

# PHOSPHORUS-BASED INTUMESCENT COATINGS

## *PINTURAS INTUMESCENTES BASADAS EN PRODUCTOS FOSFORADOS*

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### SUMMARY

*Fire is an energetic manifestation which carries undesirable consequences due to the problems that it originates. The conflagration is a disagreeable fact produced by fire.*

*The main objective of a fireproofing treatment is to make a material hardly flammable or autoextinguishable. An efficient fireproofing effect interrupts the combustion in one or more stadiums, leading the process to end in a reasonable period (preferably before ignition occurs).*

*Intumescent coatings, as a means of passive protection against fire, perform a fundamental role in this matter. Dry films of these paints, submitted to flame action, softens in a first stage and then swells due to an internal and partial loosing of non combustible gases, reaching up to 200 times of its original thickness. The charred coat, an incombustible spongy mass, protects the painted material, delays the temperature increase and avoids the access of air, and so the combustion. By means of intumescent coatings, different materials such as paper, wood, pasteboard, plastics, metals, etc. can be protected.*

*The objective of this paper was to study the influence of some formulation variables of phosphorus-based intumescent coatings, formulated and manufactured for this experiment. Chlorinated rubber coatings based on ammonium polyphosphate, pentaerythritol, melamine, 42 % chlorinated paraffin and an endothermic filler showed very high performance after ageing.*

**Keywords:** *intumescence, intumescent coating, fire resistance, thermal protection*

### INTRODUCTION

Fire loss is one of the major tragedies of modern civilization. Fire-resistant construction is an important factor since severe conflagrations have occurred in so-called fireproof buildings because highly combustible decorations and finishing materials have contributed to propagate the fire.

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Taking into account the actual methods, it is important to mention that some of them show a performance independent of the human activity and besides that they are not conditioned by the adequate functioning of the installation. These methods are included in the generic concept of “passive protection against fire”, so the decrease of material flammability performs a fundamental role.

Among these methods, the fire protection by intumescent coatings has an important place reserved. When heated, these coatings become plastic and produce non-flammable gases such as carbon dioxide and ammonia; the gases are trapped by the film converting it to a foam 50, 100 or in some cases 200 times thick in relation to the original coat film. At this stage the system solidifies, resulting in a thick, highly-insulating layer of carbon, which effectively protects the substrate from the fire.

Although, no building material is immune to the action of a fire of sufficient intensity and duration, the use of efficient fire-retardant coatings can reduce the severity of fire or delay its effects. On the other hand, the accumulation of multiple layers of conventional coatings can provide material to spread the fire.

As almost all the protecting methods, the employ of fire-retardant coatings was object at different moments of hardly controversial opinions by the protectionists since each one of these methods has both defenders and detractors. Intumescent coatings are a good example of that above mentioned; the fact of the existence of bad coatings or else of inadequate applications must not cause the disapproval. Continuous research work in this field has permitted to overcome some of these controversial aspects of the intumescent coatings.

The object of the present paper was to study the influence of some formulation variables of intumescent coatings and also to evaluate their fire-retardant properties after ageing.

## FORMULATION OF INTUMESCENT COATINGS

The formulation of an intumescent coating is difficult because of its dual role in service; it must possess adequate decorative properties but in the case of a fire, the intumescent layer must swell up within seconds to give a protective barrier on the substrate. To produce that phenomenon of intumescence, the following components were selected:

**A coal supplier or carboniferous agent.** A carbonific or a source of carbon (sometimes termed char former) is generally chosen from polyfunctional alcohols. To be effective, it must contain hydroxyl groups and a high percentage of carbon.

The combustion of pure polyalcohols is generally of exothermic type; they decompose generating different carbon oxides, water vapor and incombustible remainders. Nevertheless, polyalcohols can react under the action of heat with certain inorganic acids producing phosphorated esters. In these circumstances the degradation is difficult considering that the reaction becomes endothermic, neither flame nor flammable residues are formed, and combustible gases formation is greatly reduced; thus, fire developing is limited.

The coal supplier, which forms the carbon skeleton of the intumescent layer, must be more thermally stable than the catalyst. In this paper, **pentaerythritol** was selected since it showed a very good performance in many studies carried out by several authors [1-6].

**A dehydrating agent.** A catalyst or a source of phosphoric acid, which decomposes giving the necessary products so as to modify the pyrolysis of the coal supplier, is usually used for this purpose. The catalyst should contain a high phosphorus content and must decompose to yield phosphoric acid at a temperature below at which the carbonific does. Generally, phosphoric acid salts, polymers of these salts as well as organic compounds, derivatives or not of this acid, are used.

The dehydrating agent decomposes liberating phosphoric acid and forming esters with hydroxyl groups of the carboniferous agent, which then transform themselves in phosphoric esters showing the above mentioned characteristics against fire.

