Comments on the Measurement of "Yellowness" in Pulp and Paper

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When paper discolors with age or when it is necessary to bleach paper or pulp, the concept of yellowness arises and a need to measure the degree of discoloration. The desire to make objective measurements existed long before there was advanced instrumentation and internationally recognized colorimetric and spectrophotometric terminology. Early standards, some of which are still widely employed, are perhaps not as sophisticated as they might be in the light of present-day instrumentation. The widely cited "Tappi brightness", for example, is simply the ratio of the reflectance of pulp or paper determined by means of a filter-and-spectrophotometric-detector system with maximum sensitivity "peaked" at 457 nm (see Figure 1) relative to the reflectance reading from magnesium oxide measured with this same detector/filter combination.[1] The wavelength region and band-pass characteristics used are in the blue-wavelength region of the visible spectrum. As can be seen in Figure 1, this brightness function is similar in character to the present-day CIE color-matching function, $\bar{z}_\lambda$.

Besides the expression of Tappi brightness, Tongren[2] and McIntyre[3] suggested in the late 1930's that the Kubelka-Munk K/S value of this reflectance measured at 457 nm would be a useful measure of discoloration. Here, K/S is $(1-R)^2/2R$ and R is the reflectance of an "infinitely thick" stack of papers (reflectance, R, peaked at 457 nm as before). The reflectance of a stack of six papers is customarily used for this purpose. The difference before (zero) and after accelerated aging (time, t) multiplied by 100, i.e. $100[(K/S)_t - (K/S)_o]$, has been designated the "post-color number".

These widely used measures of the brightness or reflectivity refer only to a narrow wavelength region in the blue end of the spectrum. Such measurements do not consider the spectrophotometric characteristics of the reflected light over the entire visible region of the spectrum, that is, whether -- in a sense -- the color of the pulp is yellow, orange or brown. At the AIC meeting in Vancouver, Ruth Johnston-Feller showed some colorimetric data that suggested that lignin-colored papers may be more "orange" than the discoloration products of cellulose and hemicellulose. The data in Table I indicate that the latter materials may cause the "dominant wavelength" of papers to be on the yellow side, around 514-576 nm, whereas papers with a high lignin content may exhibit dominant wavelengths at 580 to 589 nm, more towards the orange. Perhaps this possibility is worth further consideration.

The spectral reflectance curves of a series of pulps seen in Figure 2 are rather typical of certain types of discolored papers.[4] If conservators wish to advance their understanding of the differences brought about by various bleaching treatments, it should be apparent from consideration of this figure that it is not a simple matter to evaluate the changes in spectral

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reflectance. Moreover, it would not be particularly informative if only changes in reflectance in the region of 457 nm were used to analyze the differences brought about by one treatment or the other.

It should be obvious that the information conveyed by measurements centered about 457 nm is a much abridged measure of color change in pulp and paper. Such measurements may be very useful and convenient if one is investigating the effects of different conditions on one bleaching or aging treatment and on one type of paper, where the spectral changes are all likely to be of the same type. However, if effects are to be studied with papers having different contents of lignin or with agents that may effect different chemical structures within the pulp, then consideration must be given to the response over a broad spectral region.

If further advances are to be made, it will be necessary to consider the complete spectrophotometric reflectance changes that occur, not only in the visible range from 400 to 700 nm but, as will be noted below, in the ultraviolet region. As can be seen in Figure 2, the spectral reflectance curves in the visible range of variously treated papers are often very similar. As can be seen in Figure 3, the absorption in the visible wavelengths is often no more than the "tail" of an absorption band occurring principally in the ultraviolet.

As one possible step in applying additional sophistication to analyze these results, the data may be "subtracted". Thus, the subtle differences in the curves in Figures 2 and 3 can reveal the spectral reflectance curves of the colored materials that were either removed or generated by treatments. Utilization of the Kubelka-Munk concept is particularly useful here when difference curves are considered because the K/S values are related to the concentration of colored constituents; it is the K/S values at each wavelength that are more properly subtracted, not the percentage reflectance. In the review article that this laboratory published in the Postprints from the Book and Paper Group meeting in Milwaukee, May 1982, Figure 9, p. 15, the difference curves from the work of Polcin and Rapson[4] and from the work of Silvy and LeNest[9] were shown. The latter authors used the designation PRCN for the "percent relative post-color number", or $100[(K/S)_t - (K/S)_0/(K/S)_0]$ in carrying out their subtractions.

