

CHARACTERISTICS OF FREE RADICALS IN WOOD¹

David N.-S. Hon

Assistant Professor

Geza Ifju

Professor

Department of Forest Products, Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061

and

William C. Feist

Research Chemist

Forest Products Laboratory, Forest Service, U.S. Department of Agriculture,
Madison, WI 53705

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ABSTRACT

Formation and behavior of free radicals in wood exposed to fluorescent light, terrestrial sunlight, and artificial ultraviolet light have been studied by electron spin resonance (ESR) spectroscopy. Freshly cut loblolly pine specimens (with 69% MC) did not exhibit any detectable ESR signals, strongly implying that intrinsic free radicals may not exist in green wood. Free radicals were readily produced by interaction of wood with electromagnetic radiations. At ambient temperature, for green wood specimens, a large amount of short-lived free radicals was generated by sunlight, whereas a relatively low amount of longer lifetime free radicals was generated by fluorescent light. For air-dried specimens, all light sources used were able to generate free radicals either in air (oxygen) or under vacuum. A large quantity of free radical concentration was normally generated under vacuum but free radicals decayed rapidly at ambient temperature. The interaction of free radicals with oxygen and the decomposition and termination of free radicals leading to the discoloration reaction were considered.

Keywords: Free radicals, electron spin resonance (ESR), fluorescent light, terrestrial sunlight, ultraviolet light, discoloration, loblolly pine, oxygen.

INTRODUCTION

Growth of the wood products industry in recent years has been accompanied by a significant expansion in the outdoor application of wood materials. Along with this expansion, it has become necessary to develop satisfactory methods of assessing the weathering performance of the wood materials and of the finished products. Outdoor weathering is one of the most variable and destructive forces of nature to which wood is exposed. Many factors are involved in the weathering process; and the photon energy in solar radiation is the most damaging component of the outdoor environment, serving to initiate a wide variety of chemical changes in wood materials. Consequently, photooxidation is the principal reaction in the

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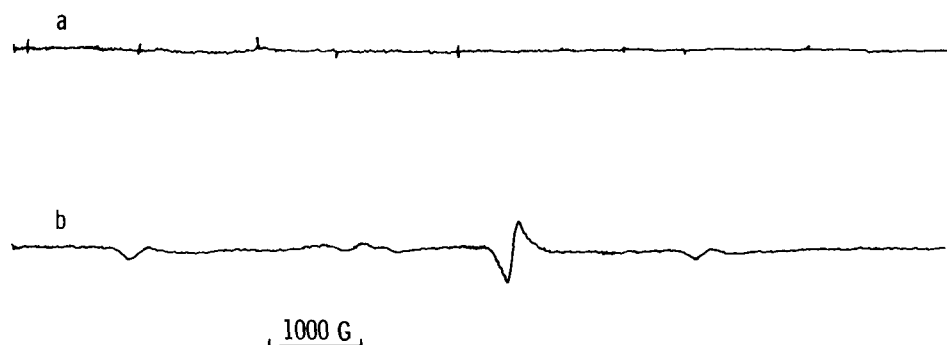


FIG. 1. ESR spectra of green loblolly pine. (a) sample prepared in dark under vacuum; (b) sample prepared in dark in presence of oxygen. ESR spectra measured at 77 K.

outdoor weathering of wood. Although chemical constituents vary widely in their resistance to photooxidation, almost every wood constituent eventually deteriorates on continued exposure to solar radiation (Hon 1979b).

Although wood is a good light absorber, penetration of ultraviolet (UV) light into wood does not traverse deeper than 75 μm (Hon and Ifju 1978). Nonetheless, wood surface reactions initiated or accelerated by light can be observed by discoloration or change in surface texture after intense UV irradiation or long-term solar irradiation (Feist 1978). It is believed that such changes of wood surface are results of UV-induced photooxidation of the chemical components, in which lignin is the key light-absorbing component (Hon and Glasser 1979a; Kalnins 1966). Further, it is generally accepted that free radicals are the primary intermediary (nonmolecular) products generated at the wood surface prior to the exhibition of discoloration and texture degeneration (Hon and Ifju 1978; Kalnins et al. 1966). Consequently, the photochemical susceptibility of wood surface has a significant bearing on the natural weathering process. Understanding the reaction mechanisms involved in weathering may shed light on developing improved coatings or surface finishing agents for wood.

