\lambda}{\int_{\lambda=0}^{\lambda=\infty} G_{\lambda} d\lambda} \text{ kiloluxhour (klxh)}.$$

The variability of daylight has given scope for ingenious calculations of its average spectral energy distribution. Here is mine. It is simpler than most and I believe sufficiently accurate.

Most of the degradation data has been obtained in a temperate climate. The daylight of a London suburb has been investigated by S.T. Henderson & D. Hodgkiss. (The spectral energy distribution of daylight. *British J. of Applied Phys.*, 14, 125-131 (1963). 15, 947-952 (1964)).

It is possible to derive from their work an approximate energy average spectral energy distribution of daylight by taking the average s.e.d. of sunny skies (correlated colour temperature 5 750 ° K) and of sunless skies (7 150 ° K) and combining them so that the contributions of these two « sources » are proportional to their relative brightness (5 to 1) and to the relative times during which each is operative (1 to 3 near London). (Data from a photographic exposure table and from The Atlas of Britain, Oxford, Clarendon Press 1963).

The two s.e.d's are combined by multiplying the reciprocals of their colour temperatures (the mired values) by 5 and 2 respectively and taking the average which, in this case, gives an s.e.d. of about 6 200 ° K against the *time* average value of 6 500 ° K. The difference is due to the great energy provided by a short period of sunlight (of low colour temperature) compared with an equal period of sunless daylight.

This result must be modified to give the s.e.d. behind window glass. (Heavy line of fig. 20).

In a sunnier climate the s.e.d. would correspond to a lower colour temperature.

Henderson & Hodgkiss found that the colour temperature of the daylight governs the s.e.d. of the light regardless of whether it comes from a hazy, cloudy or blue sky. The only factor that appears to influence the ratio of u.v. to visible radiation at a given colour temperature is the time of year. The ratio is smaller in winter.

This s.e.d. is calculated for exposure in a horizontal plane to daylight from the whole sky. The irradiation of tilted samples does not differ much from this. (L.F.C. Friele, A comparative study of natural & xenotest exposure conditions for measuring fading & degradation. *J. Soc. Dyer & Col.*, 79, 623-631, (1963)).

This is a rather crude approximation to the conditions endured by cellulose samples during photo-degradation experiments but if all the necessary corrections are made the result would be a mere sophistication of inadequate data. The xenon lamp may soon provide more accurate results.

The integrals can be evaluated graphically to give the relations :

$$1 \text{ langley} = 1.36 \text{ klxh.}$$

Experimental values range from 1.25 (Friele) to 0.86 (in winter) (E. Brunnschweiler, Prüfung der Lichtechtheit - Lichtmessungen, *S.V.F.* (Schweizerische Vereinigung von Färbereifachleuten) *Fachorgan*, 19, 521-535 (1964)).

The relation between sunlight hours and langleys can be deduced from O. Rawland, Fading of the British dyed wool light fastness standards in the U.K. : some energy measurements. *J. Soc. Dyers. Col.*, 79, 697-701 (1963). This figure (70 langleys per sunlight hour) includes periods when the sky is overcast. In sunnier climates the number of langleys per sunlight hour should be *smaller*.

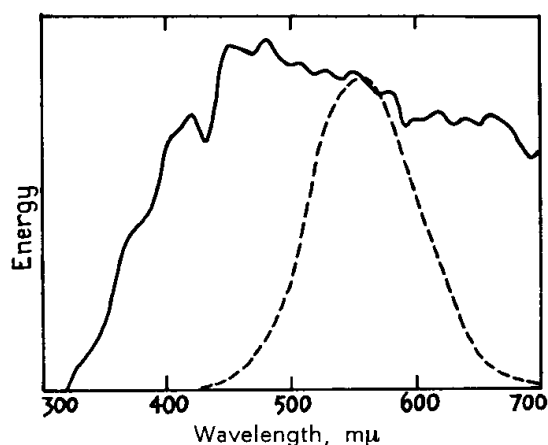


Fig. 20. — Full line : approximate energy average spectral energy distribution of sunlight through glass in a temperate region. Broken line : Full line multiplied by the standard luminous efficiency curve.

Appendix B

It is axiomatic that no photochemical reaction can occur without absorption of light. Cellulose is generally described as transparent but the rate of degradation is so slow that a scarcely measurable degree of light absorption provides sufficient energy for the reaction.

The processes that occur on absorption of light are best described in terms of the Molecular Orbital theory : The valency electrons of the atoms of a molecule are assigned to a set of molecular orbitals. Each M.O. may contain two electrons which are restricted to a definite energy and to a certain region of the space around the molecule. In the normal (ground) state of a molecule the electrons occupy a set of M.O.s such that the total electronic energy of the molecule is as low as possible.

