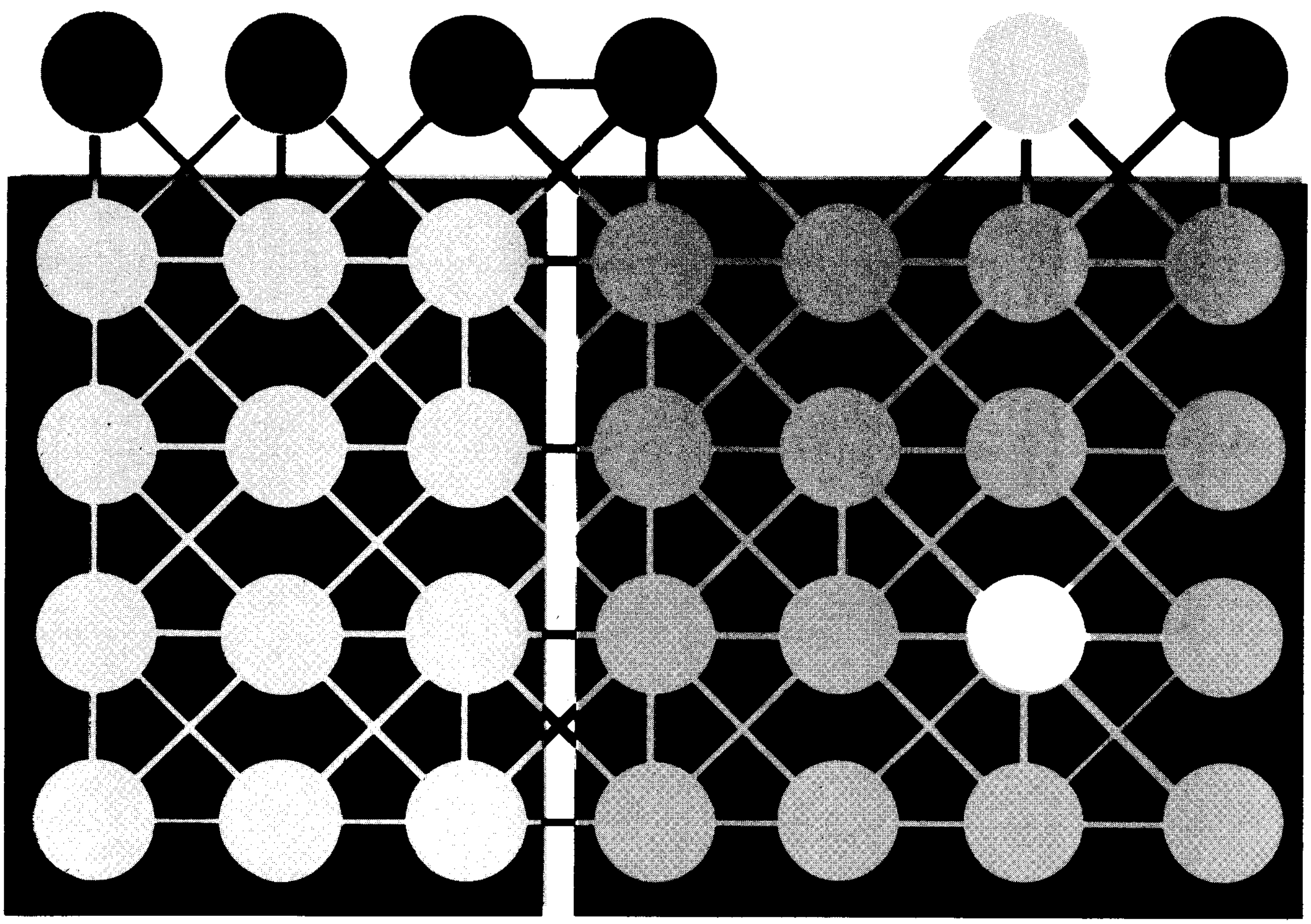
U. S. FOREST SERVICE
RESEARCH PAPER
FPL 58
OCTOBER 1966

