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Full title:

Aging of wood - Analysis of color changes during natural aging and heat treatment -

Running title:

Color changes due to ageing and heat treatment

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Abstract

The color properties of aging wood samples from historical buildings have been compared with those of recent wood samples that were heat treated at temperatures ranging from 90 to 180°C. The results of kinetic analysis obtained by the time-temperature superposition method showed that the color change during natural aging was mainly due to a slow and mild oxidation process. In other words, heat treatment could accelerate the changes in wood color that occur during aging. In one sample, the color change (ΔE^*_{ab}) after 921 years at ambient temperature was almost equivalent to that of heating (artificial aging) approximately for 6.7 h at 180°C. The results has been interpreted that the aging and the subsequent change in wood color begin at the time of tree harvesting.

Keywords

CIEL a^*b^* ; color change; heat treatment; historical building; kinetic analysis; natural aging

Introduction

Wood as a natural material can be deteriorated by biodegradation, weathering, and aging. The service life of wood can exceed thousands of years under conditions under which biodegradation and weathering is avoided. Then, aging becomes a major source of deterioration. The elucidation of the mechanism of wood aging is important not only for the preservation and restoration of wooden historical buildings but also for purposes of basic wood research. In Japan, there are many historical buildings made of wood with culturally significant properties, such as the Horyuji temple, which was constructed in the 7th century; it is the oldest wooden building in the world. Thus, the study of wood aging is of great significance in Japan, in a country with a long history of wood culture.

Aging is not well defined degradation, which proceeds slowly in wood under participation of the omnipresent oxygen and water. Some reports have described the properties of naturally aged wood in comparison with those of recent wood (Kohara and Okamoto 1955; Kohara 1958a, b; Fengel 1991; Sandu et al. 2003; Giachi et al. 2003; Viel et al. 2004; Esteban et al. 2006; Popescu et al. 2007; Yokoyama et al. 2009; Budrugaac and Emandi 2010). There is a large body of literature that reports also on the development of analytical methods suitable for studying naturally aged wood from heritages of cultural and historical importance. In an ideal case, the methods should be non-destructive, simple, and portable. Spectrometric methods were developed such as infrared or near-infrared spectrometry (Marengo et al. 2004; Tsuchikawa et al. 2005; Kandemir-Yucel et al. 2007; Castellini et al. 2008; Desnica et al. 2008; Inagaki et al. 2008a, b). There is a large progress in this field and in the development of protecting and preserving wooden cultural heritages (Falciari et al. 2003; Giorgi et al. 2005, 2009; Björdal and Nilsson 2008; Mahltig et al. 2008; Bugani et al. 2009). However, to understand the basic mechanism of wood aging, sample materials with an extended time of aging periods are needed. Kohara and Okamoto (1955, 1958a, b) widely investigated the natural aging of wood in historical buildings but a drawback in these studies was that the age of the wood was estimated based on the architectural history and style of the buildings.

During long time use of wood, possible factors of aging may be due to the combined effect of thermal oxidation by air-oxygen, which is partly dissolved in water, and acid hydrolysis by bond water and acids contained in wood. The aging mechanism of wood has been discussed by investigating heat treatment of wood, which is a kind of simulated aging. Heat under dry conditions supposed to be accompanied by thermal oxidation of wood components, while under moist conditions the more frequent participation of hydrolysis can be expected. Kohara (1958b) compared the naturally aged wood and heat-treated wood at up to 175°C un-

der both dry and moist conditions and claimed that thermal oxidation is prevalent under ambient conditions and at higher temperatures both oxidation and acid hydrolysis are active. Stamm (1956) and Millett and Gerhards (1972) also suggested that wood aging is a mild thermal oxidation at room temperature. However, few papers have evaluated the theoretical aspects and detailed mechanisms of thermal oxidation on aging.

