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Beom-Goo Lee for the degree of Master of Science in Forest Products presented on March 17, 1994

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Fungi cause wood stain by producing masses of dark hyphae in wood. Stain fungi primarily use non-structural, easily digested organic components stored in parenchyma, and cause minor losses in some wood strength properties. As a result, stained wood can be used commercially except for structural purposes. However, the aesthetic changes caused by stain fungi make the wood unacceptable to many consumers. Stain fungi cause economic losses conservatively estimated at about $ 10 million per year. Heavily stained wood has little value and this loss provides an incentive to develop stain removal treatments which permit the wood to be used where appearance is important. A variety of bleaching treatments have been developed for removing various chemical and biological stains from hardwoods, but the economic viability of these treatments for conifers is less well documented.

In this study, the bleaching effects of combinations of hydrogen peroxide, sodium hydroxide or sodium silicate were

evaluated on heavily stained ponderosa pine under various conditions.

Mean L^*-b^* gains (whiteness) of wood generally increased as peroxide concentration and treatment time increased. Increasing peroxide concentration from 1 to 2 %, and treatment time from 30 to 60 minutes markedly improved mean whiteness gains, while increasing peroxide concentration to 3 %, and treatment time to 90 minutes slightly improved mean whiteness gains. Mean whiteness gains increased as temperature increased from 50 to 60 °C, while specimens yellowed as temperature increased to 70 °C. This yellowing was associated with increased pH of the bleaching solution and decreased residual peroxide.

The ratio of sodium hydroxide to sodium silicate did not affect mean whiteness gains when pH remained under 11. However, specimens were yellowed as the ratio of sodium hydroxide increased probably because of increased pH of bleaching solution.

The results suggest that the use of a 2 to 3 % peroxide concentration at 60 °C for 60 to 90 minutes produced optimum bleaching of ponderosa pine.

REMOVAL OF FUNGAL STAIN FROM PONDEROSA PINE SAPWOOD USING PEROXIDE AND CAUSTIC BLEACHES

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Beom-Goo Lee

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Signature redacted for privacy.

Professor of Forest Products in charge of major

Signature redacted for privacy.

Head of Department of Forest Products

Signature redacted for privacy.

Dean of Graduate School

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Removal of Fungal Stain From Ponderosa Pine Sapwood Using Peroxide and Caustic Bleaches

1.0. LITERATURE REVIEW

1.1. Introduction

Wood is a natural, biodegradable substrate which can be used as a habitat by various microorganisms, including decay fungi, stain fungi, surface molds and bacteria. Decay fungi are the most important microbial colonizers of wood since they use structural components of wood for their nutrition, changing the physical and chemical characteristics of wood. In contrast, stain fungi, surface molds and bacteria primarily use non-structural, easily digested organic components of wood such as starch, pectin and protein stored in parenchyma cells and lumens. These organisms do not appreciably affect the strength of wood [Hunt and Garratt 1967], although stain fungi decrease toughness by 15 to 30 % [Chapman and Scheffer, 1940].

Wood stain is generally caused by masses of dark hyphae in the wood and occurs primarily in the sapwood when wood moisture contents exceed 20 %. Wood stain can also occur in logs and standing trees when bark beetles carry spores beneath the bark [Dowding, 1969, 1970].

Stained wood can be used commercially except for structural purposes. However, the aesthetic changes caused by stain fungi are often confused with decayed wood. Stains

annually cause economic losses conservatively estimated at about $ 10 million [Scheffer, 1973]. This serious economic loss provides an incentive to develop stain removal treatments. A variety of bleaching treatments have been developed for removing various chemical and biological stains from hardwoods [Downs 1961; Levitin, 1974, 1975 and 1976; Bounous and Carter, 1983], but the economic viability of these treatments for conifers is less well documented.

In this study, the bleaching effects of combinations of hydrogen peroxide, sodium hydroxide or sodium silicate on heavily stained ponderosa pine were evaluated under various conditions.

1.2. What is Bleaching?

The origin of the term bleach is blecan, which is the Anglo-Sexon word meaning to fade. Bleaching, therefore, means to whiten wood pulp, textiles and many other materials. Bleaching was done first by the Gauls, who bleached vegetable fibers derived from wood and vegetable ash by moistening the fibers with alkaline solution and allowing sunlight to drive the reaction [Singh, 1979].

Bleaching began on an industrial scale at the end of nineteenth century with treatment of wood chips, first with hypochlorite and later with chlorine, in combination with an intermediate alkali extraction step [Fengel and Wegener, 1984].

The main purpose of bleaching is to increase brightness. The chromophoric components absorbing light in unbleached pulp are mainly associated with functional groups of residual lignin. Chromophoric groups, therefore, must be removed or stabilized in the bleaching process. There are two possible alternatives; lignin-removal (delignification) and lignin preservation. Lignin-removal bleaching is employed for brightening chemical pulp, when high and reasonably permanent brightness is required. Chlorine, chlorine-based chemicals and oxygen are used in lignin removal bleaching. Lignin preservation bleaching usually provides only a moderate brightness increase. This process is used with high yield mechanical and semi-chemical pulps. The main reaction is to

change parts of chromophoric groups in wood or pulp. Sodium dithionite and sodium peroxide are usually used for this process [Pearl, 1967; Sjöström, 1981].

1.3. Mechanism

There are substantial differences between chromophores formed during oxidation of wood and those present in the hyphae of wood staining fungi. Understanding the nature of wood based chromophores, however, can provide insights into methods for fungal stain removal.

Wood is a chemically complex substance composed of carbohydrate and phenolic polymers. Extraneous components, such as lower molecular weight organic materials and inorganic salts occur in lesser amounts [Andrews, 1968].

The color of wood is affected by its non-carbohydrate components. Lignin, along with extraneous components, contains sites which are readily converted into chromophoric compounds [Andrews, 1968].

Lignins which are composed of guaiacyl-, syringyl-, and p-hydroxyphenylpropane units and contain p-coumaric acid esterified to terminal hydroxyl groups of the propane side chain are synthesized using L-tyrosine and L-phenylalanine as substrates by a series of enzyme-catalyzed reactions. [Higuchi, 1985].

Hydrogen peroxide is a weak acid with a dissociation constant of approximately 10^{-11} at 60 °C, and is only

negligibly dissociated below pH 9. Dissociation increases as pH increases from 9 to 13 [Hartler et. al., 1960]. Hydrogen peroxide is dissociated in aqueous solution to form hydroperoxide anion. Bleaching is performed by the nucleophilic addition reaction of hydroperoxide anions to functional groups in lignin [Gierer and Imsgard, 1977]. In this reaction, the chromophoric groups are destroyed without a concomitant breakdown of the lignin structure [Fengel and Wegener, 1984].

Hydroperoxide anions attack monomer units having aliphatic side chains possessing carbonyl groups, and p-hydroxybenzyl units possessing benzyl alcohols or their easily hydrolyzable ether groups. Secondary, unetherfied phenolic units in the absence of an oxidizable functional group on the lignin side chain are extensively oxidized in peroxide bleaching [Bailey and Dence, 1969]. As part of this degradative sequence, o- and p-benzoquinone derivatives are formed, which react further with peroxide to form colorless aliphatic substances [Reeves and Pearl, 1965; Bailey and Dence, 1969; Kempf and Dence, 1975; Singh, 1979]. However, o- and p-benzoquinone derivatives undergo condensation reactions to form other complex chromophoric products, which are more resistant to peroxide oxidation [Bailey and Dence, 1969]. Stain fungi generally discolor wood through the presence of melanins in the hyphal walls. Melanins also are synthesized from tyrosine via 3,4-dihydroxyphenyl alanine (DOPA) in culture media by various fungi and other

microorganisms. In the basidiomycotina, melanins in cell walls are synthesized using τ-glutaminyl-3,4-dihydroxy benzene (GDHB) or catechol as phenolic precursor. In Ascomycotina and related Deuteromycotina, melanins are generally synthesized using 1,8-dihydroxynaphthalene (DHN) as immediate precursor of the polymer [Bell and Wheeler, 1986]. Allomelanins, which are catechol melanins occurring in fungi, are formed by oxidation of diphenols such as catechol. Two catechols form both carbon-carbon and carbon-oxygen-carbon linkages by radical coupling reactions or nucleophilic attack. In the reactions, o-benzoquinone is used as an intermediate and catechol melanins are formed [Swan, 1973]. Melanins have o-quinone units or monomer units with aliphatic side chains which possess functional groups [Kitamura and Kondo, 1958; Swan, 1973; Bell and Wheeller, 1986; Zink and Fengel, 1990]. Melanin has the same precursor, tyrosine, as lignin. Alkaline peroxide is capable of breaking down lignin-like structures to yield colorless products [Fengel and Wegener, 1984]. Melanin can also be decolorized by treatment with hydrogen peroxide or lightened by treatment with aqueous sodium hydrosulphite [Mason, 1959; Swan, 1973], but the bleaching mechanism of melanin has not been studied.

1.4. Factors Affecting Bleaching

1.4.1. Temperature and Treatment Time

Bleaching brightness can be improved, as either temperature and treatment time or both increase within certain limits. However, bleaching brightness decreases as a result of peroxide decomposition and lignin modification when temperatures are too high. Long treatment times also cause brightness reversion as the peroxide residual disappears, causing alkali darkening [Singh, 1979].

When other conditions are the same, the time required to obtain maximum brightness depends principally on temperature. In general, bleaching time increases about two fold for every 10 °C temperature decrease [Reichert and Pete, 1949].

1.4.2. Alkalinity

Hydrogen peroxide is a weak acid which is negligibly dissociated below pH 9. Brightness increases as pH increases up to approximately 11, when other conditions are the same. Hydrogen peroxide nearly disappears at this pH, and hydrogen peroxide decomposes to produce oxygen if the pH is increased further. The oxygen reacts with lignin to create chromophoric groups such as carbon-carbon dimers that are more resistant to peroxide attack. This probably explains why the brightness drops if the pH is increased

above 11 [Martin, 1957; Hartler et al. 1960; Bailey and Dence, 1969; Singh, 1979; Fengel and Wegener, 1984]. For maximum brightness increases with minimum bleaching times, it is very important that the pH of the bleaching solution be maintained between 10.5 and 11 [Fengel and Wegener, 1984]. The pH of peroxide bleaching solution falls as the reactions proceed and carboxyl groups are formed. Buffers and stabilizers are necessary to maintain the pH of the bleaching solution within an effective range. Sodium silicate is commonly used for this purpose. As a buffering agent, the sodium silicate releases sodium hydroxide to the bleaching solution to control the pH drop. However, commercial sodium silicate contains insufficient alkali, and can not neutralize newly formed carboxyl groups, particularly in highly lignified pulps. Customarily, sodium hydroxide is included in the bleaching solution when hydrogen peroxide is used as oxidant. As a stabilizing agent, sodium silicate reacts with magnesium sulfate to form a stable colloidal suspension of magnesium silicate, which may absorb metallic decomposition catalysts to its surface and inactivate them [Andrews, 1968; Singh, 1979; Kutney, 1985].

