The Effect of Silver Nanoparticles on the Black-Stain Resistance of Acrylic Resin for Translucent Wood Coating Application

Gabrielle Boivin,[a,b,*] Anna M. Ritcey,[a] and Véronic Landry [c]

Translucent coatings applied to wood that is used for exterior applications often fail because of photodegradation and colonisation by black-stain fungi. This paper reports the effect of silver nanoparticles on the black-stain resistance of acrylic latex coatings. Acrylic latexes that contained various concentrations of silver nanoparticles were mixed with a commercial acrylic resin. The formulations were then applied to red pine (*Pinus resinosa*) sapwood, which was later evaluated for fungal resistance to *Aureobasidium pullulans*, *Sclerophoma pityophila*, and *Eppicoccum nigrum*. Latexes with silver nanoparticle concentrations as low as 0.03% (total coating formulation weight) were able to limit *S. pityophila* and *E. nigrum* growth, while higher concentrations were needed to limit the growth of *A. pullulans*. The influences of silver nanoparticles on the optical properties of the coating (*i.e*., colour, opacity, and gloss) were evaluated. It was demonstrated that the addition of silver nanoparticles to the formulation does not compromise the development of a translucent coating.

Keywords: Black-stain fungi resistance; Miniemulsion polymerisation; Silver nanoparticles; Wood coating

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INTRODUCTION

Maintaining the natural appearance of wood in outdoor applications has been a difficult problem since wood was first used, and the problem still remains today. This problem is gaining in importance with the increasing exterior use of wood in non-residential and multifamily construction. The classic grey colour of weathered wood is caused by the combined effects of sunlight bleaching and black-stain fungi growth (otherwise known as mildew or blue-stain in service). Translucent coatings containing UV absorbers, hindered amine light stabilisers (HALS), and fungicides can substantially slow the rate of the weathering process and maintain the natural wood colour for a longer time period. However, few coatings can extend the refinishing treatment intervals beyond two or three years. Furthermore, the control of black-stain fungi is becoming more difficult to achieve with the shift to low-VOC waterborne coating formulations, which require higher quantities of biocides/fungicides (Künniger *et al*. 2014). Additionally, there are fewer biocides available to add to such coating formulations because of the increasingly stringent biocide/fungicide regulatory requirements.

One cause of the need for frequent maintenance of wood coatings is the premature photodegradation of the coating components. The additives currently used in clear coatings

to protect wood against ultraviolet (UV) radiation and black-stain are organic and are often vulnerable to photodegradation, volatilisation, and leaching, which reduce the coating's long-term efficacy. As additive efficiency decreases, coatings will decompose, creating micro-cracks or small perforations that facilitate fungal colonisation (Evans *et al*. 2015). Moreover, the transparency of clear coatings makes it easier for the UV rays to reach the underlying wood, which leads to faster wood degradation. Degraded wood is a carbon source that is essential for fungal growth. The consequences of fungal growth include wood discolouration and loss of coating adhesion at the wood-coating interface. All of these factors result in the loss of the aesthetic properties of wood. Over the last decade, metal oxide nanoparticles have been shown to be effective UV absorbers (Fajzulin *et al*. 2015). However, the literature reports that the performances of coatings containing metal oxide nanoparticles are correlated with their homogeneous dispersion throughout the coating (Cristea *et al*. 2010; Weichelt *et al*. 2010; Auclair *et al*. 2011). Incorporation of nanoparticles *via* miniemulsion polymerisation could be a method to improve nanoparticle dispersion in the protective coating film.

The antibacterial properties of silver and silver salts have been recognised for a long time (Russell and Hugo 1994; Rai *et al*. 2009). There is also a renewed interest in silver and silver-containing materials that has been driven by the medical field, where more and more bacteria are showing resistance to common antibiotics. Several studies have been conducted on the antifungal activities of silver nanoparticles. These studies demonstrated that silver nanoparticles are efficient against *Cladosporium cladosporoides* and *Aspergillus niger* (Pulit *et al*. 2013), as well as *Trametes versicolor* (white-rot fungi) (Berrocal *et al*. 2015). When compared with organic biocides/fungicides, silver has numerous advantages, such as good stability at high temperature, resistance to degradation, no odor, and low volatility. Based on these advantages, silver nanoparticles are considered a good alternative to conventional organic biocides (Kaiser *et al*. 2013).

In the work reported here, miniemulsion polymerisation was used to encapsulate biocides (silver nanoparticles) in an attempt to decrease their leaching and to improve their dispersion throughout the coating. Miniemulsion polymerisation was selected over the traditional emulsion polymerisation technique to improve nanoparticle dispersion in the polymer matrix through particle encapsulation. Controlling the release and leaching of fungicides can extend the life of the coatings by ensuring that a minimum biocide concentration is always present at the coating's surface (Koleske *et al.* 2013). This polymerisation technique has already been used to encapsulate organic pigments (Steiert and Landfester 2007) and inorganic nanoparticles (Erdem *et al*. 2000; Costoyas *et al*. 2009). It was hypothesized that formulations containing silver nanoparticles prepared by miniemulsion polymerisation could protect a translucent coating from degradation by black-stain fungi.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BuA), and acrylic acid (AA) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were purified on a basic aluminum oxide column prior to their use to remove trace amounts of polymerisation inhibitors. Silver nitrate ($AgNO_3$), oleylamine, hexadecane (HD), sodium dodecylsulfate (SDS, 99%), and potassium persulfate (KPS, 99%) were also obtained from Sigma-

Aldrich; these reagents were used as received. Polyphase 678 (containing 5% iodopropynyl butylcarbamate (IPBC)) (Troy Chemical Corp.; Newark, NJ), Wocosen Technical (propiconazole) (Janssen PMP; Beerse, Belgium), AMP-95 (Angus Chemical Co.; Buffalo Grove, IL), and acrylic resin Neocryl XK-90 (DSM Coating Resins; Zwolle, The Netherlands) were all used as received.

Silver nanoparticle synthesis

Colloidally stabilized silver nanoparticles were synthesized based on the work of Chen *et al*. (2007). This synthesis generated nanoparticles that were 10 to 15 nm in size, which were then stabilised with oleylamine. In a three-neck round-bottom flask, 0.455 g of silver nitrate ($AgNO_3$) was dissolved in 3 mL of oleylamine and 60 mL of paraffin. The solution was mechanically stirred, under nitrogen, for 20 min at room temperature. The three-neck round-bottom flask was then placed in a temperature-controlled paraffin bath and heated under reflux. The temperature was gradually increased at a rate of 4 °C/min until a temperature of 180 °C was reached. This temperature was maintained for 2 h to reduce the silver present in the medium. The temperature was then decreased to 150 °C and maintained for 6 h. When the solution had returned to room temperature, 20 mL of chloroform and 60 mL of acetone were added. The solution was then centrifuged at 15,000 rpm for 15 min. After centrifugation, the supernatant was removed, and the silver nanoparticles were redispersed in less than 5 mL of chloroform. Approximately 40 mL of acetone was then added, and the suspension was mixed and centrifuged at a speed of 5000 rpm for 5 min. This acetone washing step was repeated twice.

