HEAT-INDUCED COLOR-INTENSITY CHANGE IN COASTAL DOUGLAS-FIR AND WHITE SPRUCE[1]

G. E. Troughton and *S. Chow*

Department of the Environment, Canadian Forestry Service,
Western Forest Products Laboratory, Vancouver, British Columbia

(Received 28 September 1972)

ABSTRACT

In a previous study, it was found that to reach the same degree of surface inactivation, Douglas-fir attained a much higher heat-induced color intensity at 520 nm than white spruce. To explain the heat-induced color-intensity change as a function of the above species, the present study measured the thermally induced spectral changes in the visible wavelength region for these species. The differential reflectance spectra for the sapwood and heartwood of coastal Douglas-fir and white spruce showed a peak in the 410- to 430-nm region, but only coastal Douglas-fir showed a second peak at 550 nm. Comparison of rate data for extracted and unextracted coastal Douglas-fir showed that its extractives contributed significantly to the heat-induced color-intensity change. Dihydroquercetin, a major phenolic extractive in coastal Douglas-fir upon heating produced a powerful chromophore group.

Keywords: *Pseudotsuga menziesii*, *Picea glauca*, reflectance spectrophotometry, activation energy, kinetics, chromophore, dihydroquercetin

INTRODUCTION

Ultraviolet light or heat can cause color changes in wood. Much work has been done on the photodegradation of wood and evidence has been given by various workers that chemical changes in cellulose (Rapson and Hakim 1957; Sjöström and Eriksson 1968) and lignin (Leary 1968; Lin and Kringstad 1970; Luner 1960; Van den Akker et al. 1949) are responsible for chromophore production. Barton (1968), Hillis (1969), and Wayman et al. (1968) found that certain extractives, especially polyphenols, are also a source of color-producing material. As a further complication, interactions between different chemical components in wood can affect the rate of color formation. Thus, Kringstad and Lin (1970) found that the addition of either vanillin or veratraldehyde to cellulose caused it to yellow at a much faster rate, upon exposure to ultraviolet light, than either of these components separately.

Few studies have been made on determining which chromophore groups in wood produce color upon heat treatment. Polcin et al. (1969) determined that discoloration by heat of groundwood pulps from sapwood and heartwood of western hemlock [*Tsuga heterophylla* (Raf.) Sarg.] and jack pine [*Pinus banksiana* Lamb.] was decreased by removal of extractives. Recently, using model compounds, Polcin and Rapson (1971) ranked phenolic extractives common to the above species in terms of their ability to form color upon heating in groundwood pulps.

Chow (1971) showed that color-intensity change caused by heating veneer of white spruce [*Picea glauca* (Moench) Voss] and coastal Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] could be used as a parameter to measure reduced glue-bonding ability of over-dried veneer (surface inactivation). It was found that to reach the same degree of surface inactivation, Douglas-fir attained a much higher heat-induced color intensity at 520 nm than white spruce. The 520-nm wavelength region was used, since this region was found to be more sensitive to heat-induced color-intensity change than other regions in the visible spectrum using a simple reflectance spectrophotometer.

To explain heat-induced color-intensity change as a function of wood species, the present study examines the differential re-

[1] The authors wish to thank Mr. L. R. Rozon for his technical assistance in these experiments.

flectance spectra in the visible wavelength region for white spruce and Douglas-fir over the temperature range 150 to 195 C. In particular, kinetics of heat-induced color-intensity change in white spruce and coastal Douglas-fir are determined.

EXPERIMENTAL

Materials

Wood samples: Thin sapwood and heartwood sections, approximately 50 × 50 × 0.3 mm, of coastal Douglas-fir and white spruce were dried to zero moisture content based on oven-dry weight in a vacuum oven at 50 C. The samples were obtained from one tree of each species. Five each of heartwood and sapwood sections of Douglas-fir were extracted with acetone in a soxhlet apparatus for six hr; a similar number were sequentially extracted with acetone, ethanol, and distilled water for 6 hr with each solvent. The extracted samples were dried in a vacuum oven at 50 C to remove the last traces of solvent and stored in a desiccator over phosphorus pentoxide. The extractives from the above treatments were recovered by evaporation under vacuum at 50 C. The extractives recovered from acetone were pressed into pellets at 2.5-cm diameter in a laboratory press at 1,000 kg/cm^2 for 5 min. The extractives recovered from ethanol and water were combined and similarly made into pellets.