Monoammonium phosphate was initially employed as dehydrating agent according to the satisfactory results obtained in the intumescent-isolating coat formation. Moreover, in wet zones or exteriors, coatings based on monoammonium phosphate lose their swelling capacity with time, and also show an efflorescence that alters the paint film decorative characteristics; the high solubility of this salt, that facilitates its diffusion to the surface, is the responsible of the mentioned disadvantages.

Studies trying to obtain more insoluble dehydrating agents, by polymerization of products like ammonium phosphate or by elaborating of phosphorus compounds of organic type, are carried out since a long time. Two commercial **ammonium polyphosphates** (catalysts C1 and C2), previously characterized in laboratory tests, were employed in this paper.

**Blowing agents.** These are the source of the gases; they decompose by thermal action liberating non combustible gases that swell paint film. This additive is generally based on nitrogenous products, like melamine, dicianamine or organic compounds partially halogenated like chlorinated paraffins.

The three mentioned compounds can not be chosen in an arbitrary form; the dehydrating agent or the catalyst must have a decomposition temperature near to the blowing agent. For example, if the last one works at a temperature noticeable superior to the catalyst, a carbonaceous mass without expanding would be formed, without a spongy consistence and so would not have a low thermal conductivity; on the contrary, if the blowing agent decomposition temperature is too low, gases liberate before carbonaceous mass is formed. Two different generators of gases were included in this experiment so as to extend the period of volatile products: **melamine and 42 % chlorinated paraffin**. The last one also acts as plasticiser of the selected resin.

Regarding the other components, they were:

**Resinous binder.** The film forming material must be thermoplastic. Some convertible resins, such as drying oil alkyds can not be softened sufficiently by heat to allow the foam to expand.

In this experiment, **20 cP chlorinated rubber** was employed as binder. Dry films based on this resin show a noticeable thermal decomposition at approximately 130 °C and a complete charring (without melting) at about 200 °C. Chlorinated rubber also assists as a blowing agent and a source of carbon.

To select the mentioned binder, the following properties were taken into account: it softens and decomposes below the activation temperature of the intumescent agent and also it contributes during thermal activation to the stability of the intumescent foam produced by the agent. Besides, it is nonburning and self-extinguishing when exposed to a flame.

**Pigment.** The incorporation of a non-flammable pigment leads to a limited degree of fire protection. The pigment only dilutes the combustible organic binder to the extent that the flame spread is reduced or at least is not increased. On the other hand, unpigmented coatings often show a higher flame spread than the combustible substrate. In addition to the diluting effect before mentioned, some pigments perform a physical-chemical role to control the fire.

In this paper, **rutile titanium dioxide** was used in all formulations to achieve adequate hiding power. In some compositions, titanium dioxide was partially replaced by fillers: **alumine trihydrate** or **modified barium metaborate**.

From a quantitatively point of view, considerable technical effort is required to optimize the composition since intumescent coatings not only must show excellent fire retardant properties but also adequate decorative qualities. It is necessary to incorporate large amounts of active pigments to attain the best efficiency since the fire retardancy and degree of intumescence are directly affected; however, the high loading of solids in an intumescent coating can lead to poor serviceability, simply because the film is porous if the pigment volume concentration (PVC) is too far above its critical value (CPVC). In this paper, the considered PVC values were 60 and 65 %.

The composition of six intumescent coatings is included in Table I.

## MANUFACTURE OF INTUMESCENT COATINGS

It was performed at laboratory scale in triplicate by employing a porcelain jar ball mill of 1.0 liter of total capacity. The operative conditions of the ball mill were specially considered with the aim to achieve an efficient pigment dispersion [7].

First, a solution of binder in the solvent mixture was prepared under stirring. The ball mill was loaded with the mentioned solution and the pigments were added; these components were milled for 24 hours previous incorporation of a dispersant in the quantity indicated by the manufacturer. Finally, the viscosity was adjusted in the can.

## LABORATORY TESTS

A great variety of test methods are known to evaluate the material behavior exposed to fire [8-13]. The main characteristic that distinguishes them is the way of determining the

performance of a phenomenon or situation, fire or conflagration, that does not adjust to preestablished laws and in which different variables have a great influence.

**Table I**

**Intumescent coating composition\*, % v/v**

| <b>Component</b>           | <b>I</b> | <b>II</b> | <b>III</b> | <b>IV</b> | <b>V</b> | <b>VI</b> |
|----------------------------|----------|-----------|------------|-----------|----------|-----------|
| Ammonium polyphosphate C1  | 51.5     | --        | 51.5       | --        | 51.5     | --        |
| Ammonium polyphosphate C2  | --       | 51.5      | --         | 51.5      | --       | 51.5      |
| Pentaerythritol            | 18.9     | 18.9      | 18.9       | 18.9      | 18.9     | 18.9      |
| Melamine                   | 18.2     | 18.2      | 18.2       | 18.2      | 18.2     | 18.2      |
| Titanium dioxide           | 11.4     | 11.4      | 7.4        | 7.4       | 7.4      | 7.4       |
| Modified barium metaborate | --       | --        | 4.0        | 4.0       | --       | --        |
| Alumina trihydrate         | --       | --        | --         | --        | 4.0      | 4.0       |
| 20 cP chlorinated rubber   | 62.8     | 62.8      | 62.8       | 62.8      | 62.8     | 62.8      |
| 42 % chlorinated paraffin  | 37.2     | 37.2      | 37.2       | 37.2      | 37.2     | 37.2      |