Free radical intermediates play a very important role in weathering, and the primary aim of this work is to elucidate the formation and behavior of free radicals generated in wood surfaces upon exposure to UV light irradiation. Since both oxygen and sunlight are ubiquitous in nature, the influence of oxygen on radical reactivity is also considered.

MATERIALS AND METHODS

Loblolly pine (*Pinus taeda* L.), which was harvested in Blacksburg, Virginia, in the winter of 1978, was selected for this study.

Wood specimens (earlywood), 100 μm longitudinal by 30 mm tangential by 2 mm radial, were prepared by cutting the freshly cut wood with a razor blade in a photographic darkroom. Immediately after sample preparation, they were transferred to electron spin resonance (ESR) sample tubes that were immediately sealed either in air or under vacuum. All the specimens were kept in the dark prior to carrying out any experiments. Sources of photoirradiation were a flu-

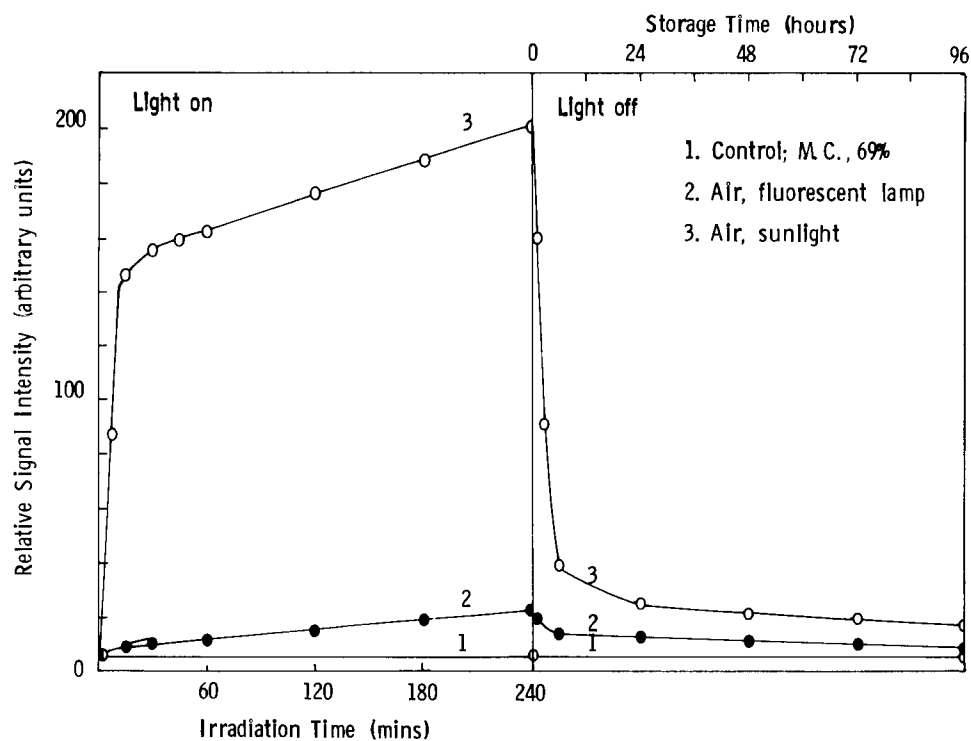


FIG. 2. ESR signal intensity of green loblolly pine as a function of irradiation time and storage time at ambient temperature. ESR spectra measured at 77 K.

orescent lamp (General Electric, cool white, 40W), an Ace-Hanovia medium pressure quartz mercury-vapor lamp (Ace Glass, Inc., 200 W), and terrestrial sunlight.

ESR spectra were measured with an X-band ESR spectrometer (Varian E-12, 100 kHz modulation). To avoid distortion of the spectra by a power saturation, ESR measurements were carried out at a microwave power of 3 mW. All spectra were recorded at liquid nitrogen temperature (77 K, -196°C) by inserting a Dewar flask with a quartz finger into the cavity.