Dihydroquercetin (DHQ) samples: A 100 × 250-mm Whatman No. 1 filter paper was weighed and then soaked with 2.0% (w/w) solution of DHQ in acetone. After the DHQ-impregnated filter paper was air-dried for 2 hr, it was again weighed. The difference in weight of the filter paper before and after impregnation with the DHQ solution indicated that it contained 2.0% DHQ on a weight basis. The DHQ-impregnated filter paper was cut into ten 50 × 50-mm samples and these samples were stored in a desiccator over phosphorus pentoxide.

Two each heartwood and sapwood sections of white spruce from the above unextracted wood samples were soaked in 2.0% (w/w) DHQ solution. These samples were air-dried for 2 hr and stored with the DHQ-impregnated filter paper samples.

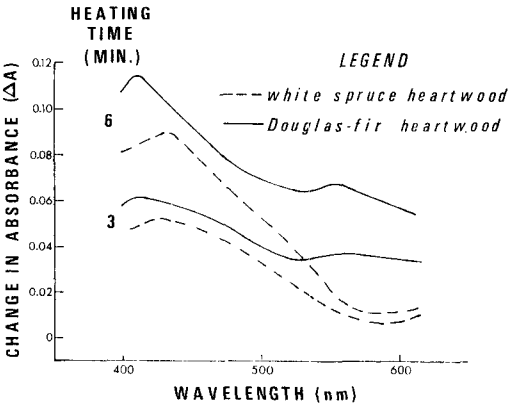

FIG. 1. Differential reflectance spectra at 195 C for coastal Douglas-fir and white spruce heartwood.

Method

For the kinetic experiments, the samples were heated in a forced-draft oven at each of the following temperatures, 150, 175 and 195 C. Samples were removed at 3- to 5-min intervals, depending on the temperature studied, to record their differential reflectance spectra and then returned to the oven. Longer time intervals were used at the lower temperatures. To determine the differential reflectance spectra of the heated samples, a Beckman DB-G spectrophotometer equipped with a reflectance attachment was used. An unheated control sample was used as a reference.

RESULTS AND DISCUSSION

Upon heating at 195 C, the differential reflectance spectrum for Douglas-fir showed peaks at 410 nm for heartwood and 430 nm for sapwood. In addition, this wood species also exhibited a broad peak at 550 nm for both sapwood and heartwood. This peak was not well resolved during the early stages of heating. In contrast, the spectrum for white spruce showed only one peak at 430 nm for both the sapwood and heartwood. With increase in heating time, the

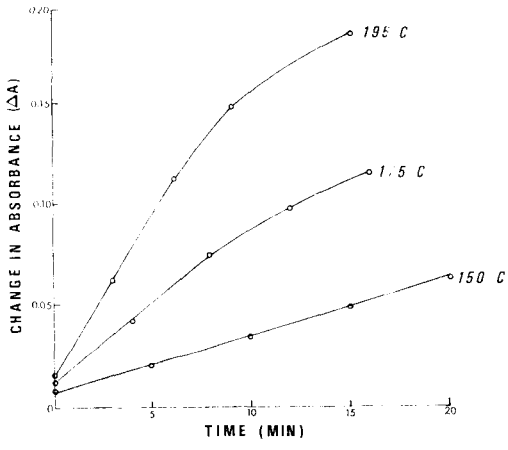

FIG. 2. Rates of color-intensity change at 410 nm for coastal Douglas-fir heartwood.

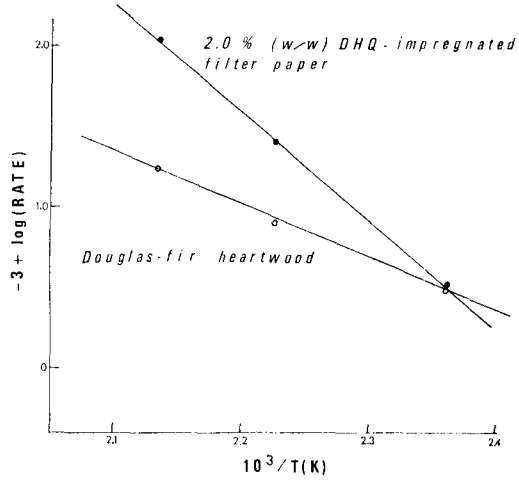

FIG. 3. Arrhenius plots for color-intensity change at 410 nm for coastal Douglas-fir heartwood and 2.0% (w/w) DHQ-impregnated filter paper.

above peaks became more sharply defined, as shown in Fig. 1.