Note: Samples with PVC 60.0 % (1.I/VI) and with PVC 65.0 % (2.I/2.VI). Solvent and diluent, C9 aromatic hydrocarbon/white spirit (4/1 ratio by weight). Additives, 2.3 and 2.4 % v/v on solids for samples 1.I/VI and 2.I/2.VI, respectively

Fire resistance can be determined by exposing the material to a small ignition or heat source. The reaction to fire embraces an extensive amount of possibilities according to test conditions, where material interaction, design and utility must be reflected.

### 1. Limiting Oxygen Index

SAE 1010 test panels (150 x 80 x 2 mm) were used. The surface (initial grade A) was sandblasted to Sa 2 ½ (SIS 05 59 00-67 Specification) attaining 20 µm maximum roughness and then degreased with toluene. The experimental intumescent coatings were brushapplied achieving about 260-280 µm dry film thickness in three coats; each coat was applied with a 48 hours period between them.

The coated panels remained at laboratory conditions for 10 days and then they were carried out to stove at 40/45 °C for 24 hours to eliminate the most quantity of the remaining solvent.

With the aim to study the intumescent coating behavior after exposure to a high humidity environment, panels were placed in an enclosed chamber containing a heated, saturated mixture of air and water vapor (100 % relative humidity chamber, ASTM D 2247-92) for 500 hours. Then the coated panels were kept in laboratory for 10 days for film drying before starting the test.

To carry out the Limiting Oxygen Index (LOI) test, the flow measuring system was calibrated by using a water-sealed rotating drum meter, the gas flow rate in the column was  $4 \text{ cm.s}^{-1}$ .

LOI test, carried out according to ASTM D 2863-87 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. It is important to mention that this method is not representative of the real behavior of a material in contact with fire but it is one method of preference in the development and improvement of fire retardant treatments due to it permits the obtainment of reproducible numerical values. This test was done in triplicate.

## **2. Intermittent Bunsen burner flame**

The necessity of determining the efficiency of the formulated coatings led to the development of a comparative method. For this aim a combustible substrate was used (*Araucaria angustifolia*). Test panels of  $200 \times 100 \times 3 \text{ mm}$  were carefully sandpapered in both faces and edges. The selected panels remained at laboratory conditions for 6 months (free of knots and any other imperfections).

Intumescent coatings were applied by brush on the panels. The first coat was constituted by the selected sample previously diluted to 50 % by weight in order to fill surface pores; the film was let to dry at laboratory conditions for 24 hours and then another two coats were applied, with 48 hours between them, reaching to a final dry film thickness about 210-230  $\mu\text{m}$ .

The conditions of film drying and exposure to 100 % relative humidity chamber were similar to those employed to determine LOI values.

The test panels were arranged in a Flame Chamber, whose characteristics are in according to UL 94 Underwriters Laboratories Standard. In this experiment, the coated panels were placed in such way that their longitudinal axes showed an inclination of 45 degrees with respect to the supporting level while their transversal axes were in a parallel position.

The test done in triplicate consisted of to submit the front bottom part of the panel to the intermittent flame of a Bunsen burner vertically disposed. Flame was adjusted so as to reach 10 mm height of blue cone. The exit hole of the burner was arranged at 15 mm of the testing surface.

The painted panel, fitted in the mentioned position, was submitted to flame action for 20 seconds, with resting periods of 10 seconds. The exposure fire/resting cycle was repeated until the flame persisted on the surface at least 5 seconds after removing the burner.

When the number of cycles with self-extinguishing behavior reached the value 30 (stage A), the flame action was extended to 50 seconds with 10 seconds of resting (stage B) and if the self-extinguishing continued after other 35 cycles in the cited conditions, the flame was kept in a constant way (stage C) until 30 minutes as maximum. The number of cycles with a self-extinguishing behavior was determined, qualifying each of them with 1 and 2 points for

stages A and B respectively and 5 points for each minute corresponding to stage C. Then, the whole amount of each panel and also the average results of the three panels were calculated.

### **3. Thermal conductivity test**

It is very important for these coatings to determine the thermal conductivity of a coated panel exposed to a fire. It is possible to evaluate the thermal isolation degree produced by the intumescent coating registering the temperature decrease on the backface of the panel.

In this experiment SAE 1010 test panels (200 x 300 x 3 mm) were used. The test was carried out on panels prepared in a similar form than those used for evaluating the Limiting Oxygen Index. The samples were placed in the before mentioned UL 94 Flame Chamber avoiding air currents.