Latex synthesis and formulation preparation

The previously synthesized silver nanoparticles were incorporated into latex polymer particles using miniemulsion polymerisation. First, monomers and 1% (with respect to monomer mass) of the hydrophobic agent (*i.e*., hexadecane) were mixed together in a beaker. In a second beaker, 30 mM of surfactant (SDS) was dissolved in ultrapure water (Nanopure® water system (Thermo Fisher Scientific; Waltham, MA)). The quantities of each component were calculated to obtain a total volume of 40 mL and 15% solid content. The organic phase was added to the aqueous phase, and the resulting solution was stirred mechanically for 1 h. The mixture was sonicated using an ultrasonic probe (Model 500 Dismembrator; Thermo Fisher Scientific; Waltham, MA) for 6 min at an amplitude of 80%, which pulsed on for 1 s and pulsed off for 1 s. In parallel, 2% (with respect to monomer weight) of initiator (KPS) was dissolved in 8 mL of ultrapure water. The sonicated miniemulsion and the KPS solution were then mixed in a three-neck round-bottom flask and purged under nitrogen for 20 min. The system was heated under reflux for 3 h at 70 °C.

The same synthesis procedure was used to prepare latexes with silver nanoparticles. The only difference was that predetermined amounts of silver nanoparticles were added to the organic phase before sonication. Latexes with 0.2%, 0.4%, and 0.6% (with respect to monomer weight) of silver nanoparticles were prepared. As the solid content of the synthesized latexes was quite low compared with commercially available resins, the synthesized latexes were mixed in a 1:1 mass ratio with a commercial acrylic resin (Neocryl XK-90). As a reference, latex was also prepared with 1.4 g of Polyphase 678 and 0.54 g of Wocosen Technical. Previous work from Stirling *et al*. (2011) reported that a combination of IPBC and propiconazole was able to control the growth of *A. pullulans* and *E. nigrum*. The compositions of all prepared latex formulations are shown in Table 1.

Table 1. Formulation Identification and Their Fungicide Concentrations

Formulation	Description	Fungicide concentration [%]*	Fungicide concentration [% final solid content]
A	Latex without fungicide	-	-
B**	Latex with IPBC and propiconazole	0.1 IPBC + 1 propiconazole	0.4 IPBC + 3 propiconazole
C	Latex with Ag NPs	0.03	0.1
D	Latex with Ag NPs	0.06	0.2
E	Latex with Ag NPs	0.09	0.3

*Of total formulation weight
**Only Formulation B contains IPBC and propiconazole

Sample preparation

Red pine (*Pinus resinosa*) sapwood was cut into 57 mm × 57 mm × 6 mm samples. The samples were lightly sanded with 80-grit sandpaper and conditioned for 2 weeks at 20 °C and 65% relative humidity (RH). Two coats of 101-µm (4 mils) thickness for each coating formulation (A to E) were applied with a foam brush on 24 samples, while the edges and the back were sealed with an epoxy (Intergard 740, Akzo Nobel). The drying time between the application of the second coat was 24 hours. Wet film thickness was measured using a wet film thickness gauge and the prepared samples were allowed to dry for two weeks at ambient temperature.

Characterisation Methods

Black-stain fungi resistance tests

Testing procedures were derived in part from the ASTM D5590 standard (ASTM 2010) and the Nordtest NT Build 338 standard (Nordtest 1988) as described by Stirling *et al*. (2011). Wood samples were first sterilised by ion beam irradiation with two passes at 17 kGy (Iotron Industries; Port Coquitlam, BC, Canada). *Aureobasidium pullulans*, *Epicoccum nigrum*, and *Sclerophoma pityophila* were selected from FPInnovations' culture collection and grown on plates of 1% malt extract agar. Individual fungi were inoculated on six replicates. After two weeks of incubation, 5 mL of a sterile 0.01% surfactant solution (Tween® 80) was aseptically transferred onto each plate, and the fungi were gently removed from the agar surface with a sterile blunt scalpel. The solution was made up to 200 mL and blended with three short pulses in a Waring Commercial Blender (Waring; Torrington, CT). The inoculum was then filtered through prewashed sterile glass wool to remove large particles that could plug the air brush. The inoculum solution was checked for the presence of spores and mycelia under a microscope at 200X magnification. The inoculum was added to an IWATA Eclipse HP-BCS airbrush (ANEST Iwata-Medea, Inc.; Portland, OR), and each sample was sprayed on the top surface with approximately 0.5 mL of the prepared solution. Inoculated samples were added to sterile pre-wetted chambers.

Samples were incubated at 22.5 °C for four weeks. After the initial two weeks, the samples were lightly sprayed with sterile water weekly. Samples were inspected for black stain fungi growth following two and four weeks of incubation. Samples were rated for black stain growth on a scale of 0 to 5, where 0 represents no growth and 5 represents extensive and intense fungal growth. Table 2 describes the rating system, which considers both the extent and intensity of fungal growth.

Table 2. Rating as a Function of Degree of Fungal Growth (Adapted from ASTM D5590)

Rating	Degree of fungal growth
0	No visible growth
1	Black stain covering up to 10% of surfaces providing growth is not as intense or coloured as to obscure the sample colour over more than 5% of surfaces.
2	Black stain covering between 10% and 30% of surfaces providing growth is not as intense or coloured as to obscure the sample colour on more than 10% of surfaces.
3	Black stain covering between 30% and 70% of surfaces providing growth is not as intense or coloured as to obscure the sample colour on more than 30% of surfaces.
4	Black stain on greater than 70% of surfaces providing growth is not as intense or coloured as to obscure the sample colour over more than 70% of surfaces.
5	Black stain on 100% of surfaces or with less than 100% coverage and with intense or coloured growth obscuring greater than 70% of the sample colour.

Optical properties (colour, opacity, and gloss)

The effect of silver nanoparticles on optical properties (*i.e.*, colour, opacity and gloss) was evaluated. To perform the optical property measurements, a uniform film of each formulation was applied on a Leneta black/white contrast chart. Formulations were applied on contrast charts to minimise the variation resulting from the wood substrate. Films of a wet thickness of 101 µm were applied with a square frame applicator (BYK-Gardner; Columbia, MD). The colour variation was evaluated using a SP60 Spectrophotometer (X-Rite; Grand Rapids, MI), which was quantified by the CIE $L^*a^*b^*$ colour space coordinates. Total colour change (ΔE^*_{ab}) was calculated for each formulation by Eq. 1,

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (1)$$

where L^*, a^*, and b^* are the CIE colour coordinates for black (0) to white (100), red (-) to green (+), and blue (-) to yellow (+), respectively. The colour changes were compared for the formulation without nanoparticles and the formulation containing silver nanoparticles at various concentrations. Percent opacity was also measured using a SP60 Spectrophotometer from X-Rite. The opacity (%) is given by the ratio of the reflectance of a film on a black surface to that of an identical film on a white substrate multiplied by 100. No differences between the reflectance on the black surface *versus* the white surface will give an opacity percentage of 100. The gloss was measured with a MG268-M2 glossmeter (KSJ Photoelectrical Instruments Co., Ltd.; Quanzhou, Fujian Province, China) at 20°.

Furthermore, to better represent the end-use, the formulations were also applied, with a foam brush (101 µm), onto red pine samples. The delta values (ΔL^*, Δa^*, and Δb^*) and total colour change (ΔE^*_{ab}) were compared for the uncoated samples and the coated samples. The colour change (ΔL^*, Δa^*, Δb^*, and ΔE^*_{ab}) was also compared for the coated samples with the formulation without nanoparticles and coated samples with formulations containing silver nanoparticles.