For the kinetic analysis, absorbance at a given peak was plotted versus time. A plot of absorbance at 410 nm versus time for Douglas-fir heartwood is shown in Fig. 2 for three temperatures. Rates of color-intensity change were calculated from these curves and are given in Table 1. It is noted that rates of reaction can be used in an Arrhenius plot to calculate activation energies provided that the initial concentration of the reactants is the same for each temperature. This latter condition was used in the kinetic experiments in this study. Using the Arrhenius equation, activation energies were calculated for heat-induced color-intensity change of Douglas-fir and white spruce. A typical Arrhenius plot is shown in Fig. 3. The activation energies for color-intensity change at 430 and 550 nm in the sapwood and 410 and 550 nm in the heartwood of Douglas-fir were similar and both were calculated to be 15 kcal/mole. The activation energies for color-intensity change at 430 nm in the heartwood and sapwood of white spruce were also similar, and both were calculated to be 11 kcal/mole.

To study the influence of extractives on chromophore formation, rates of color-intensity change at 410, 430, and 550 nm were measured at 175 C for sequentially extracted and unextracted Douglas-fir heartwood and sapwood. Table 2 shows that there is a significant decrease in the rate of color-intensity change after each solvent extraction. Thus, upon extraction of the heartwood specimens with acetone, the rate of color-intensity change at 410 nm at 175 C decreased to 50% of the unextracted rate. Upon further extraction with ethanol

TABLE 1. *Rates* of color-intensity change for coastal Douglas-fir, white spruce and 2.0%(W/W) dihydroquercetin-impregnated filter paper*

	Coastal Douglas-fir				White Spruce		
	HEARTWOOD		SAPWOOD		HEARTWOOD	SAPWOOD	DHQ-impregnated filter paper
Temp C	410 nm	550 nm	430 nm	550 nm	430 nm	430 nm	430 nm
150	0.003	0.002	0.003	0.002	0.004	0.004	0.003
175	0.008	0.006	0.007	0.006	0.007	0.008	0.025
195	0.017	0.011	0.016	0.011	0.014	0.014	0.105

* ΔA/minute where ΔA = change in absorbance

and water, the rate decreased to 40% of the unextracted rate. Upon heating at 175 C, the differential reflectance spectra for pellets made from these dried extracts showed broad peaks in the 450- and 550-nm region for both heartwood and sapwood.

Since DHQ is one of the most abundant extractives found in Douglas-fir and the above results indicated that the extractives in Douglas-fir played an important role in thermally induced color-intensity change, the chromophore properties of this compound dispersed on cellulose were studied in detail. When filter paper (cellulose) was heated by itself for 2 hr at 195 C, its differential reflectance spectrum showed a general absorbance increase in the 400- to 700-nm region without exhibiting any peaks. Also, its rate of color-intensity change in this region was much slower than the previously examined wood samples. For example, at 195 C its rate of color-intensity change at 430 nm was 0.003 ΔA/min (change in absorbance per minute) in comparison to 0.016 ΔA/min for the 430-nm peak in the sapwood of Douglas-fir. However, when the filter paper was impregnated with DHQ at the 2.0% dry weight level and heated for 2 min at 195 C, besides the general absorbance increase in the visible wavelength region, its differential reflectance spectrum showed a well-resolved peak at 430 nm and a broad peak at 550 nm. This spectrum was similar to that for Douglas-fir sapwood.

