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# Effect of Heat Treatment on Some Properties of Douglas-Fir

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**ABSTRACT.** In a study of the effect of prolonged heating on dielectric and other properties of Douglas-fir, specimens were subjected to heat treatment at 170°C. for intervals that ranged from 10 to 100 hours. Weight, dimensions, and dielectric properties were measured before and after the heat treatment at two moisture levels of 8 percent and ovendry. Surface reflectance of treated specimens was also measured. Reduction in weight and density of the wood that resulted from mild thermal decomposition did not follow a first order kinetic reaction during the first 30 hours of treatment. After that, the change in both weight and density followed a first-order reaction. Equilibrium moisture content (during absorption) of the wood at 70°F. (21°C.) and 65 percent relative humidity was reduced with increasing duration of treatment. After 100 hours of treatment, the equilibrium moisture content was reduced by 1.5 percent, based on the ovendry weight. Dielectric properties also were modified by the treatment. Dielectric properties of the wood were more sensitive to the heat treatment at low frequencies (100 Hz and 1 kHz) than at 100 kHz. There was a tendency for the dielectric loss spectrum to shift toward lower frequency with increasing duration of treatment. The logarithm of surface reflectance of treated wood showed a straight-line relation with the duration of treatment, which suggests that thermal decomposition initiates at the surface, and then penetrates gradually into the wood.

THE OBJECTIVE OF THIS INVESTIGATION WAS to determine whether prolonged heating causes changes in dielectric and other properties of wood.

Heating is one of the essential processes in converting raw material into final products in the wood industry. For example, lumber usually is dried by high temperatures. In making plywood, heat is applied when steaming veneer logs, drying veneers, and hot-pressing veneers into plywood. High-temperature treatments are also applied to form wood and fiber composites and to reduce their hygroscopic properties. Unfortunately, like many other polymeric substances, wood and cellulose are not very stable to heat, and even at moderate conditions, there is a slow thermal decomposition that results in changes of many physical and mechanical properties. Our understanding of the mechanism of thermal degradation and the effect of heat treatment on the properties of wood is, therefore, essential in using heat in a production process to improve or modify the properties of wood and fiber composites.

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## Procedure

Quarter-sawn, kiln-dried Douglas-fir lumber was machined into pieces 4 inches square by ¼-inch thick in the tangential direction, and the pieces were stored indoors for 2 years. Forty specimens were then randomly selected and were conditioned at 70°F. and 65 percent relative humidity for 3 months. After conditioning the specimens averaged 8.61 percent E.M.C. Weight and dimensions of the specimens were determined before taking dielectric measurements. Each specimen was then placed between a pair of parallel-plate copper electrodes 4 inches square, and series capacitance and loss factor of the specimens were measured using a General Radio 1610 B Capacitance Measuring Assembly. Dielectric properties of the specimens were measured at 70°F. (21°C.) at frequencies of 100 Hz (Herz), 1 kHz (kilo Herz), 10 kHz, and 100 kHz with amplitude of the sinusoidal electric field kept at 7 volts peak-to-peak at the input terminals of a capacitance bridge. After the specimens were ovendried at 105°C. for 24 hours and cooled, weight and dielectric properties were remeasured. To minimize the resorption of moisture after ovendrying, all specimens were wrapped individually in plastic sheeting immediately after their removal from the oven, and were kept in a polyethylene bag until they were placed in a high-temperature oven. Specimens were exposed to atmospheric conditions only while measuring them. By taking these precautions, moisture resorption was reduced to within 0.3 percent of the ovendry weight.

All specimens were then randomly divided into 10 groups of four specimens each, and they were assigned to 10 different durations of treatment that ranged from 10 hours to 100 hours at 10-hour intervals. Heat treatments were applied in a forced-air circulating oven controlled at 170°C. ± 3°C. At the end of the treatments, specimens were wrapped in plastic immediately upon removal from the oven, and were allowed at least 10 minutes to cool. Weight, dielectric properties, and dimensions of the specimens were then remeasured. After measuring, specimens were replaced in conditions of 70°F. and 65 percent relative humidity for 3 months. After sorption, their average E.M.C. was 7.71 percent. The dielectric properties and sorption characteristics of the specimens were re-examined.

