Annales de la Faculté des Sciences, Université de Yaoundé I. 2012, Série Physique, Vol 39 N^{0}1, pages 1-8

ABSORPTION OF IMPRALIT-KDS BY SOME TROPICAL WOODS: AND ELECTRON PARAMAGNETIC RESONNANCE STUDY

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Reçu: 11 Novembre 2011; accepté: 22 décembre 2011 ; mise en ligne: 25 janvier 2012.

ABSTRACT

We studied the retention of Impralit-KDS (a 12.5% copper-based waterborne wood preservative) by three tropical species : AYOUS (Triplochoton Sclerylonk), FRAKE (Terminalia Superra) and MOABI (Baillonnella Toxisperma). The measurements were done with an Electron Paramagnetic Resonance (EPR) spectrometer on untreated and treated samples of heartwood. The treatment was a total immersion for a duration varying from 10 minutes to 24 hours

Keywords: *EPR, Absorption, Wood, Treatment, Preservative, Immersion*

RÉSUMÉ

Nous avons étudié l'absorption de l'Impralit-KDS (concentré de sel soluble dans l'eau, à base de 12,5% d'hydroxyde cuprique, utilisé dans le traitement du bois) par trois essences tropicales bien connues sur le marché du bois camerounais. Il s'agit des essences suivantes : AYOUS (Triplochoton Sclerylonk), FRAKE (Terminalia Superra) et MOABI (Baillonnella Toxisperma). Les mesures expérimentales ont été faites au moyen d'un spectromètre à Résonance Paramagnétique Electronique (RPE) sur des échantillons traités et non traités de duramen (bois de cœur). Le traitement consiste en une immersion totale pendant un temps variant de 10 minutes à 24 heures. Le traitement a pour but de protéger le bois contre ses prédateurs naturels que sont la moisissure, les champignons et les insectes xylophages (termites), l'absorption étant un paramètre important quant à l'efficacité d'un produit de traitement. De part sa très haute sensibilité et son caractère non destructif, la technique de Résonance Paramagnétique Electronique (RPE) semble bien adaptée pour l'étude de cette absorption. Un traitement jugé efficace pour l'AYOUS et le FRAKE serait salutaire, car ces essences sont connues pour leur fragilité vis-à-vis des prédateurs du bois.

Mots clés : *RPE, Absorption, Bois, Traitement, Immersion*

INTRODUCTION

Wood is a complex cellular natural growing composite material that has no consistency from one species to another, or within a species. For a given tree, it is common for the wood found toward the center of a tree trunk (heartwood) to be quite different from that found toward the outside (sapwood). Heartwood is wood that, as a result of genetically programmed processes, has died and become

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resistant to decay, whereas sapwood is living wood in the growing tree. Wood is composed of four chemical components: cellulose (a naturally occurring thermoplastic polymer that is the main building material of the wood. It makes up about 50 % of the dry weight of wood.), hemicellulose (15 to 25 %), lignin (15 to 30 %) and extractives (organic and inorganic chemicals that make up to 15 %). These four chemical components combine to form a cellular structure [1-3]. Variations in the characteristics and volume of the four components and differences in cellular structure yield to the fact that some woods are hard and heavy and some light and soft, some strong and some weak, some naturally durable and some prone to decay [4].

Among about 30 species commonly found in tropical regions, some are said to be naturally protected (that is the case for *Baillonnella Toxisperma* called MOABI), but they are so expensive for the local population. The most accessible species are not so resistant (their resistance is rather poor or moderate) to fungi and insects, the natural enemies of wood [5]. Among them we can quote: AYOUS (*Triplochoton Sclerylonk*), FRAKE (*Terminalia Superra*). Those species that can suffer rapid biodegradation and biodeterioration, do need to undergo a preservation process.

Wood-preserving methods are of two types: - pressure processes, in which the wood is impregnated in closed vessels under pressures considerably above atmospheric pressure (vacuum pressure process) and – non pressure processes, which vary widely in the procedures and equipment used. Some of those second type methods are: spreading, fumigation, pulverization, brushing and dipping or tank immersion (by hot and cold bath), [6]. For the three species cited above, some terms related to resistance to wood predators are given in Table 1 [7].