A bare panel selected as reference was fitted in horizontal position. The measuring system (thermoelectric couple) was fixed on the superior face of the panel. The Bunsen burner was vertically disposed at the inferior face; the flame was adjusted so as to reach 10 mm height of the blue cone and the exit hole of the burner was arranged at 15 mm from the surface.

Above mentioned panel was exposed to a fire regulating the flame intensity up to cover an area of 6-8 cm diameter bringing a constant temperature of  $400 \pm 05$  °C at the backface. It is registered from the beginning the functionality of the temperature with time to develop the calibrating curve.

This operation was exactly repeated for each one of the coated panels registering the temperature evolution during 25 minutes.

For the three mentioned tests, that means for LOI, Intermittent Bunsen burner flame and thermal conductivity, a commercial alkyd paint was used as reference.

## **RESULTS AND DISCUSSION**

### **Characterization of ammonium polyphosphates**

In general, catalysts showed similar characteristics (Table II), particularly regarding high phosphorus content in their composition which could lead to a great release of phosphoric acid upon decomposition. However, the water solubility is markedly different: the ammonium polyphosphate C1 displayed the value 13.7 g/100 g at 25 °C, higher than that correspondent to catalyst C2 (4.2 g/100 g), at the same temperature.

Concerning thermogravimetric analysis (TGA), the curves obtained with the detector Shimadzu TGA-50 H (run under Argon at 10 °C/min, cell of alumina) are shown in Figures 1 and 2. Both catalysts demonstrated the highest thermal stability in the initial decomposition range (below about 200 °C); then they undergo a gradual weight loss, diminishing in rate to about 500 °C and in the limit of thermogravimetric analysis (temperature higher than 800 °C);

in this region the weight appears to be leveling off in the both cases. Moreover, in the entire temperature range of testing, the catalyst C2 showed a higher thermal stability than catalyst C1.

**Table II**  
**Characteristics of ammonium polyphosphates**

| Property                             | Catalyst C1  | Catalyst C2  |
|--------------------------------------|--------------|--------------|
| Form                                 | White powder | White powder |
| Phosphorus, % P                      | 30.6         | 31.4         |
| Nitrogen, % N                        | 14.1         | 14.3         |
| Water solubility at 25 °C, %         | 13.7         | 4.2          |
| pH of saturated solution             | 5.9          | 6.6          |
| Specific gravity, g.cm <sup>-3</sup> | 1.82         | 1.72         |
| Oil absorption, g/100 g              | 76           | 81           |
| Diameter (50.0/50.0 %), μm           | 17.2         | 22.3         |

Figure 3 displays the theoretical chemical mechanism of two dehydrating agents during a conflagration; to simplify, the composition is expressed as  $(\text{NH}_4)_2\text{HPO}_4$ .

### Thermal analysis of pigment

The determination of the endothermic and exothermic reaction temperatures for the inorganic pigments was performed by using the detector Shimadzu Differential Thermal Analyzer (DTA) at a programmed scanning of 10 °C/min under argon atmosphere. Moreover, thermogravimetric analysis (TGA) was also carried out on the pigment, in the before mentioned conditions for the catalysts.

Concerning hydrated aluminium oxide pigment, it is a white crystalline product of extremely fine and uniform particle size. Chemically, it is considered either as aluminium oxide combined with three molecules of water hydration or as aluminium hydroxide. Technically, the latter is correct since the hydrated alumina consists of three hydroxyl ions in co-ordination with an aluminium ion. However, since water molecules (34.6 % W/W) can be driver off at elevated temperatures, hydrated aluminium oxide is the commonly preferred name.

When hydrated alumina is heated to a high temperature, it releases its water of hydration that in turn acts to dissipate heat; it does not actually extinguish fire, but the heat absorbed during the release of the water of hydration increases flame resistance and retards heat build up [14].

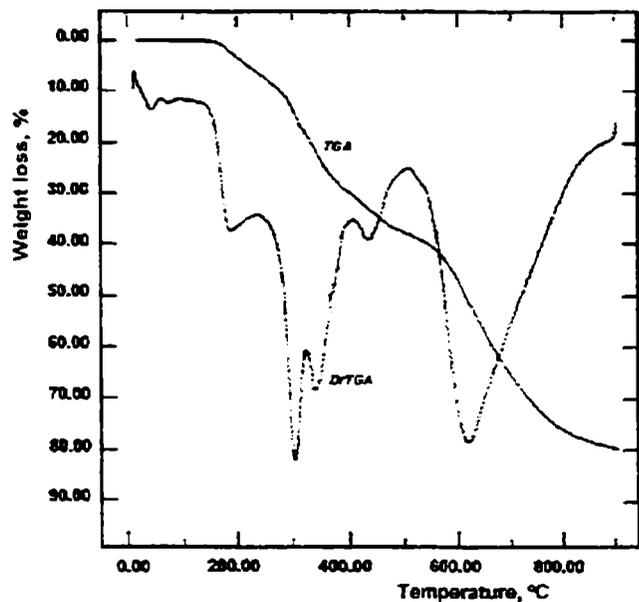


Fig. 1.- Thermogravimetric analysis (TGA) of ammonium polyphosphate C1 (heating rate 10°C/min; 30 ml Argon/min).