To determine quantitatively the darkening of the surface of the specimens caused by the heat treatment, surface reflectance of the conditioned specimens was measured with an Elrepho surface-reflectance photometer. The surfaces of the specimens were slightly sanded with a 220-grit silicon carbide abrasive paper and cleaned by high-pressure air to remove sanding dust before measuring.

Surface reflectance of the wood was measured through three filters needed to determine tristimulus values. Trichromatic coefficients were calculated from the tristimulus values (10,11). Surfaces of all heat-treated specimens were dark reddish brown, so an R68 filter was used to determine surface reflectance because this filter has an effective transmitting wavelength of 681 millimicrons and has absorption edges only towards shorter wave lengths.

## Results and Discussion

### Effect on Weight and Density

According to Stamm (7) and Kohara and Okamoto (4), the rate of thermal degradation

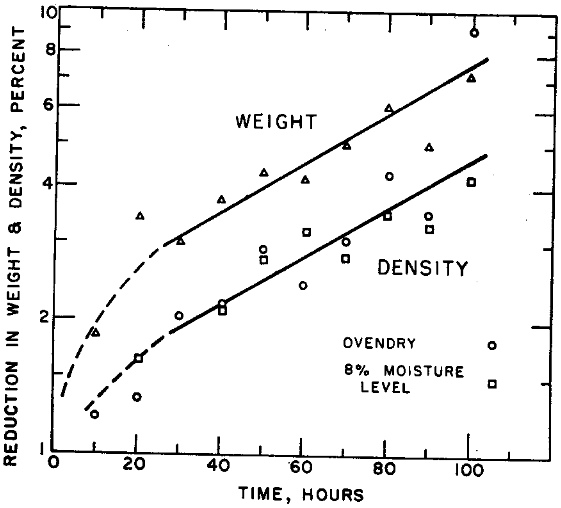

Figure 1. — Reduction in weight and density (on a logarithmic scale) of Douglas-fir wood by thermal degradation during heat treatment at 170°C., based on measurements before heating. Each point in the figure represents an average for four specimens. Note that the relations between the variables appear to deviate from linear below about 30 hours of heating.

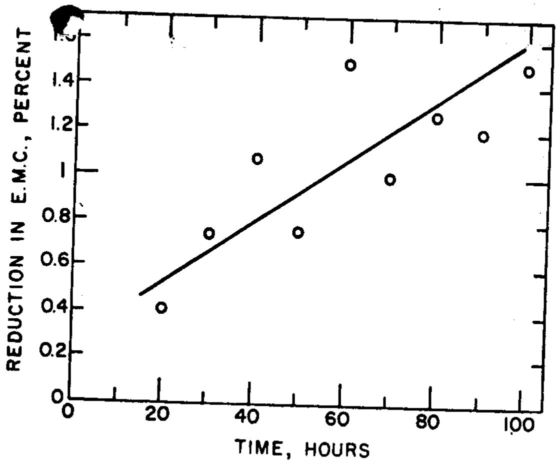

Figure 2. — Effect of heat treatment at 170°C. on the equilibrium moisture content of Douglas-fir wood in an environment of 21°C. and 65 percent relative humidity. Each point in the figure represents an average of four values. The values for E.M.C. represent reductions in percentage points from the E.M.C. before heating.

of wood follows a first-order reaction and also would follow Arrhenius' relationship. This statement is based on the observation that there is a linear relation between the logarithm of change in weight (log $\Delta W$) and the duration of heat treatment ($t$) at a constant temperature, and that the slope of the straight line is also related linearly with the reciprocal of absolute temperature.

The semi-logarithmic relation between change in weight ($\Delta W$), which is expressed in percent based on ovendry weight of unheated wood, and time is shown in Figure 1. A straight-line relation started at about 30 hours of treatment; before that time the relation was curved. Stamm (7) obtained similar results, and he considered that the initial curved relation is caused by escape of residual moisture from wood. In this study, all specimens were oven-dried before the heat treatment, and changes in weight during treatment were with respect to their ovendried weight before the test. Therefore, the curved relation between log $\Delta W$ and time may not have been caused strictly by the escape of residual water from wood, but rather because of simultaneous heterogeneous reactions of thermal degradation. A small amount of residual water and water reabsorbed after ovendrying for 24 hours at 105°C. might cause hydrolysis during the initial period of heat treatment, which would add to the complexity of the reaction. After 30 hours of treatment, thermal degradation throughout the specimen became a uniform process that may be termed a first-order reaction. The slope of the straight-line relation between log $\Delta W$ and time is calculated to be 0.0048 by linear regression analysis on those data beyond 30 hours of treatment. This value is about five times higher than that shown by Stamm (7) for wood heated at 170°C.

