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OPTIMIZATION OF A QUALITY MODEL FOR CCA INDUSTRIAL IMPREGNATION OF *PINUS RADIATA* D. DON AGRICULTURAL FENCING STAKES

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ABSTRACT

Impregnation of agricultural fencing stakes (*Pinus radiata* D. Don) using wood preservative solutions, like chromated copper arsenate (CCA-C), a water soluble salt, to protect them from decay and insect damage was investigated through the method of global modeling. Experiments were conducted using a factorial design with replicates to reduce model variability and to adjust responses to the required technical properties. Levels at which variables must be set were studied: to reduce product variability, to minimize production costs, to desensitize wood regarding the influence of uncontrollable variables, to optimize productive process and to create a global product with a higher intrinsic quality. The proposed model optimizes product retention quality and minimizes product variability, while minimizing preservative's use. Experiments were carried out by controlling wood's humidity, vacuum process duration, time of applying pressure, and preservative solution concentration, in order to allow timber to maintain its anatomical structure unchanged over time. The results of this work may be used in the optimization of similar processes in industrial plants for *Pinus radiata* D. Don stakes preservation treatments in producing countries.

KEYWORDS: Agricultural fencing stakes, chromated copper arsenate, industrial impregnation optimization, factorial design, multiple regression, global modeling.

INTRODUCTION

Pinus radiata, also known as Monterey pine, is planted extensively in the Southern hemisphere, mainly in Chile, New Zealand, Australia and South Africa. Trees can reach heights between 26 and 30 m in 20 years (Miller 1999) producing high amounts of timber; its wood has generally little durability (five years) in front of fungi and insects. Thus, preservation with chemicals or natural compounds appears to be the only way to ensure a high and prolonged durability of timber in service. However, wood preservation techniques are relatively expensive, although finally, treated wood compensates for any investment when ensuring wood durability and therefore not requiring replacement in the short term.

Chromated copper arsenate (CCA) is a mixture of copper, chromium, and arsenic formulated as oxides or salts; it preserves the wood from decay fungi, wood attacking insects, including termites, and marine borers. It also improves the weather-resistance of treated timber and may assist paint adherence in the long term. CCA is known by many trade names, including the well world-wide known Wollman CCA. Copper acts primarily to protect the wood against decay fungi and bacteria. Arsenic is the main insecticidal component of CCA. Chromium acts as a chemical fixing agent and has little or no preserving properties; it helps the other chemicals to fix in the timber, binding them through chemical complexes to the wood's cellulose and lignin.

Recognized for the greenish tint it imparts to timber, CCA has been widely used around the world often as an alternative to creosote, and pentachlorophenol that pose significant threat to health. The mentioned stain may be mitigated storing wood under cover until chemical reactions of the product with the timber take place. In order to maintain the natural color of wood, preservative pigments can be added.

AWPA (American Wood Protection Association), recognized in 1996 three types of CCA formulations (AWPA 1986), ranked by the percentage of oxides in its composition, called A, B and C, can be used. This classification was established after several experiments conducted by Smith and Williams, who observed that the maximum efficiency does not coincide with the utmost concentration of copper and arsenic (Lepage 1997).

CCA Type-C (CCA-C) Wood Preservative 60 % has the following formulation: 20.1 % arsenic pent oxide, 11.4 % copper oxide, and 28.5 % chromic acid (liquid soluble concentrate).

According to Tinto (1980), preservative treated wood posses no problems in the application of paints, varnishes and polishes when the material is dry. The incorporation of preservatives into the body wood affects its properties in a positive way, giving more resistance in front of destructive agents.

CCA treated wood has a lifetime about 15 to 40 years in service, mainly in cooling towers, piers, posts, tutorials and fences (Wilkinson 1979). On 1 January 2004 the USEPA began restricting the use of CCA for residential uses. Exceptions were allowed, including the treatment of shakes and shingles, permanent wood foundations, and certain commercial applications. It should be emphasized however that the regulatory agencies advised that CCA-treated timber products already in use pose no significant threat to health. Indeed, CCA will continue to be used in North America in a wide variety of commercial and industrial applications such as poles, piling, retaining structures and many others. The preservation industry in the USA and Canada volunteered not to use CCA for the treatment of residential timber. Following the USA and

Canada actions in restricting CCA, similar actions have been taken in other parts of the world, including the European Union and Australia.