When untreated wood is exposed to adverse conditions, nature has a series of chemistries to degrade it back to its original building blocks of carbon dioxide and water. One also talk about weathering, that is the general term used to define the slow degradation of materials exposed to the weather. Wood preservatives are used in order to prevent such damages. [8]. A preservative has an expected service life after a given treatment on a specific wood.

The choice of a treatment process shall depend on the nature of the preservative and the structural characteristics of the wood to be treated (different woods have different capacities for absorbing preservatives or other liquids). Retention, a common term used to describe the amount of chemical contained within the wood, is an important parameter regarding the treatment. Retention will vary depending upon the intended use of wood.

About chemicals used for wood treatment, since the 1970s, people are most familiar with: Chromated Copper Arsenate (CCA), Chromated Copper Borate (CCB), Ammoniacal Copper Zinc Arsenate (ACZA), Copper Azole (CA), Alkaline Copper Quaternary (ACQ), Copper Boron Azole (CBA). Copper is one of the most important and frequently used ingredients in commercial wood preservatives. Copper is typically found in the general environment within the +2 valence state only. Chromium is a fixation agent for copper and arsenic in the wood. Arsenic is a known carcinogen. The toxicity of chromium is largely a function of the oxidation state of the chromium within a corresponding molecule. The two most relevant environmental oxidation states of chromium are Cr(III) and Cr(VI). Cr(VI) has been reported to be 10 to 100 times more toxic than trivalent chromium, when ingested orally. [9]

For an efficient characterization of wood (treated or not), one needs multiscale tools [10], because annual rings are at cm scale, cells at mm scale, cell walls at µm scale, fibrils at nm scale and cellulose molecules at Å scale. Some of those tools are: ionizing radiation (X-ray, γ-ray) [11, 12], thermography [13], microwaves [14], ultrasonic, infrared spectroscopy [15-17], electron microscopy [18], nuclear magnetic resonance [19-21], and electron paramagnetic resonance (EPR).

As far as EPR is concerned, numerous studies have been done on treated wood. The EPR spectroscopy was used by Zhang and Kamdem [22] to elucidate the structure of copper complexes in a copper amine treated wood. The authors showed that the stereo-structure of copper complexes in the treated wood was either tetragonal-based octahedral or square-based pyramidal. Humar et al [23] carried out a study on the understanding of copper tolerance by some fungi. They observed that exposure of the treated samples to the fungi, significantly increased copper and chromium leaching. In another study done same year, Humar et al [24] did an EPR evaluation of copper fixation in treated wood. In a previous study done in 2000, Humar et al [25] measured the EPR spectra of (copper sulphate)-treated spruce wood. Illman and Bajt [26] obtained the EPR spectra of Mn^{2+} in four species of wood (White fir, Cottonwood, Douglas fir, and Redwood) treated by impregnation with an $MnCl_2$ aqueous solution. For some elements such as iron and manganese that are present in very small proportions in untreated woods, Lakshmi et al [27] did an EPR detection of Fe (III) and Mn (II) on the ash of the Red sandalwood.

The aim of our present study is to evaluate by the mean of EPR spectroscopy the absorption (retention) of a wood preservative named Impralit-KDS, by three tropical wood species.

MATERIAL AND METHOD

The three studied tropical species of wood material are: AYOUS (*Triplochoton Sclerylonk*), FRAKE (*Terminalia Superra*) and MOABI (*Baillonnella Toxisperma*). The original timbers were cut in a forest in Cameroon, around the town of Yaounde (Lat. 3°50'N, Long. 11°31'E, Tropical Rainforest Zone, Mean Annual Temperature 23,6°C, elevation 751 m). Samples are cylinders of 5mm diameter and 6 mm long (specially carved to fit the cavity of the EPR spectrometer), obtained from dry heartwood free from any defect, before treatment. For the three studied species, some of the specific parameters related to absorption are gathered in Table 2 [7].