Density is a function of both weight and volume. During the process of thermal decomposition, the amount of wood substances reduces with time, accompanied by a contraction in dimensions. The logarithm of density (log $\rho$) is the difference between logarithm of weight (log $W$) and logarithm of volume (log $V$), that is, $\log \rho = \log W - \log V$.

Therefore:

$$\frac{d \log \rho}{d\, t} = \frac{d \log W}{d\, t} - \frac{d \log V}{d\, t}$$

If the contraction in dimensions with treatment occurs to the same extent as loss of weight, the density should remain constant. If the slope of log $\rho$ plotted against time is the same as that of log $W$ plotted against time, then change in the volume remains constant with respect to time, which was the result for this study (Fig. 1). The average reduction in the volume of the specimens was about 1 percent and was independent of the duration of the treatment. According to Kollman and Fengel (5), Fengel (1), and Kohara and Okamoto (4), hemicellulose and holocellulose decompose rapidly when they are subjected to heat at temperatures from 100 to 160°C. Lignin is stable, compared to hemicellulose and holocellulose. The state and function of hemicelluloses in wood are not so clearly understood as those of lignin and cellulose. Timell (9) suggested that hemicellulose may serve as an intermediary between lignin and cellulose in facilitating the encrustation of the microfibrils, and perhaps influences the moisture equilibrium of the living tree. It is possible that during the process of mild thermal

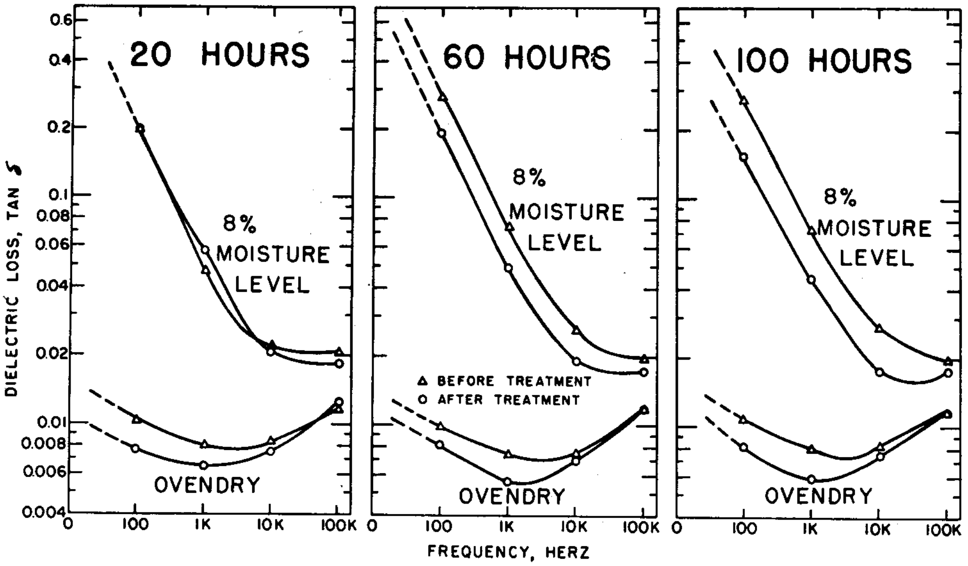

Figure 3. — Relation of frequency to loss tangent of Douglas-fir wood. Each point in the figures represents an average of four values. Loss tangent is equal to the ratio of loss current and charging current (5).

decomposition, hemicellulose and paracrystalline cellulose were depolymerized, with an accompanying initial contraction in dimension. Crystalline cellulose may be more stable than amorphous cellulose; if so, unless the crystalline cellulose is severely deteriorated, there will be no abrupt change in dimensions of the wood because of the treatment. Decomposition in paracrystalline cellulose and hemicellulose would change the hygroscopic characteristics and could possibly be the cause of the initial increases in Young's modulus and piezoelectric coefficients during the early state of heat treatment that were reported by Kohara and Okamoto (4).