1.4.3. Enzymes and Metallic Ions

Hydrogen peroxide can be catalytically decomposed by certain metallic ions and enzymes. These catalytically active materials include trace metals such as manganese, iron

and copper, and bacterial enzymes that are present in pulp [Andrews, 1968; Singh, 1979]. Bacteria can secrete peroxidase which catalyzes many oxidation reactions or catalase which accelerates the decomposition of hydrogen peroxide. Peroxidase or catalase producing bacteria can colonize mechanical pulps in high numbers, especially during warm weather [Reichert et al., 1946; Singh, 1979]. Microorganisms in the pulp and paper industry may be derived from the raw water, the pulpwood, the white water or the surrounding atmosphere [Reichert et al., 1946]. Hydrogen peroxide is produced naturally as a metabolic byproduct by many aerobic microorganisms, and has bacteriocidal properties [Reichert et al., 1946]. However, other bacteria also produce catalase, which decomposes hydrogen peroxide, as a defense mechanism against hydrogen peroxide. Pulps containing catalase can destroy peroxide thereby reducing the bleaching effect. Heavily colonized pulp may contain enough catalase to decompose nearly all peroxide, resulting in no bleaching effect [Reichert et al., 1946]. Trace metals, such as manganese, iron and copper, may enter pulp from contamination during the pulping operation, or they may be natural constituents of wood. Metals solubilized by chelating agents are catalytically active. Manganese and possibly copper are catalytically active, but iron seems to be catalytically inactive and not solubilized [Dick and Andrews, 1965]. Trace metals and enzymes can decompose peroxide catalytically, resulting in lower residual peroxide

and decreased brightness. The harmful effects of trace metals and enzymes can be largely overcome by chemical pretreatments. Enzymes are effectively inactivated by pretreating pulp with heat, chlorinating agents, oxidizing agents or bactericides, while trace metals can be inactivated with organic chelating agents such as sodium silicate or diethylenetriamine pentaacetic acid (DTPA) [Reichert and Pete, 1949; Dick and Andrews, 1965; Andrews, 1968; Singh, 1979].

1.5. Stain Fungi

1.5.1. Colonization of Wood by Stain Fungi

Stain fungi belong to the Ascomycetes and the Fungi Imperfecti [Liese, 1970; Scheffer, 1973], and typically inhabit the parenchyma tissues of the sapwood [Hunt and Garratt, 1967; Zabel and Morrell, 1992] in softwoods and hardwoods [Liese, 1970; Wilcox, 1973; Fengel and Wegener, 1984]. Wood stain can be initiated by air borne spores or spores carried by insect vectors such as bark beetles [Dowding 1969 and 1970; Panshin and de Zeeuw, 1980], previously stained stickers, and sawmill machinery which has sawn a badly stained log [Zabel and Morrell, 1992]. Under favorable conditions, spores landing on the surface of wood germinate within hours and penetrate into wood through ruptured tracheids or exposed wood rays. The hyphae then

directly penetrate the pits to rapidly colonize the parenchyma cells in the wood rays or longitudinal parenchyma surrounding the resin canals. Stain fungi often move inward along the rays from the sides to form wedge shaped stain [Liese, 1970; Zabel and Morrell, 1992]. Ophiostoma pilifera can penetrate into Pinus echinata at an approximate daily rate of 0.5, 1.0 and 4.5 mm in the tangential, radial and longitudinal direction, respectively [Lindgren, 1946]. Stain fungi form a special hyphal apex, or transpressorium, which occasionally penetrates even the lignified cell wall of tracheids using enzymes to soften the cell wall layers and hydrostatic pressure of the fungal mother cell [Liese, 1970]. These hyphae form 0.2 to 0.6 μm hyphal tips which penetrate the cell and resume growth at the normal diameter [Panshin and de Zeeuw, 1980]. Young hyphae are hyaline and smooth but become warty and bark-like with aging. Wood stain is caused by dark material deposited in the hyphal wall of these fungi in the form of globular granules 5 to 6 days after hyphal development [Zink and Fengel, 1990]. Stain fungi cause common sapwood discolorations producing shades of blue, black, and gray. Pigments secreted from fungal hyphae occasionally cause yellow, pink, purple and green stains of lesser importance. A few stain fungi can act as typical soft rot fungi and attack the S2 layer of tracheid walls [Hunt and Garratt, 1967; Scheffer, 1973; Zabel and Morrell, 1992].

Stain fungi can also depolymerize carbohydrates in wood to produce physical changes. Pine wood samples (Pinus

sylvestris) exposed to Aureobasidium pullulans for 10 weeks lost about 7 % of the cellulose, 3 to 4 % of the hemicellulose and 1.3 % of the lignin [Seifert, 1964]. Bending and compression strength decrease 1 to 5 % following exposure to stain fungi, while toughness decreased 15 to 30 % [Chapman and Scheffer, 1940]. For this reason, stained wood is not recommended for structural purposes such as utility poles, glue-laminated timbers, ladders or piling. Stain fungi also increase wood permeability by removing pit membranes, resulting in increased solution absorption and uneven finishing [Zabel and Morrell, 1992].

1.5.2. Melanin

Melanins are dark brown to black pigments of biological origin. Fungal melanins are formed in the cell wall, but generally not in the cytoplasm [Bell and Wheeler, 1986]. Melanin precursors may be secreted into the cell wall from the cytoplasm, and are oxidized to melanin [Griffiths, 1982; Bunning and Griffiths, 1984]. Melanins are copolymers containing aliphatic, aromatic and quinoid elements which contain hydroxyl, carbonyl, carboxyl and amino groups [Zink and Fengel, 1990]. Fungal melanins are formed from tyrosine, which is also used as intermediate to form lignin [Goodwin and Mercer 1983]. Melanins are insoluble in water, aqueous acid and common organic solvents; however, melanins which are extensively conjugated with carbohydrates and proteins are

water-soluble [Bell and Wheeler, 1986]. Melanins are not important in growth and development but enhance the survival and competitive abilities of species in certain environments such as areas with high levels of UV irradiation, desiccation or temperature extremes. Fungal melanins are also important for resistance to microbial attack [Bell and Wheeler, 1986]. Melanins and melanin precursors such as catechol, 5,6-dihydroxyindole, and 1,8-dihydroxynaphthalene have antibiotic effects against antagonistic organisms [Haars and Hüttermann, 1980; Pawelek and Korner, 1982]. Melanization also provides rigidity to the transpressorium and directs the development of a penetration peg [Woloshuk et al., 1980; Kubo et al., 1982; Bell and Wheeler, 1986]

2.0. OBJECTIVES

The primary objectives of the study were to;

1. Identify the optimum chemical combinations and conditions for removing fungal stain from ponderosa pine sapwood.
2. Evaluate the economics of stain removal based on experimental results.

3.0. MATERIAL AND METHODS

3.1. Wood Employed

Heavily stained ponderosa pine sapwood (Pinus ponderosa Laws) boards (2.0 x 4.4 cm) were cut into 26.4 cm long sections. Six cm on each end of the specimen was used to evaluate bleaching effects.

3.2. Effect of Peroxide Concentration, Temperature and Treatment Time

Each end (6.0 cm in length) of the wood specimen was dipped for varying periods into bleaching solutions containing 1.0, 2.0 or 3.0 % hydrogen peroxide plus 0.3 % sodium hydroxide and 4 % sodium silicate (Wt. basis). Wood specimens were dipped for 30, 60 or 90 minutes in bleaching solutions maintained at 50, 60 or 70 °C on a hot plate stirrer. Specimens were weighed before and after treatment to determine solution uptake. After treatment, wood specimens were rinsed thoroughly with cold water and sprayed with a solution containing 12 g acetic acid per 1 l of water, allowed to stand for 15 minutes, rinsed thoroughly with cold water and air-dried to neutralize any remaining sodium hydroxide [Bounous and Carter, 1983]. The degree of destaining were assessed by comparing mean L^*-b^* gains (whiteness) of specimens before and after bleaching. The

Commission International de l'Eclairage (CIE), a Paris-based international body provides quantatively measured standards for color [Brunner et al., 1990]. Measurement of the whiteness of each specimen was obtained in terms of CIELAB color space parameters [Oliver et al., 1992]. CIELAB color space co-ordinates L^*-b^* are used to measure the whiteness of specimens. The three color reflectance values, CIELAB, were obtained for each specimen before and after bleaching with a Truevision Inc. TAGRA-32 image capture board connected to a JVC BY-110 three-tube color camera. Illumination was supplied by incandescent light. The spatial resolution was 2.5 pixels/mm. The digitized images were rectangular arrays of 200 x 256 pixels, each composed of three red, green and blue components. The "L" corresponds to the light-dark and is a measure of the brightness from black(0) and white(255). The "a" is a function of the red-green difference. The "b" is a function of the yellow-blue difference [Oliver et. al., 1992; and Brunner et. al., 1990]. The depth of bleaching penetration was assessed by cutting a section from the end of each specimen and visually assessing the depth of effect. The pH of the bleaching solution was assessed using a Corning 150 pH/ion meter (Corning, Corning, NY) before and after bleaching. Residual peroxide in the bleaching solution was determined by pipeting 10 ml of the bleaching solution into an erlenmeyer flask, acidifying with 20 ml of 20 % sulfuric acid, and titrating with 0.3 N $KMnO_4$ to a faint pink end point. Each ml of 0.3 N $KMnO_4$ used equaled 1.4 g of 35 %

hydrogen peroxide per 1 l of water [Reichert and Pete, 1949]. All treatments were carried out on 5 replicates.

The data of effect of peroxide concentration, temperature and treatment time on mean L^*-b^* gains (whiteness) were analyzed using the personal computer version of SAS software [SAS Institute, 1991].

The effects of peroxide concentration, temperature and treatment time on mean L^*-b^* gains (whiteness), were compared by grouping the data by 3 peroxide concentrations, 3 temperatures and 3 treatment times to test normality and perform an analysis of variance (ANOVA). The means of each factor were then analyzed using Fisher's Protected Least Significant Difference multiple comparison t-test (FPLSD) at the 5 percent significance level.

3.3. Effect of Component Ratio on Bleaching with Peroxide

The effect of caustic component ratios in bleaching were evaluated by varying ratios of sodium hydroxide to sodium silicate, while holding peroxide content at 3 %. Sodium hydroxide and sodium silicate were tested at ratios of 0:12, 1:3, 1:6, 1:12, 2:3, 3:3 or 4:3. All treatments were carried at 60 °C for 60 minutes. After treatment, wood specimens were neutralized. The degree of destaining were assessed by comparison with the whiteness of specimens before and after bleaching using whiteness as described in section 3.2. All

experiments were carried out on 5 replicates. Component ratio effect data were analyzed statistically as described in section 3.2.