The preservative is Impralit-KDS [28-30], a copper-based waterborne heavy duty preservative, developed in Europe in the 1980's by Rütgers Organics GmbH as chromium-free preservative. It contains 12.5% copper(II) hydroxide, 8% boric acid and 10% polymeric betaine (didecyl polyoxyethyl ammonium borate, also called DPAB) as active ingredients. The DPAB belongs to the family of quaternary ammonium compounds. Impralit-KDS is a water-thinnable, dark-blue salt concentrate. Before and after fixation on wood, the colour is green. It prevents attack by wood destroying insects including termites as well as rot and fungal decay. The protection against bluestain and mould is temporary. Impralit-KDS is recognized for use in aboveground and ground-contact applications.

The concentration of the solution was 3.5 %, the minimal value for wood to be used in open with ground-contact and exposed to weather. The fixation process that depends on various factors such as wood species, dimensions of wood, absorption rate and temperature, lasts between 1 and 3 days. For special risks, Impralit-KDS is harmful if swallowed, very toxic to aquatic organisms and causes burns.

The treatment was done by total immersion of samples. We adopted four different durations of immersion for each species (10mn, 1, 10 and 24 hours). The samples were then air-dried for 72 hours (slow-drying for deeper absorption). The EPR measurements were done with a 14 Gigahertz home made spectrometer of the experimental physics III Lab. of the University of Dortmund in Germany. That frequency is above 10 GHz, the frequency of most commercial spectrometers. The calibration was done with 2,2-Diphenyl-1-pierylhydrazyl hydrated (DPPH) powder which has a density of spins of about 10^{22} cm^{-3}. DPPH is a phenolic antioxidant frequently used in EPR for settings. The paramagnetic centres are free radicals with a very short life time, such as there can be no saturation. For a given value of the current I, the regulation voltage U_r is measured, and using the Hall voltage that is linked both to U_r and B-field, one can obtained ΔB-field.

The conditions of measurements were as follow: Microwave frequency ~ 14.05 GHz, power = 6 mW, modulation current = 10mA, modulation frequency = 2 kHz, sensitivity = 2mV, time constant = 300ms, number of cycles = 10 000, number of steps = 10 000, and a B-field between 450 and 520 mT. The factor of merit (Q factor) of the cavity containing the sample was always around 700.

Table1: Terms of resistance to wood predators for some species

Species	Resistance to fungi	Resistance to dry wood insects	Resistance to termites
AYOUS	Very poor	Poor	Poor
FRAKE	Poor	Poor	Poor
MOABI	Very Good	Good	Good

RESULTS AND DISCUSSION

Some of the spectra obtained are on figures 1, 2 and 3. The absorption is in arbitrary units. One should first notice that those spectra do not show the specific signature of copper(II) or any free radical (a molecule with an unpaired electron or more) as presented for example in references [22-24]. That is not what we are looking for. Our aim is just to estimate the absorption of the solution by the wood.

Figure 1 shows the EPR spectra of FRAKE for the untreated sample and samples treated for four different immersion durations ranging from 10 mn to 24 hours. It comes out that the absorbed quantity of solution depends on the duration of the immersion. When the sample is not treated, it's spectrum simply merges with the base-line. Same behaviour was observed for AYOUS and MOABI. One can say that the EPR spectrum of a sample depends on the retention which itself can be related to the specific density of the species.

Figures 2 and 3 are both about the three species, each one for the same immersion duration. MOABI seems to be the less absorbent (whatever the immersion time is), and AYOUS the most. This can be related both to specific gravity and fibre saturation point (see table 2). Indeed, the density of MOABI is the biggest (0.87), and the one of AYOUS the smallest (0.33). On the other hand, the fibre saturation point of MOABI is the lowest (23%), and the one of AYOUS the highest (29%).