RESULTS AND DISCUSSION

Black-stain Fungi Resistance Tests

The results obtained after 2, 4, 6, and 8 weeks are shown in Figs. 1 to 3 for samples colonised by *S. pityophila*, *E. nigrum*, and *A. pullulans*, respectively.

After 8 weeks, Formulations B, C, D, and E were able to control *S. pityophila* growth, regardless of the type and amount of biocide used. *S. pityophila* growth was only present on samples coated with Formulation A (formulation without nanoparticles). In Fig. 3, it is shown that Formulations B, C, and D were efficient against *E. nigrum*. However, fungal growth was observed on some of the samples coated with Formulation E. This observation was surprising, considering that this formulation had the highest concentration of nanoparticles.

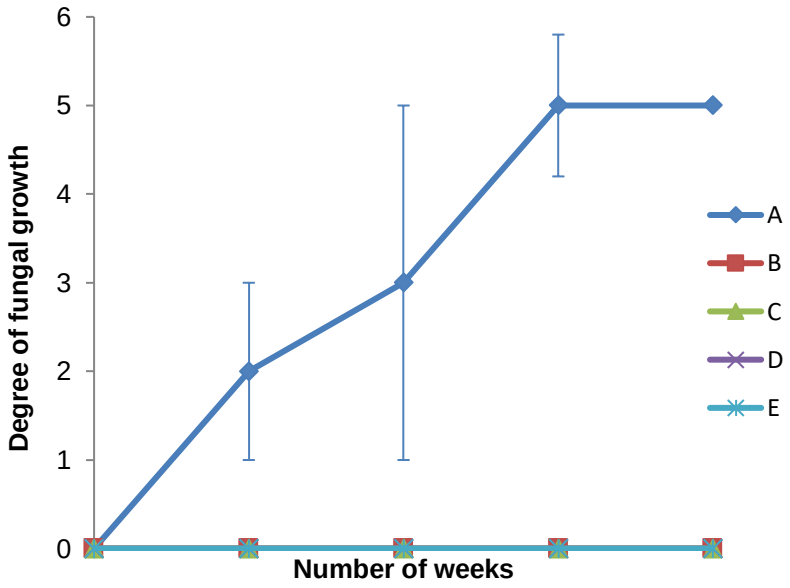

Fig. 1. Degree of fungal growth for formulations A, B, C, D, and E (as described in Table 1) to inoculated with *S. pityophila* after 2, 4, 6, and 8 weeks (error bars represent the standard deviations)

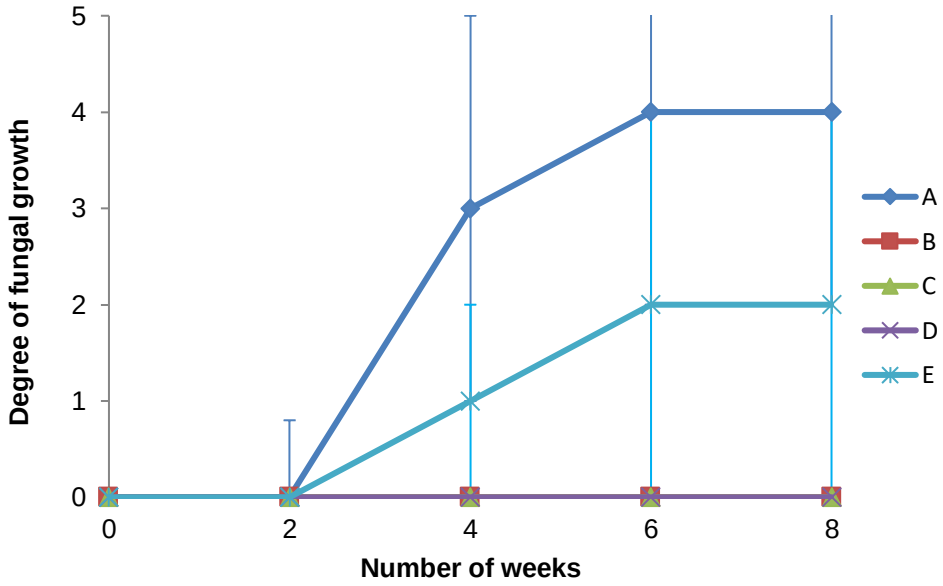

Fig. 2. Degree of fungal growth for formulations A, B, C, D, and E (as described in Table 1) inoculated with *E. nigrum* after 2, 4, 6, and 8 weeks (error bars represent the standard deviations)

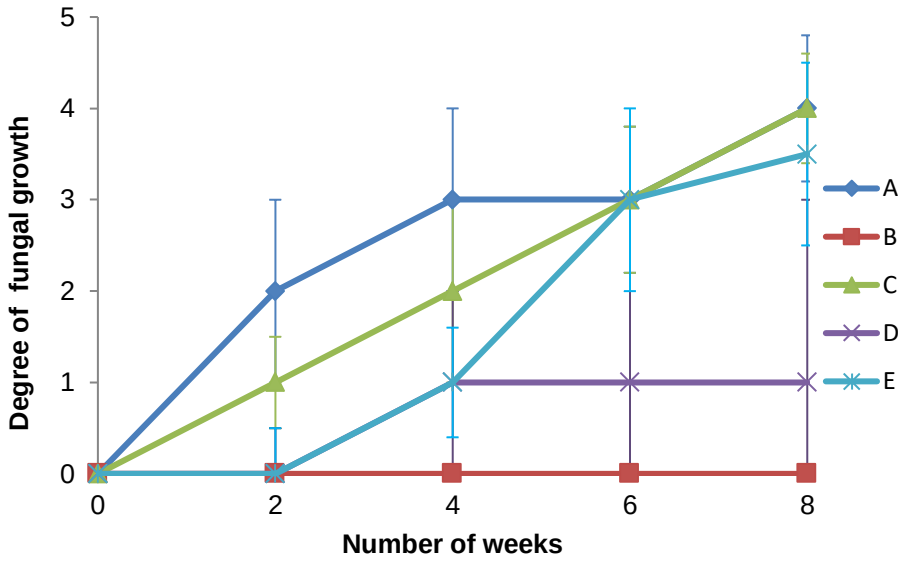

Fig. 3. Degree of fungal growth for formulations A, B, C, D, and E (as described in Table 1) inoculated with *A. pullulans* after 2, 4, 6, and 8 weeks (error bars represent the standard deviations)

A silver nanoparticle concentration below 0.09% was insufficient to control the growth of *A. pullulans* after 8 weeks (Fig. 3). However, Formulation D (0.06% silver nanoparticles) exhibited better antifungal efficiency than Formulation E (0.09% silver nanoparticles). This observation suggests that the silver nanoparticles were poorly dispersed at higher loading levels. For silver nanoparticles to effectively control *A. pullulans* growth, a high concentration of well-dispersed silver nanoparticles is required. Figure 4 shows samples inoculated with *A. pullulans* after 8 weeks.