As reviewed by Esteves and Pereira (2009) and reported in many literatures (Windeisen et al. 2009; Stanzl-Tschegg et al. 2009; Pfriem et al. 2009; Bryne and Wälinder 2010; Bryne et al. 2010), heat treatment induces various changes in wood properties: decrease in density, equivalent moisture content, and mechanical properties; improvement of dimensional stability and hydrophobicity; and both favorable and unfavorable change in color. Some properties of heat treated woods are in correlation with the inevitable color changes (Bekhta and Niemz 2003; Brischke et al. 2007; González-Peña and Hale 2009a,b)

Kinetic analysis could be an effective method for theoretical prediction and practical evaluation of natural aging of wood in comparison with accelerated aging of various materials. There are several publications on paper-aging kinetics (Zou et al. 1996a, b; Łojewska et al. 2006), but successful studies of wood-aging kinetics are rare because of the higher complexity of the problem and the lack of old wood with reliably known age.

The present study is dealing with the kinetics of color change of wood during natural aging and dry heat treatment in the context of historical buildings in Japan. It would be beneficial if significant properties of wood from the cultural heritage could be analyzed by color measurements as it is non-destructive and requires small areas. Practitioners working with wood of historical buildings and statures – such as sculptors, carpenters, and restorers – frequently evaluate the aged wood quality based on its color. Experience shows that color properties are in direct relation to aging, i.e the lightness of wood decreases and the hue is shifted slightly to red (Kohara 1958a). The same behavior in color was observed in the change induced by thermal treatment (Bekhta and Niemz 2003; Brischke et al. 2007; González-Peña and Hale 2009a,b; Matsuo et al. 2010).

In our previous study (Matsuo et al. 2010), it was possible to predict color changes that occur during aging by means of the kinetic analysis method successfully applied to color changes of wood heated. In this study, colors of wood samples of historical buildings, the ages of which were evaluated reliably by scientific methods, were evaluated. The data will be compared with the colors of wood heated under the completely dry conditions by means of kinetic analysis. The results will show whether thermal oxidation is the main factor for color change during aging.

Materials and methods

Specimens

Hinoki wood (*Chamaecyparis obtusa* Endl.), the typical wood used in traditional buildings

and Buddhist sculptures in Japan, was studied. Samples with homogeneous grain were carefully selected. The aging time and origin of eight naturally aging wood samples (A – H) collected from historical buildings are listed in Table 1. The age determined by dendrochronology, by radiocarbon dating, and data found in historical documents were in agreement. Heartwood specimens were cut out from inner parts of the samples, which were free from discoloration by bio-degradation, weathering and any stain and defect; dimensions: of 60 mm (L) x 10 mm (R) x 2 mm (T). The mechanical characteristics of these samples are described by Yokoyama et al. (2009).

The log (harvested 1988) from which the control specimens were taken, was grown from 1629 to 1988. It was dried for 18 years under ambient conditions in a shed. Its color properties were reported by Matsuo et al. (2010). The specimens were heated at temperatures ranging from 90 to 180°C in the time scale from 0.5 to 18432 h (768 days) as described in Table 2 (a). The specimens were then cooled at room temperature in a desiccator with silica-gel.

To compare the effects of natural aging, heat treatment, and a combination of natural aging and heat treatment, specimens from sample F (shown in Table 1), aged for 921 years, were heated in an air-circulating oven at various temperatures and times given in Table 2 (b) and then cooled in the same way as the heat-treated specimens. All specimens were protected from photo-discoloration by storing in a box or a desiccator in a windowless room.

TABLE 1 Naturally aging wood samples with the names of their sources and their aging times.

Sample	Source of supply	Age ^a (year)
A	Horyuji temple, Nara	1573
B	Horyuji temple, Nara	1395
C	Horyuji temple, Nara	1505
D	Horyuji temple, Nara	1470
E	Horyuji temple, Nara	1215
F	Horyuji temple, Nara	921
G	Horyuji temple, Nara	737
H	Senjuji temple, Mie	569
Control	-	19

^a Age (i.e. aging time, which was determined as the age of the outermost part of the sample detected by dendrochronology as of AD 2007.