RESULTS AND DISCUSSION

Intrinsic free radicals in wood

For many years it has been known that wood, wood fiber components, and isolated lignin contain certain amounts of free radicals that are detectable by ESR spectroscopy (Ludwig and Sarkanen 1971; Steelink 1972). However, it is not well established whether these free radicals are intrinsically extant in wood as end products of wood formation or lignification, or of wood components being attacked by fungi and enzymes. Moreover, detectable free radicals could be produced during sample preparations such as shaving, grinding, etc., or by some other means of environmentally occurring chemical and physical stresses (Ludwig and Sarkanen 1971; Hon and Glasser 1979b; Kleinert and Morton 1962). Accord-

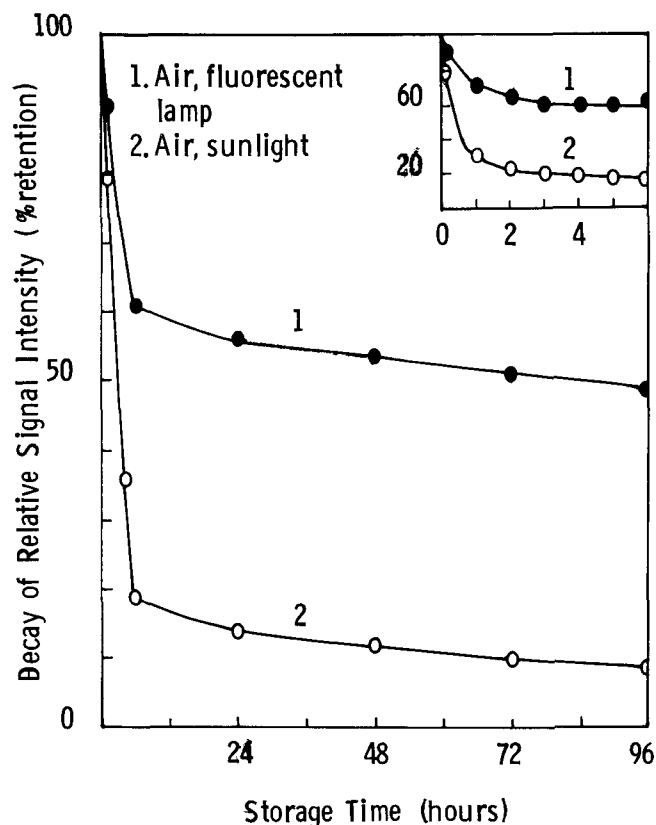


FIG. 3. Decay of ESR signal intensity of green loblolly pine as a function of storage time at ambient temperature. ESR spectra recorded at 77 K.

ingly, in order to afford a clear insight into the free radical reactions in wood, it is essential to elucidate the nature of the "intrinsic" free radicals.

A green loblolly pine was prepared for this study. Results are shown in Fig. 1. It is of interest to note that the specimen prepared in air (in darkness) and stored in the dark under vacuum did not exhibit any detectable signals of free radicals either at ambient temperature or at 77 K by ESR spectroscopy at its highest modulation settings (Fig. 1a). This indicates that free radicals were not extant in wood. A very weak signal was detected from the specimen stored in air in the dark (Fig. 1b). The ESR signal remained unchanged both at ambient temperature and at 77 K, indicating that free radicals contributing to this signal were quite stable. As a consequence of the absence of detectable free radicals in the specimen stored in vacuum in the dark, we were led to consider that oxygen in air may act as a catalyst or promoter to activate wood surfaces to create a small amount of free radicals. These free radicals are possibly phenoxy radicals resulting from oxidation of the phenol (lignin) moiety in wood (Hon 1975; Taylor and Battersby 1967). Although it is possible that certain amounts of free radicals can be generated by mechanical stress during the preparation of wood, this factor seemed unlikely to be a contributing one inasmuch as no detectable free radicals