There are thus many ways that one might report the yellowness of paper. None is the "best" or "correct" way. The purpose of these brief introductory remarks is to point out (a) that the reliance upon reflectance measurements at one principal wavelength in the blue (457 nm) is not likely to lead to significant advances in understanding of the changes brought about by one bleaching method relative to another; (b) there are potential advantages in measuring the changes in reflectance at wavelengths both in the visible and in the ultraviolet; (c) the custom in certain circles of reporting reflectance changes in terms of the change in K/S values is based on sound principles (the Kubelka-Munk theory of absorption and scattering); and (d) the reporting of differences in optical density [log (I_0/I)] or in K/S curves can indicate the character of the colored materials removed or generated in the treatment of pulp and paper.

Why mention these technical matters? Because in reading about the color changes that take place in pulp and paper, the conservator will find

that there is no one standard manner in which changes in spectral reflectance will be reported in the literature. A variety of terms will be encountered: Tappi brightness, K/S values, post-color numbers, relative post-color number $[(K/S)_t - (K/S)_0/(K/S)_0]$, specific absorption coefficient (k), scattering coefficient (s), and in the case of solutions, absorbance and optical density $[\log (I_0/I)]$. Some understanding of these terms is necessary in order to comprehend the literature.

If it may be profitable in the future to examine the changes in spectral reflectance in both the ultraviolet and visible regions of the spectrum, what can one expect to find? Figure 4 shows the results of subtracting the absorption curves of lignin (in solution) after being exposed to ultraviolet radiation and oxygen.[6] The authors show decreases in absorption at 280 and 310 nm which they attribute to changes in guaiacyl and carbonyl groups. In another wavelength region, Lorås and Rengård show that a principal spectral region of bleaching by borohydride, peroxide and dithionate is at about 360 nm (Figure 5).[7]

Interesting curves derived by subtraction were shown in our previous review[5] from the work of Claesson, Olson and Wennerblom[8] (Figures 10, 11, p. 16) and from Silvy and LeNest[9] (Figure 12, p. 17). The latter authors cited absorption peaks at 260, 310 and 420 nm in the discoloration of cellulose, attributing the absorption at 260 nm to carbonyl groups. (When the absorption of lignin is involved, Lin and Kringstad considered the absorption at 280 nm to be due to guaiacyl structures; see Figure 4.)

One of the principal absorption regions that many authors have observed during the darkening and bleaching of pulps is peaked at about 410 nm as can be clearly seen in Figure 6 and in the previously cited curves of Polcin and Rapson, Claesson, Olson and Wennerblom and of Silvy and LeNest. If one may judge from the similarity of the curves for changes in vanillin (in Figure 6), it is the components of lignin that are responsible for the changes that occur in this region of the spectrum.

Summary and Conclusions

During our opening remarks at the morning session at Vancouver, Table II was presented in order to emphasize the considerable variety of fundamental components of pulp and paper that can give rise to color. We are still not sure of many of the details of such a scheme. Nonetheless, the table should be sufficient to impress upon the conservator the fact that further advances in our understanding of the bleaching and darkening of paper will require careful experimental design and more sophisticated analytical techniques than have often been employed in the past. This is particularly true when one wishes to consider the "yellowness" of pulp and paper. Measurements of Tappi brightness and post-color number, centered principally at a narrow wavelength region in the blue (457 nm), can only provide a convenient "standard measurement". Such measurements hold little promise of increasing our understanding of the chemical changes that occur during treatment. As an initial step, the complete spectral reflectance curves in the visible spectrum should be determined. The "subtraction" of spectral absorbance curves based on this information holds some promise in elucidating the changes brought about by processes that result in bleaching or darkening. In the future, reflection or absorption measurements in the ultraviolet must be made.

References

(1) Brightness of Pulp, Tappi Standard T217 os-48, first proposed in 1941-1942.

(2) Tongren, J. C., Paper Trade J., 107, No. 8, 34-42 (1938).