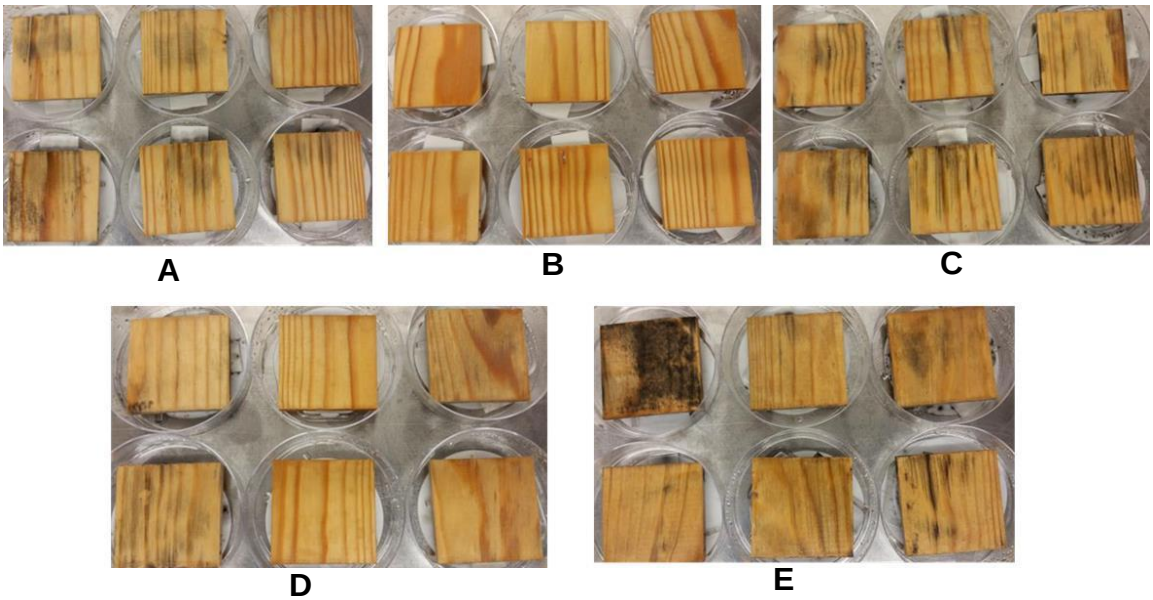

Fig. 4. Samples inoculated with *A. pullulans* after 8 weeks: (A) without silver nanoparticles, (B) with 0.1% IPBC + 1% propiconazole, (C) with 0.03% silver nanoparticles, (D) with 0.06% silver nanoparticles, and (E) with 0.09% silver nanoparticles

Optical Properties

Colour measurements on Leneta contrast charts

Maintaining low colour and gloss change, as well as low opacity, is essential in the development of a translucent coating. Delta values (ΔL^*, Δa^*, and Δb^*) and total colour change (ΔE^*_{ab}) were calculated for Formulations B through E in reference to Formulation A (without silver nanoparticles); all colour measurements for the coating were performed on Leneta charts, which are shown in Figs. 5 through 8.

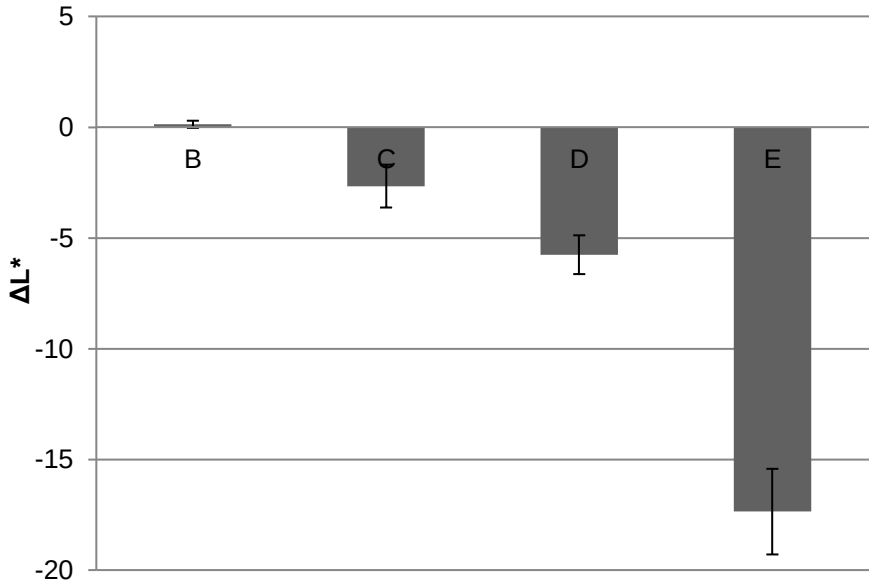

Fig. 5. Δ*L** for Formulations B, C, D, and E when compared with the formulation without silver nanoparticles (A) measured on Leneta contrast charts (error bars represent the standard deviations)

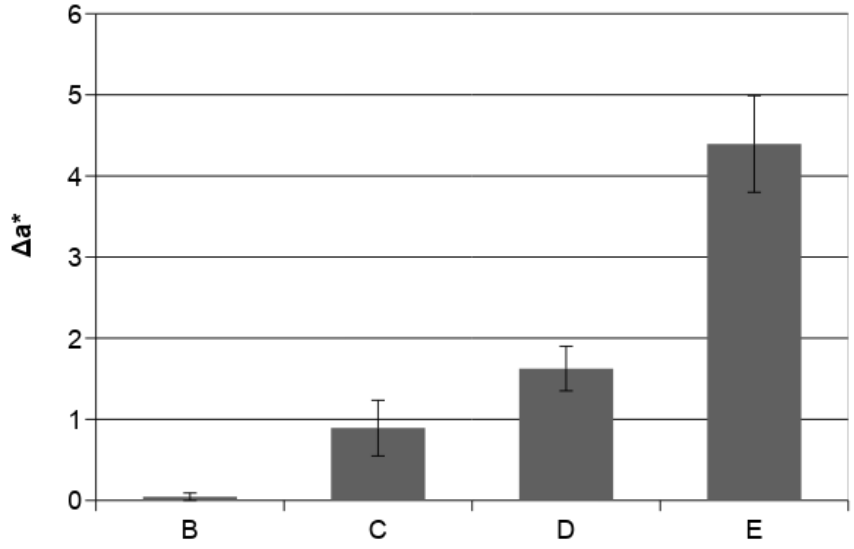

Fig. 6. Δ*a** for Formulations B, C, D, and E when compared with the formulation without silver nanoparticles (A) measured on Leneta contrast charts (error bars represent the standard deviations)

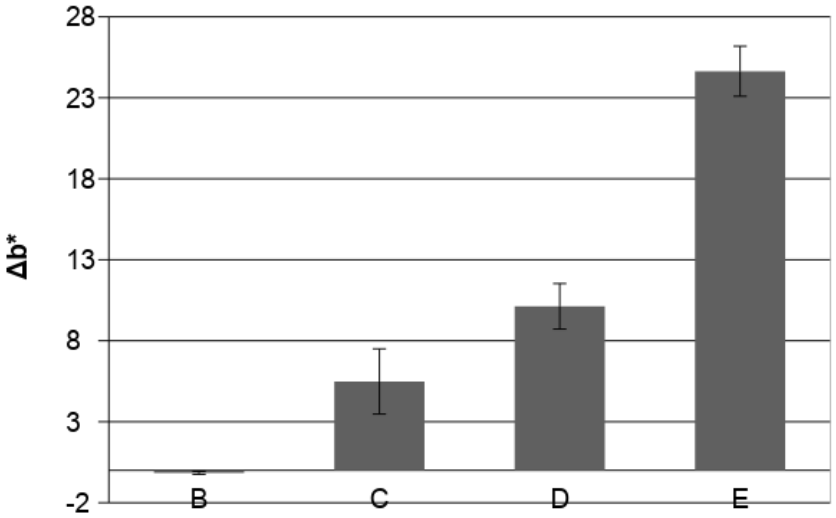

Fig. 7. Δ*b** for Formulations B, C, D, and E when compared with the formulation without silver nanoparticles (A) measured on Leneta contrast charts (error bars represent the standard deviations)

