



# Nano lithium silicates as flame-retardant impregnants for *Pinus radiata*

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## Abstract

Aqueous solutions of nano lithium silicates with 5.5/1.0 and 7.5/1.0 silica/alkali molar ratios were used to impregnate *Pinus radiata*. To obtain these impregnants, a solution of 3.5/1.0 SiO<sub>2</sub>/Li<sub>2</sub>O molar ratio was used; this ratio was increased with nanosilica solution. The impregnations were realized using Bethell process. The curing was made with dibutylamine phosphate, a divalent cation and both chemicals used sequentially. Panels were tested in oxygen index (OI) chamber and two-foot tunnel. The statistical interpretation indicates that the best economical and technical performance was reached with impregnant of the highest silica content and with zinc cation for curing.

## Keywords

lithium silicates, nanosilica, flame-retardant wood, impregnation, flammability tests

## Introduction

High-density woods show excellent fire penetration resistance since they display low thermal conductivity and an adequate capacity to form a carbonized layer allowing the maintenance of their physical and mechanical properties for longer than steel and cement.<sup>1–7</sup> Nevertheless, medium- and low-density woods and their sub-products, more widely used in the

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construction for many technical and economical reasons (i.e., fast growing), without any fire-resistant treatment, could contribute to fire propagation.

To give wood fire-resistance,<sup>8-10</sup> soluble alkaline silicates were used with a subsequent treatment with metallic salts to make insoluble the alkaline silicates;<sup>11</sup> later, on basis of previous methods, other patents were developed.<sup>12-15</sup> Nevertheless, in all cases, the silicate-based compositions can be leached from the wood by exposure to environmental water and moisture, which eventually causes that the treated wood loses its resistance against fire action.

In a previous paper,<sup>16</sup> the authors studied the flame-retardant performance of a low density wood impregnated with sodium silicates and potassium silicates of low silica/alkali molar ratios (2.5/1.0 and 3.0/1.0). To facilitate silicate polymerization inside pores of the wood, different treatments were considered; 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, which avoids only partially the leaching of impregnant in contact with water.

In other papers of the same authors,<sup>17</sup> the silicates used were of higher silica/alkali molar ratio (3.0/1.0 and 3.5/1.0). Results allowed concluding that this soluble sodium silicates previously treated with acid and then with cations lead to the formation of a lower water solubility polymeric silicates than those with a lower silica/alkali molar ratio.

Later, experiments carried out by the same working group with sodium silicate solutions placed on glass substrate allowed to infer that with higher silica content in their composition, the films show higher curing rate as well as a smaller water dissolution rate. For this reason, systems constituted by an inorganic matrix (sodium silicates) and a nanometric inorganic component (silica) distributed homogeneously in the matrix were prepared to determine their performance as fire-retardant; the new nanocomposites were formulated from 4.0/1.0 to 5.5/1.0 molar ratios.<sup>18</sup> Wood treated with nanosilicates based on high  $\text{Si}_2\text{O}/\text{Na}_2\text{O}$  molar ratio exhibited significant increasing in self-extinguishing character in relation to silica/alkali impregnants of lower silica content.

In this article, the authors continued studying aqueous alkaline silicate solutions due to their low polluting characteristic (they are free of organic solvent) and because with higher silica content in the impregnant, polymeric silicates of higher curing rate as well as of smaller water dissolution rate could be formulated.

Therefore, ecological nanocomposites of very high silica/alkali molar ratio were prepared from a commercial lithium silicate colloidal solution and nanosilica solution to be used as flame-retardant impregnants; aqueous solutions of nano lithium silicates with 5.5/1.0 and 7.5/1.0 silica/alkali molar ratios were used to impregnate *Pinus radiata* panels since it is a porous wood (oven-dry density,  $0.606 \text{ g cm}^{-3}$ ) and moderately penetrable.

## Experimental

The experiments included (1) the selection of commercial soluble lithium silicates and the curing methods to fulfill the polymerization of lithium silicates impregnated under pressure in low-density wood panels of *P. radiata*, (2) the determination of some characteristics of inorganic polymers formed by precipitation with zinc cation, (3) the operative conditions of the impregnation process and finally, (4) the laboratory tests to establish the behavior of the treated wood panels against the fire.

### *Lithium silicates and curing agents*

A commercial colloidal lithium silicate (Mejorsil, Argentina, 3.5/1.0 silica/alkali molar ratio in solution at 30% w/w) was used and an alkaline silica solution of nanodimensions (0.32% sodium oxide content), at 30% w/w, was selected to increase the silica/alkali ratio.<sup>18</sup>

The objective was the preparation, by curing inside wood pores, of systems constituted by an inorganic matrix (lithium silicate) and a nanometric inorganic component (silica) distributed homogeneously in the matrix, to determine their performance as flame retardants. The nanocomposites were manufactured with 5.5/1.0 and 7.5/1.0 molar ratios (samples A and B, respectively); both components were previously diluted until reaching 16% w/w. The adding of nanosilica solution to commercial colloidal lithium silicate solution was slowly carried out without affecting the system stability.

A sodium silicate nanocomposite of well-known performance in previous tests,<sup>18</sup> with 5.5/1.0 molar ratio and also 16% w/w, was used as reference impregnant (samples C).

To achieve the polymerization of impregnated alkaline silicates in low-density wood panels of *P. radiata*, the following methods were selected.

**Acid treatment.** It involved the use of a dibutyl amine salt and phosphoric acid (dibutyl amine phosphate). Soluble alkaline silicates contain some silanol and alkoxy groups; these silanols chemically react with hydrogen ions liberated from phosphoric acid protonating the silanol oxygen. This intermediate reacts with the silanol forming a siloxane bond. When system pH is very low, reaction rate is slow due to the repulsion between two positively charged groups (protonated oxygens). Consequently, system pH defines the dehydration rate to form polymeric silicic acid. In this experiment, a 10% dibutyl amine phosphate alcoholic solution was used for acid treatment.

**Reaction with a divalent cation.** The alkaline silicate silanol groups react with di- and trivalent cations forming metal–silanol bonds, which react to give metallic silicate polymers liberating hydrogen gas. A 10% zinc sulfate solution (0.62 M) was used.

**Acid treatment/reaction with a divalent cation.** The first stage involves the reaction of phosphoric acid with lithium silicates for allowing polymerization (formation of high molecular weight silicic acid). The second stage includes the reaction between silicic acid and metal cation to generate a metallic silicate polymer. A secondary reaction is the formation of insoluble metal phosphates that would be randomly located in the glass structure.

Table 1 displays the samples identification.

### *Inorganic polymers characteristics*

To understand some aspects of inorganic polymer formation, water-soluble salts of the selected divalent cation (10% zinc sulfate solution) was added to lithium silicate solutions. Later, X-ray studies were carried out to know some glass aspects; in addition, thermal expansion coefficients and density were measured.

**Table 1.** Samples identification

Alkaline silicates	A. Nano lithium silicate, 5.5/1.0 silica/alkali molar ratio B. Nano lithium silicate, 7.5/1.0 silica/alkali molar ratio C. Nano sodium silicate, 5.5/1.0 silica/alkali molar ratio
Treatment type	I. Impregnation with alkaline silicates alone II. Impregnation with alkaline silicates/acid III. Impregnation with alkaline silicates/zinc cation IV. Impregnation with alkaline silicates/acid/zinc cation

### Impregnation process

As mentioned, testing panels were prepared (prior to impregnation process) using *P. radiata* wood. For improving impregnation, samples were previously immersed in deionized water at 100°C for 7 days, in a closed vessel placed into a stove; the deionized water was daily changed for improving the extraction of materials (tannins, gums, cellulose, etc.). Later, the samples were exposed to laboratory environment (65% ± 2 RH, 25 ± 1°C) to reach the moisture balance (constant weight, c.a. 14.3%); these panels were identified as Reference R1. On the other hand, original panels (without any previous treatment) were identified as Reference R2.

The impregnations were carried out at 45/50°C in a vertical pressure vessel of 40 L 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 all process. The vessel was loaded in all cases with panels to impregnate; a vacuum of 400 mm Hg for 30 min was made to evacuate the cells air and water vapor.<sup>19</sup>

First, the corresponding alkaline silicate solution was added without decreasing the vacuum level. Later, the operative conditions were also considered to reach adequate retention and penetration. The pressure was gradually increased to facilitate the penetration from 1.5 to 8.5 kg cm<sup>-2</sup>; this stage elapsed for 120 min.

The next stage consisted of making a slight vacuum (approximately 50 mm Hg for 10 min) to eliminate the excess of soluble silicates (Treatment I. Impregnation with alkaline silicates alone).

Then, to promote the formation of the inorganic polymer, other impregnated panels inside the vessel were immersed in the 10% dibutyl amine phosphate alcoholic solution (this salt hydrolyzes slowly liberating phosphoric acid in contact with an alkaline solution); the pressure was gradually increased to 6.0 kg cm<sup>-2</sup> for 40 min. Then, the above-described procedure was followed again; a slight vacuum was created for 10 min (approximately 50 mm Hg) to eliminate the excess of alcoholic solution (Treatment II. Impregnation with alkaline silicates/acid).

In addition, to promote the formation of inorganic polymer, panels impregnated with alkaline silicates and exposed to a slight vacuum (approximately 50 mm Hg for 10 min) to eliminate the excess of soluble silicates were treated with a zinc sulfate solution, making another stage of impregnation in vessel at 6 kg cm<sup>-2</sup> for 30 min with a 10% zinc sulfate solution (Treatment III. Impregnation with alkaline silicates/zinc cation).

To conclude, other impregnated panels were sequentially treated with acid and with divalent cation, applying successively the impregnation stages according to the already

mentioned methodology (Treatment IV. Impregnation with alkaline silicates/acid/zinc cation).

Finally, after finishing the treatments, panels were extracted after lowering the pressure, rinsed and air-dried/cured at laboratory conditions (20–22°C; 50–55% RH) until constant weight before beginning the flammability tests, Series 1. After that, other panels were immersed in distilled water for 7 days at  $20 \pm 2^\circ\text{C}$  to study the influence of this variable (solubility of inorganic polymers) on flame-retardant efficiency, Series 2. These samples were also kept at laboratory conditions until reaching moisture balance.

### *Flammability tests*

In this study, the following tests were carried out.

**Two-foot tunnel (ASTM D 3806).** The equipment was provided by Atlas Electronic Devices Company, USA (Model TFT, Serial No. 1000). Samples size was 6 by 100 by 605 mm. The flame spread index (FSI) was computed using the equation  $\text{FSI} = (\text{Ls} - \text{Lo}) / (\text{Lb} - \text{Lo})$ , where Ls is the average of the three flame-advances, Lo the average of three flame-advances on asbestos-cement board (zero flame advance) and Lb the average of three flame advances of reference panel R2. The Panel consumption (PC, weight loss during the test) was also carried out.

**Oxygen index (ASTM D 2863).** The equipment was also provided by Atlas Electronic Devices Company, USA (Model OI, Serial No. OI-1015). Sample size was 3 by 6.5 by 70 mm. This test determines the minimum oxygen concentration in a nitrogen/oxygen mixture that supports material combustion under equilibrium conditions as candle-like burning (gas flow rate was  $4.0 \text{ cm s}^{-1}$ ).

## **Results and discussion**

### *Properties of colloidal solutions*

Nano lithium silicate solutions, of very high silica/alkali molar ratio (i.e., 7.5/1.0), are stable; nevertheless, those solutions of sodium and potassium silicates with silica/alkali molar ratio superior to 5.5/1.0, according to the present technological development, have in general a poor stability.

Nano lithium silicate solutions have the advantage (in relation to those based on sodium and potassium silicates of high silica/alkali molar ratio, i.e., 5.5/1.0) that the highest level of silicon dioxide leads to an alkalinity decrease higher than one point (for example, a pH value slightly lower to 9 for a solution 7.5/1.0  $\text{Si}_2\text{O}/\text{Li}_2\text{O}$  molar ratio of 16% w/w). This lower pH facilitates the solution manipulation and makes that the lithium silicates of high silica level do not require an acid treatment for curing because only the solubilization of  $\text{CO}_2$  from the environment is sufficient to form polymeric silicic acid of high molecular weight (protonation of the oxygen of the silanols, which reacts with the other silanol forming a siloxane bond by dehydration).

On the other hand, a disadvantage of the high silica/alkali molar ratio is that the increment of silica increases the viscosity of solutions. While the surface tension of the solution essentially defines the spontaneous penetration depth (this was adjusted in all cases, as mentioned, to  $38 \text{ dina.cm}^{-1}$ ), the viscosity particularly affects the penetration

kinetics. Consequently, to ensure an acceptable penetration and therefore a suitable impregnant retention, solutions of 7.5/1.0 Si<sub>2</sub>O/Li<sub>2</sub>O ratio were adjusted to a concentration of 16% w/w, which is lower than others used in previous works for sodium and potassium silicates solutions (5.5/1.0 silica/alkali ratio, about 20% w/w).

### *Properties of inorganic polymers*

Studies applying *X-ray* show an interatomic distance between Si and O about 1.62 Å and that each oxygen is linked to two silicon atoms or to one silicon and one metal atom. The inorganic polymer structure has a random arrangement of Si and O with cations placed into holes in the network. The other interatomic distances are 2.38, 2.68, and 3.31 Å for Li–O, O–O, and Si–Si, respectively.

Values of inorganic polymer *unidirectional thermal expansion* indicate, at first temperature intervals studied, an almost lineal increase whereas a faster rise is noted at higher temperatures. Furthermore, the volumetric coefficients, in total correspondence with those of lineal dilatation, show a reduced expansion even at temperatures between 25°C and 800°C (approximately those registered in fire): the values are 1.744% to 1.687%, respectively for 7.5/1.0 and 5.5/1.0 SiO<sub>2</sub>/Li<sub>2</sub>O molar ratios. This would promote the dimensional stability of treated wood, and consequently its mechanical resistance during conflagration.

On the other hand, *density* values at 20°C are 2.168 and 2.009 g cm<sup>-3</sup>. Regarding this property, a slight decrease in the representative values is noted as silica levels increases: the analysis of inorganic polymer density indicates that the impregnation would increase the density of treated wood according to the retention degree and the selected SiO<sub>2</sub>/Li<sub>2</sub>O molar ratio.

An additional advantage is that during combustion, the inorganic polymers would act as a layer that partially insulates the wood from the heat source (barrier action), separating the flammable materials (i.e., lignocellulose) because they promote the interfacial contact between organic and inorganic phases.

### *Retention and penetration*

After impregnation, the retentions were calculated (quantity of impregnating solution solids absorbed by wood volume unit) while the penetrations were qualitatively determined (visual and microscopic observations of cuts on the testing panels). Retention values oscillated between 76 and 81 kg m<sup>-3</sup>; the average value was 78 kg m<sup>-3</sup>.

The penetration (depth reached by the impregnating solution solids) was practically complete (the whole of the panel thickness) in all cases.

### *Fire performance*

Flammability test results are included in Table 2. A global analysis of FSI, PC, and oxygen index (OI) indicates an improved performance of all treated panels compared with the reference ones (R1, thermally treated by deionized water immersion at 100°C for 7 days; R2, original, without any previous treatment) as well as a marked efficiency difference among the different treatments.

Regarding the relative performance of the reference panels, R1 showed a better efficiency than R2 (although both of them showed the maximum value of FSI, R1 displayed smaller

**Table 2.** Results of flammability tests

Sample		Series 1			Series 2		
		Two-foot tunnel			Two-foot tunnel		
		FSI	PC (%)	OI (%)	FSI	PC (%)	OI (%)
A	I	0.21	2.63	34	0.39	3.99	31
	II	0.19	2.60	36	0.20	2.72	32
	III	0.18	2.55	40	0.17	2.55	38
	IV	0.16	2.50	43	0.15	2.49	41
B	I	0.18	2.55	36	0.22	2.80	32
	II	0.17	2.58	36	0.21	2.83	33
	III	0.12	1.95	≥46	0.11	2.00	≥46
	IV	0.12	1.94	≥46	0.12	1.98	≥46
C	I	0.23	2.75	33	0.41	4.12	31
	II	0.21	2.75	35	0.22	2.80	32
	III	0.20	2.65	40	0.19	2.62	39
	IV	0.18	2.60	43	0.18	2.59	41
Reference R1		1.00	7.38	16	1.00	7.38	16
Reference R2		1.00	8.22	12	1.00	8.22	12

value of PC and higher OI value than R2); undoubtedly the materials released by immersion in water at 100°C for 7 days are the responsible of the different performance in tests conducted.

### Statistical analysis of results

Fire performance was statistically treated according to the following factorial design: 3 alkaline silicates (A, B, and C) × 4 treatment types (I, II, III, and IV) × 2 conditions after impregnation (Series A and B), that is 24 combinations manufactured in duplicate. The variance was calculated and then the Fisher *F*-test was run. The reference tables<sup>20</sup> indicate that the considered variables (main effects) showed an important influence on performance against fire.

For the statistical analysis of the flammability tests as a whole, in a first stage the values of FSI, PC, and OI (Table 2) were turned into a scale with values from 0 to 10, which were assigned to 1.00 and 0.00 for FSI; to 8.22% and 0.00% for PC, and to 16 and ≥46 for OI, respectively (extreme values of each test); intermediate values were proportionally considered. The panel R2 (original, without any previous treatment) was considered as reference.

Later, with the aim of determining the performance of the studied variables, the average of main effects was calculated (all of them on a scale ranging from 0 to 10; Table 3) the best performance corresponds to the highest average value. The influence of each main effect is analyzed.

**Conditions after impregnation.** As expected, Series 1 (average value 7.6) displayed a significant better performance against fire than Series 2 (average value 7.1) since the



**Table 3.** Average values of main effects

Sample	Series 1	Series 2	Average (silicates/ treatment type)	Average (silicates type)
A.I	6.9	5.4	6.2	7.2
A.II	7.2	6.7	7.0	
A.III	7.7	7.5	7.6	
A.IV	8.1	7.9	8.0	
B.I	7.3	6.6	7.0	7.9
B.II	7.3	6.7	7.0	
B.III	8.8	8.8	8.8	
B.IV	8.8	8.8	8.8	
C.I	6.7	5.3	6.0	7.1
C.II	7.0	6.6	6.8	
C.III	7.6	7.5	7.6	
C.IV	8.0	7.8	7.9	
Average	7.6	7.1	7.4	7.4
Treatment type				Average
I. Impregnation with alkaline silicates alone				6.4
II. Impregnation with alkaline silicates/acid				6.9
III. Impregnation with alkaline silicates/zinc cation				8.0
IV. Impregnation with alkaline silicates/acid/zinc cation				8.2

5.5/1.0 silica/alkali ratio would be more water soluble (both alkaline oxides) than 7.5/1.0 silica/alkali ratio (lithium oxide): average values of samples A and B (lithium silicates) as well as of reference samples C (sodium silicates) were noticeably higher in Series 1 than in Series 2 for all curing treatments, except in samples B.III and IV (7.5/1.0 silica/lithium oxide) in which the average values were identical in both Series, Table 3.

The solubility of the alkaline silicates (particularly those of lower silica/alkali ratio) justifies the behavior when testing panels were previously immersed for 7 days in distilled water. Partial releasing of soluble silicates was verified determining impregnant material retention and penetration values; although the retention diminished as maximum 5% in OI test panels and 2% in Two-Foot Tunnel test panels, the depth distribution observed by microscopy indicated a very reduced presence on the surface (up to 0.4 mm, according to impregnant material type) and a growing profile toward the interior (from 1 or 2 mm of the surface, retention was totally homogeneous like in the panel core).

**Alkaline silicate type.** Panels tested in Two-Foot Tunnel showed an enhanced performance as silica/lithium oxide ratio increased. The 7.5/1.0 ratio (samples A) displayed a significant increasing of average value compared with 5.5/1.0 ratio (samples B) since they reached, respectively, average values 7.9 and 7.2, Table 3. In addition, both impregnants based on silica/lithium oxide displayed better performance against fire than references (samples C, 5.5/1.0 silica/sodium oxide ratio, average value 7.1), which were selected because they showed the best performance in all previous studies carried out by the authors.



**Treatment type for alkaline silicates curing.** Treatment IV (Impregnation with alkaline silicates/acid/zinc cation) was the best, followed by Treatments III (Impregnation with alkaline silicates/zinc cation), II (Impregnation with alkaline silicates/acid) and I (Impregnation with alkaline silicates alone), in this order.

Although the acid treatment improved the performance (average value 6.9, Table 3) in relation to wood panels treated with alkaline silicates alone (average value 6.4), this led to reduced efficiency in panels immersed in distilled water (values corresponding to Series 2 were inferior to those obtained in Series 1). This behavior could be attributed to the high solubility of those alkaline silicates polymerized only by acid treatment, which was corroborated in this case by the significant concentration of the corresponding alkaline cations (lithium or sodium according the impregnant) evaluated by atomic absorption in the solution where the panels were immersed in distilled water for 7 days.

The reaction with zinc cation would have favored the formation by dehydration of polymeric silicates of high molecular weight. In consequence, inorganic polymer of higher melting point, with reduced thermal expansion, could be responsible of improving performance against fire. Nevertheless, also in this case, when panels were immersed in distilled water before starting the flammability tests the efficiency decreased. In all cases, polymerization degree was not enough to keep the whole of impregnant into the panels after immersion; the level of alkaline cations in distilled water also demonstrated a slight solubility of impregnants A.III (average values 7.7 and 7.5, for Series 1 and 2, respectively) and C.III (average values 7.6 and 7.5, for Series 1 and 2, respectively) while a null solubility of impregnant B.III (average value 8.8 for both Series) was observed.

The partial leaching of silicates A and C was also verified by atomic absorption showing respectively the presence of lithium and sodium cations in the solution where the panels were immersed in distilled water for 7 days. On the other hand, lithium cation from panels treated with impregnant B.III practically was not detected.

Finally, panels cured sequentially with acid treatment and reaction with zinc cation showed the highest average value, 8.2. Although samples A.IV, B.IV, and C.IV displayed separately the highest average values of each curing treatment (8.0, 8.8, and 7.9, respectively), it is important to remark that in the case of sample B.IV no difference in the average values was detected in both Series: in this case, lithium from panels treated with impregnant B.IV practically was not detected by atomic absorption.

In summary, the best performance of all the panels was reached with nano lithium silicate of 7.5/1.0 silica/alkali molar ratio either by using zinc cation or acid/zinc cation for curing (samples B.III and B.IV, respectively). Nevertheless, the statistical interpretation indicates that the best performance from technical and economical viewpoint was reached with the impregnant cured only with the zinc cation since after finishing impregnation with lithium silicates, only one additional step is required for curing.

Finally, it is very important to mention that a device to measure the smoke density in the Two-Foot Tunnel was used (it includes a chimney, a light source and a photocell in the opposite point of ignition); the direct reading in percent (0–100) of light transmission received in the photocell was recorded (an opaque card was used for calibrate the zero value of scale). Results displayed a reduced smoke amount when the most efficient impregnants were tested (light transmission superior than 90% during all the test) while two reference panels R1 and R2 showed higher smoke quantity (in some moments of test, light transmission was only 5%).

## Conclusions

Visual and microscopic observations of the studied systems allowed reaching the following conclusions: (1) the nanocomposite flame-retardant mechanism is a consequence of high performance carbonaceous material-insoluble inorganic silicate system that is the build-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; (2) this residue is formed as the components of wood burns away and the silicates reappear; then, it is possible to conclude that the reduced flammability of low-density woods treated with nano lithium silicates of high silica/lithium oxide ratio is not via retention of a large fraction of carbonaceous char in the condensed phase, as there is a little improvement in residue yields, once the nanosilicates regenerate or reconstruct on the surface.

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## References

1. Athey R and Shaw P. The problem with fire. *Eur Coat J* 1999; 10: 428–431.
2. Sargent P. Multi-layer paint: the fire problem. *Pigm Resin Technol* 1998; 27(6): 361–370.
3. Horrocks A and Price D. *Fire retardant materials*. Boca Raton: CRC Press, USA and Woodhead Publishing Ltd, UK, 2001.
4. Koslowsky R and Przybylak M. In: Horrocks, Price (eds) *Natural polymers, wood and lignocellulosic materials, fire retardant materials*. UK: CRC Press, 2004, pp.293–317.
5. Factor A. Fire and Polymers. In: Nelson G (ed.) *Char formation in aromatic engineering polymers*. USA: ACS, 1990, pp.274–287.
6. Wilkie CA. The design of flame retardants. In: Nelson G (ed.) *Fire and Polymers*. Vol. 13, Washington, USA: ACS Symposium Series, 1990, pp.178–188.
7. Drysdale D. Fire safety design requirements of flame-retarded materials. In: Horrocks and Price (ed.) *Fire Retardant Materials*. Cardiff, UK: CRC Press, 2004, pp.378–397.
8. Caciolai M. Testing resistance to fire. *Anticorrosione* 1999; 7(25): 29–33.
9. Shaw RJ. The use of flame retardant coatings on wall and ceilings. *J Oil Col Chem Assoc* 1999; 72(5): 176–180.
10. Hindersinn RR. Historical aspects of polymer fire retardance. In: Nelson, G (eds) *Fire and Polymers*. Washington, USA: ACS Symposium Series, 1990, pp.87–96.
11. Lilla AG. Product and method for forming in situ insoluble metal silicates in wood pores for fire retardation and preservation: U.S. Patent. No. 3,974,318.1976.
12. Grantham et al. Method of pressure treating boards, U.S. Patent. No. 6,235,349, 2001.
13. Shiozawa K. Wood preservative composition, process for treating wood with the same, wood treated with the same, U.S. Patent. No. 5,478,598, 1995.
14. Slimak et al. Enhancing the strength, moisture resistance, and fire-resistance of wood, timber, lumber, similar plant-derived construction and building materials, and other cellulosic materials, U.S. Patent. No. 6,146,766, 2000.
15. Slimak et al. Enhancing the strength, moisture resistance, and fire-resistance of wood, timber, lumber, similar plant-derived construction and building materials, and other cellulosic materials, U.S. Patent. No. 6,040,057, 2000.
16. Giudice CA and Pereyra AM. Fire resistance of wood impregnated with soluble alkaline silicates. *Res Lett in Mater Sci*, Article ID 31956 (digital version), e-ISSN 1687-6830, DOI information 10.1155/RLMS, 2007).
17. Pereyra AM, Giudice CA and Benitez JC. Fire retardant impregnants for woods based on alkaline silicates. *Fire Saf J* 2009; 44: 497–503.
18. Giudice CA and Pereyra AM. Silica nanoparticles in high silica/alkali molar ratio solutions as fire retardant impregnants for woods. *Fire Mater* 2010; 34: 177–187.
19. Devi R and Maji. T Studies of properties of rubber wood with impregnation of polymer. *Bull Mater Sci* 2002; 25(6): 527–531.
20. Box GE, Hunter W and Hunter S. *Statistics for experimenters: an introduction to design, data analysis and model building*. USA: J. Wiley & Sons, 1978.

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