(3) McIntyre, J. W., Paper Trade J., 109, No. 24, 29-57 (1939).

(4) Polcin, J. and Rapson, W. J., "Sapwood and Heartwood of Groundwood of Western Hemlock and Jack Pine. Part III. Influence of Solvent Extraction on the Bleaching of Pulps", Pulp and Paper Magazine of Canada, 73, No. 1, 86-92 (1972).

(5) Feller, R. L., Lee, S. B. and Bogaard, J., "The Darkening and Bleaching of Paper by Various Wavelengths in the Visible and Ultraviolet", in Post-prints, Book and Paper Group, Milwaukee, 1982.

(6) Lin, S. Y. and Kringstad, "Some Reactions in the Photoinduced Discoloration of Lignin", Norsk Skogindustri, 25, No. 9, 252-256 (1971).

(7) Loråas, V. and Rengård, M. J., "Changes in Light Absorption of Mechanical Pulp", Norsk Skogindustri, 23, No. 9, 239-245 (1969).

(8) Claesson, S., Olson, E. and Wennerblom, A., "The Yellowing and Bleaching by Light of Lignin-rich Papers and the Re-yellowing in Darkness", Svensk Papperstidning, 71, No. 8, 335-340 (1968).

(9) Silvy, J. and LeNest, J. F., "Mise en évidence par diffusion de la lumiére d'un effet photochrome de la cellulose", Comptes Rendus Des Seances De L'Academie Des Sciences, Paris, Series C, Sciences Chimiques, 271, 221-224 (1970); see also "A Photochromic Effect Shown During the Ageing of a Cellulose Material by Heat and Light", Transactions of the Symposium held at Cambridge, September 1973, ed. F. Bolam. Technical Division, The British Paper and Board Industry Federation, Plough Place, Fetter Lane, London EC4A 1AL (1976).

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TABLE I

Reported Values of Dominant Wavelengths in the Color of Pulps

	Dominant Wavelength, nm		
27 Softwood and Hardwood Thiolignins			
Iiyama, Nakano and Migita, J. Jap. Wood Res. Soc., 13, 125 (1967)	576	to	589
Bleached Sulfite (low lignin content)	573.5		
Unbleached Kraft (high lignin)			580
Note in Tappi T216 os-47 "Spectral Reflectivity and Color of Pulp"			
Acetylxylan on Filter Paper (hemicellulose)	575		
Corrugated Cardboard Box (high lignin) (Our data)			584

TABLE II

Simplified Scheme:
Potential Sources of Color in Paper

Initial Components		Oxidized and Degraded Components		
		Insoluble	Soluble	
			Condensation Products	Fragments
(Cellulose, colorless)	⟶	?	✓	✓
(Hemicellulose, colorless)	⟶	?	✓	✓
Lignin (major)	⟶	✓	✓	✓
Extractives (minor)	⟶	✓	?	✓