4.0. RESULTS AND DISCUSSION

4.1. Effect of Peroxide Concentration, Temperature and Treatment Time

The degree of destaining was assessed by comparing mean L^* gains (brightness) and mean L^*-b^* gains (whiteness) of specimens before and after bleaching. Although the reason is unclear, mean L^*-b^* gains ranked specimens better than mean L^* gains, compared with visual examination. Thus, mean L^*-b^* gains were used to assess the degree of destaining. For the purposes of reporting, mean L^*-b^* gains will be referred to as mean whiteness gains throughout the discussion.

Mean whiteness gains increased as peroxide concentration increased (Table 1; Figure 1). Increasing peroxide levels from 1 to 2 % significantly improved mean whiteness gains, while increasing the concentration to 3 % did not significantly improve mean whiteness gains (Figure 1). These results suggest that further increases in peroxide concentration may increase whiteness gains, but the levels achieved probably do not justify the chemical cost. Shorter treatment times (Figure 8) or lower temperatures (Figure 5) increased mean whiteness gains as peroxide concentration increased, but the results did not significantly differ between 1 and 2 %. Treatment with 2 to 3 % peroxide appeared to be optimal for bleaching using the current solution components. The low concentration of peroxide gave the

greatest increase in mean whiteness gains on a peroxide consumption basis, even though the results were less favorable than those at higher peroxide concentrations. These results suggest that multiple bleaching in 1 percent of peroxide may produce better whiteness improvements, although this possibility was not investigated in the current study.

Mean whiteness gains generally increased as treatment temperature increased from 50 to 60 °C, but were not significantly different from one another. However, wood specimens tended to yellow as the temperature increased to 70 °C, reducing mean whiteness gains significantly in comparison with the 50 and 60 °C treatments (Figure 1). Increasing temperature for the 30 minute treatment decreased mean whiteness gains, but the effects were not significantly different from one another (Figure 8). Treatment at 50 or 60 °C appeared to be optimal for bleaching using the current system.

Higher temperatures enhanced the rate of bleaching, but also increased the rate of peroxide decomposition. As a result, peroxide consumption increased, but bleaching efficiency declined, making the process less cost effective. These reactions reflect either reactions by unchelated metal ions in the solution [Kindron, 1980] or reactions between peroxide and hydroperoxide anion [Moldenius, 1982].

Peroxide levels in the treatment solution are sensitive to a number of factors. Peroxide decomposition occurs at high temperatures or when hydroperoxide anion exceeds 0.03

mmole per liter. In the former reaction, unchelated metal ions can catalyze the decomposition of peroxide and hydroperoxide anion to produce water and oxygen [Kindron,1980]. The latter reaction produces hydroxyl group as well as water and oxygen, increasing the pH of the solution [Moldenius, 1982]. As pH approaches 11, oxygen released by the decomposition of peroxide reacts with lignin to create chromophoric carbon-carbon dimers which are more resistant to peroxide attack [Martin, 1957, Hartler et al., 1967; Bailey and Dence, 1969; Singh, 1979; Fengel and Wegener, 1984]. Specimens which were bleached at 70 °C for 90 minutes were yellowed, possibly as a result of these reactions. Thus, control of both pH and metal content are extremely important for successful bleaching.

While higher temperatures reduced the efficiency of peroxide bleaching by destroying peroxide, treatments at 50 °C resulted in reduced production of hydroperoxide anion and a corresponding reduction in the improvement in whiteness in comparison with that found at 60 °C. As a result, residual peroxides following bleaching treatments at 50 °C exceeded 40 % of the original concentration (Table 2). Therefore, long treatment times will be required at lower temperatures to obtain a bleaching effect similar to that found at higher temperatures.

Treatments at 60 °C appeared to be optimal for bleaching using the current system. The wood was nearly whitened,

although there were residual areas of staining which resisted treatment.

Mean whiteness gains generally increased as treatment time increased. Increasing treatment time from 30 to 60 minutes significantly improved mean whiteness gains, while increasing treatment time to 90 minutes produced a slight improvement which did not differ significantly from the 60 minute results (Figure 1). Mean whiteness gains at 70 °C were significantly lower for the 90 minute treatment, possibly because almost all residual peroxide was consumed or the pH exceeded 11 (Figure 7). Elevated pH levels suggested that peroxide decomposition had occurred. Treatment for 60 to 90 minutes appeared to be optimal for bleaching using the current system.

Furniture manufacturers bleach wood to obtain more uniform color, lighter color, better color stability and controlled surface characteristics [Bounous and Carter, 1983]. In this process, the bleaching effect is relatively shallow. The depth of bleaching in the current study was less than 1 mm, in virtually all specimens. This shallow treatment zone corresponds with those found in previous studies and indicates that the wood surface can only be lightly sanded to avoid exposing unbleached wood [Bounous and Carter, 1983].

Bleaching was optimum when pH was controlled between 10 and 11, and residual peroxide values ranged from 15 to 25 (Table 2). Specimens which had low mean whiteness values

before bleaching tended to experience greater improvements than those which had high initial mean whiteness values. Some specimens which were more heavily stained absorbed more bleaching solution and tended to yellow, even though these specimens were generally well bleached. The more heavily stained areas remained darker. As a result, heavily stained wood or wood with marked variations in staining may not be suitable for these treatments.

Peroxide was very rapidly decomposed at the start of bleaching and slowly decomposed as the treatment continued (Table 2). Mean whiteness gains were greatest with short treatment times. Bleaching time is reported to decrease about two fold for every 10 °C temperature increase [Reichert and Pete, 1949]. The use of wood specimens at room temperature may have cooled the bleaching solution, thereby decreasing the initial rate of bleaching. Preheating the wood surface before bleaching may reduce bleaching time and increase mean whiteness gains [Bounous and Carter, 1983].

The results indicate that treatment with 2 to 3 % peroxide solutions at 60 °C for 60 to 90 minutes produced significant improvements in mean whiteness of the specimens.

Table 1. Effects of peroxide concentration, temperature and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness).[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1			11.48(4.25)b[b]
2			14.89(4.79)a
3			15.85(4.27)a
	50		15.26(4.19)a
	60		15.72(4.17)a
	70		11.25(4.77)b
		30	12.48(4.26)b
		60	14.79(3.33)a
		90	14.94(6.07)a

a. Values represent means of 45 specimens. Values in parentheses represent one standard deviation.
b. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

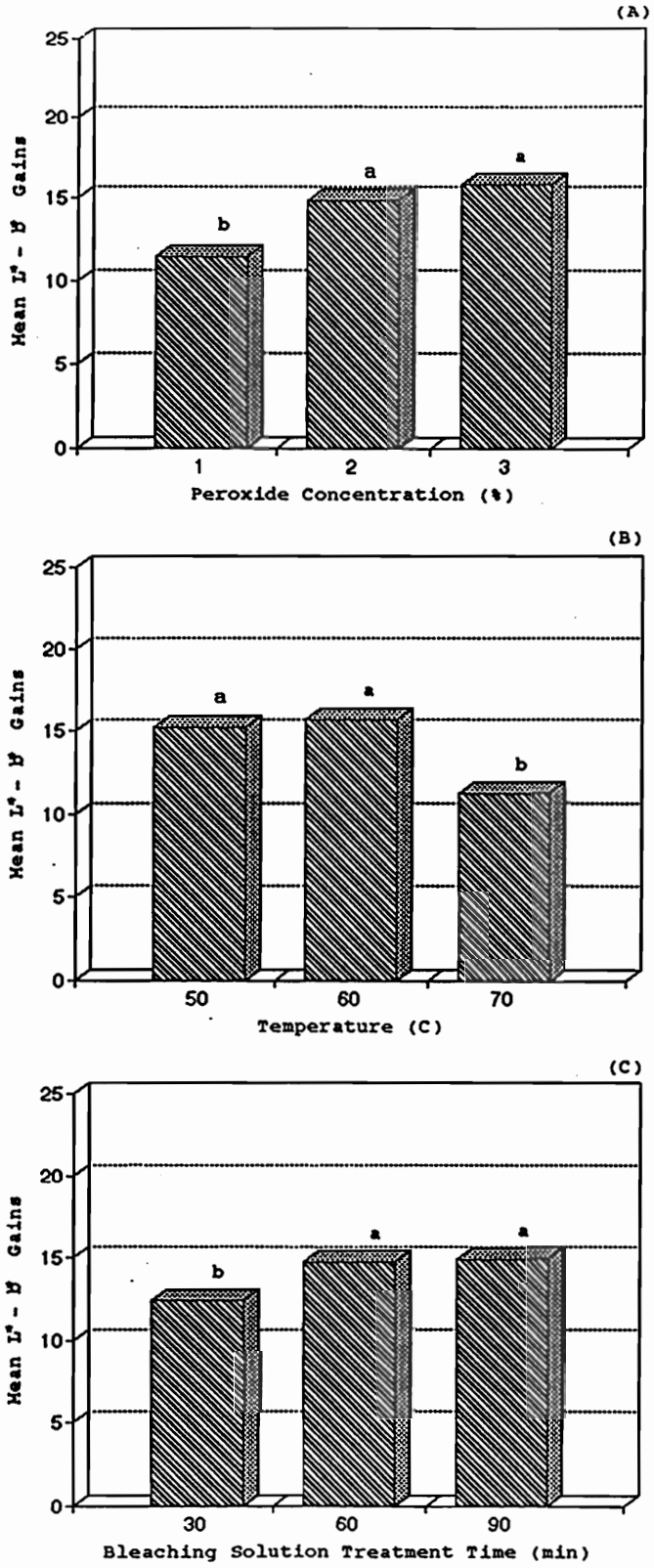


Figure 1. Effects of (A) peroxide concentration, (B) temperature and (C) bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness). Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 2. Effects of peroxide concentration, temperature and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness).[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	30	199.82	10.6	10.8	46.74	11.45(2.58)
1	50	60	150.61	10.6	10.8	47.87	12.71(1.86)
1	50	90	415.73	10.6	10.9	43.52	16.01(3.14)
1	60	30	197.20	10.5	10.8	39.04	13.01(3.13)
1	60	60	184.52	10.6	11.0	9.70	11.59(1.28)
1	60	90	157.32	10.5	11.1	7.98	13.98(2.35)
1	70	30	201.67	10.5	11.2	0.73	7.76(7.58)
1	70	60	184.51	10.4	10.9	5.92	11.01(2.20)
1	70	90	217.43	10.4	10.9	1.81	5.83(1.81)
2	50	30	127.92	10.3	10.5	59.08	13.79(5.33)
2	50	60	105.21	10.3	10.6	57.68	15.46(2.42)
2	50	90	180.35	10.3	10.7	40.43	17.69(7.54)
2	60	30	149.10	10.3	10.8	17.87	12.77(3.08)
2	60	60	127.88	10.3	10.7	23.22	18.32(2.33)
2	60	90	133.45	10.2	10.8	15.76	18.36(2.88)
2	70	30	164.83	10.4	11.1	4.19	10.71(1.17)
2	70	60	155.02	10.4	11.0	2.52	14.62(2.37)
2	70	90	198.82	10.3	11.0	1.48	12.99(7.34)
3	50	30	171.29	10.2	10.5	53.92	16.03(4.07)
3	50	60	143.19	10.2	10.6	45.65	15.13(1.59)
3	50	90	117.39	10.1	10.6	31.07	19.04(2.60)
3	60	30	154.47	10.1	10.8	11.41	12.49(2.72)
3	60	60	196.37	10.5	10.9	28.39	19.91(1.84)
3	60	90	154.47	10.1	10.6	17.34	21.02(2.73)
3	70	30	162.16	10.2	10.8	8.87	14.37(2.49)
3	70	60	202.00	10.1	10.9	3.13	14.37(2.00)
3	70	90	262.81	10.3	11.1	1.12	10.26(4.50)

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concetration.