Once impregnated, wood should be, at least, 7 days at 25°C to allow chemical reactions that fix the product; therefore, wood must be protected from rain to avoid product lixiviation from timber before fixing. Once dried, wood can be handled without risk to humans and domestic animals (Wilkinson 1979).

Over time, small amounts of CCA may leach out of the treated timber. This is particularly the case in acidic environments. The chemicals may leach from the wood into surrounding soil, resulting in concentrations higher than naturally occurring background levels. In general, most leaching takes place in the first few days and the extent and rate of leaching being highest for arsenic and copper and lowest for chromium. Available field and laboratory studies suggest that leaching of metals is highly variable and is dependent on environmental conditions. For terrestrial uses of the treated wood, environmental parameters to keep in mind include soil pH, type, texture, and organic content. Studies on sorption into soils from utility poles, have shown that the release of metals into soils/sediments from the base of treated wood, decks or utility poles or from the pressure treatment facilities, do not show a high degree of migration, either to groundwater or to the surface. In most cases, after migration of the metals a few meters down into soil, these metals attain the background level concentration of soil (EPA 2008).

A more serious risk is presented if CCA-treated timber is burnt in confined spaces such as a domestic fires or barbecues. Scrap CCA construction timber continues to be widely burnt through ignorance, in both commercial and domestic fires.

Optimization of the treatment process of wood with CCA requires joining dispersion modeling and central tendency to obtain a more robust process.

MATERIAL AND METHODS

Wood and its treatment

Wood has been legally produced and comes from responsibly managed forests of *Pinus radiata* D. Don. It is important to remember that growth and production of one tone of wood absorbs a net 1.7 tones of CO_2 from the atmosphere.

Pointed pine wooden stakes are 2.4 m long, and have diameters less than 12.5 cm; once peeled, the stakes are treated by a pressure treatment process. An aqueous solution of CCA is applied using a vacuum and pressure cycle, and the treated wood is then stacked to dry. The product used for impregnation is a chromating copper arsenate CCA-C that is prepared in aqueous solution at two different concentrations (1.43 and 1.84 %) according to the testing method described below.

A Bethell cell type or full is used for impregnation following the sequence:

a) Introduction of timber in the autoclave and sealing
b) Vacuum - 68649 Pa initial minutes during each treatment as determined
c) Admission of the preservative
d) Pressurized to 980700 Pa minutes during each treatment as determined
e) Vacuum for 30 minutes.

The process can apply varying amounts of preservative at varying levels of pressure to protect the wood against increasing levels of attack. Increasing protection can be applied, in increasing order of attack and treatment, for exposure to the atmosphere, implantation within soil, or insertion into a marine environment.

During the process, the mixture of oxides reacts to form insoluble compounds, helping with leaching reduction. If the process is carried out correctly, very little preservative is left on the surface of the wood, and the safety hazard from surface pollutants is minimized.

Pressure processes are the most permanent method for preserving timber life. These processes have a number of advantages over the non-pressure methods. In most cases, a deeper and more uniform penetration and a higher absorption of preservative is achieved. Another advantage is that the treating conditions can be controlled so that retention and penetration can be varied.

Controlled variables

After 48 h of the process of cutting, for each load processed in the autoclave are drawn 20 units, which have previously been identified, referring to his state of moisture, with a drill; it is increased by one each dowel's sample of 5 mm diameter and 25 mm long according to (INN 2003).

Wood samples are taken at the laboratory in the form of dowels, which are dried at 103 ± 2°C and milled for 2 h, and then analyzed by Spectroscopic X-ray Fluorescence (AWPA A9, Standard method for analysis of treated wood and treating solutions by X-Ray Spectroscopy.). This analysis provides the value of the response variable, known as retention, which is measured in kilos oxide per m^3 of CCA treated wood (kg ox $CCA.m^{-3}$) for each one of the experiments (Tab. 1).

Tab. 1: Variables according to the fixation's level.

Variable	Low level (-1)	High level (+1)
A: Concentration of solution (%)	1.430	1.837
B: Initial vacuum time (min)	10.1	30.2
C: Time pressure (min)	10.4	30.6
D: Humidity of wood (%)	12.9	31.3

The information is collected through a two-level factorial design replicated. It is firstly modeled estimating the effective dispersion coefficients using the method of least squares and then get the model for the central tendency. Both are contrasted by the semi-normal probability graph (Daniel 1959), to construct the global model, which allows process optimization.

