Preferred citation: J. Silvy and J.F. Le Nest. A photochromic effect shown during the ageing of a cellulose material by heat and light. In **The Fundamental Properties of Paper Related to its Uses**, *Trans. of the Vth Fund. Res. Symp. Cambridge, 1973*, (F. Bolam, ed.), pp 755–760, FRC, Manchester, 2018. DOI: 10.15376/frc.1973.2.755.

A PHOTOCHROMIC EFFECT SHOWN DURING THE AGEING OF A CELLULOSE MATERIAL BY HEAT AND LIGHT

J. SILVY and J. F. LE NEST, Ecole Française de Papeterie, Université de Grenoble, France

The main results of this were given in a note to the C.R.A. at its meeting of 15th July 1970

Introduction

THE yellow colouration that occurs when a cellulose material is exposed to heat and light is considered to be an indication of its degradation.⁽¹⁻³⁾ By using diffuse reflection spectra techniques, we have been able to determine the absorption bands that appear when cellulose is heated in darkness. We have also been able to demonstrate the reversibility of the colouration effect, as this disappears if the cellulose material is exposed to daylight at ambient or low temperature.

Photorestoration can be used for obtaining a higher degree of whiteness than in the initial state; in addition, the colouration effect returns if the unprocessed cellulose initially subjected to light action is placed away from light (post-irradiation effect) and it is more intense if the temperature is increased.

The bleaching of cellulose materials by light has been remarked by several research workers,⁽⁴⁻⁷⁾ but, to our knowledge, the photochromic nature of these colour reactions was not demonstrated following these observations. During the course of our investigations, we have noticed that this phenomenon occurs for various cellulose materials whether it be lignified cellulose such as newsprint or cellulose in the most pure form we have been able to procure.

Testing methods and interpretation of light diffusion measurements

SAMPLES of paper and very pure, 'Avicel' quality, powdered cellulose⁽⁸⁾ are placed in dark surroundings and heated to a temperature of 120° C. Under such conditions, no cellulose mass loss occurs.

In order to induce discolouration of the samples, a xenon arc lamp is used

Under the chairmanship of Dr H. G. Higgins

with a filter system enabling D-type daylight to be obtained at an ambient temperature of less than 35° C. A Beckman DK2A integrating sphere spectrophotometer is used for tracing, in the 2 300–7 000 Å range, the diffuse reflection factor (R_{∞}) curves of the samples following their exposure to heat or light.

The ratio between the specific absorption Σ_a (cm⁻¹) and the specific scattering coefficient Σ_s (cm⁻¹) of the material can be calculated from these measurements using the following formula⁽⁹⁾—

$$\frac{\Sigma_a}{\Sigma_s} = \frac{3}{4} \left(\frac{1 - R_\infty}{1 + R_\infty} \right)^2$$

Using these values, the post-relative colour number is calculated for various exposal periods t—

P.R.C.N., per cent =
$$\frac{\frac{\sum_{a}}{\sum_{s_{t}}} - \frac{\sum_{a}}{\sum_{s_{o}}} \times 100}{\frac{\sum_{a}}{\sum_{s_{o}}} \times 100}$$

The plus or minus sign of this value signifies the increase or reduction in the specific spectral absorption of the material. The influence of the $1/\Sigma s$ factor is not apparent on the spectral curves drawn as we have verified.

Experimental results

THE spectra of the Σ_a/Σ_s ratio for cellulose materials show strong absorption in the ultra-violet range as indicated in Fig. 1: curve 1 represents pure cellulose and curve 2 lignified cellulose; shoulders can be seen on the curves at 2 600 Å and 3 500 Å.

Fig. 2 shows the variation in relative spectral absorption (P.R.C.N., per cent) of pure cellulose exposed for various periods of time in heated surroundings in darkness, then in daylight: curves 1, 2 and 3 correspond to the cellulose exposed to heat for 13 h, 148 h and 3 months, respectively; curves 3–6 correspond to the cellulose then exposed to daylight for 0 min, 40 min, 6 h and 70 h, respectively.

During exposure to heat, the absorption range of cellulose increases progressively to 2 600 Å, then 3 100 Å and 4 200 Å. The latter absorption band is responsible for the yellow colouration of the sample. During exposure to light, the absorption at 4 200 Å and 3 100 Å decreases in the reverse order: the cellulose bleaches.