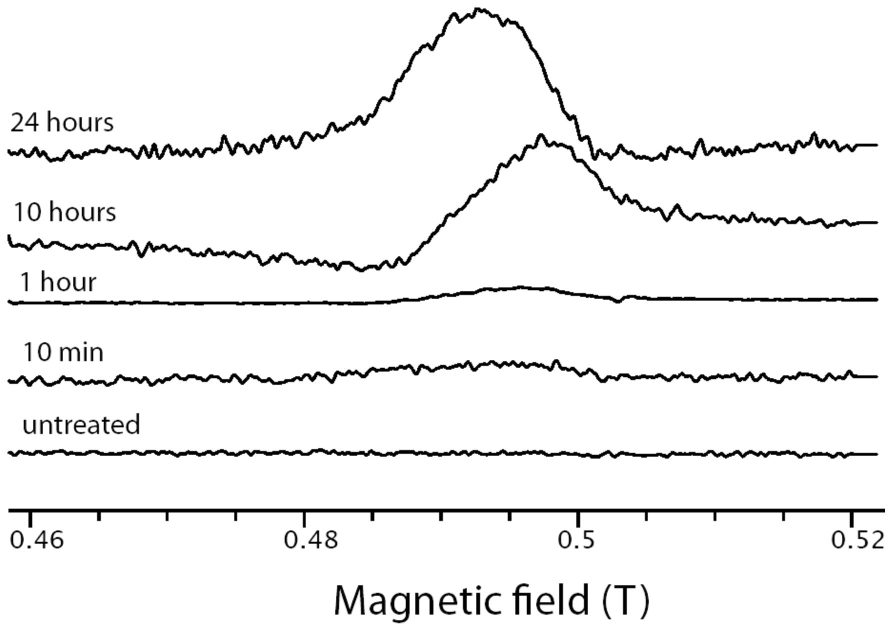

Figure 1: EPR spectra of FRAKE: untreated, 10 mn, 1 h, 10 h, and 24 h treatment by total immersion in Impralit-KDS. The amount of absorption (in arbitrary units) depends upon the length of time it remains immersed.

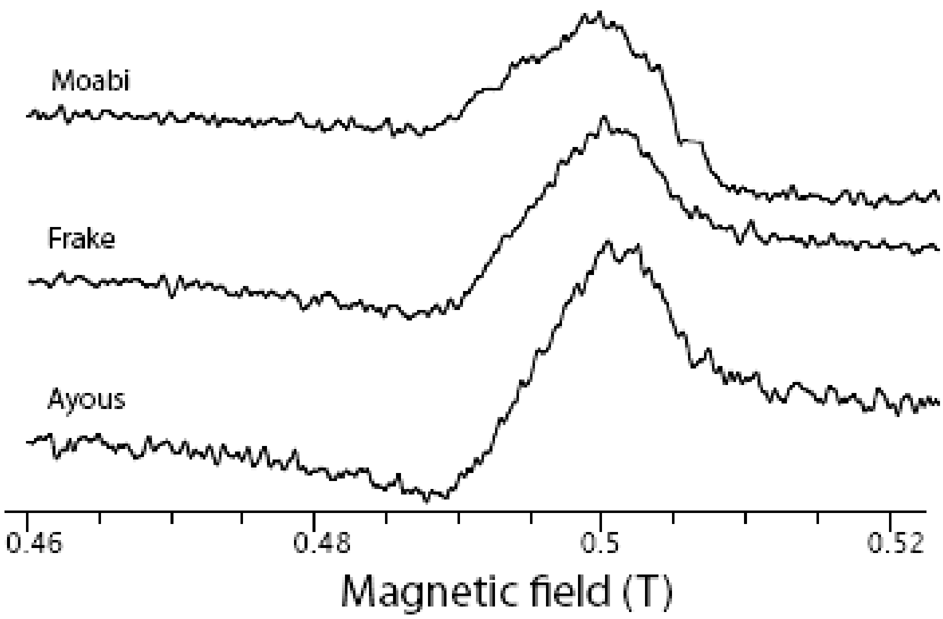

Figure 2: Comparative absorption of AYOUS, FRAKE, and MOABI after a 10 hours treatment by total immersion in Impralit-KDS.