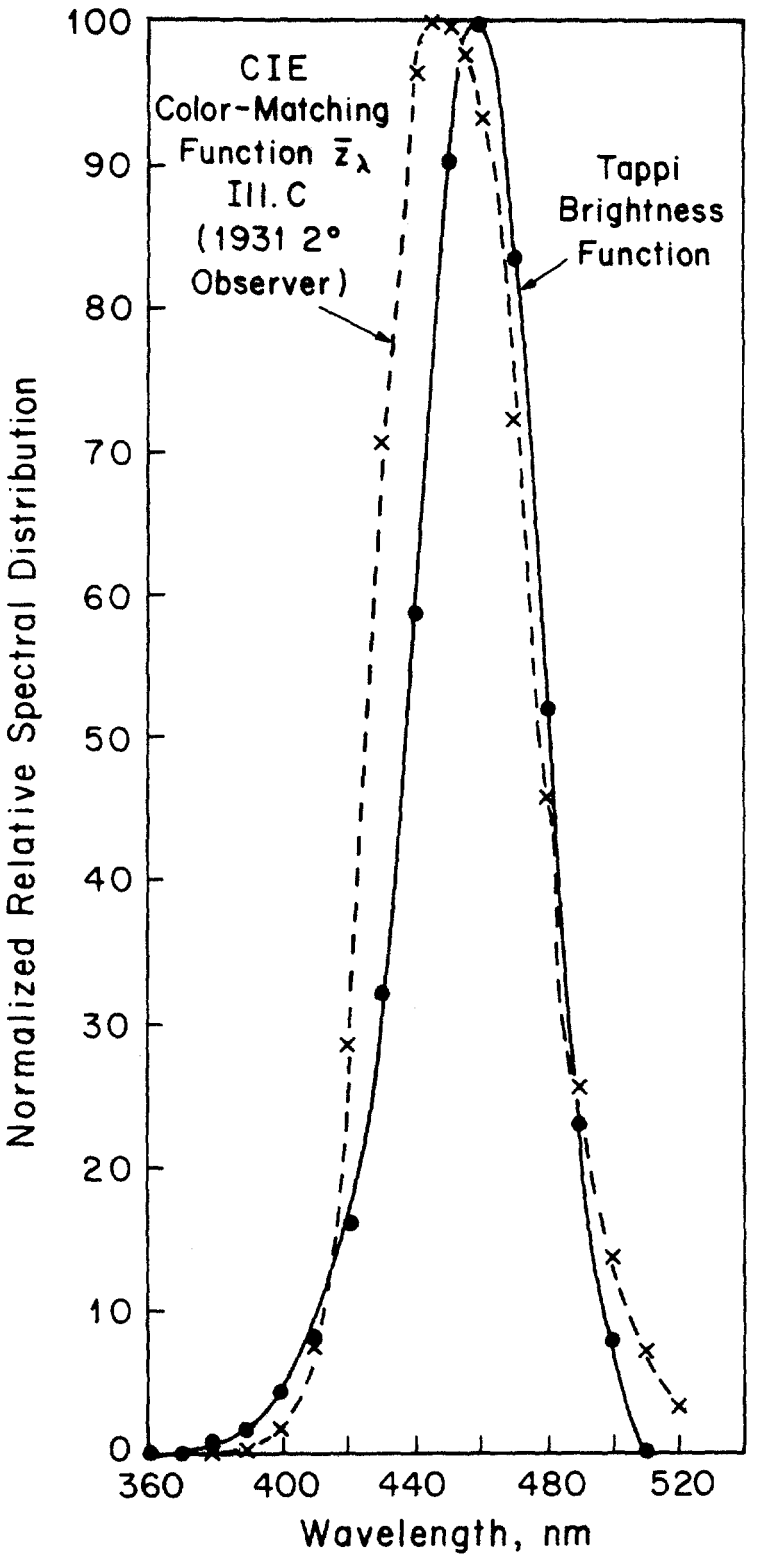


Figure 1

Relative Spectral Distribution of Filter/Detector System in the Tappi Brightness Meter Compared to the CIE Color-Matching Function, $\bar{z}_\lambda$.

These Data Also Appear in "The Measurement of Appearance", R. S. Hunter and R. W. Harold, J. Wiley, 2nd Ed., 1987, Figure 10.6.

Polcin and Rapson (1972)