U. S. DEPARTMENT OF AGRICULTURE · FOREST SERVICE · FOREST PRODUCTS LABORATORY · MADISON, WIS.

LIGHT-INDUCED FREE RADICALS IN WOOD



ABSTRACT

The formation of free radicals in wood by exposure to light was detected by electron-spin resonance spectroscopy. Wood that had been kept in the dark had a very low radical concentration. Exposure to daylight, and especially ultraviolet light increased the radical content in wood. In vacuum or in an inert atmosphere the radicals were stable. In the presence of oxygen the radicals rapidly decomposed.

Light-induced free radicals in wood

by
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INTRODUCTION

In this work we sought to determine whether exposure of wood to light results in the formation of free radicals and consequently in increased surface reactivity of wood. An understanding of the photochemical reactivity of wood surfaces has a bearing on the development of improved finishes and glues for wood.

"A free radical is a molecule or part of a molecule in which the normal chemical bonding has been modified so that an unpaired electron is left associated with the system" (1, p. 2).[3] The reactivity of the molecule is thus increased and the uncompensated spin of the electron results in a magnetic moment, which makes instrumental detection possible.

Free radicals are formed in the course of numerous reactions, but in complex materials their detection has been difficult. The development of electron spin resonance spectroscopy has made the detection of free radicals possible in polymeric materials.

Evidence has been presented for the generation of free radicals in cellulose by irradiation with ultraviolet light (2). The existence of stable free radicals in lignin has also been demonstrated (4, 5, 7). The formation of free radicals in wood by ionizing radiation has been shown (3), but the generation of free radicals in wood resulting from exposure to light has not been previously reported.

In the present study wood specimens were examined by electron-spin resonance spectroscopy before and after exposure to light, and evidence of light-induced free radicals was obtained. Some indication of their stability in various atmospheres was also observed.

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[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[3] Underlined numbers in parentheses refer to Literature Cited at the end of this report.

PROCEDURE AND RESULTS

Wood specimens were placed in the cavity of a Varian 4500 spectrometer.[4] The specimens were irradiated either before such placement or while they were inside the cavity. A typical electron-spin resonance (ESR) signal is shown in figure 1. It is obtained as a derivative curve of a microwave absorption phenomenon. For our purpose, the most important qualitative aspect was the vertical trough-to-peak distance, which is a rough measure of the free radical content. The absolute value of the distance should not be taken literally, because it depends on many factors including exposed surface area and "gain" of the instrument. The relative values, however, are of interest.

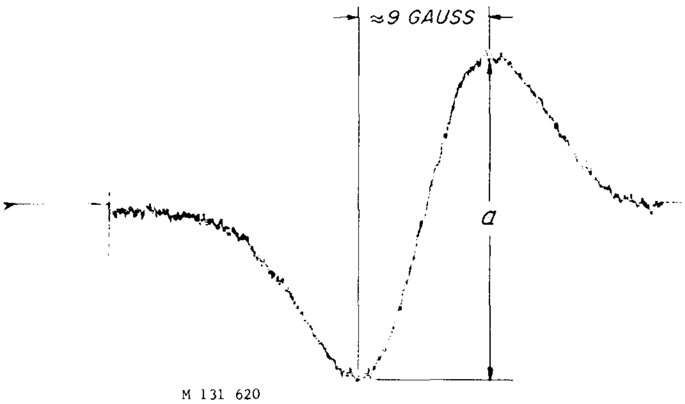

Figure I.--Typical electron-spin resonance signal. The vertical trough-to-peak distance (a) is a relative measure of the free radical concentration in the specimen. The 9 value was approximately 2 and the horizontal trough-to-peak distance was about 9 gauss.

Free Radical Formation

Birch wood.--A sliver of yellow birch veneer was placed in a quartz tube (3 millimeters in diameter), and the electron-spin resonance spectrum was obtained. The sample was irradiated in the spectrometer cavity for 2-1/2 minutes with a 254-millimicron ultraviolet light. Measurements of the ESR signal were made periodically after the light was turned off. The signal continued to increase to a maximum followed by a gradual decrease (fig. 2).