These results are in agreement with those obtained by Salamah and Zaitun [31] in a study of dry salt retention (DSR) by wood samples of some Malaysian non-durable timbers treated with a CCA solution. They found that the DSR was inversely proportional to the density of wood

Woods such as MOABI that are resistant to penetration (by the preservative) may be incised before treatment to permit deeper and more absorption. The effectiveness of incising depends on the fact that preservatives usually penetrate

Table2: Specific characteristics of studied species

Species	Specific density	Fibre saturation point
AYOUS	0.33	29%
FRAKE	0.54	27%
MOABI	0.87	23%

into wood much farther in the longitudinal direction. Owoyemi and Kayode [32] have shown how the preservative absorption capacity of Gmelina arborea (a tropical species) wood could be enhanced through incision.
Let us also mention that some studies [33, 34] have shown that the absorption of preservatives by woods can be enhanced by an ultrasonic pre-treatment with an acoustic horn that increases the specific permeability coefficient in both radial and tangential direction.

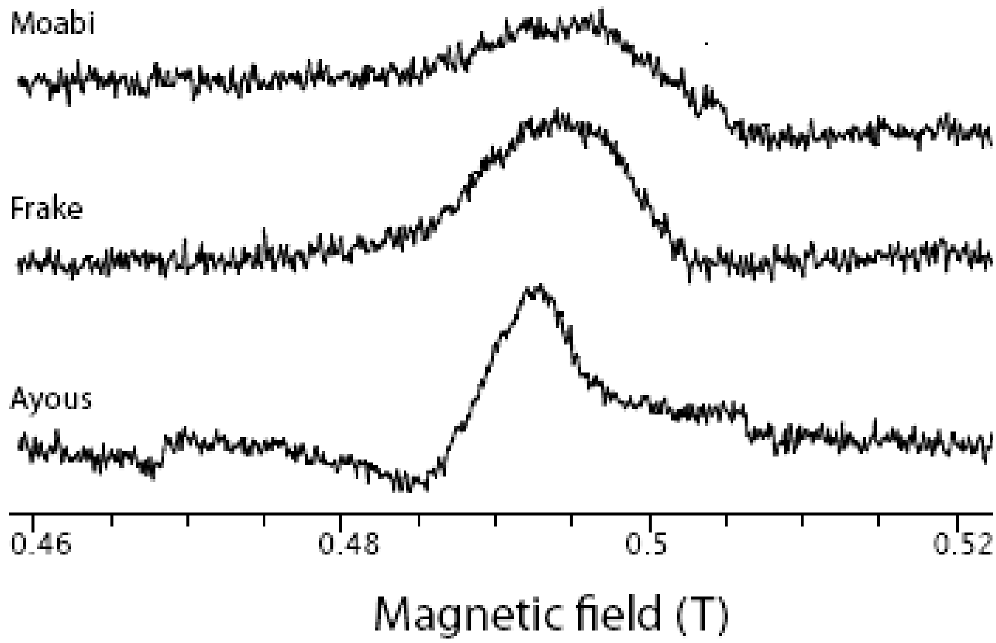

Figure 3: Comparative absorption of AYOUS, FRAKE, and MOABI after a 24 hours treatment by total immersion in Impralit-KDS.

CONCLUSION

An EPR study of absorption of a copper-based wood preservative named Impralit-KDS has been done for three tropical species: AYOUS (*Triplochoton Sclerylonk*), FRAKE (*Terminalia Superra*) and MOABI (*Baillonnella Toxisperma*). We found that for a given species, as far as the saturation limit has not been attained, the amount of absorption depends upon the length of time it remains immersed. For identical durations of immersion, the absorption amount depends both on the specific density and the fiber saturation point of the species.

ACKNOWLEDGEMENT

It was a great pleasure being at the Experimental Physics III Laboratory of the University of Dortmund for two months. Many thanks to the DAAD for sponsoring this stay.

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