Occasionally, when using photorestoration techniques, the sample becomes whiter than the original unprocessed sample⁽¹⁰⁾—see results in Table 1. This shows that our observations and measurements are relative and that the unprocessed cellulose had already started to age.



The photochromism of pure cellulose is also demonstrated in Fig. 3, where it can be seen that yellowing occurs after exposure to heat for 3 months: curve 1 followed by bleaching after exposure to light for 70 h; curve 2 and then a much more pronounced yellowing effect after re-exposure to heat in darkness for 25 days.

Electronic paramagnetic resonance measurements carried out at ambient temperature have shown that the initial unprocessed cellulose acts as a diamagnetic substance. Conversely, during exposure to heat, it becomes paramagnetic and a signal can be observed in the form of a single 10 Gs wide absorption ray characterised by a factor g = 2.0192. The signal is amplified when heating is performed under vacuum in a sealed tube. In addition, the concentration of paramagnetic centres in cellulose increases during photorestoration.



Of the three absorption bands discovered during heating in darkness, the one centred on 2 600 Å is not reversible when exposed to light. On the other hand, the 3 100 Å and 4 200 Å absorption bands characterise a photochromic effect that can be observed in the visible spectrum.

We think that the 2 600 Å absortpion band corresponds to the characteristic transition $n-\pi^*$ of carbonyl groups, as can be observed in cellulose dialdehyde prepared by oxidation using sodium meta-periodate. Fig. 4 shows the variation in P.R.C.N., per cent after this chemical treatment for unprocessed unoxidised cellulose (curve 1). In conjunction with this ultra-violet absorption (P.R.C.N. >0), a bleaching in the visible spectrum is observed (P.R.C.N. <0), which could be equivalent to the daylight exposure effect. If the same cellulose dialdehyde is then exposed to heat (curve 2), it exhibits considerable absorption in the 2 600 Å, 3 100 Å and 4 100 Å bands, very close to that observed in the case of unoxidised cellulose.

Conclusions

This study explains the complexity of the ageing process of cellulose materials, which has already been greatly emphasised in the literature. In addition, it indicates the reversible character of certain phenomena and this is of primary importance in the choice of parameters for the study of accelerated ageing for standardisation.

The following recommendations have to be made-

I. During ageing in light, it is necessary to make a distinction between temperature effects and those of luminous radiation and, as such, the temperature has to be defined and controlled during irradiation.

2. In the choice of light source for the accelerated ageing tests in light, the spectral distribution of the light source should be strictly comparable with that of the total radiation of D-type daylight. The use of unfiltered sources having a spectrum of superimposed rays on a continuous background is dangerous when one considers the relative importance of certain rays in the spectrum.

The in-depth study of photochromic mechanisms of cellulose should result in a host of practical consequences and in fundamental information, especially about the influence of our natural environment on the behaviour of cellulose materials.

References

- 1. Rash, R. H., J. Res. Nat. Bur. Stand., 1931, 7, 456
- 2. Roudier, A., Saulquin-Bisson, A., ATIP Bull., 1959, (3), 109; Roudier, A. and Sauret, G., Ibid., 1959, (4), 187
- 3. French standards Q 03-036 and Q 03-037 (January 1969)
- 4. Poulle, E., Escher, J., Desrivières, M. and Peteri, R., *Gazette des Archives*, 1959, (26), 33
- 5. Hudson, F. L. and Edwards, C. J., Paper Tech., 1966, 7 (1), 27-28

- 6. Nolan, P. H., Van den Akker, J. A. and Wink, W. A., Paper Trade J., 1945, 121 (11), TS101
- 7. Claesson, S., Olson, E. and Wennerblom, A., Svensk Papperstidn., 1968, 71 (8), 335
- 8. Battista, O. A. and Smith, P. A., Ind. Eng. Chem., 1962, 54 (9), 20
- 9. Silvy, J., Revue d'Optique, 1961, 40 (10), 495
- 10. Le Nest, J. F., Silvy, J. and Chêne, M., 39th Congress of Industrial Chemistry, Bucharest, September 1970

Transcription of Discussion

Discussion

Dr K. Ebeling I would like to congratulate Dr Graminski on an excellent presentation. It seems to me that here we have direct experimental evidence for the mechanisms proposed in my paper to account for the dissipation of energy during the straining of paper. May I add that we should not look at fibre-to-fibre bonds alone. We should not forget the bulk of the cell wall. Similar phenomena are taking place there between the fibrils and the lamellae.