Table 3. Effects of temperature and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 1 % peroxide concentration.[a]

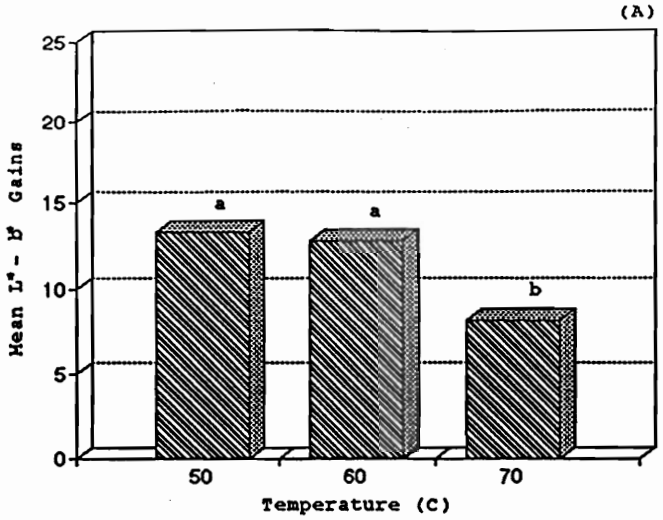
H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	30	199.82	10.6	10.8	46.74	11.45(2.58)bc[c]
1	50	60	150.61	10.6	10.8	47.87	12.71(1.86)c
1	50	90	415.73	10.6	10.9	43.52	16.01(3.14)ab
1	60	30	197.20	10.5	10.8	39.04	13.01(3.13)cd
1	60	60	184.52	10.6	11.0	9.70	11.59(1.28)a
1	60	90	157.32	10.5	11.1	7.98	13.98(2.35)a
1	70	30	201.67	10.5	11.2	0.73	7.76(7.58)c
1	70	60	184.51	10.4	10.9	5.92	11.01(2.20)c
1	70	90	217.43	10.4	10.9	1.81	5.83(1.81)d

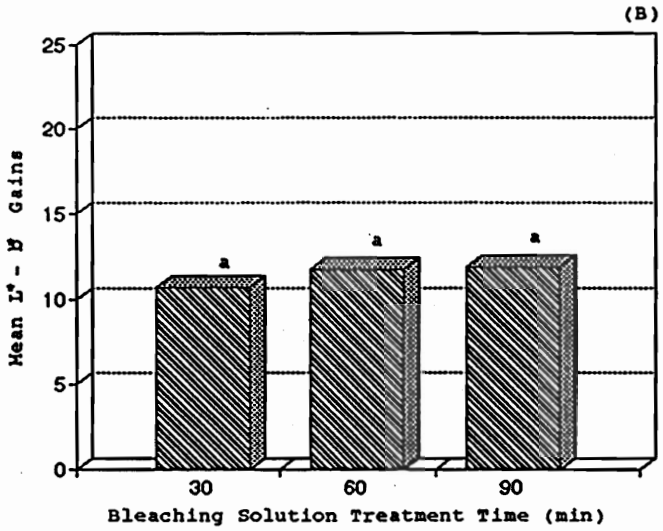
a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 4. Effects of temperature and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 1 % peroxide concentration.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1	50		13.39(3.11)a
1	60		12.86(2.42)a
1	70		8.20(4.86)b
1		30	10.74(5.13)a
1		60	11.77(1.84)a
1		90	11.94(5.10)a

a. Values represent means of 15 specimens





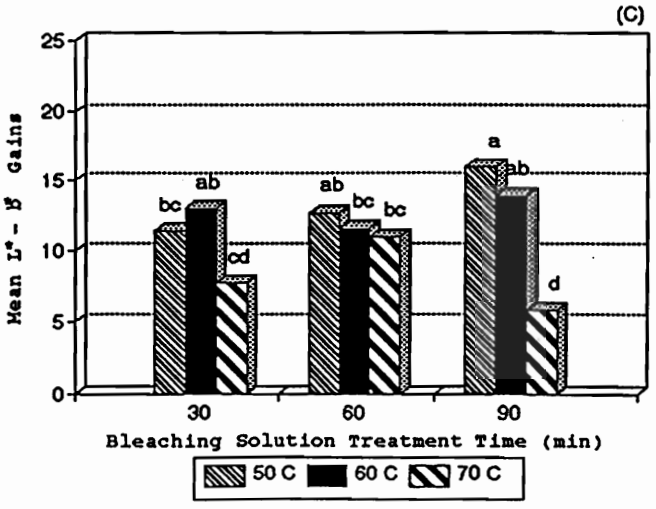


Figure 2. Effects of (A) temperature, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 1 % peroxide concentration. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 5. Effects of temperature and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 2 % peroxide concentration.[a]

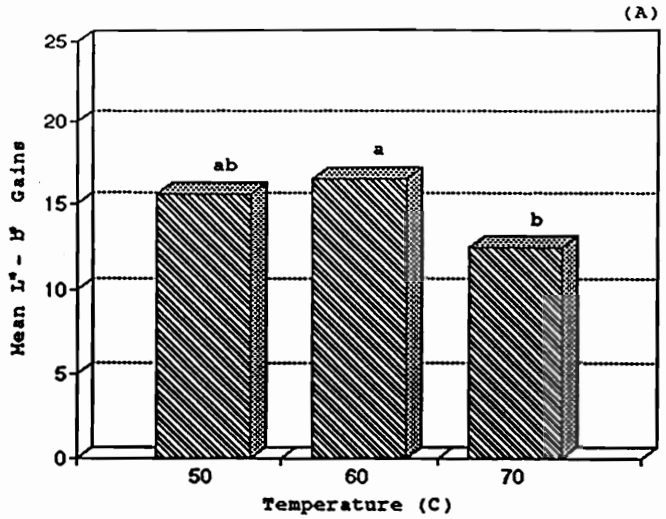
H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
2	50	30	127.92	10.3	10.5	59.08	13.79(5.33)abc[c]
2	50	60	105.21	10.3	10.6	57.68	15.46(2.42)abc
2	50	90	180.35	10.3	10.7	40.43	17.69(7.54)ab
2	60	30	149.10	10.3	10.8	17.87	12.77(3.08)abc
2	60	60	127.88	10.3	10.7	23.22	18.32(2.33)a
2	60	90	133.45	10.2	10.8	15.76	18.36(2.88)a
2	70	30	164.83	10.4	11.1	4.19	10.71(1.17)c
2	70	60	155.02	10.4	11.0	2.52	14.62(2.37)abc
2	70	90	198.82	10.3	11.0	1.48	12.99(7.34)bc

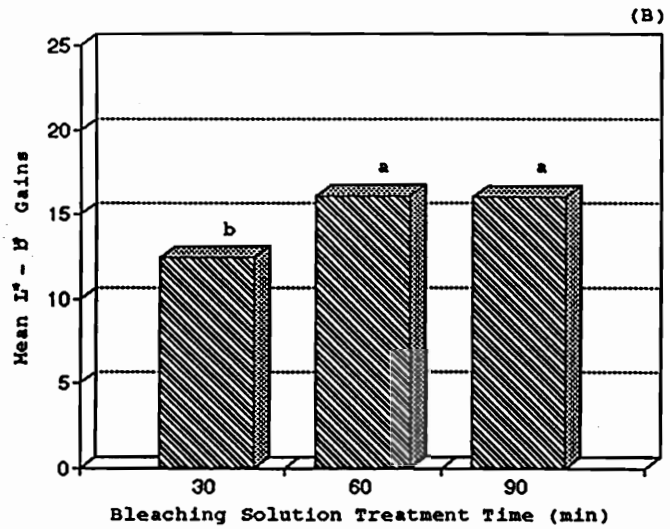
a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 6. Effects of temperature and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 1 % peroxide concentration.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
2	50		15.65(5.36)ab
2	60		16.48(3.75)a
2	70		12.54(4.49)b
2		30	12.42(3.60)b
2		60	16.13(2.74)a
2		90	16.11(6.47)a

a. Values represent means of 15 specimens.





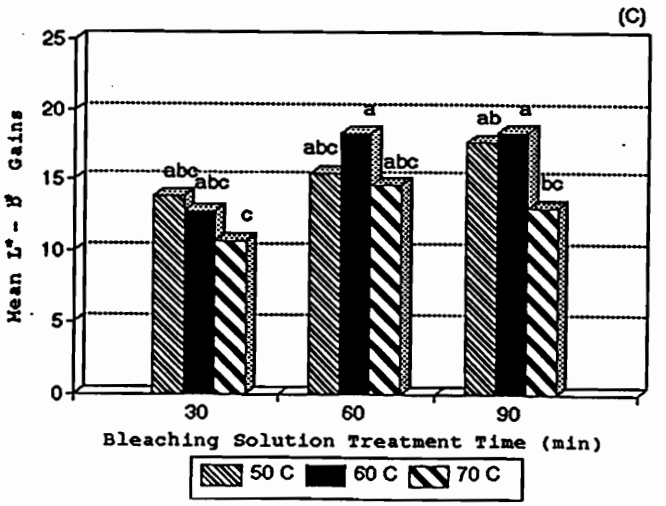


Figure 3. Effects of (A) temperature, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 2 % peroxide concentration. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 7. Effects of temperature and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 3 % peroxide concentration.[a]