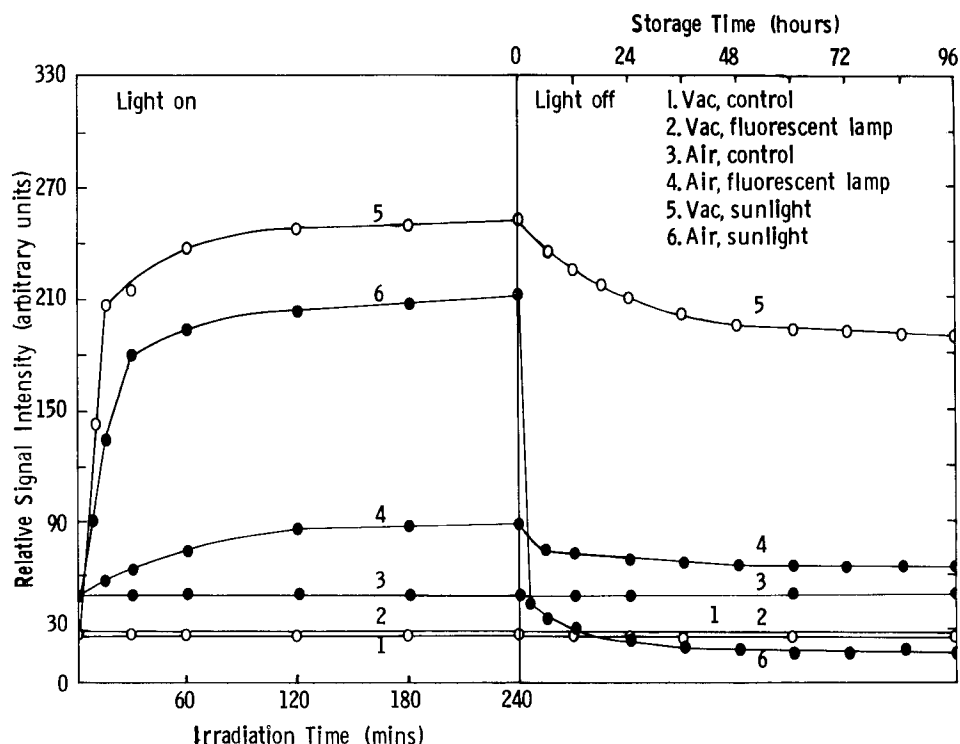


FIG. 4. ESR signal intensity of air-dried loblolly pine as a function of irradiation time and storage time at ambient temperature. ESR spectra recorded at 77 K.

were produced from the sample stored in vacuum. Consequently, it is quite possible that green wood may not contain any intrinsic free radicals, or they are present only in a very small quantity not detectable by ESR spectroscopy. This directly implies that "intrinsic free radicals" in wood is not a proper term. Similar results were obtained from the classic studies by Rex (1960) and Ranby et al. (1969).

Further, the detectable amount of free radicals in wood is likely to be generated by absorbing suitable energy available in the immediate environment. This energy may originate from oxygenation reactions, mechanical stress, or photons of light. Of these energy sources, light appears to be the most critical one in producing wood free radicals, as will be discussed in a subsequent section.

Light-induced free radicals in fresh wood

Although there is only a small amount of free radicals generated in freshly prepared wood specimens in the presence of oxygen and in the absence of light, electromagnetic radiation, e.g., light, is able to generate free radicals readily in wood.

When a wood specimen was exposed to an indoor-type fluorescent lamp, the increment of ESR signals of free radicals as a function of exposure time was observed (similar results have been observed by Kalnins et al. (1966)); and the