TABLE 2 Treatment temperatures and times of sample F, aged 921 years, (a) heat-treated recent wood samples and (b) heat-treated historical naturally aging wood (sample F).

	Treatment times for samples F heated to			
	the temperatures			
	90°C	120°C	150°C	180°C
	(h)	(h)	(h)	(h)
a) Recent	256~18432 ^a	32~7680	4~960	0.5~120
b) Sample F	-	384~2696	54~560	4~42

^a The treatment at 90°C is now in process with a planned treatment time limit of 61440 hours.

Color measurement

The color of the specimens was measured with a spectrophotometer (KONICA MINOLTA CM-2600d) under a D65 light source and an observer angle of 10°. The sensor head of the spectrophotometer was 8 mm in diameter, which was sufficient to eliminate the influence of variation of earlywood and latewood on color values because the average annual ring width was 1.0 mm (Yokoyama et al. 2009; Matsuo et al. 2010), and the specimens had a homogenous grain. The CIELAB color parameters (L^* , a^* , b^*) and the color differences (ΔE^*_{ab}) were used for the kinetic analysis. The differences in ΔL^* , Δa^* , and Δb^* and the total color differences ΔE^*_{ab} were calculated using the following formulas (JIS 2008, 2009):

$$\Delta L^* = L^* - L_0^*; \quad \Delta a^* = a^* - a_0^*; \quad \Delta b^* = b^* - b_0^* \quad (1)$$

$$\Delta E^*_{ab} = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \quad (2)$$

where L^* is the lightness and a^* and b^* the color coordinates under any testing condition, and L_0^* , a_0^* , and b_0^* the corresponding reference values obtained as the average of 83 untreated specimens. L_0^* , a_0^* , and b_0^* were 82.0, 7.20, and 22.2, respectively. Nine to 16 specimens of naturally aging wood, 3 to 5 specimens of heat-treated wood, and 1 to 2 specimens of heat-treated naturally aging wood were tested at each condition. Three locations in each specimen were measured, and the average values with standard deviations were calculated for the whole set of measurements at the given condition.

Results and discussion

Color changes

Figure 1 shows the specimen images. The naturally aging and heat-treated wood became darker with increasing aging and treatment time, respectively. The color changed uniformly from the outside to the middle of the specimens. Table 3 gives the changes in the L^* , a^* , b^* , and ΔE^*_{ab} values of naturally aging wood, and Figure 2 compares ΔE^*_{ab} of natural aging wood to that of heat-treated wood (Matsuo et al. 2010). In both recent and naturally aging wood, L^* decreased and a^* , b^* , and ΔE^*_{ab} increased with aging time. The measured color values of

control specimens were near to the reported values and color changes and the data between natural aged woods and those of heat treated recent woods are sufficiently larger than the reported variations in color of hinoki wood (Mitsui et al. 2001, 2005; Tsushima et al. 2006).

TABLE 3 Number of specimens and CIE data concerning L^* , a^* , b^* , and ΔE^*_{ab} of naturally aging wood with standard deviations in parentheses.

Sample, age	# Specimens	L^*		a^*		b^*		ΔE^*_{ab}	
A, 1573	16	62.11	(1.39)	11.36	(0.38)	27.82	(0.75)	21.11	(1.35)
B, 1395	10	58.31	(1.68)	12.01	(0.50)	26.66	(0.79)	24.62	(1.62)
C, 1505	11	59.34	(1.14)	11.19	(0.25)	26.29	(0.78)	23.40	(1.07)
D, 1470	15	57.62	(1.59)	11.95	(0.32)	26.47	(1.22)	25.25	(1.46)
E, 1215	15	63.25	(0.96)	11.09	(0.39)	27.23	(0.81)	19.82	(0.97)
F, 921	15	65.66	(1.01)	10.56	(0.40)	27.00	(0.71)	17.39	(1.02)
G, 737	9	67.41	(0.56)	10.91	(0.26)	27.70	(0.60)	16.04	(0.56)
H, 569	15	73.20	(0.77)	9.37	(0.43)	25.89	(0.65)	9.81	(0.88)
Cont., 19	83	82.01	(0.84)	7.20	(0.61)	22.22	(1.03)	0.00	-