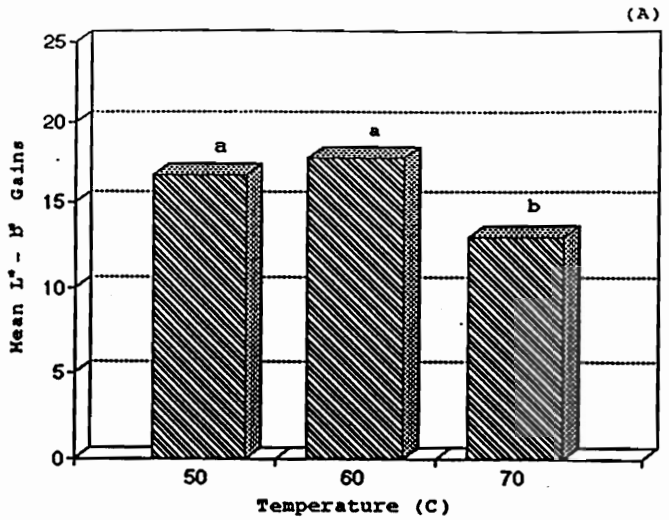
H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
3	50	30	171.29	10.2	10.5	53.92	16.03(4.07)bc[c]
3	50	60	143.19	10.2	10.6	45.65	15.13(1.59)c
3	50	90	117.39	10.1	10.6	31.07	19.04(2.60)ab
3	60	30	154.47	10.1	10.8	11.41	12.49(2.72)cd
3	60	60	196.37	10.5	10.9	28.39	19.91(1.84)a
3	60	90	154.47	10.1	10.6	17.34	21.02(2.73)a
3	70	30	162.16	10.2	10.8	8.87	14.37(2.49)c
3	70	60	202.00	10.1	10.9	3.13	14.37(2.00)c
3	70	90	262.81	10.3	11.1	1.12	10.26(4.50)d

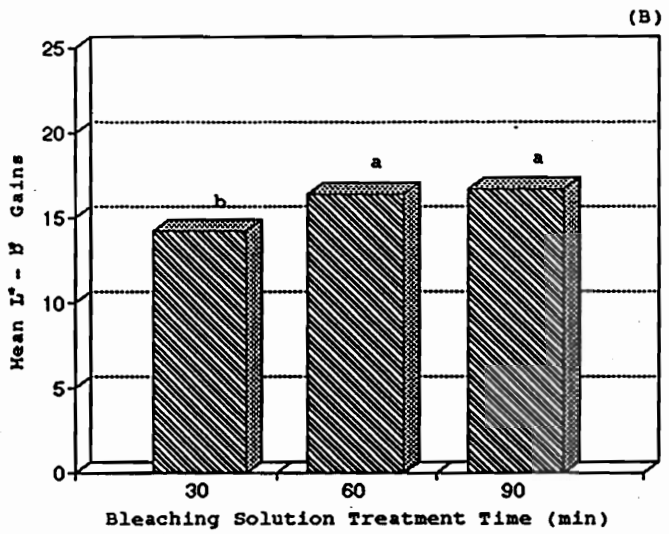
a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 8. Effects of temperature and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 3 % peroxide concentration.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
3	50		16.73(3.22)a
3	60		17.80(4.54)a
3	70		13.00(3.57)b
3		30	14.30(3.30)b
3		60	16.47(3.04)a
3		90	16.77(5.77)a

a. Values represent means of 15 specimens.





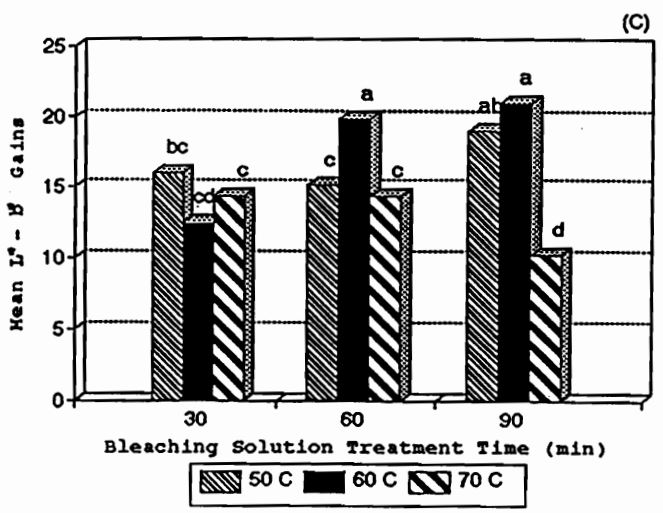


Figure 4. Effects of (A) temperature, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 3 % peroxide concentration. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 9. Effects of peroxide concentration and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 50 °C.[a]

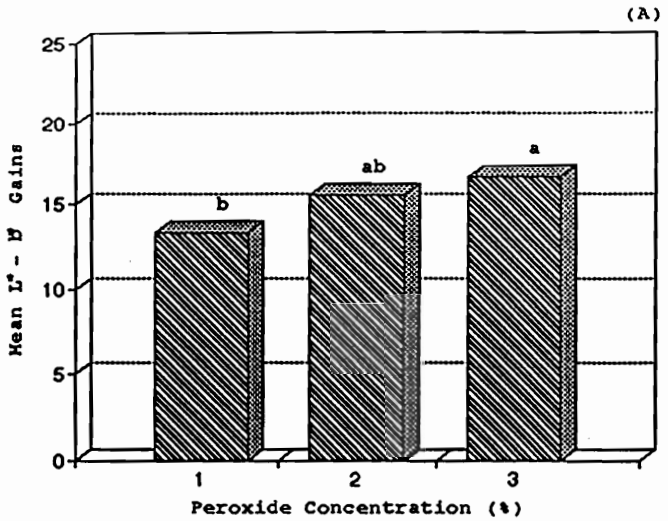
H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	30	199.82	10.6	10.8	46.74	11.45(2.58)c[c]
1	50	60	150.61	10.6	10.8	47.87	12.71(1.86)bc
1	50	90	415.73	10.6	10.9	43.52	16.01(3.14)abc
2	50	30	127.92	10.3	10.5	59.08	13.79(5.33)bc
2	50	60	105.21	10.3	10.6	57.68	15.46(2.42)abc
2	50	90	180.35	10.3	10.7	40.43	17.69(7.54)ab
3	50	30	171.29	10.2	10.5	53.92	16.03(4.07)abc
3	50	60	143.19	10.2	10.6	45.65	15.13(1.59)abc
3	50	90	117.39	10.1	10.6	31.07	19.04(2.60)a

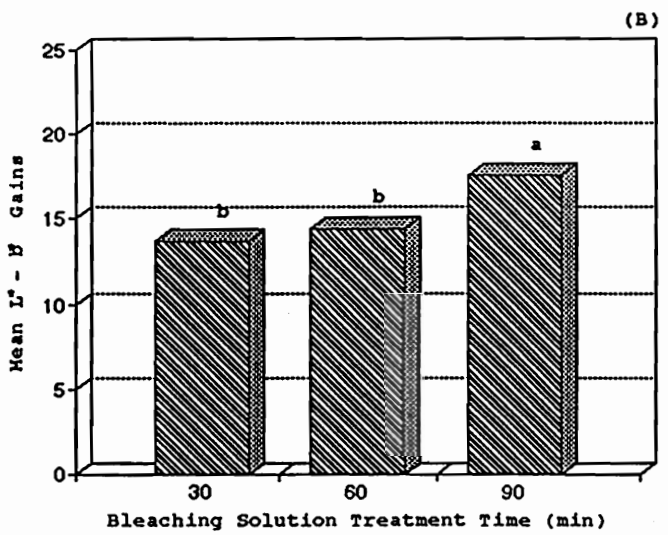
a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 10. Effects of peroxide concentration and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 50 °C.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1	50		13.39(3.11)b
2	50		15.65(5.36)ab
3	50		16.73(3.22)a
	50	30	13.76(4.30)b
	50	60	14.43(2.23)b
	50	90	17.58(4.76)a

a. Values represent means of 15 specimens.





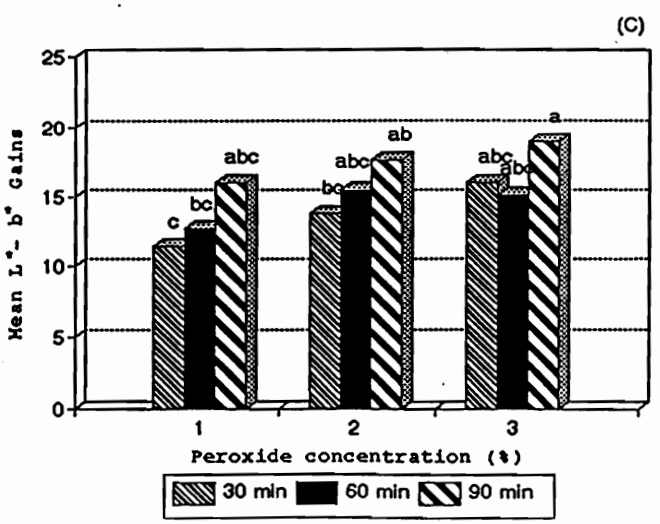


Figure 5. Effects of (A) peroxide concentration, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 50 °C. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 11. Effects of peroxide concentration and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 60 °C.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	60	30	197.20	10.5	10.8	39.04	13.01(3.13)b[c]
1	60	60	184.52	10.6	11.0	9.70	11.59(1.28)b
1	60	90	157.32	10.5	11.1	7.98	13.98(2.35)b
2	60	30	149.10	10.3	10.8	17.87	12.77(3.08)b
2	60	60	127.88	10.3	10.7	23.22	18.32(2.33)a
2	60	90	133.45	10.2	10.8	15.76	18.36(2.88)a
3	60	30	154.47	10.1	10.8	11.41	12.49(2.72)b
3	60	60	196.37	10.5	10.9	28.39	19.91(1.84)a
3	60	90	154.47	10.1	10.6	17.34	21.02(2.73)a

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 12. Effects of peroxide concentration and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 60 °C.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1	60		12.86(2.42)b
2	60		16.48(3.75)a
3	60		17.80(4.54)a
	60	30	12.75(2.77)b
	60	60	16.61(4.11)a
	60	90	17.79(3.89)a

a. Values represent means of 15 specimens.