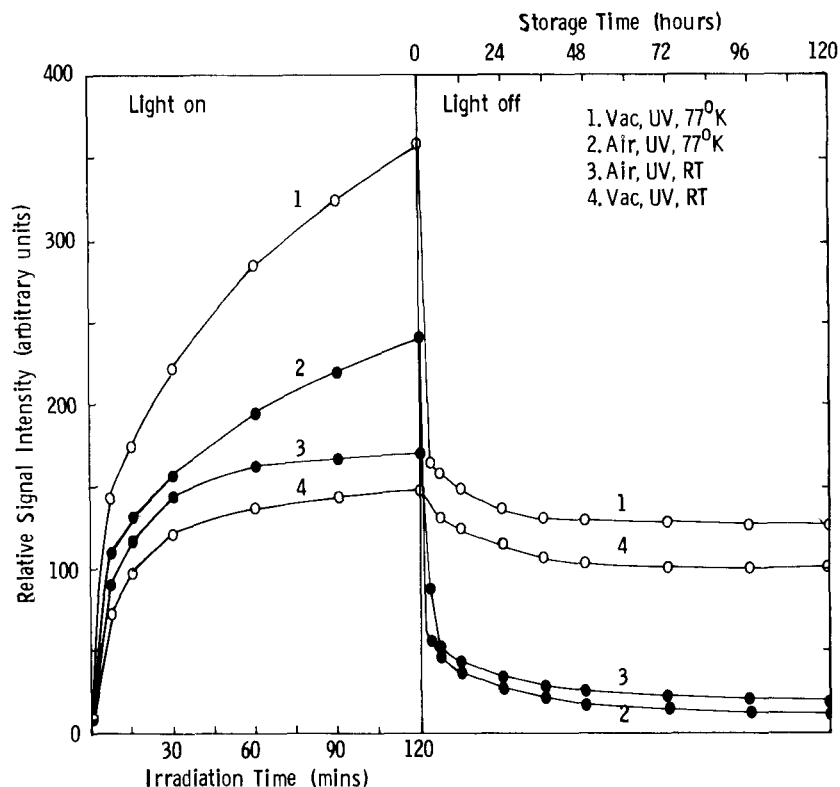


FIG. 5. ESR signal intensity of air-dried loblolly pine as a function of UV irradiation time and storage time at ambient temperature. ESR spectra recorded at 77 K.

increment was further enhanced when the specimen was exposed to sunlight. Results are shown in Fig. 2. It is obvious that the latter light source generated an almost tenfold stronger signal intensity than those generated by the former light and fortyfold stronger than that of the control (unexposed) specimen. This clearly demonstrates that more wood free radicals were generated by irradiation with sunlight than with fluorescent light.

When specimens were removed from either sunlight or fluorescent light, the ESR signal intensity decreased rapidly during the first hour of storage at ambient temperature (Figs. 2 and 3). Apparently, approximately 70% and 25% of the original ESR signal intensity (which corresponds to the concentration of free radicals) decayed at ambient temperature for 60 min for the specimen exposed to sunlight and fluorescent light, respectively. When these specimens were further stored at ambient temperature for 96 h, the intensity decayed to 18% and 48% of their original values for sunlight and fluorescent light-exposed samples, respectively. This observation implies that exposure of wood to sunlight generates a large amount of relatively short-lived free radicals, whereas fluorescent light is able to generate a small amount but long-lived free radicals.

In short, these findings imply that freshly cut wood, in its wet (green) state (69% MC), is susceptible to interaction with fluorescent light and sunlight leading

to generation of free radicals. The customary observation of the existence of "intrinsic free radicals" in wood may well be an artifact. The "intrinsic free radicals" are probably produced during wood preparation as well as from the wood's being exposed to electromagnetic radiation.

Light-induced free radicals in air-dried wood

It is of primary interest to study the formation of free radicals in air-dried wood (with 6–7% MC) and to compare to those in freshly cut wood with 69% MC.

When a vacuum specimen (MC may drop a little due to the vacuum system) being prepared in the dark was exposed to a fluorescent light, only a small amount of free radical formation was recognized from ESR studies (Fig. 4). When the vacuum specimen was irradiated with sunlight, a significant amount of free radical formation was observed. Likewise, when specimens were exposed to fluorescent light or sunlight in the presence of air, the increment of free radical concentration was recognized for both light sources, in which a significantly higher concentration of free radicals was obtained from the specimen treated with sunlight (Fig. 4).