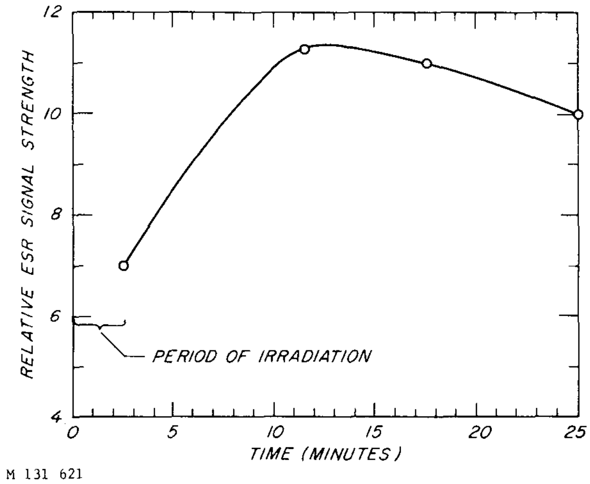

Figure 2.--Plot of ESR signal from yellow birch veneer after 2-l/2 minutes of ultraviolet irradiation,

The increase of the signal after irradiation suggests the existence of an activated species A* that decomposes into two or more radicals:

$$A^* \rightarrow R_1\cdot + R_2\cdot$$

The existence of a signal in the nonirradiated wood may have been due to the reported presence of stable free radicals in lignin (4, 5, 7) or to the effect of visible light on the wood during normal handling. To investigate the effect of normal lighting, toothpicks from an unopened box were placed in quartz tubes in a dark room with only dim red lighting. One sample was kept on a laboratory desk for 2 days, (exposure to indirect sunlight through a north window and to overhead fluorescent lighting) while the other sample was kept in total darkness. The ESR signals were measured. The results are shown in figure 3A.

Both samples were then irradiated for 5 minutes with light from a "blacklight" lamp that had a peak intensity at about 350 millimicrons and a range of wavelengths from about 300 to 400 millimicrons. Increased signal strength resulted, indicating that longwave ultraviolet light produced free radicals in the samples (fig. 3B). The data suggest that the effects of room light and blacklight are cumulative.

Yellow-poplar sapwood.--Sapwood samples of yellow-poplar veneer, about 0.2 millimeter thick and 5 centimeters long, were placed in quartz tubes as before. One of the samples was placed in an

[4] The facilities used in this work were made available through the generosity of Professor John Willard of the University of Wisconsin.

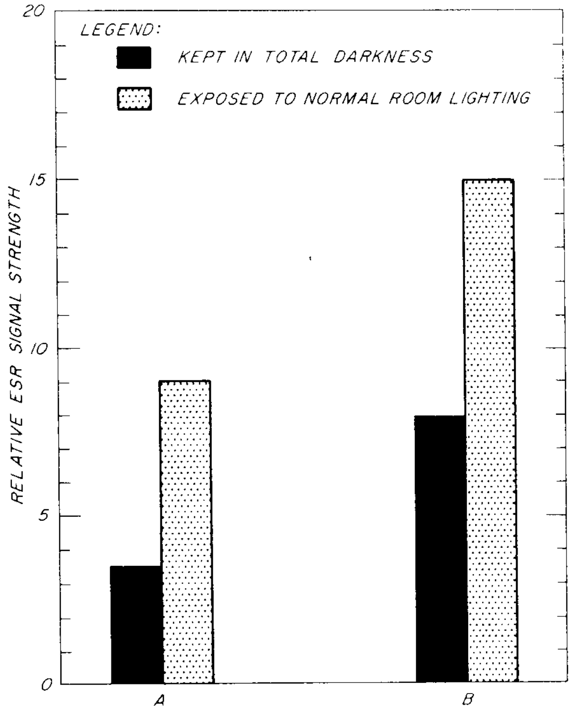

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Figure 3.--Comparison of ESR signals from toothpicks, A--before, and B--after irradiation with longwave ultraviolet light.

open-ended quartz tube and was handled entirely in the dark. A second sample in an open-ended tube was exposed to daylight from a north window and to the usual fluorescent artificial lighting in the room. A third sample, in a closed tube which had been flushed with helium, was also exposed to the normal light. As before, ESR measurements were taken before and after irradiation with longwave ultraviolet (b l a c k l i g h t). The relative signal strengths are shown in figure 4.