Dr N. K. Bridge Although many of us are interested in this paper because of its theoretical points of view, there is a practical point to question. I find it inconceivable that banknotes receive the amount of flexing you appear to be giving them in your test—something like 20 000 flexes, which is ten times a day for several years!

 $Dr \ E. \ Graminski$ The number of flexes reported in this paper are more than necessary to determine durability. We have revised our flexing procedures. At the time that this work was started, we were unsure what the flexing procedure should be or what factors were important, so we flexed the paper for a long time. We find that as few as a thousand flexes or less than 10 min of flexing is all that is required to estimate durability.

Dr A. B. Truman This reminds me of some work done in 1963* when we were looking for a similar effect. We used the technique that Derek Page had developed for detecting and measuring the size of fibre-to-fibre bonds. We passed strips of paper at constant load over a sharp edge, we followed the pattern of the breakage of bonds and we tried to quantify it. Your results support our findings on structural change.

Dr D. H. Page In your apparatus, I think it is rather important whether or not the paper at the inner side of the flexing cylinder is going into compression or is still in tension. If it goes into compression (and can you calculate this?), there is opportunity for micro-compressions to be produced in the

* Jackson, M. and Truman, A.B., Paper Tech., 1965, 6(3), T45-T51 Under the chairmanship of Dr H. G. Higgins

Discussion

fibres and that would lower the modulus of the paper. Do you get different results at different tensions?

Dr Graminski We have performed experiments in which the restraining force was varied from 400 g to 1 000 g and found no significant difference in the results. The side facing the rollers may go into compression, but you must remember that, as flexing proceeds, the side in compression eventually goes into tension and vice versa. It is unlikely that micro-compressions account for the decline in modulus, since papers that exhibit good stiffness and modulus retentions do not exhibit a large increase in air permeability. There is an excellent correlation between decline in stiffness and increase in air permeability. We have not calculated whether the paper facing the roller goes into compression.

Dr J. Grant There is a very important factor determining the durability of papers that have to be bound in books (and you were talking about ledger papers)—the way in which the sheets are bound up. Theoretically, in order to get the maximum durability for a bound book and the sheets contained in it, it should be bound up with the machine-direction running across the double page. In practice, this is not done, because the binders do not like it; you cannot open the book flat. If you open it in the centre, the pages will not stay open. Consequently, the machine-direction usually runs down the sheet, which of course makes the paper weak at the fold of the double page. If it is possible to devise a paper that would open flat, the book could be bound up with the machine-direction running across the book instead of down. The durability of bound ledgers would thus be increased tremendously and the increase would far transcend anything that can be done on the papermaking side, including the effect of flexing resistance.

Dr Graminski In designing documents, it would be advantageous for the cross-direction of the paper to run in the direction that will receive the most flexing. It is the cross-direction of paper that retains its properties most during flexing.

Mr J. R. Parker May I comment on the possible effects of thickness. I assume that the paper, as it passes round the rollers, conforms closely to their curvature. The strain variation at the paper surface during the test will therefore be proportional to the paper thickness. Have the effects of this been observed? In addition, what were the thicknesses of the paper samples for which the results have been presented?

Effect of flexing on paper

Dr Graminski I am sorry that the thickness values were not included in the preprint. They were 3.8 thousandths of an inch for the newsprint, 4.2 for the ledger paper and 4.8 for the high grade rag paper. Presumably, the thickness of paper will have a bearing on the results, but we have not investigated this factor specifically.

Mr Parker May I suggest an experiment? If papers of different thicknesses were used, then the excursion of the strain could be varied in relation to the radius of bending, so that the effect of flexing (which might cause stiff fibres and shives to break away from the paper surface) could be distinguished from the effects of strain in the test direction.

 $Dr \ Graminski$ Yes, this could be done. In fact, I have observed that, when interfibre debonding occurs as a result of flexing, there is a larger decline in physical properties in the direction opposite to flexing than when little or no interfibre debonding takes place.

Dr C. T. J. Dodson Did you observe partial failure of fibre-to-fibre bonds? Have you also investigated an effect of moisture? If so, did you see cracks in the matrix at higher moisture contents?

Dr Graminski We did not flex at high humidity conditions, but the conditions in the test room had gone down accidentally to a very low humidity one winter's day and the matrix deteriorated severely. Yes, moisture has a definite effect.