To use the two-level factorial design and to generate an orthogonal design matrix it is necessary to codify variables according to the following transformation:

$$X_i = \frac{\text{unit variable - average}}{(\text{width of interval})/2} \tag{1}$$

then:

$$A = \frac{\% - 1.6335}{0.2035} \quad B = \frac{\text{min} - 20.15}{10.05} \quad C = \frac{\text{min} - 20.5}{10.1} \quad D = \frac{\% - 22.1}{9.2}$$

These variables was performed with a 2^4 factorial design with 4 repetitions of each experiment, with a total of 64 experiments, by measuring each retention expressed as kilograms of oxides $CCA.m^{-3}$ as response value, see Tab. 2.

Tab. 2: CCA-C retention values.

Experiment Nº	Variables				Retention (kg.ox CCA.m^{-3})			
	A	B	C	D	R1	R2	R3	R4
1	–1	–1	–1	–1	5.13	5.28	5.32	5.34
2	+1	–1	–1	–1	6.96	5.36	7.21	6.47
3	–1	+1	–1	–1	4.94	6.85	5.95	5.35
4	+1	+1	–1	–1	6.66	6.74	6.80	8.26
5	–1	–1	+1	–1	6.52	6.04	7.05	8.34
6	+1	–1	+1	–1	8.25	8.06	9.41	9.92
7	–1	+1	+1	–1	4.55	5.87	7.36	7.36
8	+1	+1	+1	–1	7.93	9.78	9.16	8.57
9	–1	–1	–1	+1	5.87	4.48	4.60	4.20
10	+1	–1	–1	+1	8.56	7.01	7.16	5.63
11	–1	+1	–1	+1	4.03	4.42	4.96	4.79
12	+1	+1	–1	+1	7.16	6.33	6.86	9.43
13	–1	–1	+1	+1	5.34	4.32	4.64	6.45
14	+1	–1	+1	+1	7.62	7.44	8.44	7.51
15	–1	+1	+1	+1	4.89	6.01	6.10	6.12
16	+1	+1	+1	+1	7.33	9.48	8.50	6.39

RESULTS AND DISCUSSION

A theoretical development was conducted by Pepió and Polo (1996) that improves the work done of Nair and Pregibon (Nair and Pregibon 1988) to model a joint variability and central tendency of an industrial production process using factorial design of the type 2^p, which allow variables to consider p two levels each, with a total of $n=2^p$ treatments or tests, codified in the lines specified in the matrix design, replicated r times.

Being mi the average and σ^2_i the variance of observations for the i^{th} treatment (i-th line of the array design), modeling is to relate the mean and variance with the β_k factors and their interactions through coefficients location β_k and dispersion θk with:

$$m_i = \sum_{k=1}^{n} a_{ik}\beta_k \quad y \quad \ln(\sigma^2{}_i) = \sum_{k=1}^{n} a_{ik}\theta_k \tag{2}$$

where: ln - the Neperian logarithm,
a_{ik}, k=1,2,...,n - the elements of the i-th line of the matrix model.

This model allows expressing the responses and the sums of squared differences in terms of the coefficients by:

$$Y_{ij} = \sum_{k=1}^{n} a_{ik}\beta_k + \varepsilon_{ij} \quad y \quad \ln(X_i) = \sum_{k=1}^{n} a_{ik}\theta_k + \mu_i$$
$$i = 1,2,\ldots,n \ ; \ j = 1,2,\ldots,r \qquad (3)$$

where: $X_i = \sum_{j=1}^{r}(y_{ij} - \bar{y}_i)^2$

Given that the estimated location coefficients β_k differ depending on whether the variances σ^2_i can be considered statistically the same or not, it is first necessary to estimate the coefficients of dispersion and explore its significance.