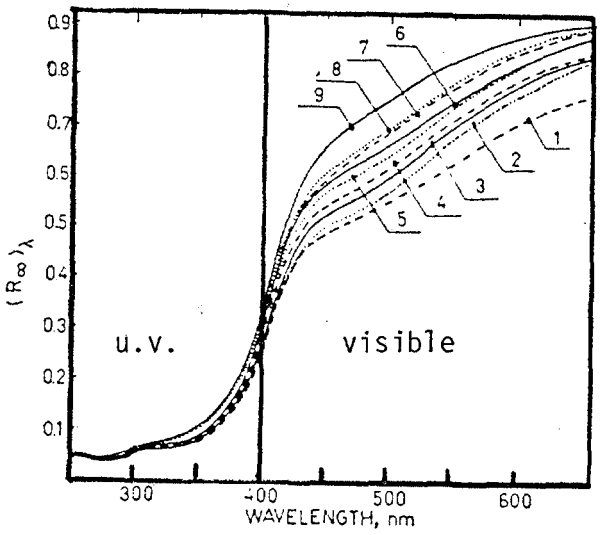
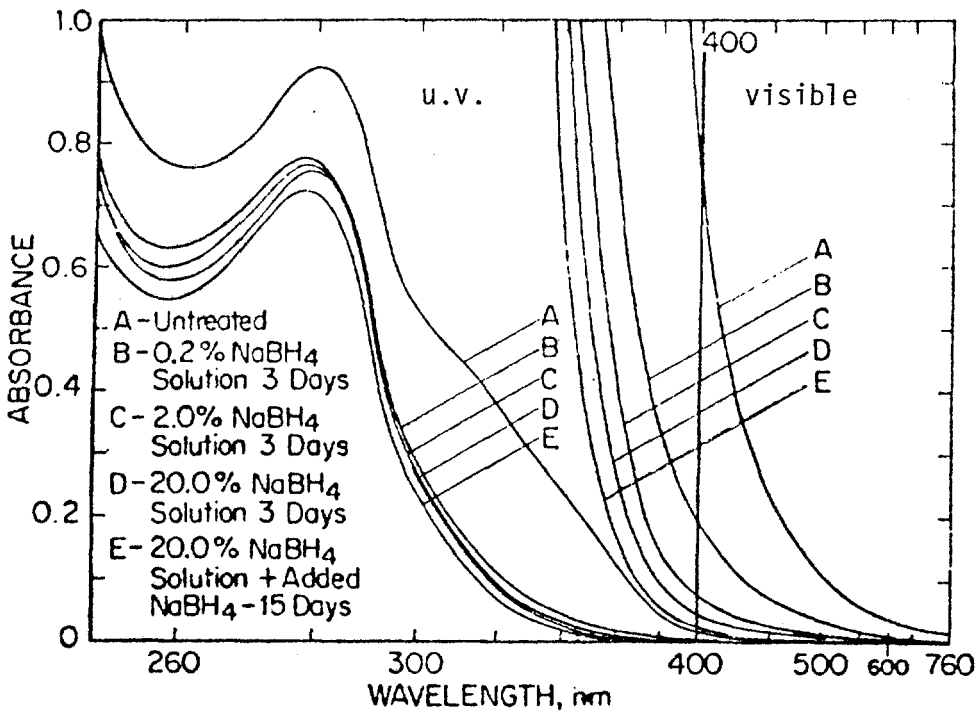


Figure 2

Reflectivity Curves of Western Hemlock Sapwood Groundwood Pulp Which Had Undergone Various Bleaching Treatments with 2% Dithionate and Hydrogen Peroxide

Color of Coniferous Lignin

Pew and Connors
Tappi, 54 (1971), 245-251

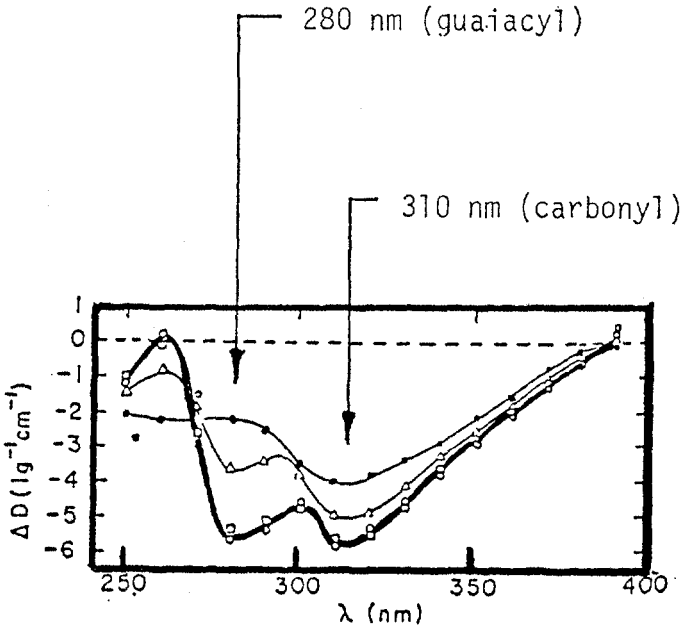


Absorption Spectra of Solutions of Spruce Cellulolytic Enzyme Lignin Before and After Treatment with $NaBH_4$. Right, 200 mg and left, 5 mg of lignin/100 ml of 70% Aqueous Methyl Cellosolve.