## Effect on Equilibrium Moisture Content

Effect of heat treatment on the reduction in equilibrium moisture content (E.M.C.) of wood at 70°F. and 65 percent relative humidity during the sorption process is shown in Figure 2. After 20 hours of heat treatment at 170°C., the average E.M.C. of wood was 0.4 percentage point lower than the average E.M.C. of the same specimens before the treatment. The reduction in E.M.C. increased 1.5 percentage points when wood was treated for 100 hours. According to Yashiro (11), differential heat of wetting of wood treated up to 150°C. is reduced 90-160 cal. per gm of water, which is from about ⅛ to ⅕ of the values for untreated wood. The integral heat of wetting of heat-treated wood is also reduced about the same. Yashiro (11) considered that the reduction in heat of wetting could be attributed to the reduction in number of adsorption sites in wood because of the treatment. Heat may drive residual moisture out of wood and form strong hydrogen bonding in paracrystalline regions, or may even increase the degree of crystallinity of wood (10). Heat may also reduce the accessibility of water molecules by decomposing "sorption sites." In any event, the sigmoid shape of the relation between E.M.C. and relative humidity of wood and fiber composites will not be influenced by the treatment, because the sigmoid relation is caused by multilayer sorption of water molecules by wood. According to this multilayer sorption model for wood and cellulose (3), the number of multilayer sorption sites is governed by the number of primary sorption sites. Water sorbed by primary sites in turn serves as the secondary sorption sites. A reduction in the number of primary sites reduces the number of secondary sites, which in turn reduces consecutive sites of higher order, but it will not affect the sigmoid relation.

### Effect on Dielectric Properties

Dielectric properties, which are measures of the interaction of matter with an electric field, have been explained previously (6).

The effects of heat treatment on dielectric properties of wood are shown in Figures 3 through 7. In Figures 3 and 4, the dielectric frequency spectrum of specimens before and after heating is presented only for representative intervals of heating. In Figure 3, which shows on a logarithmic scale the frequency dependence of loss tangent of wood before and after heating, the loss tangent of heat-treated wood is smaller than that before the treatment when the frequency is at 100 Herz and at 1 kH (kilo Herz), but the difference is very much smaller at a frequency of 10 kHz. At 100 kHz, the difference in loss tangent before and after the treatment is difficult to discern. By viewing the effect of treatment on the over-all frequency spectrum, the spectrum shows the tendency for ovendry wood to shift toward the lower frequency side. The shift in spectrum is not pronounced for wood at the 8 percent level, especially for the specimens treated less than 60 hours at 170°C. The effect of heating on shifting in the frequency spectrum was not measured precisely because of limitation in the range of the capacitance measuring assembly used. Degree of heat treatment, however, did not show a consistent influence on the loss tangent of wood. Figure 4 shows the relation between frequency of the external electric field and the dielectric constant before and after heating. The dielectric constant of wood after the treatment was consistently low compared to that before the treatment. The rate of change in the dielectric constant of ovendried wood (Fig. 5) increased gradually up to 60 hours of treatment; after that, the dielectric constant remained constant even though weight and density of the wood decreased continuously with time (Fig. 1).

Reduction in dielectric parameters and shift in the spectrum of tan δ at the ovendried condition because of heating can be explained as follows: The dielectric properties of a material are functions of the number of polarizing elements and the freedom of rotation of the elements. During the initial process of heat treatment, both the number of polarizing elements and the freedom of their rotation are reduced because of the treatment. Reduction in the freedom of rotation of polar groups would tend to shift the frequency spectrum toward a lower frequency. After 60 hours, however, there may be formation of shorter chain molecules because of depolymerization of wood substances, which counterbalances the reduction in polar groups caused

