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Zinc borates as flame-retardant pigments in chlorine-containing coatings

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Abstract

This paper discusses the influence of zinc borates with molecular formulas of $2ZnO\cdot3B_2O_3\cdot3.5H_2O$ and $2ZnO\cdot3B_2O_3\cdot7.5H_2O$ used for substituting antimony trioxide on the performance of chlorinated alkyd, flame-retardant coatings.

Experimental coatings were manufactured on a laboratory scale, applied by brush on wood panels (Araucaria Angustifolia) and finally tested in a limiting oxygen chamber (LOI values), in a flame cabinet (intermittent bunsen burner rating) and in a two-foot flame tunnel (flame-spread index, panel consumption, after-flaming and after-glow).

Results of laboratory tests indicated that coatings with a chlorine-containing resin used as the film-forming material, zinc borates can act as a flame retardant. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Flame-retardant coatings; Chlorinated alkyd resin; Antimony trioxide; Zinc borates; Limiting oxygen index; Two-foot flame tunnel

1. Introduction

Fire is a complex phenomenon; its evolution and severity depends on several inter-related variables. An uncontrolled fire on a macroscale involves different stages: *initiation* (heating, decomposition and ignition or gas combustion), *growth* (spread or propagation leading to substrate combustion), *steady state* (fire fully developed) and finally *decay* (fire extinguished by itself) [1].

The growth stage is most easily controlled when an efficient flame-retardant coating is used. In the steady state, the coating can protect the structural stability of a building [2].

Flame-retardant coatings are designed for application over a range of combustible or non-combustible surfaces and they offer improved aesthetics. Since coatings with thin films can delay flame spreading (flaming combustion along a surface) and smoke generation, they are often used in living and work spaces where safe egress is essential [3]. On the other hand, if a conventional paint is applied over walls and ceilings of a room and a fire takes place in an object in this space, flames can reach the surface of the wall and, as a consequence, generate more heat and flammable vapors. Flames can then reach the ceiling, and a significant amount of heat is radiated

* Corresponding author. Present address: CIDEPINT, CIC-CONICET, Research and Development Center for Paint Technology, Av. 52 e/121 y 122, 1900 La Plata, Argentina. again. When the flammable vapors instantaneously ignite, a flash-over takes place. This is a point of no return.

Flame-retardant coatings are distinguished by their ability to release non-flammable gases when contacted by fire or when heat is generated. These gases interfere with the rate of spreading flame and also reduce its intensity [4]. The fire resistance effect can be obtained by adding a halogen source to the composition or by chemically building it into the film-forming polymers. To improve fire retardancy, antimony trioxide is usually used as a synergistic additive.

Recently, many studies have been carried out to substitute, in part or completely, antimony trioxide since the char analysis shows that about 80–95% of antimony volatilizes. It also increases smoke production. Other reasons for replacement are to achieve a better cost/performance balance and to reduce concern for the possible toxicity of antimony oxide [5,6].

This paper has the fundamental aim of studying the replacement of antimony oxide with zinc borates of molecular formulas $2ZnO\cdot3B_2O_3\cdot3.5H_2O$ and $2ZnO\cdot3B_2O_3\cdot7.5H_2O$ in flame-retardant coatings based on chlorinated alkyd resins to achieve improved performance in laboratory tests.

2. Formulation of flame-retardant coatings

Coating compositions formulated for the present study are included in Table 1.

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Table 1 Composition of flame-retardant coatings, % by volume on solids^a

Component	1	2	3	4	5	6	7	8	9
Titanium dioxide	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
Iron oxide	_	_	_	_	-	_	_	_	9.0
Antimony trioxide	9.0	6.0	6.0	6.0	3.0	_	_	_	_
Zinc borate ^b	-	3.0	_	1.5	3.0	4.5	9.0	_	_
Zinc borate ^c	_	_	3.0	1.5	3.0	4.5	_	9.0	_
Micronized talc	22.4	22.4	22.4	22.4	22.4	22.4	22.4	22.4	22.4
Chlorinated alkyd resin (solids) ^d	52.4	52.4	52.4	52.4	52.4	52.4	52.4	52.4	52.4
Bentone (gel)	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Additives	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9

^a PVC (pigment volume concentration), 42.9%.

 b 2ZnO·3B₂O₃·3.5H₂O.

^c 2ZnO·3B₂O₃·7.5H₂O.

^d 24.9% chlorine content.

2.1. Binder

In all cases a chlorinated alkyd resin was employed as film-forming material (24.9% by weight of chlorine on solids), which was manufactured on a laboratory scale by means of soya oil, chlorendic anhydride and pentaeritritol [7–10]. Preparation technique and general characteristics of the final product are mentioned in a previous work [11].

The chlorinated alkyd resin acts in the gaseous phase, decomposing by heat action to give free radicals which combine with air oxygen by complex reactions, in such a way that gases of oxidation generated by the decomposing substrate remains inhibited; its efficiency depends on the possibility of releasing water vapor at material decomposition temperature so as to generate incombustible gases.

The performance of this resin is not only limited in general to its action on the gaseous phase since it also increases the carbonaceous remainder during polymer pyrolysis. In this way a fire-retardant action in the solid phase is shown.

2.2. Pigment

Antimony trioxide, titanium dioxide (rutile) and talc were used. Zinc borates were used as substitute for antimony trioxide. Antimony trioxide is a well-known pigment for its fire resistance action. However, it by itself, is not effective; nevertheless, in combination with halogenated organic compounds, it shows an adequate flame-retardant behavior. Its mechanism of action is attributable to the interference on flame spreading velocity that produces antimony trichloride and/or antimony oxychloride generated during the fire spreading reaction.

Titanium dioxide improves the films hiding power; it also shows an important physical activity generated by decreasing the concentration of the organic part, dividing the material in isolated pieces by occupation of pores and amorphous polymer regions. Accordingly, a higher amount of heat is necessary in order to reach the pyrolysis temperature [12]. Talc has a satisfactory efficiency due to its high specific heat and low thermal conductivity. It contributes to adequate antisettling properties, excellent paintability, satisfactory levelling and also good water, humidity and chemical resistance.

The mechanism of action of each specific pigment is its predominant activity. However, from a practical point of view, fire-retardant pigments act combining one or more mechanisms.

Concerning zinc borates as partial or complete substitutes for antimony trioxide, they were prepared in the laboratory by reacting zinc oxide with boric acid according to these formulas: $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and $2ZnO \cdot B_2O_3 \cdot 7.5H_2O$. These pigments contain no free zinc oxide as to avoid the negative effect on the thermal stability of some halogenated compounds.

2.3. Pigment/binder ratio

In all cases, the pigment volume concentration (PVC) was 42.9% and, as a consequence, there was identical chlorine content in all of the paints.

2.4. Other components

Zirconium and cobalt naphtenates were used as drying agents, an electroneutral additive as dispersant and gel of bentone as thickener. White spirit was employed as the solvent.

3. Coating preparation

In the first stage, pigment, dispersant and thickening agent were added to the alkyd resin in solution (50% by weight in white spirit). Then, dispersion took place by employing a high speed bead mill and, finally, the drying agents were incorporated.

4. Fire retardancy evaluation

Test panels were prepared using a combustible material (Araucaria Angustifolia), which was conditioned for 6 months in a laboratory (average humidity, 6.8% and density, 0.497 g cm⁻³). Previous to the coating application, panels were carefully sandpapered on the faces and edges. Panels which showed knots or imperfections were not used. The first coat was applied diluting the sample with white spirit to 50% by weight. After 24 h of drying, two additional coats were given with a 24 h lapse between them. Final dry film thickness was 70–80 μ m. In all cases, application was done by brush.

After 10 days of air drying, panels under study were heated at 45–48°C for 24 h to eliminate the remaining solvent. A commercial alkyd paint, employed as the finishing coat of a conventional non-retardant scheme, was selected as the control. The performance of these paints were evaluated in a limiting oxygen chamber (LOI values), in a flame cabinet (Intermittent Bunsen Burner Rating) and in a two-foot flame tunnel (flame-spread index (FSI), Panel Consumption, after-flaming and after-glow).

5. Results and discussion

5.1. Thermal analysis of zinc borates

The thermogravimetric analysis (TGA), of zinc borates used as fire resistance pigments in the formulated flameretardant paints, was performed in a cell of alumina run under argon at 10° C/min (Fig. 1). The 2ZnO·3B₂O₃·3.5H₂O (2:3:3.5) shows high thermal stability: the water of hydration was retained up to 290°C, which indicates an absence of intersticial water in the crystal. A weight fraction of about 85.5% remained at 800°C displaying the highest weight loss between 290/510°C (the maximum rate of weight reduction was observed at 395°C). On the other hand, the $2ZnO\cdot3B_2O_3\cdot7.5H_2O$ (2:3:7.5) had an initial decomposition range lower than 2:3:3.5: the water of hydration stayed in the crystal up to 150°C; the total weight loss was 26.6% at 800°C and the highest rate was at about 195°C (the range of water loss was 150/620°C).

These TGA results were confirmed by using a differential thermal analyzer (DTA) at a programmed scanning rate of 10°C/min under an argon atmosphere: endothermic areas were observed at temperature ranges where weight loss took place.

5.2. Limiting oxygen chamber

To carry out the limiting oxygen index (LOI) test, the flow measuring system was calibrated using a water-sealed rotating drum meter; the gas flow rate in the column was 3.2 cm s^{-1} .

The LOI test, carried out according to ASTM D 2863 Standard, determines the minimum concentration of oxygen in a mixture with nitrogen that will just support combustion of a material under equilibrium conditions of candle-like burning. This method is not representative of the real behavior of a material in contact with fire but it is one method used in the development and improvement of fire-retardant treatments because it permits the obtainment of reproducible numerical values. This test was done in triplicate.

Results at 20°C of the LOI test are shown in Fig. 2. The experimental limit to qualify a sample as self-extinguishing is a LOI of 28% [7] and consequently all samples fulfilled that test requirement. Moreover, the analysis of results indicated a significant influence of fire-retardant pigments on



Fig. 1. TGA of zinc borates.



Fig. 2. LOI (commercial alkyd paint - LOI: 13%; coating: 9; LOI: 20%).

LOI values: it is preferable to use zinc borate in conjunction with antimony oxide for improving the coating performance (samples 2 through 5). A maximum LOI value was obtained with coating 5 including antimony oxide/zinc borate 2:3:3.5/zinc borate 2:3:7.5 as fire-retardant pigment (1/1/1 ratio), followed by coating 3 (antimony oxide/zinc borate 2:3:3.5/zinc borate 2:3:7.5, 2/1/1 ratio).

The total replacement of antimony oxide with zinc borates was in coatings 6–8. They also showed a self-extinguishing capability since their LOI values were higher than 28%, although inferior to coating 1 based on antimony oxide alone.

Coating 9 (iron oxide substituted completely antimony oxide and/or zinc borates) displayed a LOI value less than 28% and therefore it cannot be defined as self-extinguishing. In the absence of fire-retardant pigments the halogen-containing coating failed the LOI test.

Finally, the commercial alkyd used as a reference did not fulfill the test requirement and showed the lowest LOI value, 13%.

5.3. Flame cabinet

Table 2

The wood test panels of Araucaria Angustifolia (200 mm \times 100 mm \times 3 mm) were arranged in a Flame Cabinet according to UL 94 (Underwriters Laboratories Standard). The longitudinal axes of the coated panels were set with an inclination of 45° with respect to the supporting level while their transversal axes were in a parallel position.

The test, done in triplicate, consisted of submitting the front bottom area of the test panel to the intermittent flame of a bunsen burner vertically disposed. Flame was adjusted so as to reach 10 mm height of the blue cone. The exit hole of the burner was 25 mm of the testing surface.

The painted panel, in the above-mentioned position, was submitted to flame action for 10 s with resting periods of 20 s. The exposure cycle fire/resting was repeated until the flame did not extinguish during the latest stage. The number of self-extinguishing cycles was determined qualifying each of them with the scale included in Table 2. Then, the total points for each panel and the average of the three panels were calculated. The qualification and classification of paints were made according to what is established in Table 3.

Results of the exposure to the intermittent flame test are shown in Table 4. The values obtained in these experiments corroborate the conclusions reached in the LOC in relation with the influence of studied variables. Thus, when the Table 3

Qualification and classification of the coatings

Average rating in intermittent flame test	Coating qualification	Coating classification	
100 or more	Passed	Class A	
70–99	Passed	Class B	
30–69	Failed	Class C	
29 or less	Failed	Class D	

Table	4
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Intermittent flame test res	ults (qualification a	and classification of	f coatings)
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Sample	Rating ^a	Coating qualification	Coating classification
1	127	Passed	Class A
2	132	Passed	Class A
3	135	Passed	Class A
4	127	Passed	Class A
5	142	Passed	Class A
6	112	Passed	Class A
7	107	Passed	Class A
8	117	Passed	Class A
9	48	Failed	Class C
Commercial alkyd paint	2	Failed	Class D

^a Average of three values.

replacement of antimony trioxide by zinc borates was partial (coatings 2–5), generally, formulated paints showed an improvement in their performance (coating 1). The effect of endothermic zinc borates was also very significant both to increase the fire resistance and to control the flame spreading in this test.

The total substitution of antimony oxide with zinc borates led to samples (coatings 6–8) which passed this test, although with reduced performance. All samples with antimony oxide and/or zinc borates were classified in Class A.

Sample 9 and the commercial alkyd paint failed and they were located in Classes C and D, respectively. Both of them continued to burn on completion of the test and they are considered to be highly flammable.

5.4. Two-foot flame tunnel

The apparatus consists of a $600 \text{ mm} \times 100 \text{ mm}$ section of angle iron with a central channel 64 mm wide. The angle iron, which is inclined 28° from the horizontal, is boxed underneath. The specimen is placed with the coated side

Classifica	tion used for evaluating coating behavior ^a
10	During the test there is no flame except the burner. The carbonized zone does not exceed 3 cm^2
7	Five seconds after the burner flame is shut off, there is no persistent flame on the surface. The carbonized zone does not exceed 6 cm^2
5	Five seconds after the burner flame is shut off, there is no persistent flame on the surface but in ignition points over the carbonized zone that lingers for 10s as maximum lapse of time. The carbonized zone does not exceed 12 cm^2
2	Five seconds after the burner flame is shut off flame persists: the test is considered a failure

^a The fire/resting exposition cycle is repeated if the qualification is equal or superior to 5.

Table 5			
Two-foot tunnel	test performance	of experimental	coatings ^a

Number of sample	FSI	Panel consumption (%)	After-flaming (s)	After-glow (s)
1	0.39	2.82	0	0
2	0.31	2.33	0	0
3	0.15	2.31	0	0
4	0.23	2.42	0	0
5	0.08	2.01	0	0
6	0.49	3.23	1	0
7	0.54	3.52	1	0
8	0.51	3.47	1	1
9	0.65	4.12	1	1
Commercial alkyd paint	1.23	9.78	160	4
Bare substrate (Araucaria Angustifolia)	1.00	7.18	2	1

^a Average of three values.



(a)



(b)



(c)

Fig. 3. (a) Coating 5, based on antimony trioxide/zinc borate 2:3:3.5/zinc borate 2:3:7.5 (1/1/1 ratio), showed the best performance in two-foot tunnel test (FSI 0.08). (b) Coating 3, based on antimony trioxide/zinc borate 2:3:7.5 (2/1 ratio), displayed a very good efficiency in two-foot tunnel test (FSI 0.15). (c) Bare substrate (Araucaria Angustifolia), left, and commercial alkyd paint, right, tested in two-foot tunnel (FSI 1.00 and 1.23, respectively).

down on the angle iron over a burner and exposed to the flame for 4 min; then the mean of the three highest consecutive readings in inches of the flame advance is calculated (measured at 15 s intervals). The FSI is computed by using the following equation:

$$FSI = \frac{L_s - L_a}{L_b - L_a}$$

where FSI is the flame spread of painted panels, L_s is the mean of three-flame advance readings of painted panel, L_a the mean of three flame advance readings of asbestos-cement board (zero-flame spread) and L_b the mean of three flame advance readings of bare wood panel (Araucaria Angustifolia).

Other measurements were also carried out to evaluate the comparative performance of experimental flame-retardant coatings:

Panel consumption: measure of the weight of material consumed during the test (it includes both losses of the substrate and any of the fire-retardant chemicals).

After-flaming time: time, in seconds, that flaming continues on the face of the test panel after the burner flame is shut off (it operates for an additional 60 s after making the last of the readings every 15 s).

After-glow time: additional time, in seconds, that the surface of the panel continues emitting light (glows) after the flame is shut off.

Results obtained in the two-foot flame tunnel are displayed in Table 5 and are the average of three determinations. These values also indicate differences in the behavior of the experimental coatings. The FSI shows that the best performance corresponded to sample 5 (the lowest value of the series, Fig. 3a), followed by coatings 3 (Fig. 3b), 4, 2 and 1, in this order (antimony oxide/zinc borates as the fire-retardant pigment). On the other hand, the worst behavior of experimental coatings was displayed by sample 9 (without fire-retardant pigment); coatings 6, 7 and 8 had an intermediate performance.

The commercial alkyd paint showed even a lesser effectiveness than paint 9; its FSI was higher than 1 which implies that the reference paint increased the fire-spreading of bare substrate (Fig. 3c).

The FSI and the other measurements in the two-foot tunnel (Table 5) are in close agreement. Besides, they corroborate the conclusions attained in the LOC and in the flame cabinet.

6. Conclusions

 After burning, paints including zinc borates in their composition as fire-retardant pigment generate anhydrous compounds which undergo vitrification inhibiting further oxidation of the char; on the other hand, antimony oxide (a vapor-phase flame retardant) has little effect on char formation.

- Antimony oxide as a synergistic additive in chlorinecontaining resin and the zinc borates, due to endothermic behavior, is the main argument for explaining the excellent performance of some experimental paints determined by the various procedures mentioned in this paper.
- Zinc borate 2:3:7.5 outperforms the behavior of 2:3:3.5. This fact would be explained by the results of thermal analysis. The higher number of hydrated water molecules, when released at high temperatures, can diffuse and absorb a greater amount of heat (2:3:7.5 cools the surface better than the 2:3:3.5) which increases flame resistance and retards heat built up.
- Interestingly, the total substitution of antimony oxide with zinc borates allows the formulation of successful flame-retardant paints, although with an inferior performance but with a better cost/efficiency ratio.
- The chlorinated alkyd resin used in this experiment releases only 0.28% (w/w) of HCl gas in the complete combustion (the carbon–chlorine bonds on the aromatic chlorendic anhydride are relatively strong and require severe conditions for HCl to be produced). Although this amount of HCl is very low, it could produce an intense metallic corrosion after the conflagration by dissolving in condensed water on surfaces (i.e. on electronic systems where the clean up after the fire is very difficult). The presence of zinc borates in flame-retardant coatings would give the following chemical reaction of neutralization:

$$2\,ZnO\cdot 3B_2O_3+12\,HCl$$

$$\rightarrow$$
 Zn(HO)Cl + ZnCl₂ + BCl₃ + 3HBO₂ + 4H₂O

and, consequently to avoid or at least to control the HCl volatilization during the combustion. Experimental coating 1 released about 0.10% (w/w) of HCl in a total combustion while in the other samples this value was less than 0.02% (w/w).

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