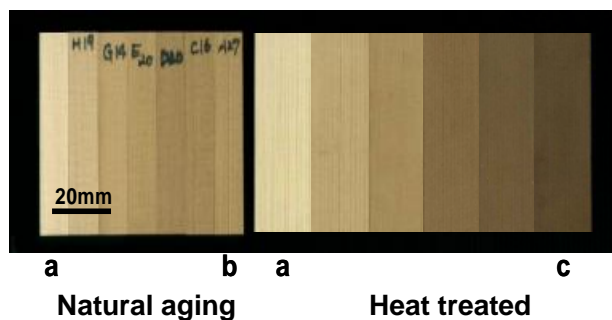


FIGURE 1 Color change of naturally aging and heat-treated wood (a: control (untreated wood), b: aged for 1573 years, c: treated at 180°C for 120 h). The specimens are arranged in order of increasing aging or treatment time.

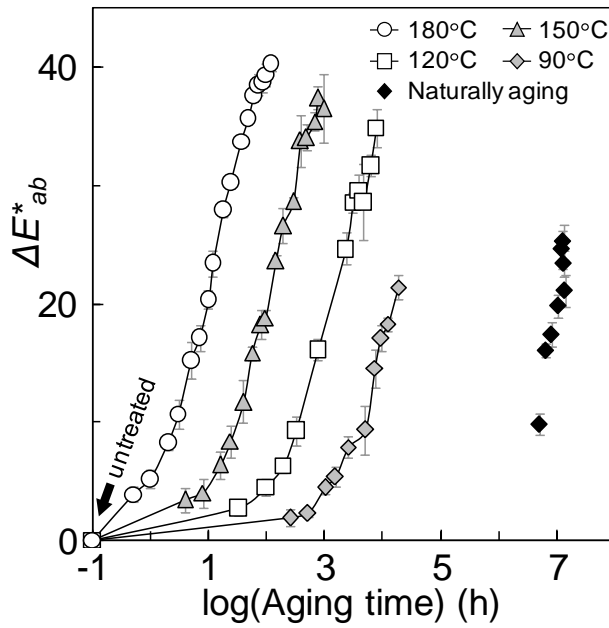


FIGURE 2 Changes of ΔE^*_{ab} during natural aging and heat treatment as a function of time and temperature. (error bar: standard deviation)

Kinetic analysis and color changes of natural and accelerated aging

Kinetic analysis using the time-temperature shift factor (a_T) was adopted to predict the color change during natural aging in our previous article (Matsuo et al. 2010). The brief description of the analysis is as follows.

Generally, it is known that a chemical reaction can be described by an Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where k is the rate constant of the chemical reaction, A the frequency factor, E_a the apparent activation energy, R the gas constant, and T the absolute temperature of the reaction. The apparent activation energy is then obtained from the slope of the Arrhenius plot, which is the logarithm of the determined time versus the reciprocal of treatment temperature (Atkins and Paula 2010). The regression line of the Arrhenius plot allows the determination of the reaction rate at any temperature. To determine the activation energy based on all of the data, the time-temperature superposition principle (TTSP) (Ding and Wang 2007) is often applied. According to the TTSP, when the curves of the measured material parameter vs. logarithmic treatment time at different temperatures can be superimposed by proper scale changes on the log time axis, the shift distance along the logarithmic time axis is called the time-temperature shift factor a_T , given by

$$a_T = t_T / t_{ref} \quad (4)$$

where t_{ref} is the test time at a reference temperature T_{ref} , and t_T is the time required to give the