Polo and Pepió estimated the effects of scattering and estimate the variances associated with each treatment from the model.

$$\ln(X_i) = \sum_{k=1}^{n} a_{ik}\theta_k + \mu_i \ , \ i = 1,2,\ldots,n \qquad (4)$$

and is chosen as estimator of the variance of each treatment:

$$\hat{\sigma}^2_i = \frac{\hat{X}_i}{r-1} = \frac{\exp\left[\sum_{k=1}^{n} a_{ik}\,\theta_{k(\text{min-quad})}\right]}{r-1} \qquad (5)$$

using the minimum quadratic estimators of the coefficients of dispersion. It can increase the efficiency of estimation by maximum credible for the estimators.

The analysis of the impact location is not verified when the assumption of equal variance of the treatment is done by the linear model:

$$Y_{ij} = m_i + \sigma_i\varepsilon_{ij} = \sum_{k=1}^{n} a_{ik}\beta_k + \sigma_i\varepsilon_{ij} \ , \ j = 1,2,\ldots,r \qquad (6)$$

Tab. 3 shows the average values for the retention of each treatment and values of $\ln X_i$.

Tab. 3: Average retention values, X_i, $\ln X_i$, standard deviation and W_i.

I	A	B	C	D	R_1	R_2	R_3	R_4	Average	X_i	$\ln X_i$	σ_i	W_i
1	-1	-1	-1	-1	5.13	5.28	5.32	5.34	5.268	0.027	-3.609	0.320	16.467
2	1	-1	-1	-1	6.96	5.36	7.21	6.47	6.500	2.016	0.701	0.817	7.955
3	-1	1	-1	-1	4.94	6.85	5.95	5.35	5.773	2.064	0.725	0.320	18.045
4	1	1	-1	-1	6.66	6.74	6.80	8.26	7.115	1.758	0.564	0.817	8.708
5	-1	-1	1	-1	6.52	6.04	7.05	8.34	6.988	2.949	1.082	1.141	6.124
6	1	-1	1	-1	8.25	8.06	9.41	9.92	8.910	2.428	0.887	1.007	8.845
7	-1	1	1	-1	4.55	5.87	7.36	7.36	6.285	5.494	1.704	1.141	5.509
8	1	1	1	-1	7.93	9.78	9.16	8.57	6.800	1.885	0.634	1.007	8.795
9	-1	-1	-1	1	5.87	4.48	4.60	4.20	7.050	1.647	0.499	0.486	9.856
10	1	-1	-1	1	8.56	7.01	7.16	5.63	9.410	4.304	1.459	1.241	5.715
11	-1	1	-1	1	4.03	4.42	4.96	4.79	7.360	0.513	-0.667	0.486	9.368
12	1	1	-1	1	7.16	6.33	6.86	9.43	9.160	5.607	1.724	1.241	6.001
13	-1	-1	1	1	5.34	4.32	4.64	6.45	5.188	2.669	0.982	0.751	6.904
14	1	-1	1	1	7.62	7.44	8.44	7.51	7.753	0.647	-0.436	0.664	11.685
15	-1	1	1	1	4.89	6.01	6.01	6.12	5.758	1.011	0.011	0.751	7.662
16	1	1	1	1	7.33	9.48	850	6.39	7.925	5.459	1.697	0.664	11.945

The estimated effects for the dispersion model are:

Average = 0.497; A = 0.813, B = 0.603, C = 0.646, D = 0.323, AB = -0101, -1062 AC =, AD = 0.092, BC = -0220, -0538 BD = CD = -0836. The estimated standard error of the effects is +/- 0.727 and the estimated standard error is the average +/-0.364 with 5 degrees of freedom (t = 2.571).

From these effects, ordered in absolute value, its significance was studied using the method of half-normal probability plot described by Daniel (1959), obtaining statistically significant results, from most to least important, the interactions AC, CD and variables A and C, see Fig. 1.

The equation of the model is given by:

$$\ln X = 0.497+0.407A+0.323C-0.531AC-0.418CD \tag{7}$$

i.e.