Figure 3

Lin and Kringstad

Norsk Skogindustri, 25 (1971), 252-256



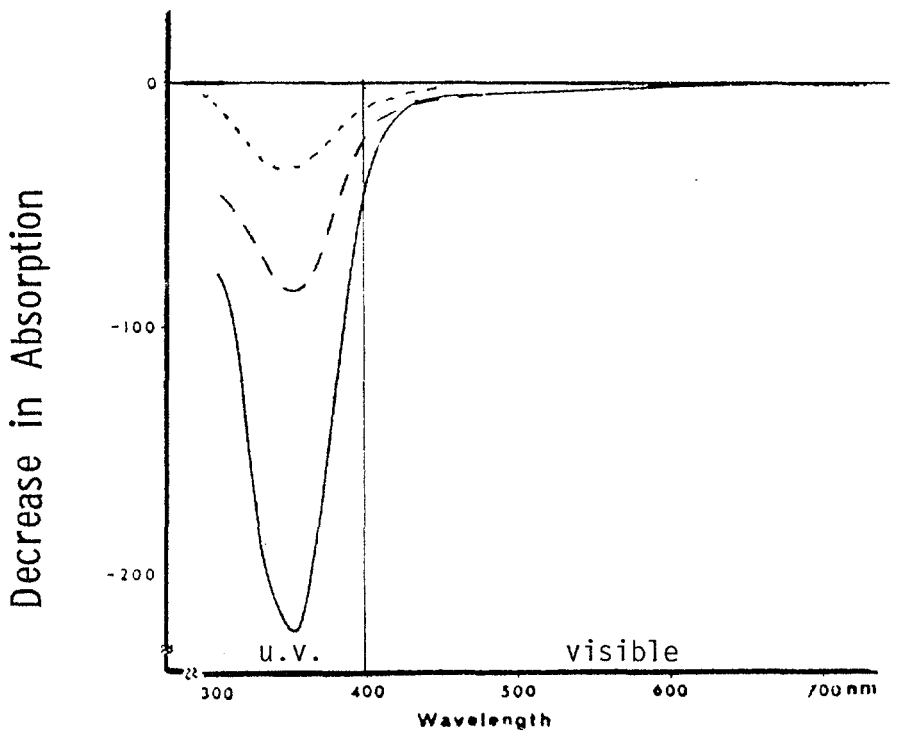
Effect of oxygen on the spectral change of spruce milled wood lignin (in methylcellosolve-water 7:3, v/v):

- **-0- irradiated in air for 6 hours**
- **-•- irradiation under vacuum of 5×10^{-4} torr for 6 hours**
- **-△- same solution opened to air and irradiated for 3 hours**
- **-□- same solution irradiated for additional 3 hours**

ΔD = change in optical density

Figure 4

Loråas and Rengård
Norsk Skogindustri, 23 (1969), 239-245



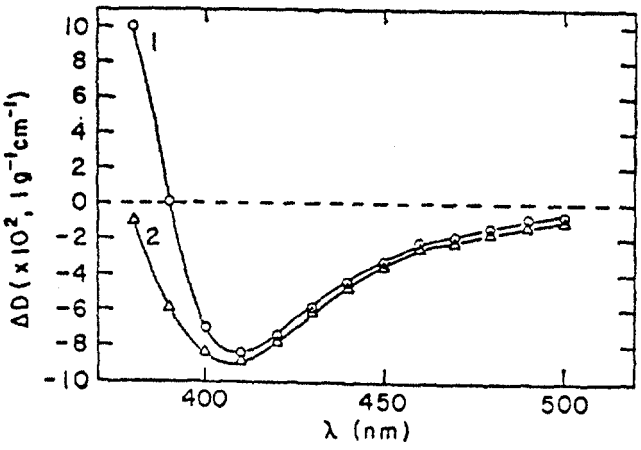
Decrease in absorption of light by bleaching of groundwood pulp.

Legend:

——— borohydride bleaching
- - - - - - - peroxide bleaching
..... dithionite bleaching

Figure 5

Lin and Kringstad (1971)



$NaBH_4$-reduction △D-curves of colored products obtained from oxidation of vanillin with $NaIO_4$(1), and with near ultraviolet irradiation (2).
△D = change in optical density

Figure 6