When a molecule absorbs light one of these electrons acquires the energy of the light quantum and moves into a vacant orbital where it has a greater energy and occupies a different region in space. A molecule will absorb light of such a wavelength that its quanta provide exactly this energy difference.

The molecule is now said to be in an excited state. It can return to the ground state by a variety of processes which involve release of the extra energy as heat, sometimes accompanied by re-emission of light (fluorescence). The excitation energy may also be transferred to another molecule. (Simons, J. P. The reactions of electronically excited molecules in solution. *Quarterly Reviews*, 1959, 13, 3-29).

In the case of the action of light on dyed cellulose, deactivation without chemical reaction is by far the commonest process. The ratio of the number of chemical bonds broken to the number of quanta absorbed is about one in ten thousand, or less (7).

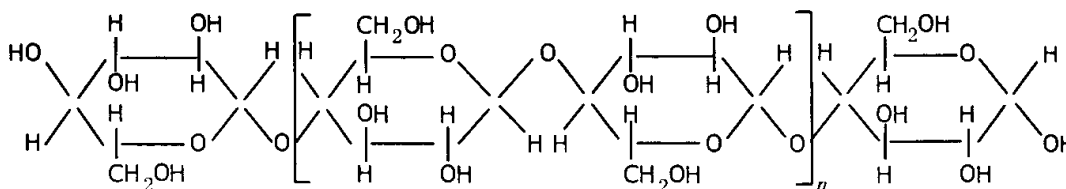
Chemical change occurs when the excited electron is transferred to another molecule or when another electron occupies the position left vacant by the excited electron. The molecule is now an ion or a radical or both and is very reactive.

For more profound information on the fundamental processes of photochemistry see (60) and : Symposium on photochemistry in relation to textiles. *J. Soc. Dyers & Colourists*, 1949, 65, 585-788.

Glossary

α-cellulose. The percentage of a cellulose sample which fails to dissolve in 17.5 % sodium hydroxide solution at 20 ° C. This residue is considered to be cellulose of high molecular weight which contributes usefully to the strength of the fibre.

Cellulose. A polymeric molecule consisting of up to several thousand anhydroglucose units linked through glycosidic bonds :



The strength of the fibre must be related in some way to the great length of the cellulose molecule but the way in which these molecules pack together to form the visible fibre is not yet known. The natural fibres may be divided into numerous long, thin microfibrils by beating. These each contain many molecules. The major part of each molecule is aligned with the microfibril. According to the various micelle theories the molecules lie roughly parallel and come together at intervals into a crystalline, ordered, parallel arrangement. These theories are now being challenged and the whole subject of the fine structure of the cellulose fibres is under review.

The general properties & structure of cellulose and its products are described in several general works :

OTT E., SPURLIN H. M. & GRAFFLIN M. W. (eds.) *Cellulose and Cellulose derivatives*. 2nd. edn. 3 vols. N.Y. Interscience, 1954.

HONEYMAN J. *Recent advances in the chemistry of Cellulose and starch*. London, Heywood, 1959.

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Copper Number. Oxidation of the hydroxyl groups and scission of the cellulose molecule gives rise to carbonyl groups whose number is estimated from the weight of copper reduced from the cupric to the cuprous state by 100 grams of cellulose. This number is only roughly proportional to the number of carbonyl groups because it depends on the way the test is conducted and on the position of the carbonyl groups on the cellulose molecule.

Degree of Polymerisation (DP). The average number of anhydroglucose units in the cellulose molecule. The average can be taken in several ways and the various methods of determining it give different averages. The most common way of estimating DP is to measure the viscosity of a solution of cellulose. The relationship between viscosity and DP varies with the nature of the reaction responsible for the change in DP. Several different methods of conversion have been published which, of course, derive different DP's from the same viscosity. Many authors therefore prefer to publish figures for the change in viscosity (or fluidity) without making any assumptions about the cause of the change. The relation between fluidity and tensile strength also varies with the nature of the degradation reaction and with the nature of the fibre.

Fluidity. See DP.

Fold endurance. A machine repeatedly bends and unbends a piece of paper until it breaks. Various angles of bend and tensions are employed for this test. The number of bends endured by the paper is its fold endurance.

Methylene Blue absorption. Oxidation of the hydroxyl groups of the cellulose molecule results in the formation of aldehyde, carbonyl and carboxyl groups (cf. Copper Number). The carboxyl group is acidic and the number of such groups can be estimated by measuring the absorption of the basic dye Methylene Blue.

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