$$X = EXP\,(0.497+0.407A+0.323C-0.531AC-0.418CD)$$

Therefore, the estimated variance is:

$$\sigma^2{}_i = \frac{X_i}{3} = EXP(-0.601+0.407A+0.323C-0.531AC-0.418CD) \tag{8}$$

and the estimated standard deviation is:

$$\sigma_i = EXP(-0.301+0.203A+0.161C-0.266AC-0.209CD) \tag{9}$$

Because there are significant effects and interactions in modeling variability, to modeling central tendency requires a change of variable, consisting in dividing each value of the average response by its corresponding standard deviation. Are used as values of σ_i their estimates, resulting from the dispersion model in this way the new model of the effects of central tendency is given by:

$$W_{ij} = \frac{Y_{ij}}{\sigma_i} = \sum_{k=1}^{n} a_{ik}\, \beta^*_k + e^*_{ij} \;,\; i=1,2,\ldots,n \tag{10}$$

where: Yij - distributed $N(m_i,\sigma^2{}_i)$ then W_{ij} - $N(m_i/\sigma_i,1)$ with constant variance, the linear model is transformed such that it works with the matrix model without transform, as components of this matrix is orthogonal, the estimators of β^* - independent to be the diagonal matrix of variances-covariances.

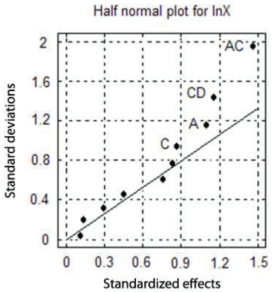

Fig. 1: Half-normal plot method.

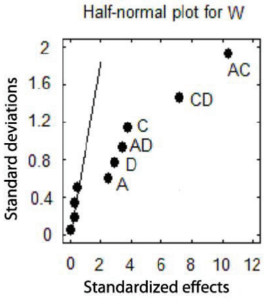

Fig. 2: Half-normal probability plot.

Obtaining estimates of the standard deviation of each treatment through the resulting model are calculated the values of variable W_i. Tab. 3 shows the estimated values of the estimated standard deviation of each treatment given by the model and the values of W_i.

Entering these values in Statgraphics, we get the following estimates for the variable effects W_i:

Average = 9.349, A= -0.643, B=0.155, C= -0.915, D=-0.707, AB= 0.001, AC= 2.527, AD= 0.837, BC= -0.053, CD= 1.823.

The estimated standard error of the effects is +/- 0.495 and the estimated standard error is the average +/- 0.247 with 5 degrees of freedom (t = 2.571).

Applying the half-normal probability method plot, statistically significant results are obtained, sorted from most to least important, the interactions AC, CD, the variable C, AD interaction, the variables D and A, see Fig. 2.

The equation of the model for W_i is given by:

$$W_i = 9.349 - 0.643A - 0.915C - 0.707D + 2.527AC + 0.837AD + 1.823CD \tag{11}$$

as: $W_i = Y_i / \sigma_i$ then $Y_i = W_i\, \sigma_i$ is given by:

$$Y_i = (9.349 - 0.643A - 0.915C - 0.707D + 2.527AC + 0.837AD + 1.823CD)\\ \mathrm{EXP}(-0.301 + 0.203A + 0.161C - 0.266AC - 0.209CD) \tag{12}$$

To optimize this process known model, should take into account two considerations, the first relates to the value required by the technical standard which is 6.4 (kg.ox.m^{-3}) and the second is to reduce the cost of the process.

Setting the variable humidity of wood at a low level, D = - 1, the model is reduced to:

$$Y_i = (10.056 - 1.480A - 2.738C + 2.527AC)\ \mathrm{EXP}(-0.301 + 0.203A + 0.370C - 0.266AC) \tag{13}$$

In the response surface of Fig. 3 are showed the different values of retention of the timber depending on the values that set the variables of concentration and time pressure, if both variables are set at high level, retention is higher, but does not meet the standard, by tracing the corresponding level curves, we obtain the Fig. 4., see value transformations in Tab. 2.

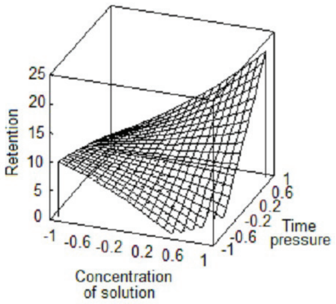

Fig. 3: Response surface with D=-1.

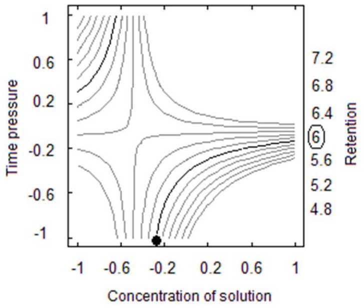

Fig. 4: Level curves with D=-1.