Rates of color-intensity change at 430 nm for the DHQ-impregnated filter paper are shown in Table 1. Thus, the addition of 2.0% (w/w) DHQ to the filter paper increased its rate of color-intensity change at 430 nm by a factor of 35 at 195 C. Using the Arrhenius equation, an activation energy of 31 kcal/mole was calculated for the color-intensity change at 430 nm in DHQ-impregnated filter paper. An activation energy was not calculated for the 550-nm peak, since this peak was not well resolved and hence was difficult to measure accurately. An Arrhenius plot for DHQ-impregnated filter paper is shown in Fig. 3.

To study the effect of DHQ on white spruce, which does not naturally contain this extractive, heartwood and sapwood samples were impregnated with 2.0% (w/w) DHQ solution. As anticipated, besides the peak at 430 nm, their thermally induced spectra now showed a second peak at 550 nm. The presence of the 550-nm peak in Douglas-fir and its absence in white spruce would explain the finding of previous work (Chow 1971) that when these wood species reach the same degree of surface inactivation, coastal Douglas-fir attains a much higher color intensity at 520 nm than that for white spruce.

TABLE 2. *Rates* of color-intensity change at 175 C for extracted and unextracted coastal Douglas-fir*

Condition	HEARTWOOD 410 nm	HEARTWOOD 550 nm	SAPWOOD 430 nm	SAPWOOD 550 nm
unextracted controls	0.008	0.006	0.007	0.006
acetone extracted	0.004	0.003	0.005	0.004
acetone, ethanol and water extracted	0.003	0.002	0.003	0.003

* ΔA/minute where ΔA = change in absorbance

CONCLUSIONS

Activation energies for heat-induced color-intensity change in the sapwood and heartwood of coastal Douglas-fir were calculated to be 15 kcal/mole as compared with 11 kcal/mole for white spruce. Differences in behavior for the above species were attributed to the presence of dihydroquercetin (DHQ), a major phenolic extractive in Douglas-fir but absent in white spruce. An activation energy of 31 kcal/mole was calculated for the thermally induced color-intensity change in 2.0% (w/w) DHQ-impregnated filter paper.

REFERENCES

BARTON, G. M. 1968. Significance of western hemlock phenolic extractives in pulping and lumber. For. Prod. J. 18(5):76–80.

CHOW, S. 1971. Determining veneer surface inactivation by a reflectance colorimeter. For. Prod. J. 21(2):19–24.

HILLIS, W. E. 1969. The contribution of polyphenolic wood extractives to pulp colour. APPITA 23(2):89–101.

KRINGSTAD, K. P., AND S. Y. LIN. 1970. Mechanism in the yellowing of high-yield pulp by light. TAPPI 53:2296–2301.

LEARY, G. U. 1968. The yellowing of wood by light: Part II. TAPPI 51:257–260.

LIN, S. Y., AND K. P. KRINGSTAD. 1970. Photosensitive groups in lignin and lignin model compounds. TAPPI 53:658–663.

LUNER, P. 1960. Brightness of high yield pulps. II. Reductive bleaching of cold soda pulp from white birch with sodium borohydride. TAPPI 43:819–826.

RAPSON, W. H., AND K. A. HAKIM. 1957. Carbonyl groups in cellulose and colour reversion. Pulp Paper Mag. Can. 58(8):151–157.

POLCIN, J., M. WAYMAN, C. B. ANDERSON, AND W. H. RAPSON. 1969. Sapwood and heartwood groundwood of western hemlock and jack pine. Part 1. Influence of extractives on optical properties. Pulp Paper Mag. Can. 70(7):T410–T417.

POLCIN, J., AND W. H. RAPSON. 1971. Sapwood and heartwood groundwood of western hemlock and jack pine. Part II. Heat stability of extractives. Pulp Pap. Mag. Can. 72(10): T324–T330.

SJÖSTRÖM, E., AND E. ERIKSSON. 1968. The influence of carboxyl and carbonyl groups on the brightness stability of bleached pulps. TAPPI 51:16–19.

VAN DEN AKKER, J. A., H. F. LEWIS, G. W. JONES, AND M. A. BUCHANAN. 1949. The nature of the colour changes in groundwood. TAPPI 32:187–192.

WAYMAN, M., C. B. ANDERSON, AND W. H. RAPSON. 1968. Bleaching characteristics of heartwood and sapwood groundwood of jack pine and western hemlock. Pulp Pap. Mag. Can. 69(5): T225–T234.