Wood kept in the dark for 1 week gave an extremely weak signal (fig. 4, a) that was very close to the resolving power of the instrument. Exposure of a similar sample to laboratory lighting conditions for 1 week, however, produced a well-defined signal (e). As a first approximation, there was little difference in signal strength in wood exposed to laboratory light and air (e), and to laboratory light and helium (f). Continued exposure to blacklight caused a continuing increase insignal strength (d and h).

Decrease of Free Radical Concentration with Time

The decrease of the ESR signal in yellow-poplar sapwood with time was examined. Thin samples of veneer (0.2 millimeter thick, about 5 centimeters long) were placed in quartz tubes. Two of the tubes were open to air and the third was closed after being flushed with helium gas. The samples were then irradiated with blacklight for 2 hours, and the ESR signals were measured. One of the tubes open to air was flushed with oxygen after the first reading. Decrease in the signal strengths is shown in figure 5.

Free radical concentration was nearly constant in helium and little decay of signal occurred. Continuing decay of signal occurred in the specimens exposed to air and to oxygen.

Further Stability Measurements

Sapwood samples of yellow-poplar veneer were placed in quartz tubes as before. One sample tube was swept with helium for several days, evacuated with a vacuum pump, and was then sealed. Two other sample tubes were left open to air; one was stored in the dark and the other in normal laboratory light. The light-exposed tube and the sealed tube were irradiated for a half hour, and the ESR signals were measured. After 7 days, stronger signals were desired and the samples were irradiated again for an additional 12 hours. To reduce experimental errors due to variations of spectrometer settings or sample positioning, a diphenylpicrylhydrazyl (DPPH) standard was used. The radical concentration in the standard is known to remain nearly constant over long periods of time. The signal obtained from wood samples was divided by the signal obtained from the standard in each case. The decay in free radical concentration (decreasing signal ratio) is shown in figure 6 for the sample under vacuum and for the sample exposed to air. Figure 7 shows the decrease in signal ratio for the sample initially kept in the dark.

After irradiating for the additional 12-hour period only a slight increase in signal strength was observed for the sample exposed to air. The signal for the s a m p l e sealed in vacuum, however, increased by about 60 percent.

The signal from the sample sealed in vacuum remained fairly constant for at least a week. The signal from the sample open to air decreased very rapidly; the signal from the sample open to air but in darkness was very small. After exposure to room light for 7 days, an increased signal ratio was noted in the sample initially stored in darkness, but it was weak and decreased rapidly with time.