The level curves show the values of retention for different values of the variables. Since the goal is the value required by the technical standard which is 6.4 (kg.ox.m^{-3}), indicates that the line highlighted in any of its points can be achieved by the value of this standard.

Noted in the upper left with a point, the status of the process to minimize the cost of it since, setting the concentration solution to the lowest level and time pressure at 0.19, which is equivalent according to function processing time using a pressure of 22.42 minutes, which is slightly greater than the value 20.5 minutes, which is used in this process, further making the least variability for setting D = -1.

Setting the variable humidity of wood in the high level, D = 1, is the general model is reduced to:

$$Y_i = (8.642+0.194A+0.908C+2.527AC)\ EXP(-0.301+0.203A-0.048C-0.266AC) \qquad (14)$$

In the response surface of Fig. 5 shows the different values of retention of the timber depending on the variables of concentration and time pressure, by tracing the corresponding level curves, we obtain Fig. 6.

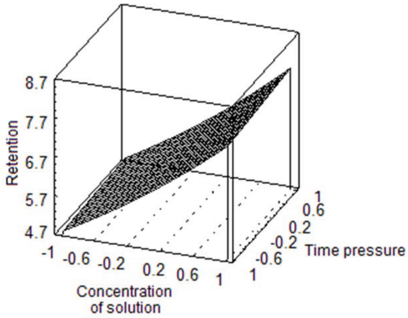

Fig. 5: Response surface with D=1.

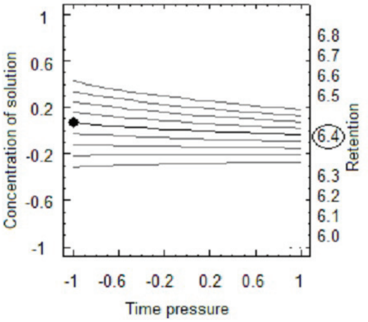

Fig. 6: Level curves with D=1.

In Fig. 6, on the highlighted line any of its points can achieve the value required by the standard: 6.4 (kg ox.m^{-3}). The black point at the left hand side shows the optimum values of controlled parameters to minimize the cost of the process, through a substantial solute reduction.

At 0.1 it is possible to reduce from 1.65 to 1.63 %, the needed product concentration, working at the lowest levels of the time-pressure curve and wood humidity; the concentration variability is slightly higher when using higher humidities (D =1).

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REFERENCES

1. AWPA, 1986: Standard P5/86. Standards for waterborne preservatives.
2. Daniel, C., 1959: Use of half-normal plots in interpreting factorial two-level experiments. Technometrics 1(4): 311-341.
3. EPA 739-R-08-006, 2008: Reregistration eligibility decision for chromated arsenicals. List A. Case No. 0132.
4. Instituto de Normalización (INN), 2003: Preserved wood. Extraction of samples, Santiago, Chile, (Madera preservada. Extracción de muestras.) 7 pp (in Spanish).
5. Lepage, E.S., 1986: Manual of nutrition of woods. Technological Research Institute of the State of Sao Paulo. (Manual de Preservaçao de madeiras. Instituto de Pesquisas Tecnologicas do Estado de Sao Paulo), 7 pp (in Spanish).
6. Miller, R., 1999: Characteristics and availability of commercially important woods. Forest Products Laboratory. Wood Handbook. Wood as an engineering material. Department of Agriculture, Forest Service, Forest Products Laboratory. Madison, WI. E.E.U.U. Chapter 1.
7. Nair, V.N., Pregibon, D., 1988: Analyzing dispersion effects from replicated factorial experiments. Technometrics 30(3): 247–257.
8. Pepió, M., Polo, C., 1996: Design and optimisation of processes. Statistical laboratory, ETSEIT-UPC, (Disseny i optimització de processos. Laboratori d'Estadística ETSEIT-UPC). Terrassa, Spain (in Spanish).
9. Tinto, J.C., 1980: Manual for protective treatments of forest products. Argentina. General Investment Council. (Manual para tratamientos protectores de productos forestales. Argentina. Consejo General de Inversiones) (in Spanish).
10. Wilkinson, J.G., 1979: Industrial Timber Preservation. The Rentokil Library, Associated Business Press, London, 532 pp.

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