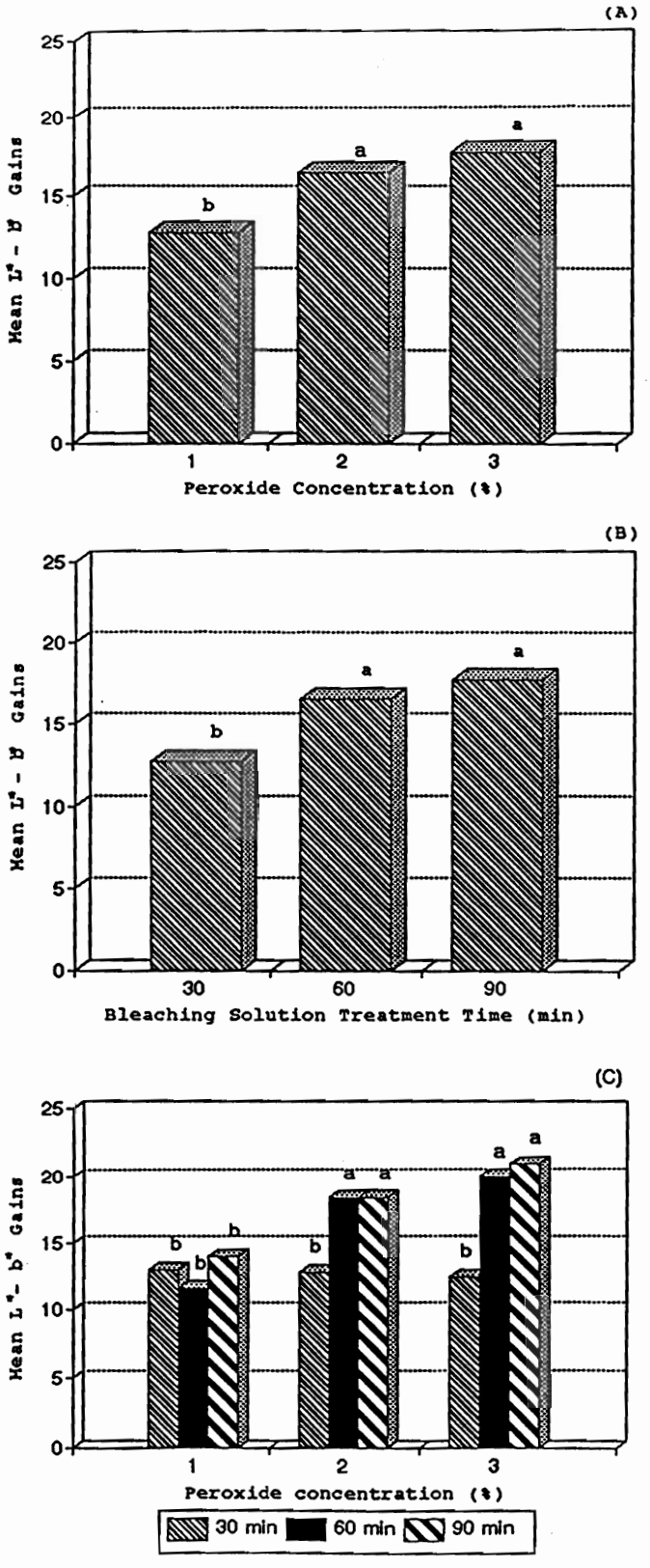


Figure 6. Effects of (A) peroxide concentration, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 60 °C. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 13. Effects of peroxide concentration and bleaching solution treatment time on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) at 70 °C.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	70	30	201.67	10.5	11.2	0.73	7.76(7.58)bc[c]
1	70	60	184.51	10.4	10.9	5.92	11.01(2.20)abc
1	70	90	217.43	10.4	10.9	1.81	5.83(1.81)c
2	70	30	164.83	10.4	11.1	4.19	10.71(1.17)abc
2	70	60	155.02	10.4	11.0	2.52	14.62(2.37)a
2	70	90	198.82	10.3	11.0	1.48	12.99(7.34)ab
3	70	30	162.16	10.2	10.8	8.87	14.37(2.49)a
3	70	60	202.00	10.1	10.9	3.13	14.37(2.00)a
3	70	90	262.81	10.3	11.1	1.12	10.26(4.50)abc

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 14. Effects of peroxide concentration and bleaching solution treatment time on mean L^*-b^* (CIELAB) gain (whiteness) at 70 °C.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1	70		8.20(4.86)b
2	70		12.54(4.49)a
3	70		13.00(3.57)a
	70	30	10.95(5.14)ab
	70	60	13.33(2.66)a
	70	90	9.46(5.47)b

a. Values represent means of 15 specimens.

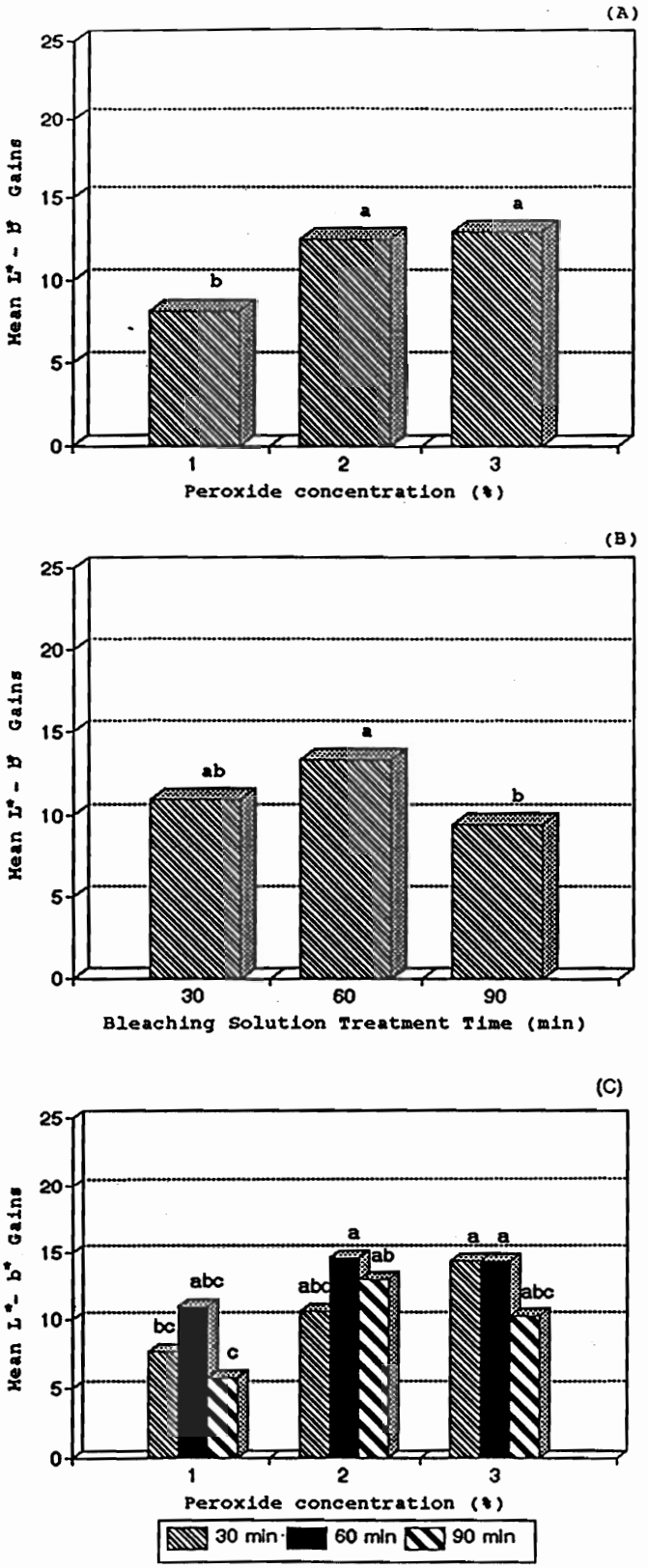


Figure 7. Effects of (A) peroxide concentration, (B) bleaching solution treatment time or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) at 70 °C. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 15. Effects of peroxide concentration and temperature on bleaching solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) for 30 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	30	199.82	10.6	10.8	46.74	11.45(2.58)abc[c]
1	60	30	197.20	10.5	10.8	39.04	13.01(3.13)ab
1	70	30	201.67	10.5	11.2	0.73	7.76(7.58)c
2	50	30	127.92	10.3	10.5	59.08	13.79(5.33)ab
2	60	30	149.10	10.3	10.8	17.87	12.77(3.08)abc
2	70	30	164.83	10.4	11.1	4.19	10.71(1.17)bc
3	50	30	171.29	10.2	10.5	53.92	16.03(4.07)a
3	60	30	154.47	10.1	10.8	11.41	12.49(2.72)abc
3	70	30	162.16	10.2	10.8	8.87	14.37(2.49)ab

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 16. Effects of peroxide concentration and temperature on mean L^*-b^* (CIELAB) gain (whiteness) for 30 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1		30	10.74(5.13)b
2		30	12.42(3.60)ab
3		30	14.30(3.30)a
	50	30	13.76(4.30)a
	60	30	12.75(2.77)a
	70	30	10.95(5.14)a

a. Values represent means of 15 specimens.