same response at the test temperature T . Combining Eqs. (3) and (4) gives

$$a_T = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (5)$$

where both T and T_{ref} are absolute temperatures. Plotting $\ln(a_T)$ vs. $1/T$ is another way to calculate E_a and to predict changes in properties under ambient conditions. In the present study, a logistic function was chosen to describe the changes of L^* and ΔE^*_{ab} and a polynomial expression for those of a^* and b^* . All parameters of the functions were estimated using a non-linear iterative curve-fitting method and the coefficient of determination R^2 is determined to express the goodness of fit:

$$R^2 = \frac{\sum_{i=1}^n (\hat{Y}_i - \bar{Y})^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2} \quad (6)$$

where the values \hat{Y}_i are measured values, Y_i the modeled values, and \bar{Y} the average of measured data. The measured color properties of the naturally aging wood were superposed by using the multiplying factor a_T on the time axis to fit the regression curve at 180°C. The proper a_T values were determined by the non-linear iterative curve fitting method. Figure 3 shows the superposed data with the regression curve. A well-superposed curve implied that the color changes might have been caused by the same process irrespective of natural aging or heat treatment. Regression curves fit well along the whole data set ($R^2 > 0.99$ in L^* and ΔE^*_{ab} , and $R^2 > 0.87$ in a^* and b^*). Our previous study showed that the calculated apparent activation energies of heat-treated wood on L^* , a^* , b^* , and ΔE^*_{ab} were 117, 94.3, 116, and 114 kJ mol⁻¹, respectively. The quoted study also concluded that the color change during the heat treatment was explained as thermal oxidation irrespective of treatment temperature. The color change in the ambient condition was predicted based on these results and compared with the change measured in naturally aging wood. That is, the Arrhenius plots were extrapolated to the temperature of 15°C, i.e. to the annual mean air temperature in historical buildings in Nara, Japan (Nagata 1970, 1971a, b). Then, the a_T calculated from the extrapolation was compared with the a_T determined from empirical data. The Arrhenius plot of ΔE^*_{ab} is presented in Figure 4 (1) as an example, but the plots of L^* , a^* and b^* exhibited similar features.

The a_T calculated from empirical data was lower than that calculated from the extrapolation, implying that the plot did not necessarily keep a linearity over the reaction temperature range. Such a non-linearity of the Arrhenius plot has been observed for the mechanical properties of various polymeric materials (Celina et al. 2005; Ding and Wang 2008). Gillen et al. (2005) and Bernstein and Gillen (2010) ensured the existence of a non-Arrhenius behavior by

comparing the naturally aging polymer samples with the samples treated at widely-ranged temperatures. Or, as applied for a lot of accelerated deterioration tests, the lower a_T of the naturally aging samples may result in that the change was accelerated because of the moisture in the cell wall which induces the hydrolysis, the repetition of drying and wetting, and the repetition of hot and cold periods.

However, the analysis by using the linear correlation of the Arrhenius plot is an effective way to predict the lifetime (Rowe and Rimal 2008; Rowe et al. 2010; Arrieta et al. 2010). The regression lines for the plots including both heat treatment and natural aging (Figure 4 (2)) showed fairly good linearity ($r > 0.99$) in all color parameters. Based on the good linearity, we can conclude that the color change during natural aging was similar to that of the heat treatment, namely the thermal oxidation. This conclusion needs further inspection concerning the linearity of Arrhenius behavior for exact prediction and elucidation of wood aging. Conceivable experiments are, for example, heat treatment at the temperature below 90 °C or accelerated deterioration test considering moisture in the cell wall.