It is of great interest to learn that the rates of free radical formation are dependent upon the light sources used as well as on the exposure atmosphere. This is quite plausible because of the stronger energy emitted from the sun than from the fluorescent light. Hence, more free radicals were produced from the specimen treated with sunlight. The presence of air (oxygen) seems to be a prerequisite for free radical formation in wood exposed to fluorescent light. As described earlier, oxygen may function as a catalyst or promoter to activate wood surfaces for free radical formation. A similar phenomenon was observed from cellulose fiber (Hon 1975, 1976, 1979a).

When the wood specimens were exposed to sunlight, a higher amount of free radical concentration was able to be accumulated under vacuum than in air (oxygen). This indicated that oxygen in the system would probably terminate certain amounts of sensitive (unstable) free radicals. Consequently, the rate of decay of free radicals increased. It is worthwhile to mention here that during the irradiation period, competitive reactions of free radical formation and decay undoubtedly took place throughout the reaction, and the rate of formation was always greater than that of decay. Moreover, interaction between free radicals and oxygen molecules probably leads to the formation of peroxides that are unstable toward heat and light, and are usually transformed into carbonyl and carboxylic groups (Hon 1979a). These secondary reactions then lead to a gradual change of texture and discoloration of the wood surface.

The reactivity of free radicals produced in wood by the two light sources either under vacuum or in air was different when samples were stored in the dark. Results are shown in Fig. 4. The decay of free radicals took place rapidly for the specimens treated in air either by sunlight or by fluorescent light. The rate of decay was rather slow for samples treated under vacuum. This observation further supports the observation that labile free radicals are very sensitive to oxygen. They react with oxygen rapidly to stabilize themselves, as described earlier.

It is of importance to point out here that those free radicals that were detectable by ESR spectroscopy from the specimens treated at ambient temperature are the relatively stable ones. Most of the short-lived free radicals are unable to survive at such temperatures.

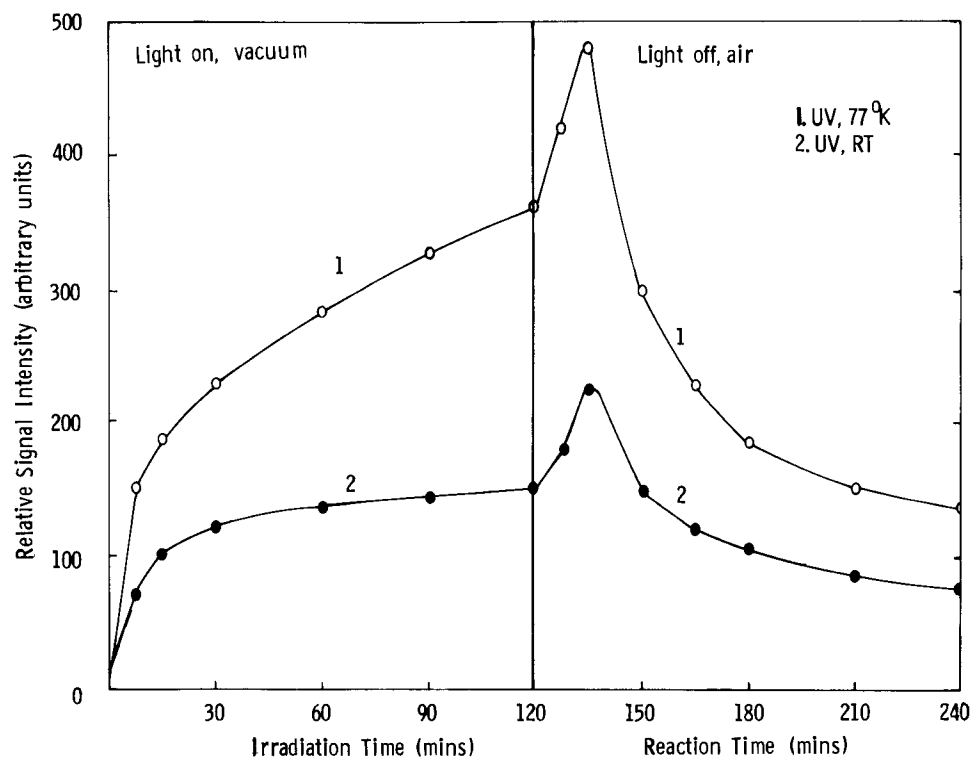


FIG. 6. Increment of ESR signal intensity of vacuum-treated specimen interacted with oxygen in air at ambient temperature. ESR spectra recorded at 77 K.