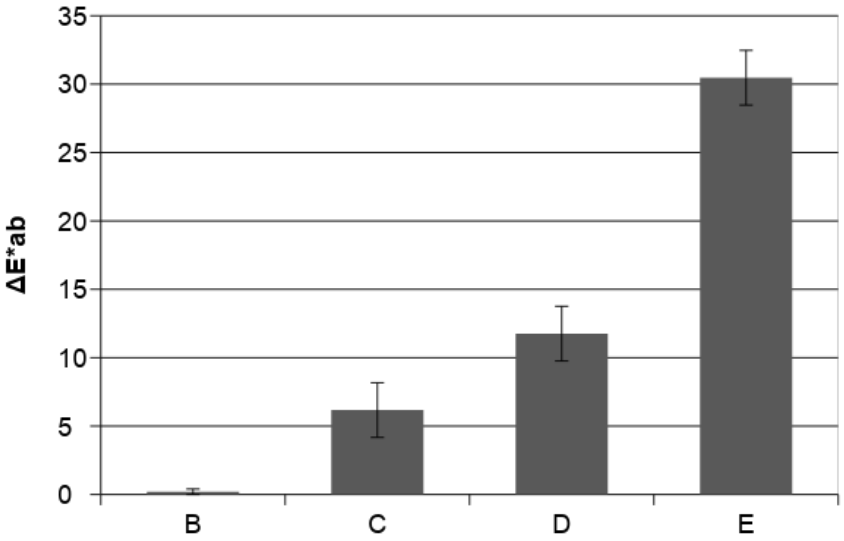

Fig. 8. Total colour change (ΔE^*_{ab}) for Formulations B, C, D, and E when compared with the formulation without silver nanoparticles (A) measured on Leneta contrast charts (error bars represent the standard deviations)

The organic fungicides (IPBC + propiconazole; formulation B) used as the reference did not alter the colour of the film, as the ΔL^*, Δa^*, Δb^*, and ΔE^*_{ab} values were all near zero. However, this trend was not observed for Formulations C, D, and E, containing silver nanoparticles. These formulations exhibited colour changes that increased as the silver nanoparticle concentration increased. Despite the small loadings of silver nanoparticles, the colour change of the film can be appreciable because of the localised surface plasmon resonance (LSPR) effect. Indeed, LSPR can result in unusually strong light scattering and absorption properties. This could explain why silver nanoparticles are extraordinarily efficient at light absorption and scattering, and unlike many dyes and

pigments, why they have a colour that depends upon the size and the shape of the particles (Bhattarai *et al*. 2011).

Figure 9 shows the five formulations applied on Leneta contrast charts. The addition of silver nanoparticles darkened Formulations C, D, and E, as they had ΔL^* values of -3 ± 1, -6 ± 1, and -17 ± 2, respectively. The Δa^* values for Formulations C and D were below 2, whereas for Formulation E, the value was 4 ± 1. Silver nanoparticles considerably affected the Δb^* values; Formulation C had a Δb^* of 5 ± 2, Formulation D had a Δb^* of 10 ± 1, and Formulation E had a Δb^* of 25 ± 2. At only 0.03% silver nanoparticle concentration, formulation C had a ΔE^*_{ab} of 6 ± 2. Formulation D, with twice the concentration of silver nanoparticles (0.06%) as Formulation C, had a ΔE^*_{ab} of 12 ± 2. Formulation E exhibited the highest ΔE^*_{ab}, with a value of 30 ± 2. These are considerable colour changes in comparison with Formulation A when one considers that an unexperienced observer will perceive a difference in colour at a ΔE^*_{ab} value greater than 2 (Mokrzycki and Tatol 2011).

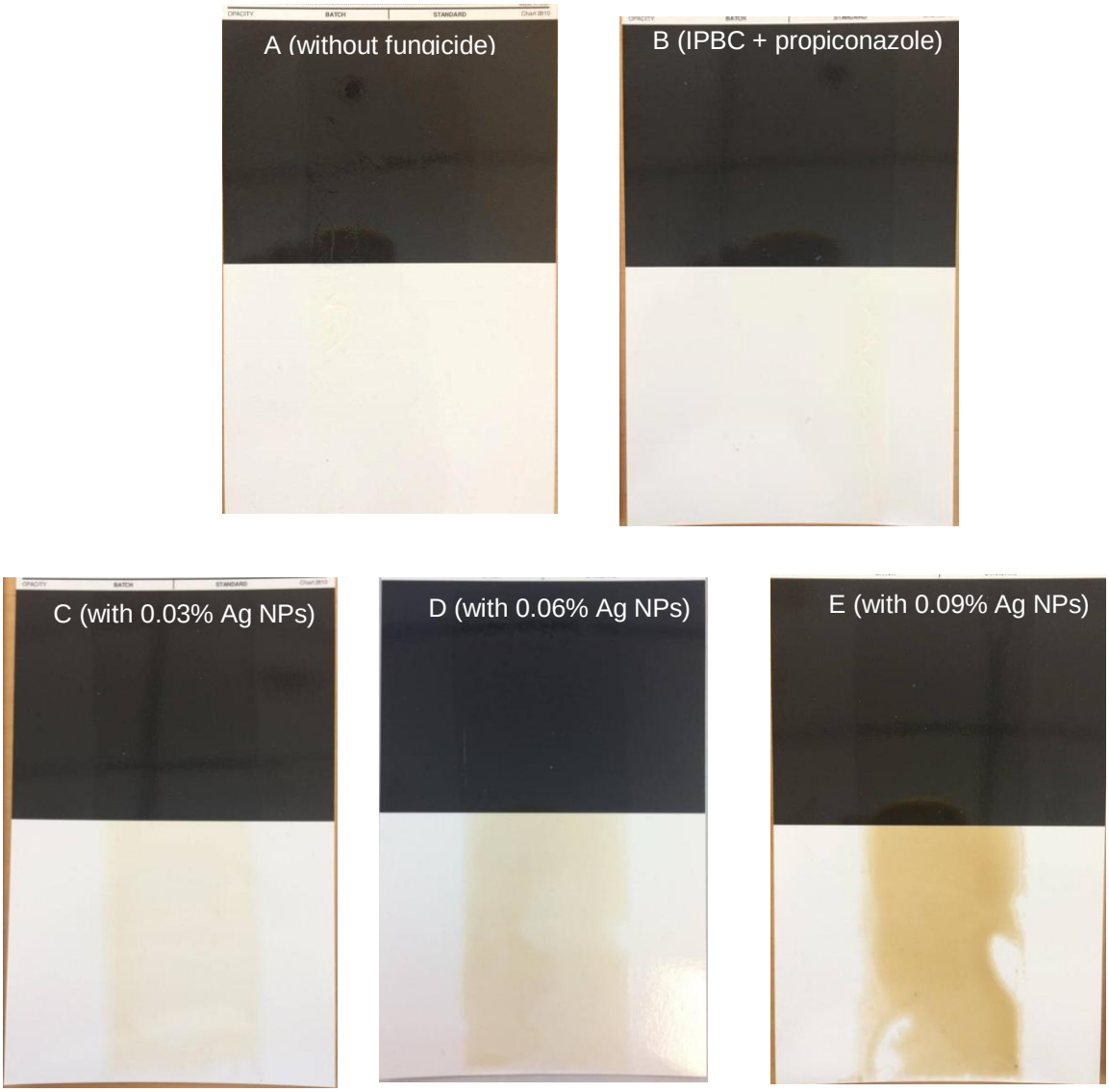

Fig. 9. Leneta contrast charts for the five coating formulations given in Table 1