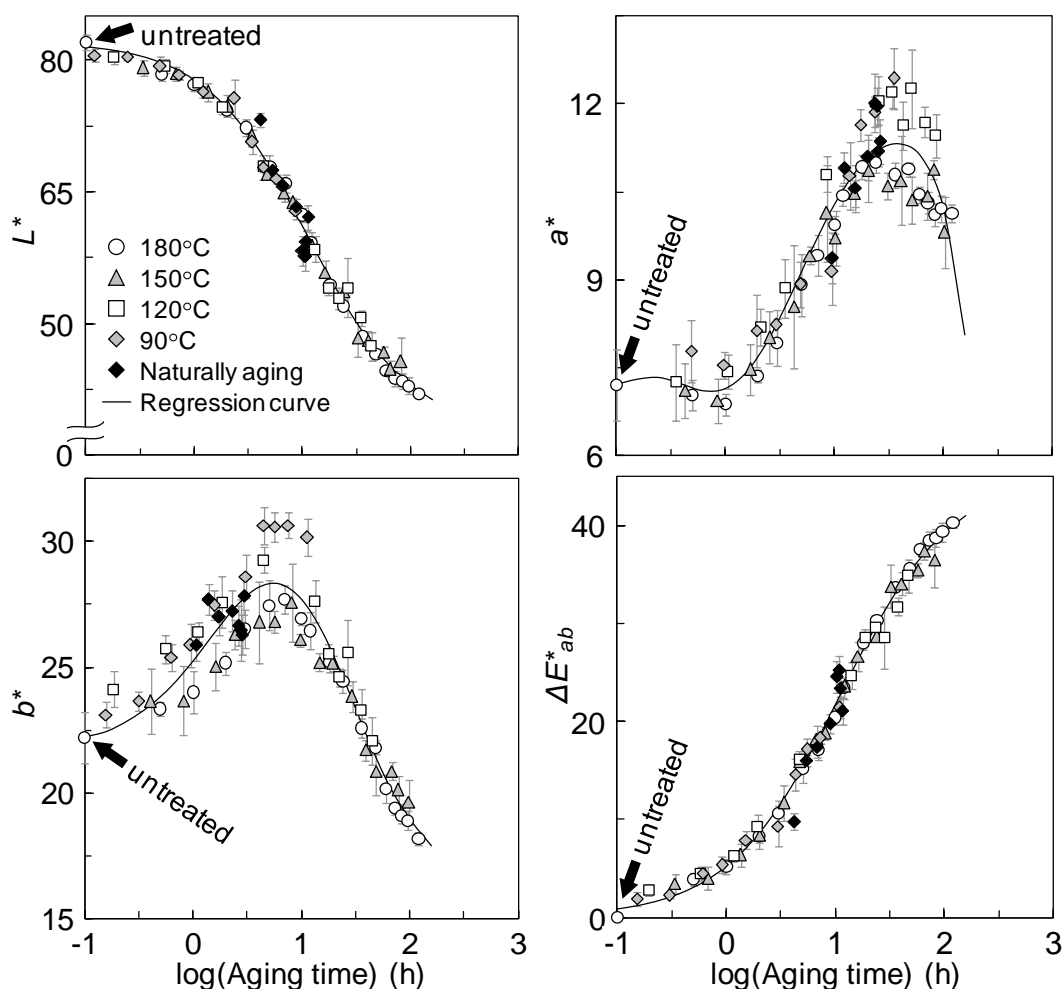


FIGURE 3 Superposed color properties with master curves using a_T at each temperature. (error bar: standard deviation)