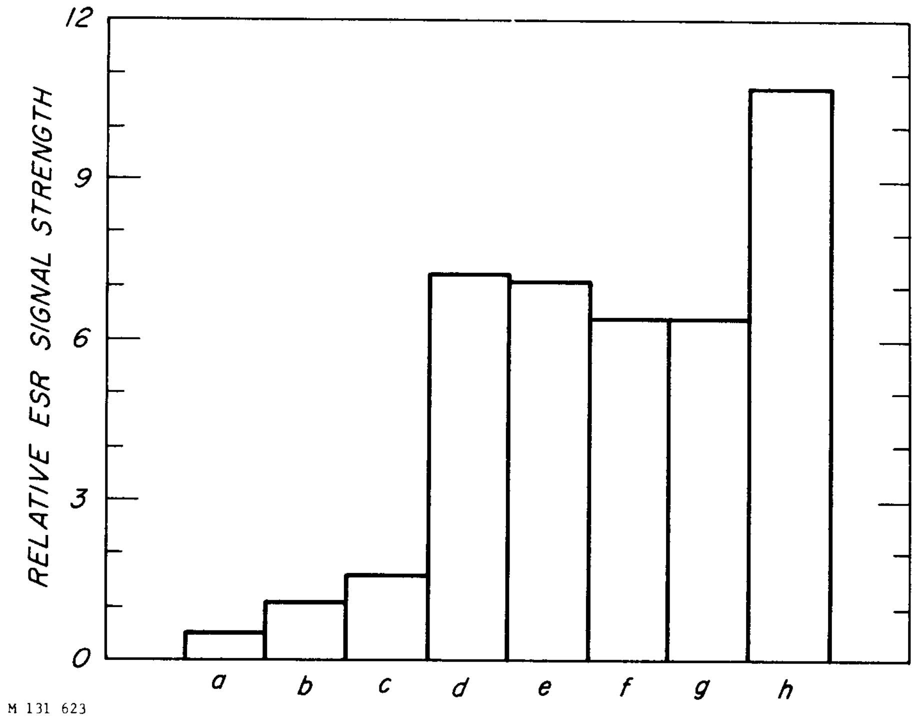

Figure 4.--Comparison of maximum ESR signals from yellow-poplar veneer exposed according to the conditions described below.

Exposure conditions for samples of yellow-poplar veneer

Veneer sample	Exposure	Exposure time	Distance of light from specimen	Atmosphere
a	dark	1 week	--	air
b	blacklight	5 min.	45 cm.	"
c	"	10 min.	"	"
d	"	15 min.	5 cm.	"
e	normal light	1 week	--	"
f	" "	"	--	helium
g	blacklight	7 min.	45 cm.	"
h	"	20 min.	5 cm.	"

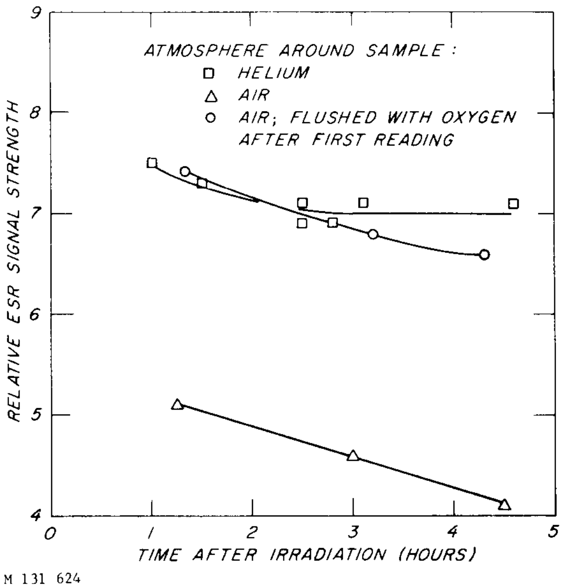

Figure 5.--Plot of ESR signal from samples of yellow-poplar veneer after exposure to ultraviolet irradiation for 2 hours. The samples were irradiated in various atmospheres.