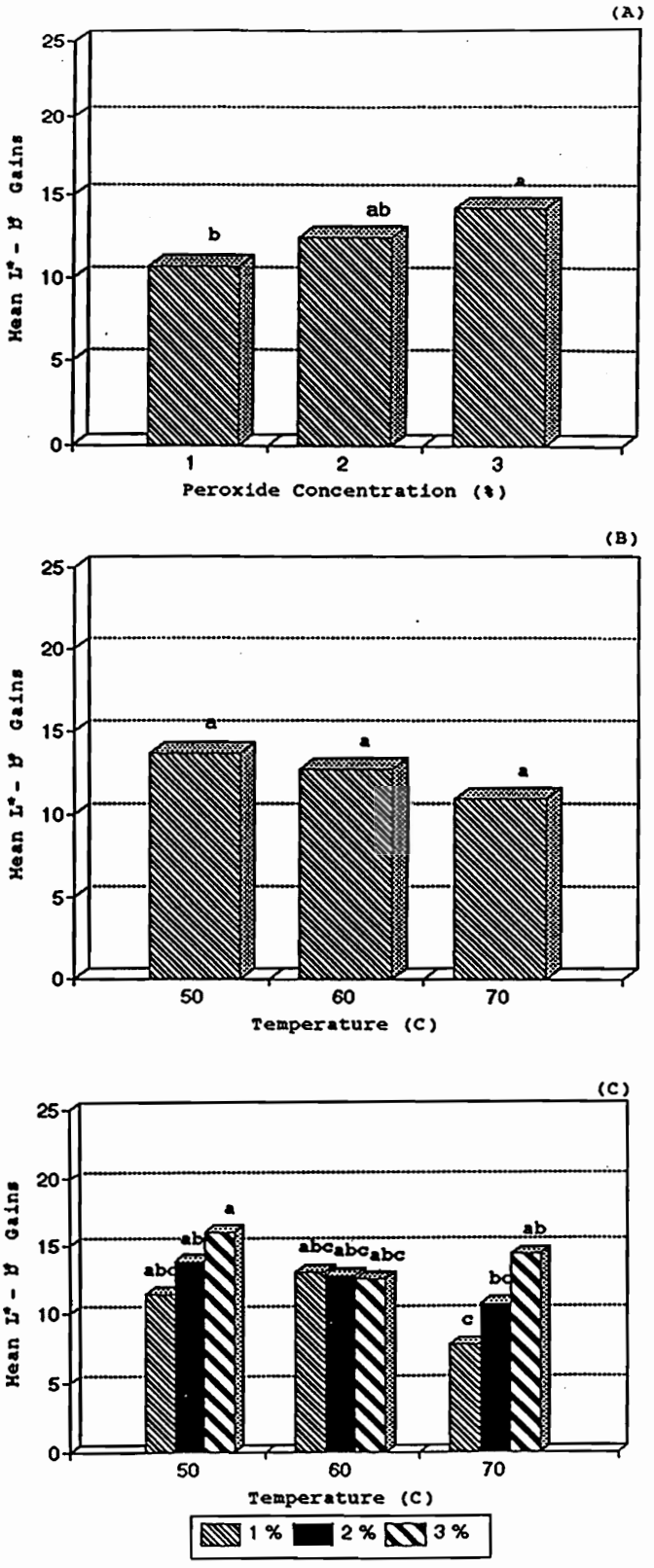


Figure 8. Effects of (A) peroxide concentration, (B) temperature or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) for 30 minute treatment. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 17. Effects of peroxide concentration and temperature on bleaching solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) for 60 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	60	150.61	10.6	10.8	47.87	12.71(1.86)cd[c]
1	60	60	184.52	10.6	11.0	9.70	11.59(1.28)d
1	70	60	184.51	10.4	10.9	5.92	11.01(2.20)d
2	50	60	105.21	10.3	10.6	57.68	15.46(2.42)b
2	60	60	127.88	10.3	10.7	23.22	18.32(2.33)a
2	70	60	155.02	10.4	11.0	2.52	14.62(2.37)bc
3	50	60	143.19	10.2	10.6	45.65	15.13(1.59)bc
3	60	60	196.37	10.5	10.9	28.39	19.91(1.84)a
3	70	60	202.00	10.1	10.9	3.13	14.37(2.00)bc

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 18. Effects of peroxide concentration and temperature on mean L^*-b^* (CIELAB) gain (whiteness) for 60 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1		60	11.77(1.84)b
2		60	16.13(2.74)a
3		60	16.47(3.04)a
	50	60	14.43(2.23)b
	60	60	16.61(4.11)a
	70	60	13.33(2.66)b

a. Values represent means of 15 specimens.

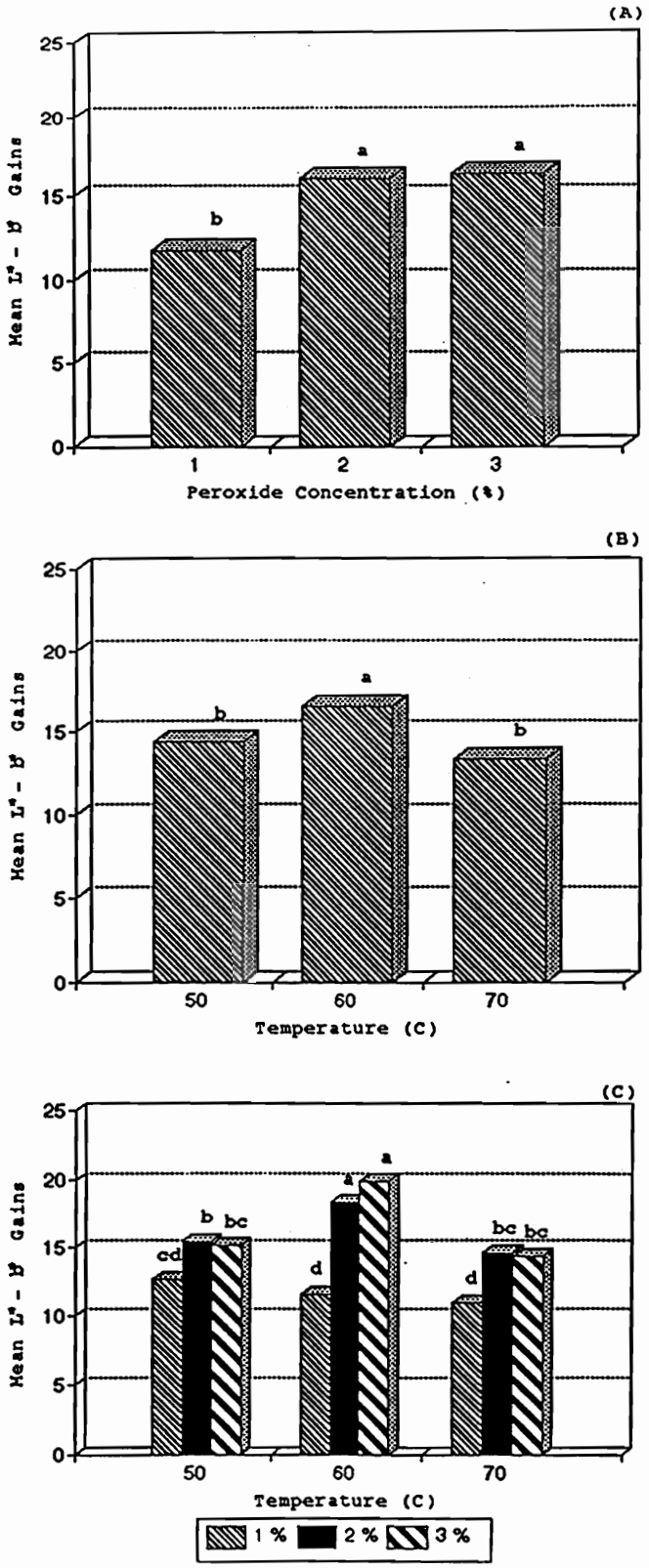


Figure 9. Effects of (A) peroxide concentration, (B) temperature or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) for 60 minute treatment. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

Table 19. Effects of peroxide concentration and temperature on bleaching solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness) for 90 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
1	50	90	415.73	10.6	10.9	43.52	16.01(3.14)abc[c]
1	60	90	157.32	10.5	11.1	7.98	13.98(2.35)bcd
1	70	90	217.43	10.4	10.9	1.81	5.83(1.81)e
2	50	90	180.35	10.3	10.7	40.43	17.69(7.54)abc
2	60	90	133.45	10.2	10.8	15.76	18.36(2.88)ab
2	70	90	198.82	10.3	11.0	1.48	12.99(7.34)cd
3	50	90	117.39	10.1	10.6	31.07	19.04(2.60)ab
3	60	90	154.47	10.1	10.6	17.34	21.02(2.73)a
3	70	90	262.81	10.3	11.1	1.12	10.26(4.50)de

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

Table 20. Effects of peroxide concentration and temperature on mean L^*-b^* (CIELAB) gain (whiteness) for 90 minute treatment.[a]

H_2O_2 (%)	Temperature (°C)	Treatment time (min)	L^*-b^* (CIELAB) gain
1		90	11.94(5.10)b
2		90	16.11(6.47)a
3		90	16.77(5.77)a
	50	90	17.58(4.76)a
	60	90	17.79(3.89)a
	70	90	9.46(5.47)b

a. Values represent means of 15 specimens.

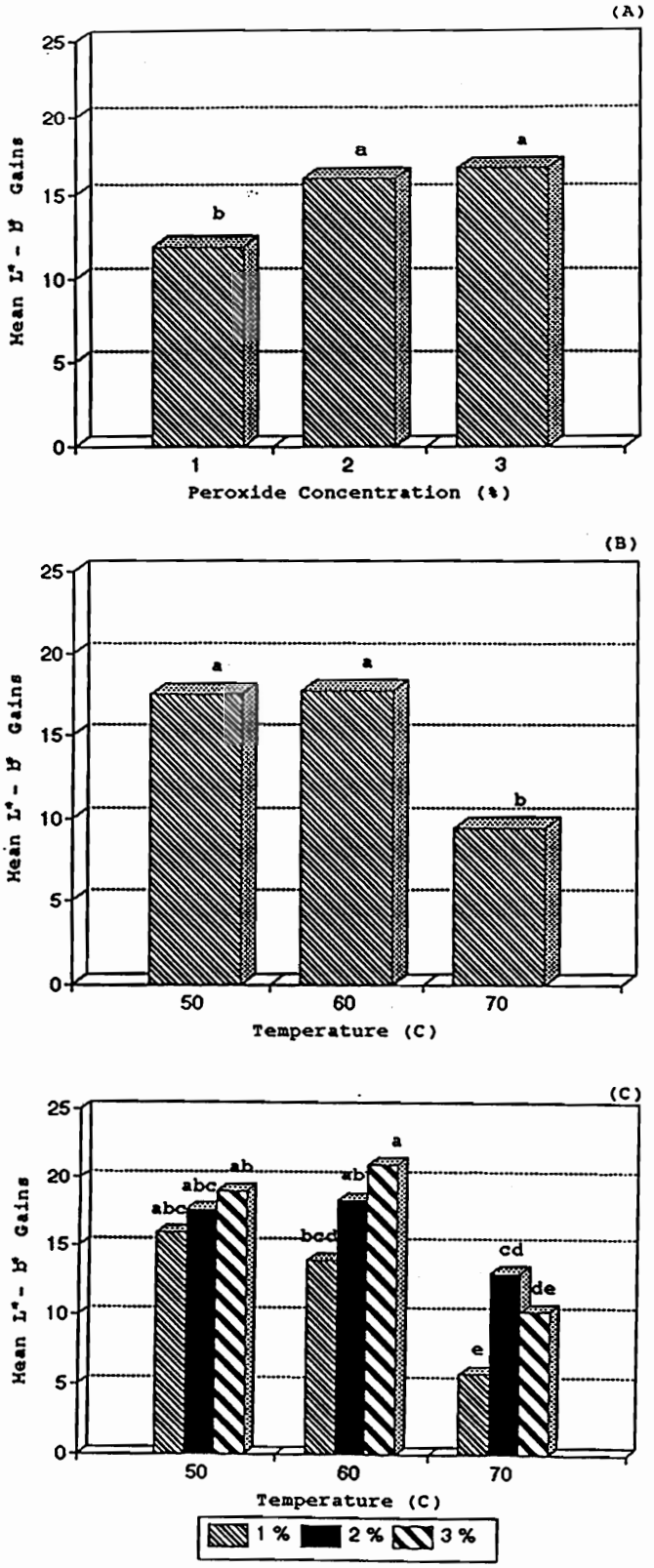


Figure 10. Effects of (A) peroxide concentration, (B) temperature or (C) both on mean L^*-b^* (CIELAB) gain (whiteness) for 90 minute treatment. Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

4.2. Effect of component ratio on bleaching with peroxide

Mean whiteness gains were not affected by changes in the ratio of sodium hydroxide to sodium silicate when pH remained below 11 (Table 21). Mean whiteness gains were highest at a 1:3 ratio; however, except for the 1:6 ratio, specimens treated with solution ratios of 0:12, 1:3, and 1:12 did not significantly differ from one another (Figure 11).