Ultraviolet light-induced free radicals in air-dried wood

When wood specimens were irradiated with an artificial ultraviolet (UV) light bearing wavelengths of >254 nm, the generation of free radicals was particularly noticeable at 77 K. The highest amount of free radical concentration was registered from specimens treated under vacuum at 77 K. The depression of free radical formation to a certain extent by oxygen was recognized when specimens were treated in such atmosphere. Again, the role of oxygen in stimulating secondary radical reactions can be visualized even at 77 K.

Lower amounts of free radical concentration were detected from specimens treated with UV light at ambient temperature either under vacuum or in oxygen. This implies that labile free radicals are not able to be trapped at ambient temperature. Only those relatively stable free radicals are able to survive and to be detected by ESR studies. Further, when specimens were exposed to UV light at ambient temperature, higher amounts of free radical concentration were always detected from specimens treated in air (oxygen) than those treated in vacuum. Similar observations were obtained from specimens treated with fluorescent light at ambient temperature.

The decay patterns of free radicals at ambient temperature for specimens irradiated with UV light at ambient temperature and at 77 K are shown in Fig. 5.

It is obvious that free radicals generated in vacuum either at 77 K or at ambient temperature had a longer lifetime than those produced in the presence of air (oxygen). This clearly indicates that oxygen-activated free radical species are unstable at ambient temperature; most of them decayed rapidly at such temperature.

The role of oxygen in promoting free radical formation is further substantiated by an experiment set forth as follows:

Immediately after specimens were irradiated with UV light under vacuum at 77 K and at ambient temperature, air was allowed to reach the specimens at ambient temperature. A different feature is of interest. Results are shown in Fig. 6. Apparently, for specimens treated at 77 K and at ambient temperature, the free radical concentration increased rapidly and reached its peak at ca. 20 min of reaction. However, the newly formed free radicals continuously underwent secondary reactions, which led to the decay of free radicals beyond 20 min of reaction. This implies that oxygen is capable of promoting free radical formation. These free radicals are decomposed and stabilized themselves readily after 20 min of reaction at ambient temperature. It should be added here that Kalnins *et al.* (1966) observed the increase of signal intensity after UV light was turned off for the sample irradiated in the presence of oxygen.

CONCLUSIONS

Wood is a good light absorber. It is capable of absorbing electromagnetic radiation energy to produce free radicals. The formation and behavior of wood free radicals are greatly dependent upon the light sources used as well as on the exposure atmosphere. The following conclusions may be drawn from this study:

1. Green wood (with 69% MC) may not contain any free radicals. The customary observed "intrinsic" free radicals in wood may well be an artifact. Wood free radicals are feasibly created during mechanical preparations as well as from wood exposure to electromagnetic radiations, *i.e.*, terrestrial sunlight and indoor fluorescent light. A high amount of free radical concentration was registered from wood specimens treated with sunlight, but most of the free radicals were relatively unstable. Alternately, a low amount of free radicals was created from specimens treated with fluorescent light. These radicals were relatively stable at ambient temperature.
2. Air-dried wood specimens readily interact with natural sunlight, fluorescent light, and artificial UV light to produce free radicals, either in the presence of air or under vacuum. Higher amounts of free radicals were generated under vacuum than in air for all light sources. Oxygen is likely to be a mandatory element to activate wood surfaces for promoting free radical formation when fluorescent light or UV light irradiation is used at ambient temperature.
3. For all systems, free radicals generated under vacuum have a relatively long lifetime compared to those generated in the presence of air. Addition of oxygen to samples treated under vacuum seems to be able to promote free radical formation, but the lifetime of these free radicals was relatively short. The decomposition and termination of wood free radicals are believed to have a significant bearing on discoloration reactions and the natural weathering process.

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