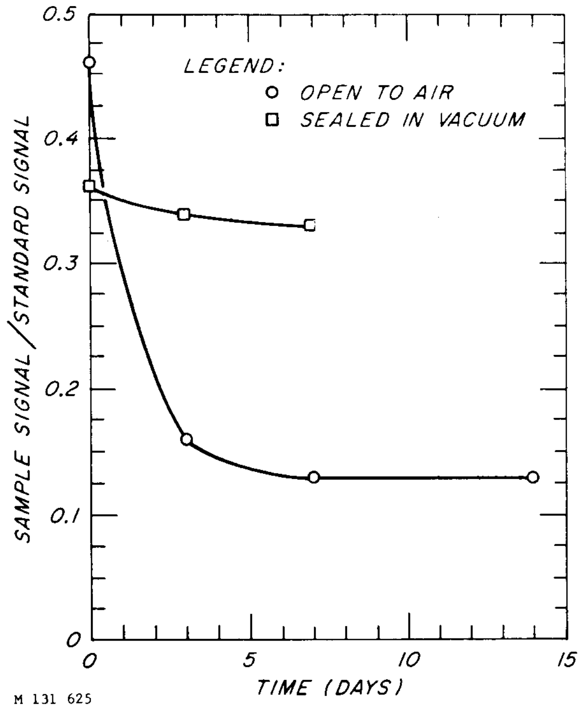

Figure 6.--ESR signal decay after samples of yellow-poplar veneer were irradiated for 12 hours.

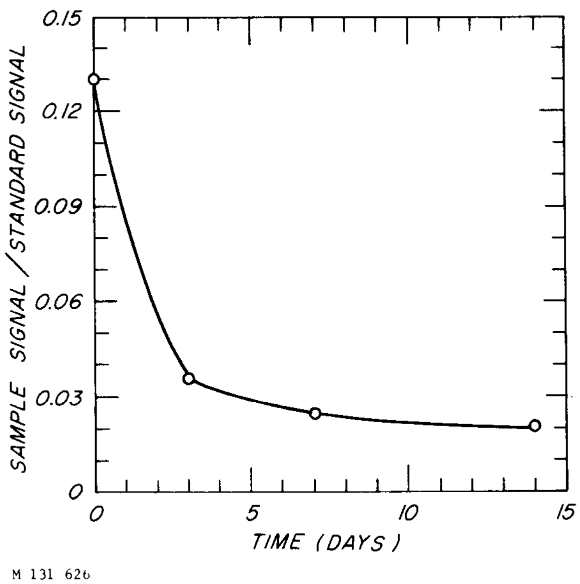

Figure 7.--ESR signal decay after sample of yellow-poplar veneer that had been kept in the dark was exposed to normal room light for 7 days.

DISCUSSION AND CONCLUSIONS

The ESR signal was extremely weak in the wood samples that had been kept in the dark over a long period of time. Normal laboratory illumination produced a definite increase in the free radical content of wood. The illumination included laboratory fluorescent light as well as daylight (no direct sunlight). The amount of ultraviolet light that was present under these "normal lighting" conditions could not have been very large, but may have been sufficient to produce the extremely weak signal.

Irradiation of wood samples with ultraviolet light produced a marked increase in the concentration of free radicals. This was observed with both middle ultraviolet (about 254 millimicrons) and near ultraviolet (primarily 350 millimicrons) radiation. In one case (fig. 2) the concentration of free radicals increased for about 10 minutes after irradiation, and then decreased, suggesting the formation of several free radicals from the light-activated molecular species. The effective concentration of radicals as indicated in figure 1 appears to be approximately 10^{-6} to 10^{-5} molar.

Free radicals were produced in wood by irradiation in atmospheres of air, helium, and in vacuum. It is likely that in the presence of air, alkoxyl and peroxyl radicals are produced in addition to alkyl radicals.

In helium and in vacuum the radicals appeared to be relatively stable, while in the presence of oxygen a measurable decay of radical concentration was observed. Apparently the post-irradiation reactions involve the combination of radicals with oxygen when it is available. In vacuum or in the presence of helium gas, some other deactivation mechanism is operative.

The considerable stability of the radicals (in the absence of oxygen) and the low energy requirement for their formation (as judged by their generation in daylight) suggests that these radicals may be stabilized chemically. Steelink (6) has reported the existence of a relatively stable radical, syrinoxyl, that resembles a portion of lignin structure. Possibly similar types of stabilized radicals are formed in wood by light.

Although the observations made from the work reported here are cursory, they do suggest the course of future work. Some of the problems which could be studied profitably are:

1. Effect of specific wavelengths
2. Effect of extractives or other substances in wood
3. Kinetics and effect of environment on signal decay
4. Surface reactivity of wood with a high free-radical content.

It is hoped that such an expanded program of research can be pursued.

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