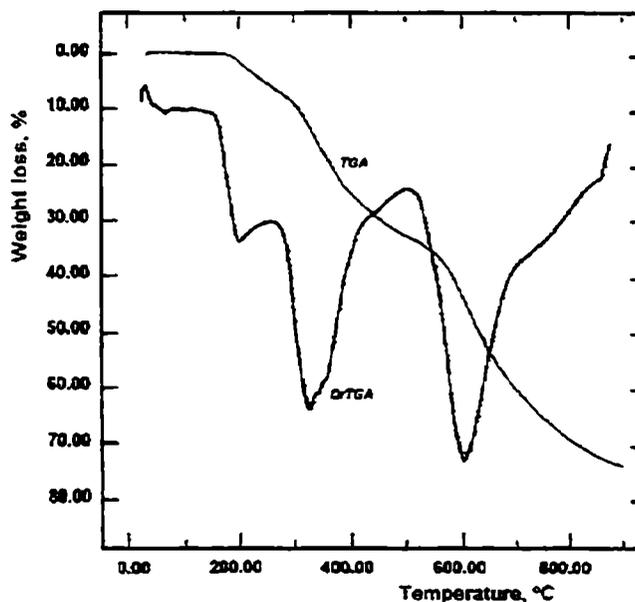


Fig. 2.- Thermogravimetric analysis (TGA) of ammonium polyphosphate C2 (heating rate 10°C/min; 30 ml Argon/min).

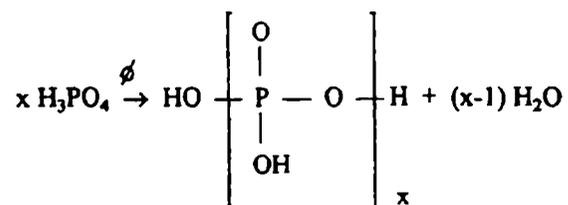
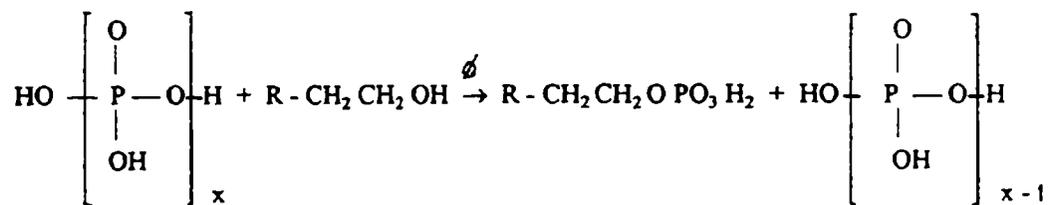
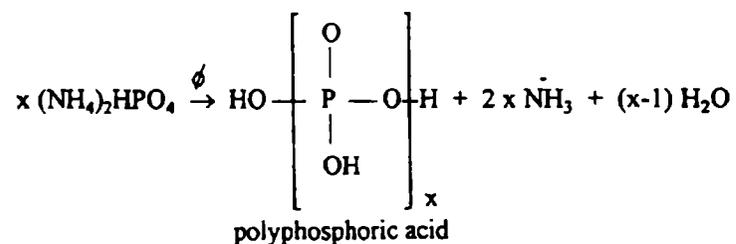


Fig. 3.- Theoretical reactions between the catalyst and the coal supplier

The DTA and TGA curves of the hydrated aluminium oxide are shown in Figures 4 and 5, respectively. The Fig. 4 indicates three regions of endothermic activity; the first occurs at about 242 °C, the second appears from 250 to 350 °C with a maximum endothermic peak approximately at 311 °C and the other near to 538 °C. These results were confirmed by TGA which also shows a weight fraction of 64.5 % remaining at 800 °C for this endothermic filler.

In relation with barium metaborate used as filler in some intumescent coatings, its commercial form is a modified pigment that contains a minimum of 90 % of barium metaborate calculated as  $BaB_2O_4 \cdot H_2O$ . It acts as both a flame retardant and an afterglow inhibitor and has a mode of action typical of all boron compounds.

Figure 6 displays the differential thermal analysis of modified barium metaborate; it can be seen from the thermal profile obtained that this filler does not indicate a large exothermic or endothermic behavior in the desired temperature range.

Moreover, from thermogravimetric analysis of this pigment it is possible to conclude that it has good heat stability since it does not decompose at high temperatures. Figure 7 shows near to 9.0 % weight loss at 600 °C with a heating rate of 10 °C/min.

It is important to mention that both fillers, hydrated aluminium oxide and modified barium metaborate, have low water solubility and hence a great permanence in the film under exterior weathering conditions. Moreover, they do not produce toxic fumes when heated.

Finally, rutile titanium dioxide used as pigment in all the formulations can yield a high refractive index as well as chemical and physical stability. Its ability to opacity might be considered a major optical property. TGA indicates that titanium dioxide is extremely stable at high temperatures, Figure 8. This exceptional stability can be attributed to the strong bond between the tetravalent titanium ion and the bivalent oxygen ions. Moreover, it is water insoluble.

### **100 % relative humidity testing**

The degree of blistering and film adhesion were assessed on coated metallic panels aged in a 100 % relative humidity chamber for 1500 hours. The mean values are indicated in Table III.

The degree of blistering was evaluated according to ASTM D 714-87. The blister size is qualified with reference standards from 10 to 0, where 10 represents no blistering, 8 is the smallest blister size easily seen by the unaided eye, 6, 4 and 2 indicate progressively larger sizes. The frequency is qualitatively defined as F (few), M (medium), MD (medium dense) and D (dense). Observed blistering corresponded to the osmotic phenomenon, that is the blistering exclusively developed by water diffusion through the paint film and not from rusting.

As expected, the blister resistance was significant due to the high permeability showed by the coatings formulated with high PVC values: in these films the water can readily escape to the outside surface without the loss of film adhesion.

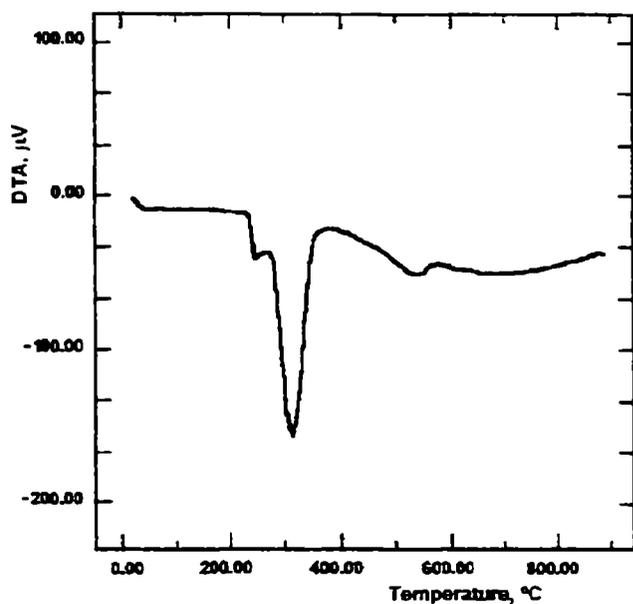


Fig. 4.- Differential thermal analysis (DTA) of hydrated aluminium oxide (heating rate 10 °C/min; 30 ml Argon/min; sample weight 20.25 mg).

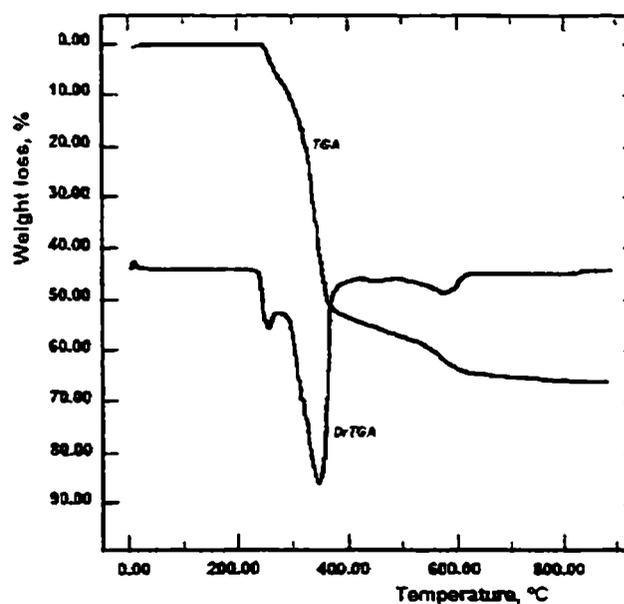


Fig. 5.- Thermogravimetric analysis (TGA) of hydrated aluminium (heating rate 10 °C/min; 30 ml Argon/min).

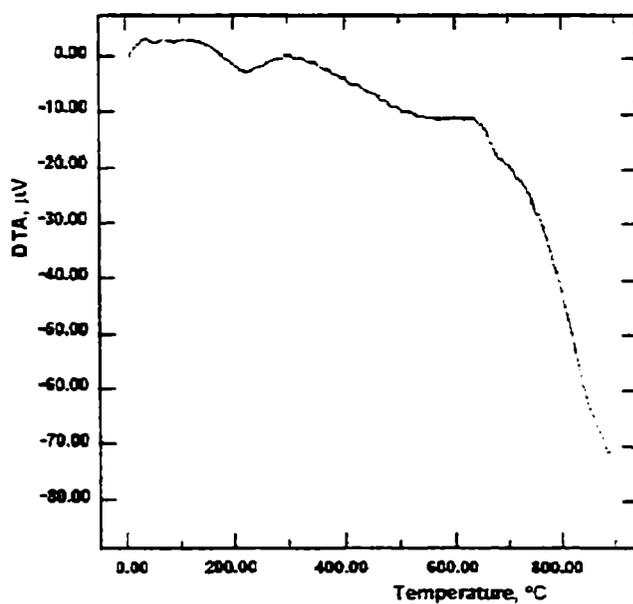


Fig. 6.- Differential thermal analysis (DTA) of modified barium metaborate (heating rate 10 °C/min; 30 ml Argon/min; sample weight 9.52 mg).

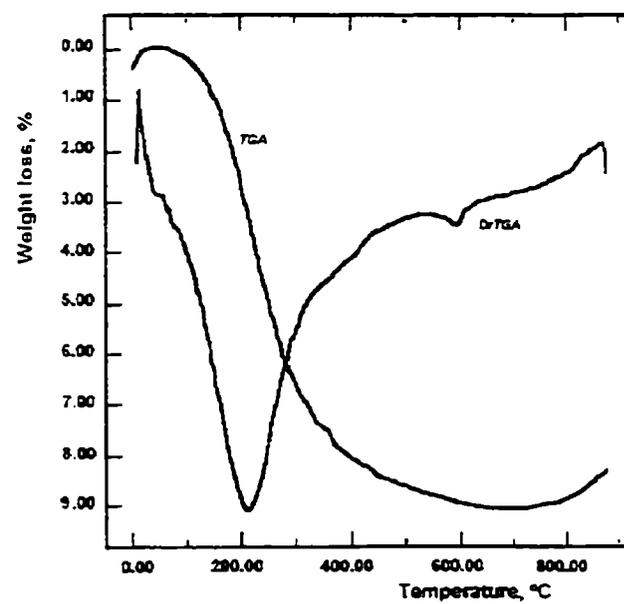


Fig. 7.- Thermogravimetric analysis (TGA) of modified barium metaborate (heating rate 10 °C/min; 30 ml Argon/min).

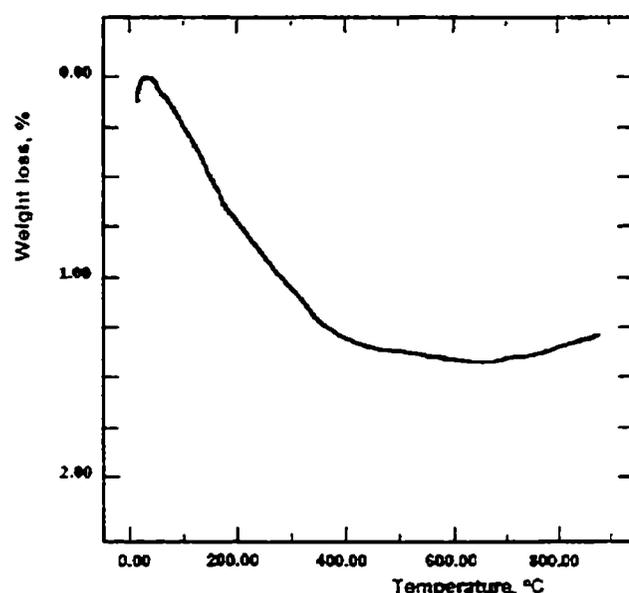


Fig. 8.- Thermogravimetric analysis (TGA) of titanium dioxide (heating rate 10 °C/min; 30 ml Argon/min).

To determine film adhesion, the Elcometer Tester Model 106 was used. The dolly bonded to the coating under test is subjected to progressively increasing stress at a constant rate until it fractures: dragging indicator retains the maximum pull of force reached. Near to 20 determinations at room temperature ( $20 \pm 2$  °C) were made for each intumescent coating to minimize the scattering of the results. The fracture values were expressed related to corresponding original coating (adimensional unit), Table III.

Table III

**Degree of blistering and film adhesion  
Limiting Oxygen Index**

| Coating                | PVC, % | Degree of blistering<br>(1) | Film adhesion<br>(1, 2) | LOI <sup>**</sup> (3), % |
|------------------------|--------|-----------------------------|-------------------------|--------------------------|
| 1.I                    | 60.0   | 9-F                         | 0.7                     | > 50                     |
| 1.II                   |        | 9-F                         | 0.9                     | > 50                     |
| 1.III                  |        | 10                          | 0.8                     | > 50                     |
| 1.IV                   |        | 10                          | 0.9                     | > 50                     |
| 1.V                    |        | 9-F                         | 0.7                     | > 50                     |
| 1.VI                   |        | 10                          | 0.9                     | > 50                     |
| 2.I                    | 65.0   | 10                          | 0.8                     | > 50                     |
| 2.II                   |        | 10                          | 0.9                     | > 50                     |
| 2.III                  |        | 10                          | 0.7                     | > 50                     |
| 2.IV                   |        | 10                          | 0.9                     | > 50                     |
| 2.V                    |        | 10                          | 0.7                     | > 50                     |
| 2.VI                   |        | 10                          | 1.0                     | > 50                     |
| Commercial alkyd paint |        | 4-D                         | 0.5                     | 13                       |

(1) 100 % relative humidity chamber (ASTM D 2247-92). 500 hours

(2) Relative to original coating (adimensional unit)

(3) Normal velocity, 4.0 cm.s<sup>-1</sup>

Results display high values of film adhesion, since they range between 0.7 and 1.0, that is the coatings retained approximately from 70 to 100 % of the original fracture values after ageing.

Since all coated panels showed a reasonable behavior in the two tests carried out after ageing, the whole of them were selected for evaluating their fireproof capacity.

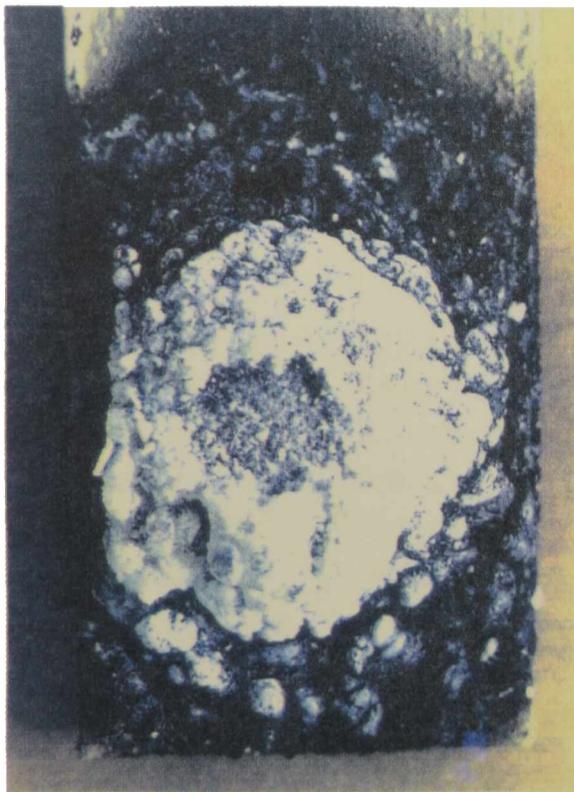
### **Limiting Oxygen Index**

Experimental results corresponding to LOI test are also shown in Table III; all samples were tested in triplicate at about 20 °C and showed a self-extinguishing capability since their Limiting Oxygen Index was higher than that corresponding to the experimental limit for this type of chamber LOI 28 % [3].

This test did not allow to establish the influence of the formulation variables considered in this study since all the intumescent coatings displayed a very good performance, LOI > 50 %.

### **Intermittent Bunsen burner flame**

Coating qualification and classification was carried out according to Table IV. Average results of the exposures to the intermittent flame test are shown in Table V.



**Fig. 9.- View of panel for testing. Coating 2.II after finishing Intermittent Bunsen burner flame.**



**Fig. 10.- View of reference panel protected with commercial alkyd paint, Intermittent Bunsen burner flame test.**

All the experimental coatings showed a significant intumescence and a quite uniform development. Only in a few cases a slightly depression attributable to the flame pressure was observed; the insulating layers remained firmly adhered to the substrate in all the panels.

Referring to average height of the intumescence, values ranged between 5 and 9 mm for coatings 1.I/1.VI (PVC 60.0 %) and between 11 and 16 mm for coatings 2.I/2.VI (PVC 65.0 %), Table V. Fig. 9 shows a panel protected with coating 2.II after finishing the test.

**Table IV**

**Coating classification**

| Average rating in intermittent flame test | Coating Qualification | Coating classification |
|---|-----------------------|------------------------|
| 200 or more                               | Passed                | Class A                |
| 100 to 199                                | Passed                | Class B                |
| 70 to 99                                  | Passed                | Class C                |
| 30 to 69                                  | Failed                | Class D                |
| 29 or less                                | Failed                | Class E                |

Pigment volume concentration had a definite effect both on flame retardant properties and on the height of the intumescence. Moreover, the type of catalyst showed a significant influence on fireproofing capacity of films exposed to adverse humidity conditions. Coatings with the best performance in this test were formulated with ammonium polyphosphate C2: the whole of them were classified as class A and in all cases their behavior as fire retardant was higher than samples with ammonium polyphosphate C1 in their composition.

**Table V**

**Intermittent flame test results**

| Coating    | Average value | Intumescence, mm | Coating qualification | Coating classification |
|------------|---------------|------------------|-----------------------|------------------------|
| 1.I        | 140           | 5/6              | Passed                | Class B                |
| 1.II       | 205           | 8/9              | Passed                | Class A                |
| 1.III      | 175           | 6/7              | Passed                | Class B                |
| 1.IV       | 225           | 8/9              | Passed                | Class A                |
| 1.V        | 155           | 5/6              | Passed                | Class B                |
| 1.VI       | 245           | 8/9              | Passed                | