Silica nanoparticles in high silica/alkali molar ratio solutions as fire-retardant impregnants for woods

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SUMMARY

The objective of this paper is to know the fire performance of wooden panels (*Pinus radiata*) impregnated with silica nanoparticles added to silica/alkali colloidal solutions. Two series of impregnated panels were prepared with diverse penetrations and retentions (a) after drying/curing the impregnants at laboratory conditions until reaching constant weight and (b) after finishing this stage with prior distiller water immersion for seven days and a later air exposition for attaining moisture balance. Panels were tested in a limiting oxygen chamber and in a two-foot tunnel. Some results displayed a high fire-retardant efficiency. Copyright © 2009 John Wiley & Sons, Ltd.

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1. INTRODUCTION

High-density woods present excellent resistance to fire penetration as they display low thermal conductivity and adequate capacity to form a charred layer; the latter allows the maintenance of their physical and mechanical properties for a longer time than steel and cement structures [1–7]. Nevertheless, medium- and low-density woods and their sub-products are widely used in construction for various technical and economical reasons (i.e. fast growing); consequently, without any fireproofing treatment they can contribute to fire propagation.

In a previous paper [8], the authors studied the flame-retardant performance of a low-density wood (Araucaria angustifolia) impregnated with sodium silicates and potassium silicates of low

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silica/alkali molar ratios (2.5/1.0 and 3.0/1.0). To facilitate silicate polymerization inside the pores of the wood, different treatments were considered: (a) air dried in laboratory (20–22°C; 50–55% relative humidity) until constant weight; (b) thermal treatment in forced draft oven for 24 h at 90°C; (c) acid treatment with a 10% alcoholic solution of dibutyl amine phosphate and finally (d) combined treatment (acid and heating). The results indicated that some treatments with these silicates of low silica/alkali molar ratios were sufficient to make the silicic polymers slightly insoluble or at least of reduced water-solubility; the latter avoids only partially the leaching of impregnation in contact with water.

In another paper of the same authors [9], the silicates used were of higher silica/alkali molar ratio (3.0/1.0 and 3.5/1.0) than in the previous experiments; an acid treatment was also used to form, in the first stage, a silicic polymer of elevated molecular weight and then, in the second stage, a treatment with several cations (aluminum, copper, zinc, magnesium and calcium) to form a metallic silicic polymer of high insolubility. The results concluded that the soluble alkaline silicates previously treated with an acid and then with cations led to the formation of metal silicate polymers of much reduced water-solubility than those obtained in the above-mentioned paper.

On the other hand, because the alkaline-soluble silicates studied earlier have similar essential disadvantage of a very high alkalinity of the aqueous solutions, which demand special attention for their manipulation, in other paper [10] the authors used solvent-based organic silicates as impregnants. For this study, taking into account the inorganic characteristics and the excellent physical–mechanical properties of the zinc-alkyl silicate films, ethyl silicates with different hydrolysis degrees were selected to impregnate panels of a porous wood (*A. angustifolia*) with the purpose of improving the behavior against fire action; very good performances were also obtained with some of these samples.

In the present paper, the authors took up again the studies with the aqueous alkaline silicate solutions considering their aspect of being less polluting to be free of organic solvent and also because experiments with the mentioned alkaline silicate solutions spread on glass allowed to infer that with a higher silica content in their composition, the films would show a higher curing rate as well as a smaller water dissolution rate. Therefore, ecological nanocomposite systems of very high silica/alkali molar ratio were prepared from a commercial sodium silicate colloidal solution and nanosilica solution to be used as fire-retardant impregnants. Testing panels were prepared on *Pinus radiata* as it is a porous wood (oven-dry density, $0.606\,\mathrm{g\,cm^{-3}}$) and moderately penetrable; it is important to mention that no significant differences were determined between *A. angustifolia* (0.497 gcm⁻³) used in earlier tests and *P. radiata* when both of them without any prior treatment were subjected to flammability tests.

2. EXPERIMENTAL PART

2.1. Alkaline silicates

A commercial-soluble sodium silicate (3.5/1.0 silica/alkali molar ratio in solution at 30% w/w) was used [11, 12]; it is defined as a soluble silicate as it dissolves in water forming viscous solutions with a high stability degree.

A colloidal silica solution of nanodimensions, alkaline type (0.32% sodium oxide content), also at 30% w/w, was used for increasing the silica/alkali ratio. This silica sol, also known as hydrosol

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silica, is a colloidal solution of highly hydrated silica particles dispersed in water; it is odorless, insipid and nontoxic, with a pH value of 9.2 and density of 1.25 g cm⁻³ at 25°C.

The nanosilica has a molecular chemical formula mSiO₂·nH₂O. Nanometric colloidal silica may be obtained by several chemical processes; the most important methods include the hydrolysis of alkoxysilane esters, the combustion of silica halides and the precipitation from the aqueous solution of sodium metasilicate [13, 14].

The nanosilica used in this paper has a density of ρ 2.31 g cm⁻³. The morphology and size of the associated particles were evaluated with SEM with the specific area using the BET method; in both cases, the samples were heated at 300°C for 2 h prior to the measurements to produce thermal desorption of the adsorbed organic substances used during manufacture as they may block active centers of the silica surface and therefore lower N_2 adsorption takes place during estimation of BET isotherm.

The aggregates of individual particles have an effective diameter of 1022 nm (SEM); the specific area displayed a value of $216 \,\mathrm{m}^2\,\mathrm{g}^{-1}$ (BET). The $6/\mathrm{d}.\rho$ ratio, indicating precisely the specific area of particles, suggests that individual particles have an average diameter đ of approximately 12 nm.

The objective was to prepare, by curing the inside of the pores of wood, systems constituted by a matrix inorganic (alkali silicates) and a nanometric inorganic components (silica) distributed in a homogeneous form in the mentioned matrix, to determine their performance as being a fire retardant.

The new nanocomposite systems were prepared with $\frac{4.0}{1.0}$, $\frac{4.5}{1.0}$, $\frac{5.0}{1.0}$ and $\frac{5.5}{1.0}$ molar ratios; the adding of nanosilica solution in alkaline silicate colloidal solution was easily carried out.

In previous laboratory tests, the formation of inorganic polymer by acid silicification starting from soluble silicates and zinc cation to provide water insolubility (several water-soluble salts of the above-mentioned cation were added to the soluble silicate solutions) indicated a quick formation of gel at the interface followed by a propagation of the reaction into the aqueous phase. Then, a coagulated mass separated out and the precipitates were predominantly amorphous.

In addition, the quoted inorganic polymer was characterized by applying X-rays. These studies show an interatomic distance between Si and O of about 1.62 Å, and besides that each oxygen is linked to two silicon atoms or to one silicon and one metal atom. The structure of glass has an Si and O random arrangement with cations placed into holes in the network. Unpublished previous experiments carried out by the authors showed that larger ions and those with higher valence are held more strongly in the network; the relative size and charge of the ions influence the solubility of inorganic polymer generated by silicification.

Impregnant systems were previously diluted until reaching the 20% w/w. Then, the aqueous solutions used for the impregnation were characterized through density, pH and viscosity at 20°C, Table I; the surface tension was adjusted in all solutions with a tensioactive agent (sodium dodecyl sulphate) to $30 \,\mathrm{dyne}\,\mathrm{cm}^{-1}$.

The properties of glasses (density and refraction index) were studied, Table I. Regarding these properties, a slight decrease in their representative values was noted as silica in the composition increased: the analysis of the density values of the glasses indicated that in all cases the impregnation would increase the density of the treated wood according to both the obtained retention degree and the silica/alkali ratio selected, whereas the refraction indexes attained reduced values (similar to the extenders used in coatings).

The values of thermal expansion of the unidirectional expansion indicate, in the first intervals of temperature studied, an almost linear increase whereas a faster rise was noted at higher temperatures. Moreover, the volumetric coefficients, in total correspondence with those of lineal dilation, show

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	Solutions				Glasses			
Sample	Silica/alkali ratio	Density, °Be	Viscosity, cP	pН	Density, g cm ⁻³	Refraction index		
A	3.5/1.0	22.2	12.5	11.2	2.427	1.495		
В	4.0/1.0	21.5	14.2	11.0	2.395	1.492		
C	4.5/1.0	21.0	16.8	10.8	2.373	1.488		
D	5.0/1.0	20.3	32.1	10.5	2.322	1.482		
E	5.5/1.0	20.0	76.8	10.3	2.284	1.479		

Table I. Some properties of the sodium silicates at 20°C.

a reduced expansion inclusive at temperatures between 25 and 800°C (approx. those registered in a fire): the values ranged from 1.744 to 2.587%. This would favor the dimensional stability of the treated wood, and consequently of its mechanical resistance during a conflagration.