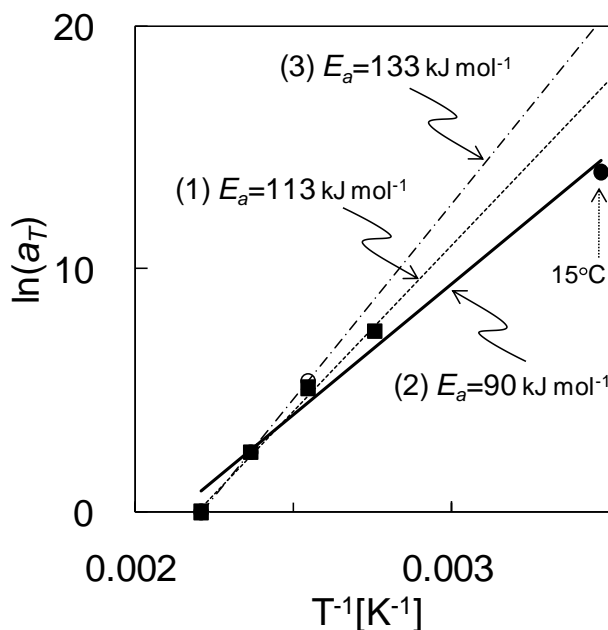


FIGURE 4 Arrhenius plots of shift factors from empirical superposition of the change of ΔE_{ab}^* , regression lines and apparent activation energies for the plots of (1) heat-treated wood, (2) heat-treated wood and naturally aging wood, and (3) heat-treated naturally aging wood. (■: heat-treated, ●: natural aging, ○: heat-treated after natural aging)

Color changes during heat treatment of naturally aging wood

In the preceding section, the conclusion was that color changes during natural aging could be explained mainly as thermal oxidation, and they could be accelerated by heating. The hypothesis is that color changes during natural aging involves similar processes as those observed during accelerated aging by heating. This means that the heat treatment of sample F (Table 2 b), which included a combination of natural aging and heat treatment, should cause a color change similar to that of natural aging or heat treatment only. According to the shift factor calculated, the color change (ΔE_{ab}^*) after 921 years in the ambient temperature was almost equivalent to that of approximately 6.7 h at 180°C. Therefore, the total color change that occurred during natural aging for 921 years and during 180°C treatment for x h was plotted as the change for $(6.7 + x)$ h. Figure 5 shows the superposed data obtained by the shift factors calculated from the color changes of heat-treated wood.

The aging time in the figure represents the total treatment time calculated as aging at 180°C. The changes of heat-treated naturally aging wood were well-superposed on those of heat-treated wood. This confirms the hypothesis that the mechanism of the color change during heat treatment might be the same as that occurring during natural aging. The values of the

apparent activation energies are summarized in Table 4. Although those of heat-treated naturally aging wood were somewhat higher than the others, those of L^* and ΔE^*_{ab} were within the framework of reported values (Stamm 1956; Millett and Gerhards 1972). The higher energies of a^* and b^* means that they change more slowly than L^* and ΔE^*_{ab} . However, the range of these data was not sufficient to evaluate them more accurately.

TABLE 4 Apparent activation energies (E_a) and correlation coefficients (r) calculated from the shift factors of (1) heat-treated wood, (2) heat-treated wood and naturally aging wood, and (3) heat-treated naturally aging wood.

CIE data	Activation energies E_a for samples no.			Regression coef. r for samples no.		
	(1) ^a (kJ mol ⁻¹)	(2) (kJ mol ⁻¹)	(3) (kJ mol ⁻¹)	(1) ^a	(2)	(3)
L^*	117	90	135	0.998	0.990	1.000
a^*	95	84	154	0.993	0.997	0.998
b^*	114	99	153	0.996	0.997	0.999
ΔE^*_{ab}	113	90	133	0.997	0.992	1.000

^a data from Matsuo et al. (2010)