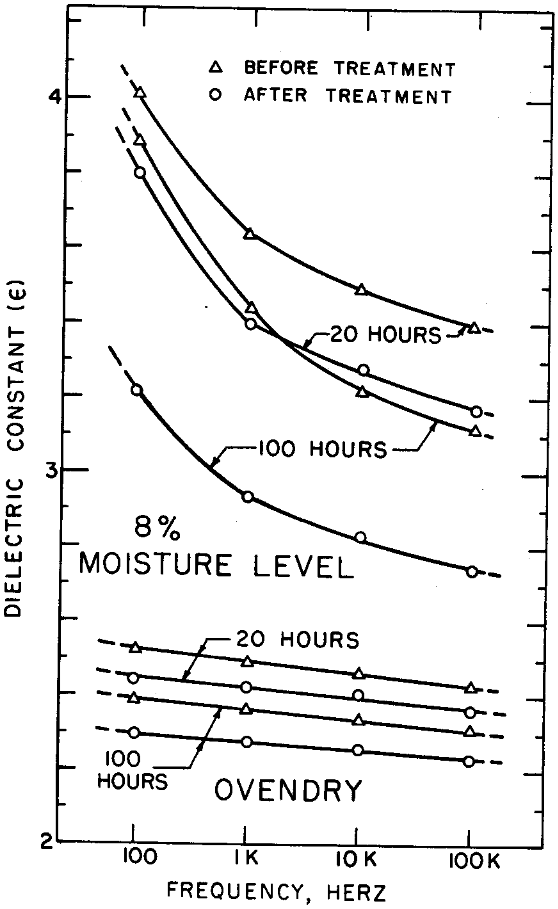

**Figure 4. — Dielectric constant for Douglas-fir at several frequencies before and after heating at 170°C. for 20 or 100 hours. Each point in the figure represents an average of four values. The dielectric constant is the ratio between the charge held by a capacitor with electrodes separated by a dielectric substance and the charge held by similar electrodes separated only by vacuum (5).**

by heating. As a result, there is no substantial change in dielectric properties after 60 hours of treatment.

Effect of heat treatment on the dielectric properties of a wood-water aggregate was twofold. One was a primary effect of the heating, which caused a change in polar groups of wood substances and was measured under ovendried condition as has been described previously. The other was a secondary effect, which resulted in reduction in E.M.C. of the wood because of heating. The secondary effect was estimated from the empirical relation between dielectric constant and moisture content at 1,000 megaherz (6), with dielectric constant $= 3.93(10^{0.0242M})$. Change in the dielectric constant caused by reduction in the E.M.C. of wood at various durations of treatment was then calculated, with the dielectric constant of wood at 8.6 percent moisture content as standard. This is the average E.M.C. of wood before heating. The expected reduction in dielectric constant of wood-water aggregate would be the sum of the primary and secondary effects (Fig. 5).

At 10 kHz and 100 kHz, the change in dielectric constant of wood-water aggregate agreed closely with the sum of the primary and the secondary effects. At 100 Hz and 1 kHz, the observed change in dielectric constant was consistently higher than the sum of the primary and the secondary effects, and this was especially so at 100 Hz. There are two possible causes.

One is that the estimated secondary effect is based on the empirical relation at the megaHerz region. The effect of moisture content on the dielectric constant of wood at audio frequencies may be higher than that at radio frequencies.

The second possible cause is that the interfacial polarization of wood (6) may appear at frequencies below 1 kHz when the moisture content is about 8 percent. This polarization may be more sensitive to the number of polar groups that will form interface upon application of an external field than to the freedom of motion of polar groups. At the frequency of 1 kHz, the increase in duration of treatment is not so pronounced as that at 100 Hz, perhaps because the frequency of 1 kHz may be the limit of interfacial polarization of wood at this moisture level.