Mean whiteness gains decreased as the ratio of sodium hydroxide increased to raise the pH of bleaching solution (Table 21). Specimens from the 4:3 ratio treatment had significantly lower mean whiteness gains than those from the 2:3 or 3:3 ratios (Figure 11).

In this experiment, pH had the greatest effect on whiteness and any factor which altered pH produced a corresponding change in whiteness. At pHs between 10 and 11, mean whiteness gains were not significantly different from one another. However, mean whiteness gains decreased as pH increased above pH 11 (Table 21).

Hydrogen peroxide is a weak acid. It is very important that the pH of the bleaching solution is maintained between 10.5 and 11. The pH of a peroxide bleaching solution falls as the reaction proceeds and carboxyl groups are formed. Thus, a buffer and a stabilizer such as sodium silicate or sodium hydroxide are used to maintain the pH of bleaching solution. Although the reason is unclear, peroxide decomposition occurred in all experiments, and so pH rose as

treatment time increased. Peroxide decomposition may be caused more by the reaction between peroxide and hydroperoxide anion since pH increased in the bleaching solutions even when specimens were not present (data not shown). Therefore, in the current system, the addition of sodium hydroxide to the bleaching solution may be unnecessary and the amount of sodium silicate may be reduced.

Caution should be used in interpreting solution uptake rates, since the specimens had a higher end-grain to radial or tangential grain than would be found on most lumber. In addition, some solution was absorbed upward from the 6 cm long section, increasing total solution uptake. Solution uptake was highest when wood specimens were treated with 1 % peroxide solution at 50 °C for 90 minutes (Table 2); however one of the five specimens absorbed 3 times the bleaching solution, compared with the other specimens.

The results indicate that bleaching solutions with a sodium hydroxide : sodium silicate ratio of 1 to 3 produce the most significant improvements in mean whiteness gains, when specimens were bleached with 3 % peroxide at 60 °C for 60 minutes.

Table 21. Effects of the ratio of sodium hydroxide to sodium silicate on solution uptake, pH, peroxide consumption and mean L^*-b^* (CIELAB) gain (whiteness).[a]

Ratio of NaOH : Na_2SiO_3	Solution uptake (Kg/m^3)	pH initial	pH final	H_2O_2 residual (%)[b]	L^*-b^* (CIELAB) gain
0 : 12	132.96	10.2	10.7	14.97	20.63(2.71)ab[c]
1 : 3	235.76	10.1	10.9	32.17	21.40(3.27)a
1 : 6	141.86	10.4	11.2	13.28	17.72(1.53)bc
1 : 12	196.37	10.5	10.9	28.39	19.91(1.84)ab
2 : 3	225.45	10.7	12.4	7.30	15.35(0.49)cd
3 : 3	147.50	11.1	12.5	19.09	14.35(2.80)d
4 : 3	222.73	11.4	12.9	6.27	8.94(2.42)e

a. Values represent means of 5 specimens. Values in parentheses represent one standard deviation.
b. As a percent of original peroxide concentration.
c. Mean values with the same letter are not significantly different by Fisher's Least Significant Difference test at $\alpha = 0.05$.

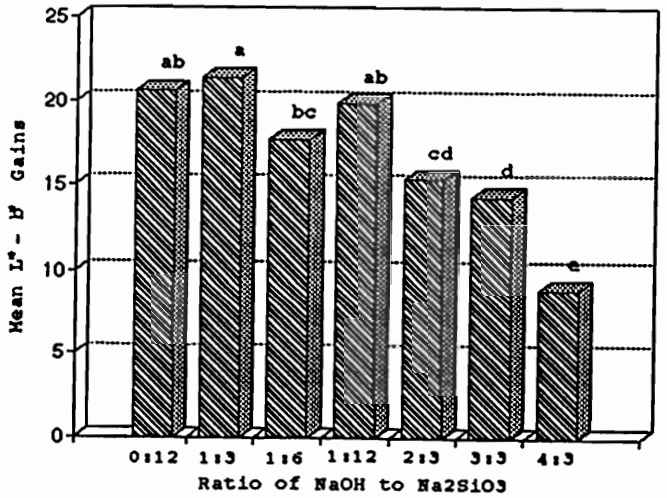


Figure 11. Effects of the ratio of sodium hydroxide to sodium silicate on mean L^*-b^* (CIELAB) gain (whiteness). Bars with the same letter(s) are not significantly different by Fisher's Least Significant Difference Test at $\alpha = 0.05$.

4.3. Economics of Bleaching

While bleaching produced marked improvements in wood appearance, the costs of such treatments must be reasonable. A preliminary economic assessment of the process used the following initial chemical costs:

Hydrogen peroxide (50 %)	: $ 0.88 per kg
Sodium Silicate	: $ 0.48 per kg
Sodium Hydroxide	: $ 0.29 per kg

For the purposes of the analysis, heat input was not included because the volumes of wood in these studies were so small that minor differences in heating rate would dramatically alter results. Finally, capital costs for the treatment facilities were not included, although the use of enclosed dipping facilities with some circulation of solution would not be expected to add markedly to the costs.

The results suggest that treatment with 2 to 3 % peroxide appears to be optimal for bleaching using the current system with 4 % sodium silicate and 0.3 % sodium hydroxide (Figure 1). Bleaching using 2 % peroxide solution would cost $ 0.53/m^2 of board, while increasing peroxide levels to 3 % increases the cost to $ 0.70/m^2 (Table 22). These translate to costs of $ 117.73 and $ 155.22 per thousand board feet for 2 and 3 % peroxide, respectively. As noted earlier, the increases in brightness with an increase in peroxide from 2

to 3 % were not significant. As a result, the increased costs of higher peroxide levels are not justified.

Changes in the ratio of sodium hydroxide to sodium silicate did not affect mean whiteness gains when pH remained below 11 (Table 21). Based upon our results, bleaching using a 3 % peroxide solution at 60 °C for 60 minutes using a sodium hydroxide : sodium silicate ratio of 1:3 produced the highest improvements in mean whiteness at a cost of $ 0.56/m^2 (Table 23). As expected for treatments, costs would vary with chemical composition.

Table 22. Expected chemical costs for bleaching ponderosa pine sapwood at selected temperatures and conditions.

Treatment Temperature (°C)	Treatment Time (min)	H_2O_2 Conc (%)	H_2O_2 Cost ($/m²)	NaOH Conc (%)	NaOH Cost ($/m²)	Na_2SiO_3 Conc (%)	Na_2SiO_3 Cost ($/m²)	Total Chemical Cost ($/m²)
50	30	1	0.17	0.3	0.01	4	0.18	0.36
50	60	1	0.17	0.3	0.01	4	0.18	0.36
50	90	1	0.17	0.3	0.01	4	0.18	0.36
50	30	2	0.34	0.3	0.01	4	0.18	0.53
50	60	2	0.34	0.3	0.01	4	0.18	0.53
50	90	2	0.34	0.3	0.01	4	0.18	0.53
50	30	3	0.51	0.3	0.01	4	0.18	0.70
50	60	3	0.51	0.3	0.01	4	0.18	0.70
50	90	3	0.51	0.3	0.01	4	0.18	0.70
60	30	1	0.17	0.3	0.01	4	0.18	0.36
60	60	1	0.17	0.3	0.01	4	0.18	0.36
60	90	1	0.17	0.3	0.01	4	0.18	0.36
60	30	2	0.34	0.3	0.01	4	0.18	0.53
60	60	2	0.34	0.3	0.01	4	0.18	0.53
60	90	2	0.34	0.3	0.01	4	0.18	0.53
60	30	3	0.51	0.3	0.01	4	0.18	0.70
60	60	3	0.51	0.3	0.01	4	0.18	0.70
60	90	3	0.51	0.3	0.01	4	0.18	0.70
70	30	1	0.17	0.3	0.01	4	0.18	0.36
70	60	1	0.17	0.3	0.01	4	0.18	0.36
70	90	1	0.17	0.3	0.01	4	0.18	0.36
70	30	2	0.34	0.3	0.01	4	0.18	0.53
70	60	2	0.34	0.3	0.01	4	0.18	0.53
70	90	2	0.34	0.3	0.01	4	0.18	0.53
70	30	3	0.51	0.3	0.01	4	0.18	0.70
70	60	3	0.51	0.3	0.01	4	0.18	0.70
70	90	3	0.51	0.3	0.01	4	0.18	0.70

Table 23. Expected chemical costs for bleaching ponderosa pine sapwood at selected ratios of sodium hydroxide to sodium silicate.

Ratio of NaOH : Na_2SiO_3	H_2O_2 Conc (%)	H_2O_2 Cost ($/m²)	NaOH Conc (%)	NaOH Cost ($/m²)	Na_2SiO_3 Conc (%)	Na_2SiO_3 Cost ($/m²)	Total Chemical Cost ($/m²)
0 : 12	3	0.51	0.0	0.00	3.6	0.16	0.67
1 : 3	3	0.51	0.3	0.01	0.9	0.04	0.56
1 : 6	3	0.51	0.3	0.01	1.8	0.08	0.60
1 : 12	3	0.51	0.3	0.01	3.6	0.16	0.68
2 : 3	3	0.51	0.6	0.02	0.9	0.04	0.57
3 : 3	3	0.51	0.9	0.03	0.9	0.04	0.58
4 : 3	3	0.51	1.2	0.04	0.9	0.04	0.59

5.0. CONCLUSIONS

Mean whiteness gains markedly improved as peroxide levels increased from 1 to 2 %, while increasing peroxide concentration to 3 % produced a diminished rate of improvement which would probably not justify the additional cost of chemical. Low peroxide concentrations produced good mean whiteness gains when specimens were treated at low temperatures for long periods. Increasing treatment temperatures from 50 to 60 °C increased mean whiteness gains, while increasing temperature to 70 °C yellowed wood specimens as residual peroxide decreased and the pH of bleaching solution increased.

Increasing treatment time from 30 to 60 minutes markedly improved mean whiteness gains, while gains were slightly improved as treatment time increased to 90 minutes.

Mean whiteness gains were not affected by changes in the ratio of sodium hydroxide to sodium silicate, provided the pH of bleaching solution remained below 11. However, specimens yellowed as the ratio of sodium hydroxide increased as a result of increased pH of bleaching solution.

The results suggest that a 2 to 3 % peroxide solution at 60 °C for 60 to 90 minutes, where the pH remained less than 11, and the residual peroxide were between 15 and 25 % produced the best mean whiteness gains.

Although specimens were treated under optimum conditions, the wood was nearly whitened, and lost its natural color. In

addition, the blue stained zone remained slightly visible. The effects were most noticeable for unevenly stained specimens since the clean area was lightened more than heavily stained zone. The results indicate that evenly stained wood would be most suitable for bleaching. As a result, bleaching is probably most useful for wood which is lightly or heavily stained, but not for material intermediate between these extremes. Bleaching remains, however, a viable option for upgrading the value of discolored pine and merits further trials.

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