It is also worth noting that the ΔE^*_{ab} difference is far more important between Formulations D and E when compared with the ΔE^*_{ab} difference between Formulations C and D. However, the difference in nanoparticle concentration among all of the formulations is 0.03%.

Colour measurements on red pine samples

Despite the high total colour change (ΔE^*_{ab}) observed on Leneta contrast charts with formulations containing low concentrations of silver nanoparticles, the colour variation might not be as perceivable to human eyes when the formulations are applied onto wood substrates. Hence, tests were conducted with red pine samples coated with Formulations A, B, C, D, and E. Some red pine samples were also left uncoated. The colour coordinates (L^*, a^*, and b^*) were measured on the coated and uncoated red pine samples. The ΔL^*, Δa^*, Δb^*, and ΔE_{ab}^* values were calculated based on the differences between the coated samples and the uncoated samples. Additionally, ΔL^*, Δa^*, Δb^*, and ΔE_{ab} values were calculated based on the difference between the red pine samples coated with Formulations B to E, with biocide(s), and Formulation A, without biocide. These results are presented in Figs. 10 to 13.

In Fig. 10, the ΔL^* values were negative ($\Delta L^* < 0$), irrespective if referenced to the uncoated wood sample or to coated wood with Formulation A (without biocide). A negative ΔL^* means that the wood coating darkened the samples. The ΔL^* value was proportional to the concentration of silver nanoparticles in the coating formulation.

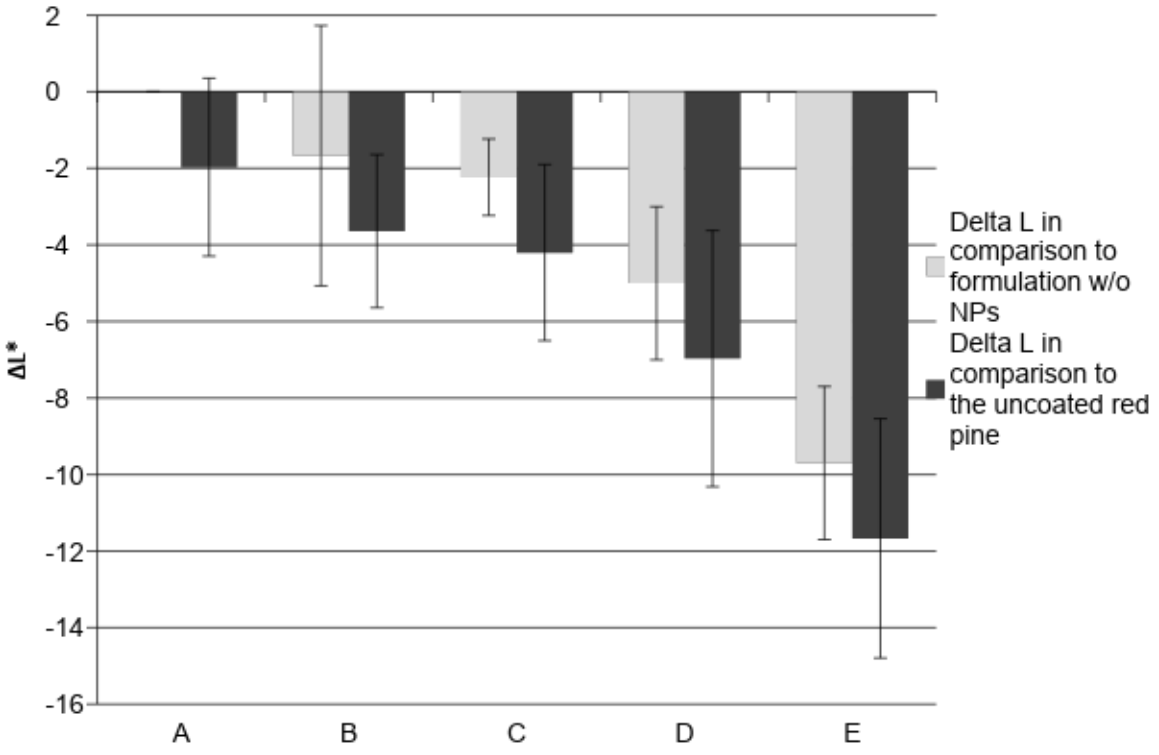

Fig. 10. ΔL^* for Formulations B, C, D, and E when compared with Formulation A (pale grey), and ΔL^* for Formulations A, B, C, D, and E when compared with uncoated red pine (dark grey); NPs indicates silver nanoparticles (error bars represent the standard deviations)

The Δ*a** values (Fig. 11) were not appreciably affected by the application of the formulation without nanoparticles or the formulations containing silver nanoparticles, except for Formulation E (0.09% silver nanoparticles), which presented Δ*a** values higher than 4.

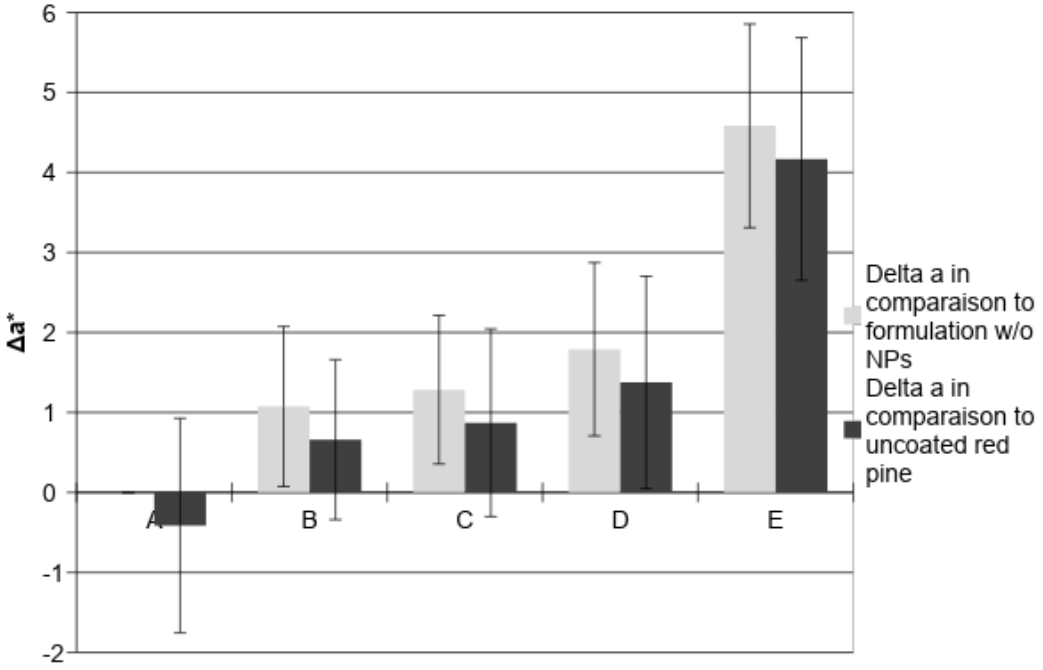

Fig. 11. Δ*a** for Formulations B, C, D, and E when compared with Formulation A (pale grey), and Δ*a** for Formulations A, B, C, D, and E when compared with uncoated red pine (dark grey); NPs indicates silver nanoparticles (error bars represent the standard deviations)

The application of the formulations (A to E) onto red pine samples, regardless of the presence or absence of silver nanoparticles, tended to make the wood samples more yellow, as the Δ*b** values were positive (Fig. 13; dark grey bars). However, the presence of silver nanoparticles did not influence Δ*b**, in comparison with the formulation without nanoparticles, as the Δ*b** values (Fig. 13; pale grey bars) were nearly zero. In brief, the change in Δ*b** was primarily attributed to the resin contained in the coating formulation, rather than the addition of silver nanoparticles.

Figure 13 presents the ΔE^*_{ab} values calculated in reference to wood coated with Formulation A, and in reference to uncoated wood. It is worth noting that the total colour change *versus* the uncoated wood was mostly due to the Δ*b** component (Fig. 13; dark grey bars). The ΔE^*_{ab} values calculated *versus* Formulation A, without silver nanopaprticles (Fig. 13; pale gray bars), were much lower. Even though these ΔE^*_{ab} values are small, they are still perceptible to the human eye. According to Landry (2012), the total colour change (ΔE^*_{ab}) calculated between a commercial semi-transparent acrylic coating applied on spruce and uncoated spruce had a value of 36. When comparing the same semi-transparent coating applied on white pine to uncoated white pine, the ΔE^*_{ab} was 31. The ΔE^*_{ab} calculated between the red pine samples coated with Formulation E (highest silver nanoparticle concentration) and the uncoated samples was 18; in this comparison, it can be assumed that the addition of silver nanoparticles to a coating formulation did not compromise the development of a semi-transparent or translucent coating.

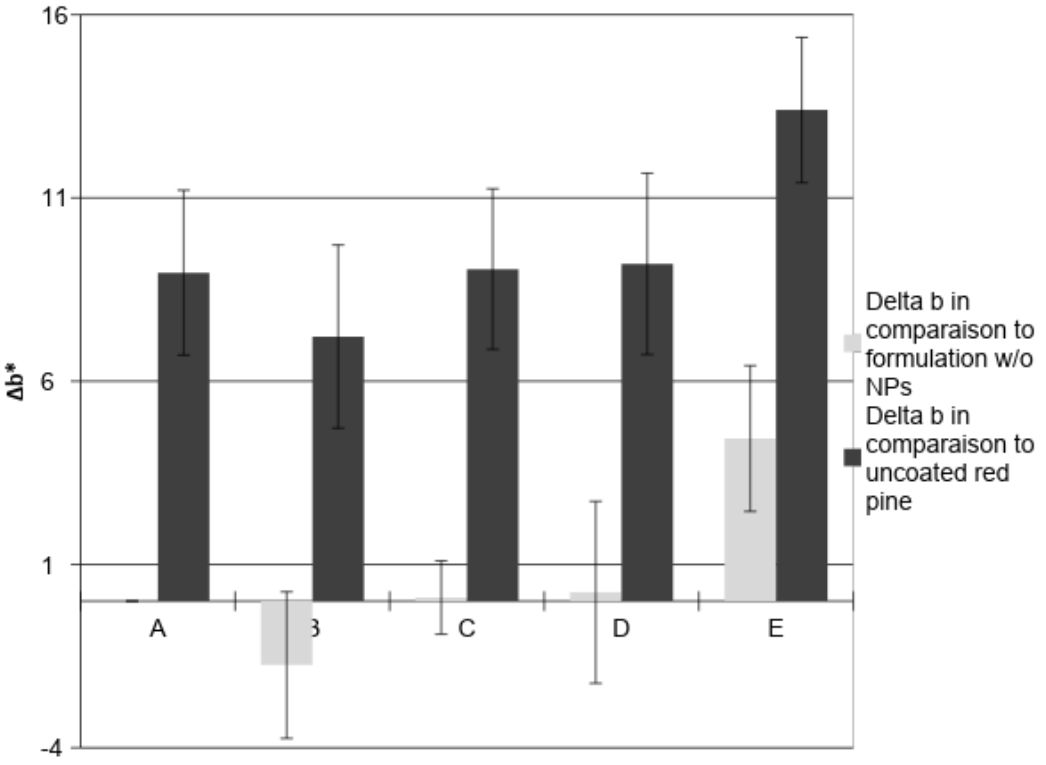

Fig. 12. Δ*b** for Formulations B, C, D, and E when compared with Formulation A (pale grey), and Δ*b** for Formulations A, B, C, D, and E when compared with uncoated red pine (dark grey); NPs indicates silver nanoparticles (error bars represent the standard deviations)

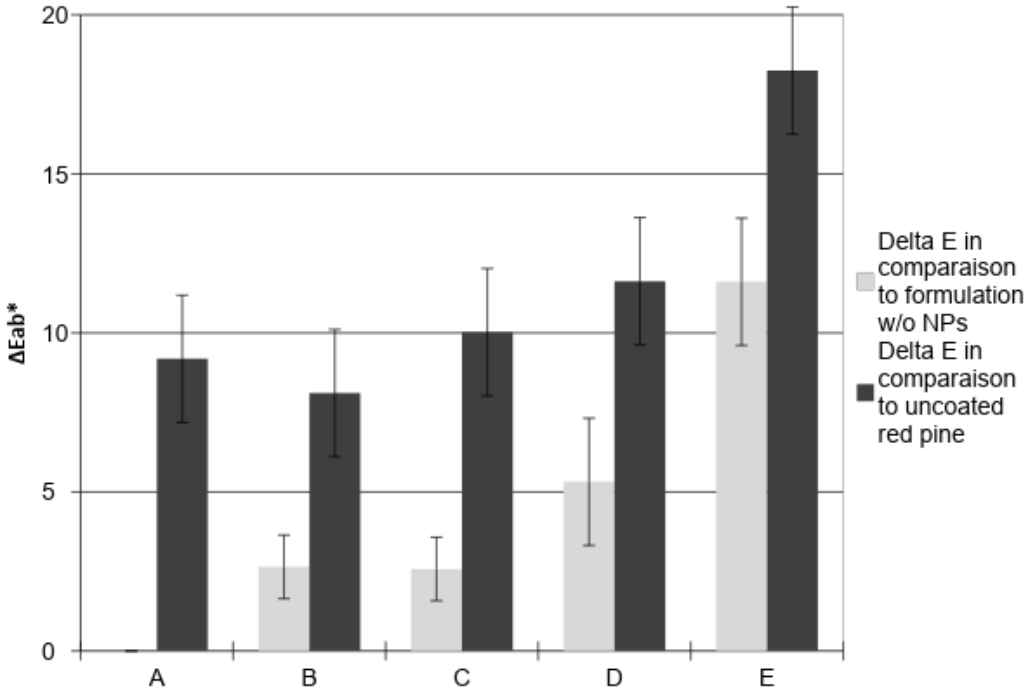

Fig. 13. ΔE^*_{ab} for Formulations B, C, D, and E when compared with Formulation A (pale grey), and ΔE^*_{ab} for Formulations A, B, C, D, and E when compared with uncoated red pine (dark grey); NPs indicates silver nanoparticles (error bars represent the standard deviations)

Opacity and gloss on Leneta contrast charts

Because silver nanoparticles are known for their strong light scattering and absorption properties, it is important to measure the opacity of the prepared formulations to determine if the grain and texture of wood substrates will be obscured. The opacity measurements of the five prepared formulations are presented in Fig. 14, where 0% represents completely translucent and 100% represents completely opaque.

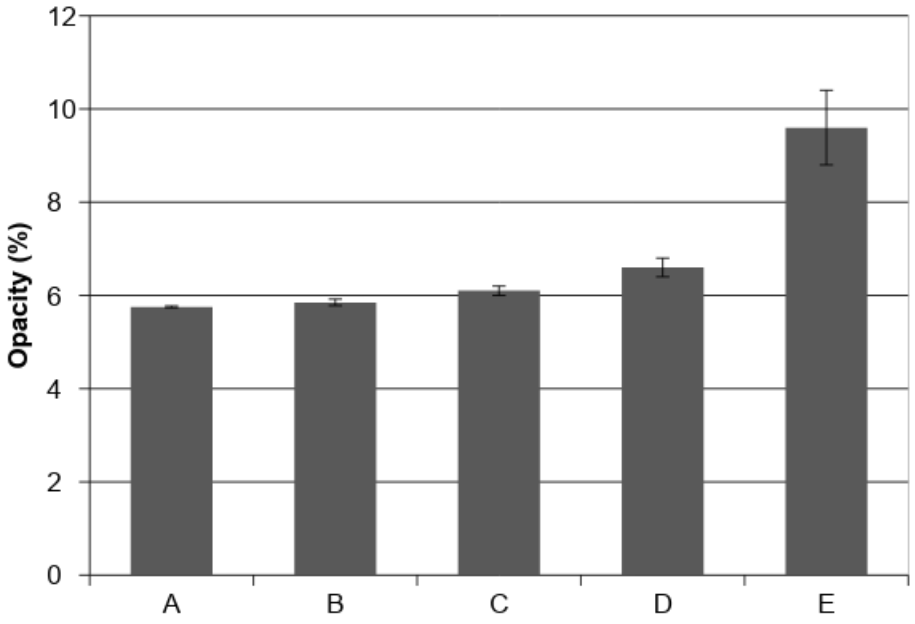

Fig. 14. Opacity measurements for Formulations A, B, C, D, and E (error bars represent the standard deviations)

Formulations A, B, C, and D exhibited opacity values that ranged from 5.8% ± 0.2% to 6.6% ± 0.2%. The highest opacity values were observed for Formulation E (9.6% ± 0.8%). As was observed with the colour changes, the opacity differences were more apparent between Formulations D and E than between Formulations C and D, even though the difference in silver nanoparticle concentration was the same. For all the prepared formulations, the opacity value was below 10%. Clear coatings are known to slightly obscure the substrate, as is shown in the opacity values of the coatings of this study; hence, the prepared formulations should maintain the aesthetic properties of wood. However, there is no distinct opacity value or range of values that denotes clear, semi-transparent, and opaque classes.

Gloss values at an angle of 20° were also measured (Fig. 15). When comparing the results obtained for Formulations A, C, D, and E, there were no appreciable differences among the gloss values, which indicates that the addition of silver nanoparticles at concentrations below 0.09% did not affect the optical property of the coating. A lower gloss value was observed for Formulation B, which indicated that IPBC and propiconazole could cause a matting effect with respect to the coating.

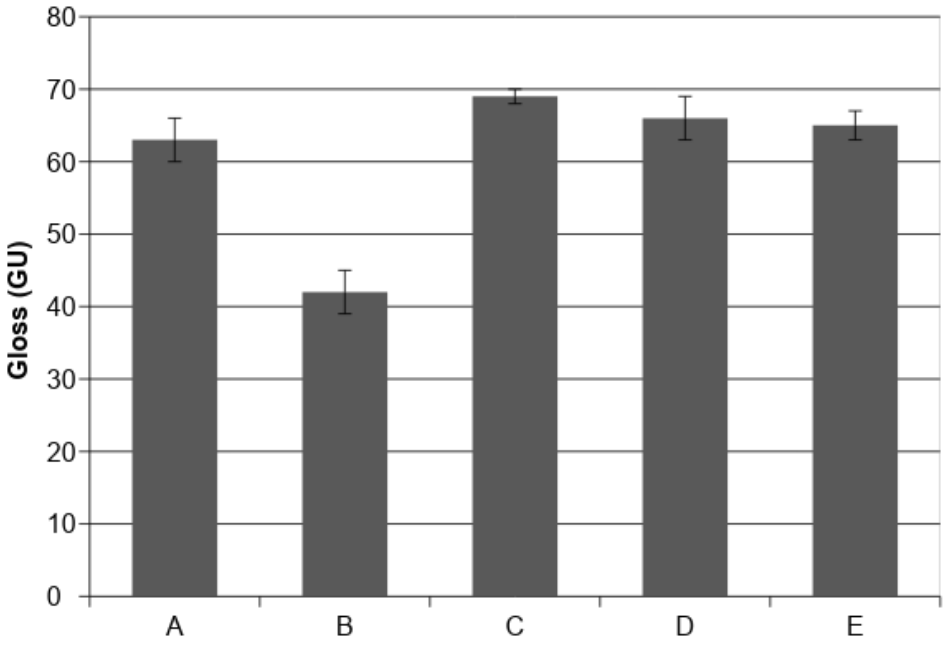

Fig. 15. Gloss values at 20° for Formulations A, B, C, D, and E

CONCLUSIONS

1. Miniemulsion polymerisation can be used to synthesize an acrylic latex coating containing silver nanoparticles, which will limit the growth of black-stain fungi.
2. Latexes coatings with a concentration of silver nanoparticles as low as 0.03% were able to limit the growth of *S. pityophila* and *E. nigrum* as efficiently as the reference formulation (0.1% IPBC + 1% propiconazole) after eight weeks.
3. Silver nanoparticle concentrations lower than 0.09% were not as effective as the reference formulation (B) with organic fungicides to control *A. pullulans* growth. However, samples coated with the formulation containing 0.06% silver nanoparticles exhibited better antifungal results after eight weeks than formulations containing 0.09% silver nanoparticles.
4. The addition of silver nanoparticles into a latex coating formulation affected the film's colour. However, the ΔE^*_{ab} change caused by 0.09% silver nanoparticles addition was lower than the ΔE^*_{ab} of a semi-transparent acrylic coating applied onto white pine and spruce. The other optical properties of the coating film were not influenced by the presence of silver nanoparticles. Therefore, the addition of silver nanoparticles into a coating formulation does not compromise the development of a translucent coating.

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