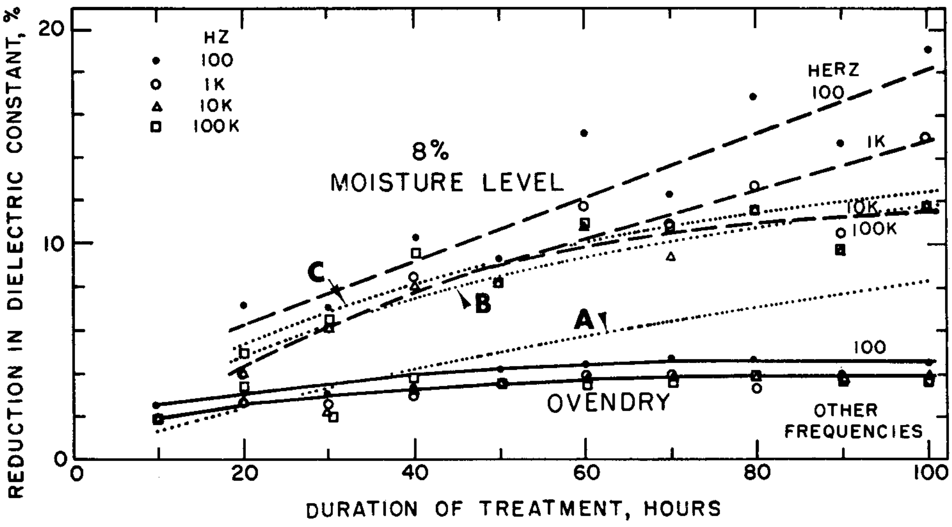

Figure 5. — The relation between duration of heating and reduction in dielectric constant of Douglas-fir wood because of heating at 170°C. Each point in the figure represents an average for four specimens. The calculated secondary effect on dielectric constant, curve A, plus the primary effect on ovendry wood, produces the combined effect shown for 100kH in curve B and for 100 H in curve C.

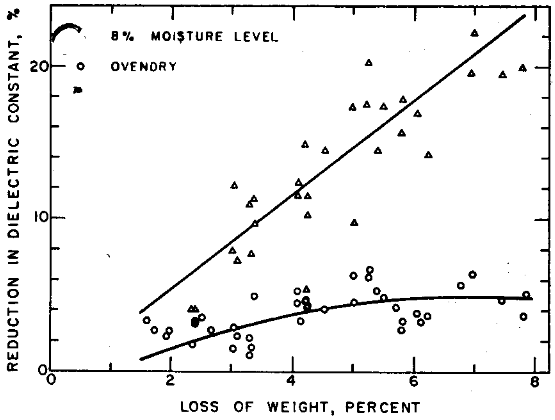

**Figure 6. — Relation of reduction in dielectric constant at 100 Herz of Douglas-fir heated at 170°C. to reduction in weight caused by the heating.**

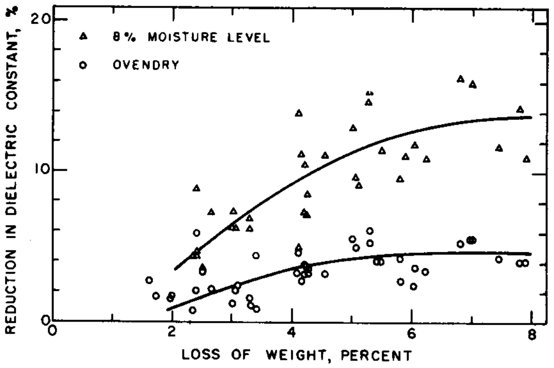

**Figure 7. — Relation of reduction in dielectric constant at 100,000 Herz of Douglas-fir heated at 170°C. to reduction in weight caused by the heating.**

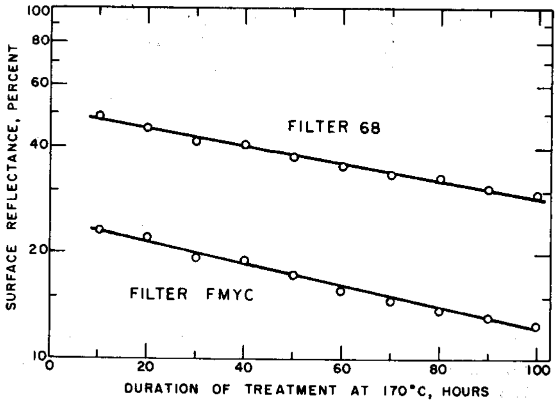

**Figure 8. — Relation of surface reflectance (on a logarithmic scale) of Douglas-fir heated at 170°C. to duration of heating. Each point in the figure represents an average for four specimens.**