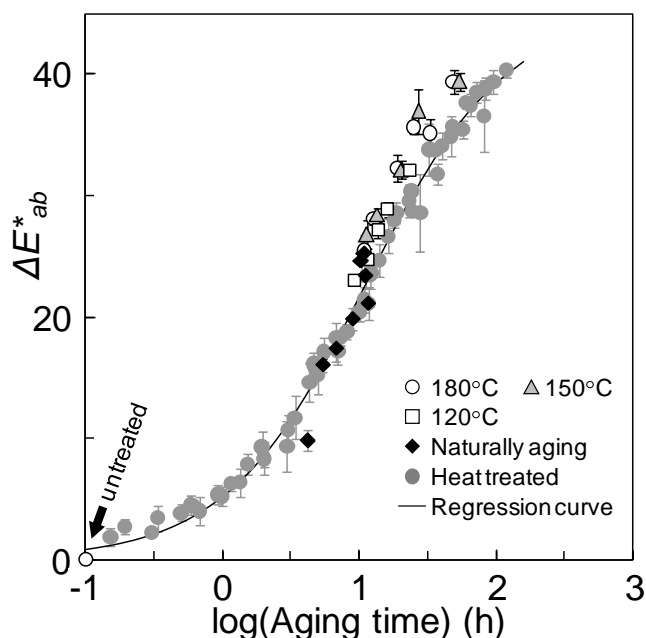


FIGURE 5 Superposed data of heated wood after aging for 912 years using a_T calculated from heat-treated wood (●: heat-treated wood at 90-180°C superposed by a_T , error bar: standard deviation).

The beginning of wood aging

Fengel (1991) indicated that the aging of wood begins with the cutting of a tree and that alterations of the wood substances begin shortly after a tree has been cut. Moreover, chemical changes after heartwood formation, i.e. the formation of a physiologically dead part of the xylem (Panshin et al. 1964), play probably also a role in wood aging. This section discusses the beginning of wood aging based on the results of the former section.

In our previous study, in which color changes were measured in a recently harvested wood sample (Matsuo et al. 2010), there was a slight change in the color parameters with the time of heartwood formation. Figure 6 shows the L^* variation within the recently harvested wood sample as compared with that variation predicted with E_a of 90 kJ mol^{-1} , which was calculated from the a_T of both heat treatment and natural aging. There was little change in L^* within the range of approximately 160 years from which almost all specimens were cut out. The variation within the wood sample was much smaller than the predicted change. This can be interpreted that most wood aging that is responsible for color changes begins with tree harvesting and wood processing. This conclusion also requires further examination, including an examination of the question how to evaluate the tree cutting time from wood samples that do not have their outer-most annual rings.

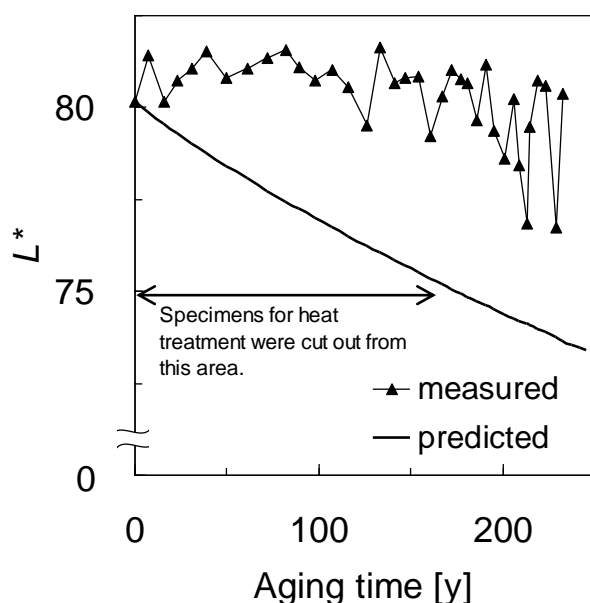


FIGURE 6 The L^* value measured along the radial direction on the radial section from the sapwood/heartwood boundary toward the pith as compared with predicted natural color changes. Aging time was determined as the time from heartwood formation. The arrow indicates the area from which the specimens for heat treatment were cut out.

Conclusions

The color changes of naturally aging wood samples were measured and kinetically analyzed. The value of L^* decreased and those of a^* , b^* , and ΔE^*_{ab} increased with the aging time both for natural and artificial aged wood by heat-treatment. As a result of the kinetic analysis, the color changes during natural aging could be mainly explained as a mild thermal oxidation. This result was also supported by analyzing the color changes of heat-treated naturally aging wood. Predictions of natural color changes were interpreted that most wood aging responsible for color changes begins not with heartwood formation but with tree harvesting and wood processing.

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