2.2. Impregnation process

As mentioned, testing panels were prepared on P. radiata [15].

For improving impregnation, samples were previously immersed in deionised water at 100° C for seven days, in a closed vessel placed on a stove; the deionised water was daily changed for improving the extraction of extraneous materials (tannins, gums, cellulose, etc.). At a later stage, the samples were left exposed in the laboratory environment ($65\% \pm 2$ RH, $25\pm 1^{\circ}$ C) to reach the moisture balance (constant weight, ca. 14.3%).

The impregnations were carried out at $\frac{45}{50}^{\circ}$ C in a vertical pressure vessel of 401 capacity, provided with a vacuum pump and an air compressor. The selected 3/1 wood/impregnant solution ratio assured in all steps that the testing panels were completely submerged during the whole process. The vessel was loaded in all cases with pretreated panels to impregnate and a vacuum of 400 mmHg during 30 min was made to evacuate the air and the water vapor of the cells.

First, the alkaline silicates solution was added without decreasing the vacuum level. Later, the operative conditions were also considered to reach several retentions and penetrations: the pressure was gradually increased to facilitate the penetration from 1.5 to 6.5 kg cm⁻²; this stage elapsed from 15 to 120 min.

The next stage consisted of creating a slight vacuum (approximately $50 \, \text{mmHg}$ for $10 \, \text{min}$) to eliminate the excess of soluble silicates. Then, to promote the formation of the inorganic polymer, the samples inside the vessel were immersed in the 10% dibutyl amine phosphate alcoholic solution (this salt hydrolyzes slowly to liberate phosphoric acid in contact with an alkaline solution); the pressure was gradually increased to $4.0 \, \text{kg} \, \text{cm}^{-2}$ for $20 \, \text{min}$.

Then, the procedure described above was followed again, that is, a slight vacuum was created to eliminate the excess of the alcoholic solution (approximately 50 mmHg for 10 min) and after 10% solution of zinc cation was added. A pressure of 4.0kg cm⁻² was held for 10 min.

Finally, panels were extracted after lowering the pressure, rinsed and air dried/cured in the laboratory (20–22°C; 50–55% RH) until constant weight before beginning the fire evaluation tests, Series 1. In Series 2, after having executed the mentioned stages, panels were immersed in distilled water for 7 days to study the influence of this variable (solubilization of the inorganic polymer) on the fire-retardant efficiency; in this series, samples were also kept in the laboratory until reaching moisture balance.

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2.3. Flammability tests

[16–18]. In this study, the following trials were carried out:

- Two Foot Tunnel (ASTM D 3806 St.): The Flame spread index (FSI) was computed by using the equation FSI = (Ls Lo)/(Lb Lo), where Ls is the average of the three flame-advance, Lo the average of three flame-advance of asbestos-cement board (zero flame-spread) and Lb the average of three flame-advance of the reference panel R1. The Panel consumption PC (loss of weight during the test) was also carried out.
- Limiting Oxygen Index, LOI (ASTM D 2863 St.): Determines the minimum oxygen concentration that just supports combustion of a material under equilibrium conditions such as candle-like burning (gas flow rate was 4.0 cm s⁻¹).

3. RESULTS

The wood panels before and after the extraction with water were observed by SEM: cuts in three directions were made using a joinery saw equipped with small fibers; finally, a polishing with thick wool cloth was made. Thereby, samples surface were previously coated with gold, Figure 1; in this figure, the morphologically hollow spaces are cleaner. In addition, in EDX determinations before immersion, the axial duct and rays were observed to be covered by calcium and carbon associated with organic and inorganic compounds; however, after immersion, a large proportion of these two elements was removed.

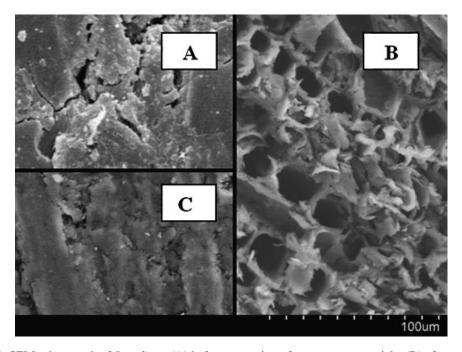


Figure 1. SEM micrograph of *P. radiata*: (A) before extraction of extraneous materials; (B) after extraction with boiling water; and (C) after impregnation.

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Fire Mater. 2010; **34**:177–187 DOI: 10.1002/fam With the aim of determining the performance of each studied variable, in the first stage the values of FSI, PC and LOI were established on a scale that ranged between 0 and 10. Thereby, the values 0 and 10 were, respectively, assigned to 1.00 and 0.00 (FSI); to 7.38 and 0.00% (PC) and to 16 and \geqslant 46 (LOI); the panel R1 (thermally treated by deionised water immersion at 100°C for seven days) was considered as the reference. It is important to mention that in all the cases, value 0 corresponded with the lowest one obtained in each test while for LOI determination a result of \geqslant 46 was the best performance registered.

Then, fire performance was statistically treated according to a factor design of 5 silica/alkali ratios, 3 impregnation levels and 2 conditions after impregnation, that is 30 combinations manufactured in duplicate. The variance was calculated and then the Fisher F test was run. The reference tables [19] indicate that the quoted variables considered (main effects) in this study showed an important influence on the performance against fire.

The results of the flammability tests are included in Table II. For their interpretation, the average of the main effects was calculated, Table III. The best performance for the considered variables corresponds to the highest average value.

3.1. Retentions and penetrations

After having concluded the impregnation, the retentions were calculated (gravimetric determination), whereas the penetrations were carried out from a qualitative point of view (visual and microscopic observations of cuts on the testing panels).

		Series 1		Series 2			
	Two foot tunnel			Two foot tunnel			
Sample	FSI	PC, %	LOI, %	FSI	PC, %	LOI, %	
A, Group I	0.35	3.35	41	0.64	5.03	23	
B, Group I	0.31	3.15	41	0.48	4.03	31	
C, Group I	0.29	3.03	42	0.32	3.32	38	
D, Group I	0.27	2.97	43	0.27	3.06	42	
E, Group I	0.26	2.93	43	0.25	2.96	43	
A, Group II	0.30	3.05	42	0.52	4.17	25	
B, Group II	0.27	2.98	42	0.41	3.49	32	
C, Group II	0.25	2.91	43	0.30	3.06	38	
D, Group II	0.23	2.82	43	0.24	2.82	43	
E, Group II	0.22	2.74	44	0.22	2.80	44	
A, Group III	0.28	3.00	42	0.46	4.21	27	
B, Group III	0.26	2.87	42	0.35	3.70	35	
C, Group III	0.24	2.80	43	0.27	3.20	40	
D, Group III	0.22	2.72	43	0.21	2.87	43	
E, Group III	0.20	2.65	≥46	0.19	2.62	≥46	
Reference R1*	1.00	7.38	16	1.00	7.38	16	
Reference R1**	1.00	8.22	12	1.00	8.22	12	

Table II. Results.

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^{*}R1, thermally treated by deionised water immersion at 100°C for seven days.

^{**}R2, original, without any previous treatment.

	Series 1								
Sample	Group I	Group II	Group III	Average	Group I	Group II	Group III	Average	Average
A	6.76	7.18	7.27	7.07	3.08	4.05	4.46	3.86	5.46
В	6.99	7.31	7.39	7.23	4.87	5.50	5.94	5.44	6.34
C	7.22	7.48	7.60	7.43	6.54	6.73	6.99	6.75	7.09
D	7.42	7.63	7.70	7.58	7.27	7.59	7.67	7.51	7.55
E	7.48	7.80	8.14	7.81	7.49	7.64	8.18	7.77	7.79
Average	7.17	7.48	7.62	7.42	5.85	6.30	6.65	6.26	
Impregnation level			Average series 1		Average series 2			Total average value	
Group I		7.17		5.85			6.51		
Group II	7.48		6.30			6.89			
Group III			7.62		6.65			7.24	

Table III. Average values of main effects.

The several specimens were classified in three groups according to the retention reached. These values, that is the quantity of solids of the impregnant solution absorbed by the unit of volume of wood, oscillated between $\frac{70}{80}$ (Group I), $\frac{105}{115}$ (Group II) and $\frac{125}{135}$ kg m⁻³ (Group III); the average values were, respectively, 72, 109 and 132 kg m⁻³. Concerning penetration, that is the depth that attained the impregnant solution, this was very irregular, partial and complete (the whole of the panel thickness) in Groups I, II and III, respectively.

3.2. Fire performance

3.2.1. Series 1. FSI indicates an improved performance of all the treated panels in relation with the reference ones (R1: thermally treated by deionised water immersion at 100°C for seven days; R2: original, without any previous treatment) as well as a marked difference in the efficiency of the designed treatments.

Regarding the relative performance of the reference panels, R1 showed a better efficiency than R2 (although both showed the maximum values of FSI, R1 displayed a smaller value of PC and a higher LOI value than R2); undoubtedly the materials released by immersion are responsible for the different performances in the tests conducted.

The panels showed an enhanced performance (decreasing FSI values) as the silica/alkali ratio and impregnation level increased. For example, specimen E-Group III-Series 1 (the best one) showed a significant decrease of the FSI with regard to the reference panels (FSI=1.00, which implies a flame-advance along the whole of the panel length), reaching a 0.20 value (that is 112 mm beyond the flame-advance registered on the panel of asbestos-cement whose average value was 50 mm). The values of PC corroborated the conclusions reached when analyzing the FSI; thus, the best specimen E-Group III-Series 1 lost only 2.65% while the reference panels R1 and R2 reached values of 7.38 and 8.22%, respectively.

LOI results also showed an increasing effectiveness, starting from the reference panels as the silica/alkali ratio and impregnation level increased. For example, panel R1 displayed an LOI of 16% (sample easily combustible), whereas the treated panels exhibited in all cases higher values, between 41 and \geq 46%. The latter allows classifying all samples of Series 1 as self-extinguishing as they require a higher oxygen concentration that is available in air.

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3.2.2. Series 2. These panels also exhibited better effectiveness than the reference panels R1 y R2. Samples treated with high silica/alkali ratio displayed a similar behavior as Series 1, whereas those treated with silicates of less silica content showed worse success (higher FSI and PC and less LOI values).

The solubility of the studied alkaline silicates (particularly those of lower silica/alkali ratio) justifies the quoted behavior as the testing panels were previously immersed for 7 days in distilled water [20, 21]. A partial releasing of the soluble silicates was verified determining the retention and penetration values of the impregnant material; although the first ones diminished as maximum 7% in the panels for the LOI test and 3% for those used in Two Foot Tunnel test, the distribution in depth observed by microscopy indicated a very reduced presence on the surface (up to 0.5 mm, according to the impregnant material type) and a growing profile toward the interior (starting from 1 or 2 mm a similar homogeneous retention existent in the core of the sample was detected).

It is very important to mention that using the smoke density attachment that Two Foot Tunnel used for experiment has (it includes a chimney and in addition a light source and a photo cell mounted at the opposite end point of ignition) the direct reading in percent (0-100) of light transmission received in the photo cell recorded (an opaque card was used for calibrating the zero value of scale). The results displayed a reduced smoke amount when the most efficient impregnants were tested (light transmission superior than 90% during all the tests), whereas both reference panels R1 and R2 showed a higher smoke quantity (in some moments light transmission test was only 5%).

3.3. Statistical analysis

Table III: Concerning impregnates composition, the highest value obtained by averaging the fire testing results was shown for sample E: 7.79; diminishing values were attained as silica/alkali ratio decreased until reaching the value 5.46 which corresponds to the lowest ratio considered (sample A).

In relation with the second main effect studied, Group III (the highest retention value) displayed the best average value: 7.24.

As expected, Series 1 (7.42) had a significant better performance against fire than Series 2 (6.26) as the alkaline silicates of less silica/alkali ratio are lightly water soluble.

Finally, it is important to mention that non-uniformity of panels (both in the wood and in the impregnant) test working conditions and operator are the main sources of error in both the tests carried out in this experiment.

Thus, in the case of Two Foot Tunnel Method, the degree of repeatability depended on the level of flame spread ratings; standard deviation of duplicate results was 0.04 and 0.06 for the lowest and highest FSI (0.19 and 0.64, respectively). In addition and for the lowest and highest PC values (2.62 and 5.03%, respectively) determined in the mentioned test, standard deviation of duplicate panels was 0.21 and 0.35, respectively.

The standard deviation of the mean of replicates in the LOI Chamber for samples with oxygen index of 23% (the lowest value) and 46% (the highest one) were, respectively, 0.6 and 1.4.

4. ANALYSIS OF FIRE-RETARDANCY MECHANISM

Combustible materials such as woods, natural and synthetic polymers, etc., when exposed to a source of sufficient heat, decompose releasing flammable volatiles; thermal decomposition developed in anaerobic conditions or in an atmosphere poor in oxygen is called pyrolysis. The mixing

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of the above-mentioned flammable volatiles with air, if temperature is high enough, leads to the ignition.

In addition, if the heat evolved by this ignited flame is sufficient to keep the decomposition rate of the wood above that required to maintain the concentration of the combustible volatiles, within the flammability limits for the system, a self-sufficient combustion cycle is established.

The major interest is not that the woods burn but how to make them more difficult to ignite and, if they are ignited, to make the burning less efficient.

The impregnation of *P. radiata* panels by means of no leachability inorganic silicates demonstrated, in trials carried out, the wood flame retardancy. These impregnants in the form of nanocomposites would lead to separation of the flammable material (i.e. lignocellulose present in the wood) as they maximize the interfacial contact between organic and inorganic phases. An additional advantage is that during combustion, the silicates remain intact at very high temperatures (minimum thermal expansion) and moreover, they act as a layer that partially insulates the wood from the heat source (barrier action).

In summary, the nanocomposite flame-retardant mechanism is a consequence of high-performance carbonaceous material-insoluble inorganic silicate system that is built-up on the surface during burning, which insulates the underlying material and slows down the mass loss rate of the decomposition products (i.e. smoke, etc.), imparting in this way a self-extinguishing character to it.

This residue forms as the components of wood burn away and the silicates reappear. Then, it is possible to conclude that the reduced flammability of low-density woods treated with inorganic nanosilicates is not via retention of a large fraction of carbonaceous char in the condensed phase, as there is little improvement in the residue yields once the nanosilicates regenerate or reconstruct on the surface.

5. CONCLUSIONS

- Nanocomposites constitute a new development in the idea of flame retardancy and offer significant advantages over the conventional compositions used as impregnants. Wood treated with nanosilicates exhibited significant increases in its self- extinguishing character. When heated they soften at relativity high temperatures and when cooled they keep their amorphous original form. The soluble nanosilicates demonstrated their compatibility with the components of wood as superficial tension was previously adjusted.
- The improved fire resistance of the treated panels could be supported in the whole of the impregnants constituted by the non-combustible components placed inside the pores of the wood, which makes it a 'more inorganic' material, by separating the flammable components of the wood. In summary and according to the mechanism described earlier, the control of pyrolysis and combustion of wood panels treated with nanosilicates could be based mainly on both barrier effects (no flammable exposed areas from silicates and char from combustion of wood components). The authors did not discard the possible thermal action (conductivity diminution of treated woods) that would also contribute to fire retardancy while the high chemical stability of nanosilicates makes the chemical interaction between the impregnants and the most combustible components of the wood improbable.
- The slight differences of behavior in Series 1 could be attributed to the less volumetric expansion coefficients (that is higher-dimension stability) demonstrated by those silicates

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- of elevated silica content as they would avoid the generation of microcracks, which is an enlargement of the specific area (substrates more vulnerable to the fire action).
- The major difference between fire resistances detected in the tests carried out in the Two Foot Tunnel could be explained as what determines the comparative burning characteristics by evaluating the flame spread over the surface when ignited under controlled conditions, whereas the LOI Chamber determines the relative flammability by measuring the minimum concentration of oxygen required to support combustion.
- The significant advantages of the alkaline silicates for the treatment of woods are the high fire-retardant efficiency, the minimum thermal expansion, the reduced generation of smoke during the conflagration and the low cost. The most essential disadvantage of the inorganic silicates is the high alkalinity of the solutions that demands special care for their manipulation.
- In this study, no tests were performed with soluble inorganic silicates of high silica/alkali molar ratios prepared from pure silica and sodium oxide by melting to obtain colloidal solutions (but not nano-structured systems) to be used as impregnants. As only soluble silicates of high silica content were prepared in the laboratory starting from a commercial colloidal sodium silicate solution (3.0/1.0 silica/sodium oxide molar ratio) and a nanosilica solution, the comparison of the performance as fire-retardant impregnants between nano and microsilicates could not be done. At the moment, the authors take up a study to decide on the influence of this variable (nano and microsilicates).
- Although colloidal silica was used to prepare the alkaline silicates used as impregnants for wood, these silicates during the proposed treatment cure form, as mentioned, metallic inorganic polymers. Therefore, minimal or null amount of silica should be free after curing to be released as micro or nanomaterials along with the smoke during a conflagration; corroborating the above-mentioned, it is important to point out that preliminary thermo-gravimetric analysis indicated that these metallic inorganic polymers cured under laboratory conditions are extremely stable at high temperatures: the loss of alkali by volatilization showed very reduced values at 800°C (inferior to 0.1% w/w). Despite these silicates having no danger from silicosis and in addition that the silicate dust does not accumulate in the lungs, this subject must be carefully studied in other experiments, knowing the problems that all materials in the form of small particles suspended in the air can generate in human beings.

REFERENCES

- 1. Athey R, Shaw P. The problem with fire. European Coating Journal 1999; 10:428-431.
- 2. Sargent P. Multi-layer paint: the fire problem. Pigment and Resin Technology 1998; 27(6):361-370.
- 3. Horrocks A, Price D. Fire Retardant Materials. CRC Press: U.S.A., Woodhead Publishing Ltd: U.K., 2001.
- 4. Koslowsky R, Przybylak M. Natural polymers, wood and lignocellulosic materials. In *Fire Retardant Materials*, Horrocks A and Price D (eds). CRC Press: U.K., 2004; 293–317.
- Factor A. Char formation in aromatic engineering polymers. In Fire and Polymers, Nelson G (ed.). ACS: U.S.A., 1990; 274–287.
- 6. Wilkie CA. The design of flame retardants. In Fire and Polymers, Nelson G (ed.). ACS: U.S.A., 1990; 178-188.
- 7. Drysdale D. Fire safety design requirements of flame-retarded materials. In *Fire Retardant Materials*, Horrocks A and Price D (eds). CRC Press: U.K., 2004; 378–397.
- 8. Giudice CA, Pereyra AM. Fire resistance of wood impregnated with soluble alkaline silicates. *Research Letters in Materials Science*, Volume 2007, Article ID 31956 (version digital); e-ISSN 1687-6830; DOI information 10.1155/RLMS.
- 9. Pereyra AM, Giudice CA, Benitez JC. Fire retardant impregnants for woods based on alkaline silicates. *Fire Safety Journal*, DOI: 10.1016/j.firesaf.2008.10.004.

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Fire Mater. 2010; **34**:177–187 DOI: 10.1002/fam

- Pereyra AM, Giudice CA. Ethyl silicates with different hydrolysis degree like non-flammable impregnating material for wood. *Maderas. Ciencia y Tecnología* 2008; 10(2):113–127.
- 11. Tsai M, Yang Ch, Huang P. Effects of seeds concentration on the formation of colloidal silica. *Materials Science and Engineering* 2005; **123**:238–241.
- 12. Tsai M, Huang P, Wu W. The study of formation process of colloidal silica. *Materials Research Bulletin* 2005; 40:1609–1616.
- 13. Jesionowski T, Krysztafkiewicz AJ. Properties of highly dispersed silicas precipitated in an organic medium. *Dispersion Science and Technology* 1999; **20**:1609.
- Krysztafkiewicz A, Jesionowski T, Binkowski S. Precipitated silicas modified with 3-aminopropyltriethoxysilane. Colloids Surfaces, A 2000; 173:73.
- 15. Devi R, Maji T. Studies of properties of rubber wood with impregnation of polymer. *Bulletin Materials Science* 2002; **25**(6):527–531.
- 16. Caciolai M. Testing resistance to fire. Anticorrosione 1999; 7(25):29-33.
- 17. Shaw RJ. The use of flame retardant coatings on wall and ceilings. *Journal of Oil and Colour Chemist Association* 1999; **72**(5):176–180.
- 18. Hindersinn RR. Historical aspects of polymer fire retardance. In *Fire and Polymers*, Nelson G (ed.). ACS: U.S.A., 1990; 87–96.
- 19. Box GE, Hunter W, Hunter S. Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building. Wiley: U.S.A., 1978.
- Dietzel M. Dissolution of silicates and the stability of polysilicic acid. Geochimica et Cosmochimica Acta 2000; 64(19):3275-3281.
- 21. Papisova I et al. Structural effects in matrix polycondensation of silicic acid. European Polymer Journal 1999; 35:2087–2094.

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