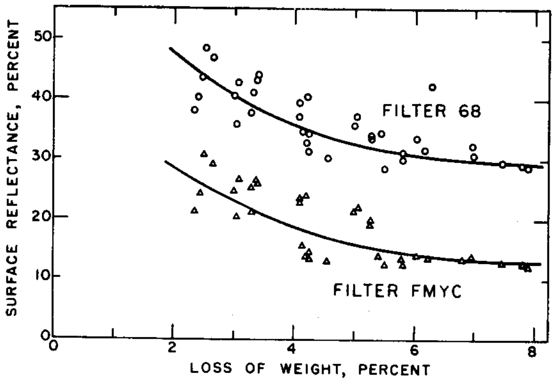

**Figure 9. — Relation of surface reflectance of Douglas-fir heated at 170°C. to reduction in weight caused by the heating.**

## Surface Reflectance

Surface reflectance of matter is usually compared with MgO powder as a standard. The reflectance shown in Figures 8 and 9 is, therefore, the relative surface reflectance of treated wood compared to the reflectance of compressed MgO powder as 100 percent. As shown in Figure 8, there is a very good linear relationship between the logarithm of reflectance and the duration of heat treatment, starting at 10 hours of treatment and extending through 100 hours of treatment. This result contrasts with the change in weight or density of wood (Fig. 1), in which the plot of log *W* and time is not a straight line up to 30 hours of treatment. During sanding to obtain a uniform surface for optical measurement, the color of treated wood at from 1 to 2 mm below the surface of the specimen was noted to be lighter than that at the surface. The surface of wood contaminated by natural resin in the wood during the process of treatment retained almost the original color of the specimen before the treatment. These findings indicated that the degree of thermal decomposition varies inversely with depth from the surface, and it agrees with the statement by Stamm (7) that the degradation reaction is at the surface of a solid. This could explain the deviation from a first-order reaction observed with change in weight during the initial period. Thermal decomposition of the wood specimens followed first-order kinetics

Table 1. — AVERAGE TRICHROMATICITY COEFFICIENTS AND LUMINANCE FACTOR OF HEAT-TREATED WOOD AT 170°C.

| Duration of treatment (hours) | x | y | z | Luminance factor (%) |
|---|---|---|---|---|
| 0[1] | 0.358 | 0.373 | 0.269 | 38.95 |
| 20 | .408 | .372 | .220 | 21.91 |
| 40 | .415 | .374 | .210 | 19.16 |
| 60 | .414 | .374 | .212 | 15.74 |
| 80 | .416 | .374 | .210 | 13.72 |
| 100 | .415 | .369 | .216 | 12.59 |

[1] Measurements were made on surplus specimens that were not heated.

as reported by Kohara and Okamoto (4), and by Stamm (7). It initiated at the surface of the wood and gradually progressed towards the interior. It probably took about 30 hours for the specimens to reach the point where decomposition progressed at a uniform rate throughout the specimen. The degree of decomposition, however, would appear in different degrees, depending on the depth below the surface. A temperature gradient may have been created across the thickness of the specimens by radiation and exothermic reaction during heating. Such a gradient, if it existed, was considered insignificant compared to fluctuations of temperature in the forced-air oven.

Table 1 shows trichromatic coefficients of heated wood. Trichromatic coefficients of treated wood were low compared to those of untreated wood. There was no appreciable difference among the periods of treatment. Y-stimulus, which is the surface reflectance measured using a FMY/C filter, is also known as luminance factor. The luminance factor of wood becomes less as duration of heating increases. The difference in the color characteristics of heated wood resulted mainly from reduction in the luminance factor.

## Conclusion

Mild thermal decomposition in a forced-air oven is a surface reaction. Loss in weight of wood and loss in surface reflectance follows a first-order reaction. The effect of thermal decomposition on dielectric properties of wood does not follow first-order kinetics.

Heating reduces hygroscopic properties of wood, probably because the number of water sorption sites in the cell walls has been reduced. This conclusion is based on Yashiro's observation (11) on the reduction in heat of wetting in wood that has been heated, and on the observation in this experiment that heating reduces the E.M.C. of wood.

Heating has more effect on the dielectric constant of wood at low than at high frequencies. Additional investigation may lead to the possibility that changes in the dielectric constant of wood may be measured to indicate intensity of degradation by heat. There was a considerable change in wood properties during the initial 20 hours of treatment. Future investigations should consider this fact.

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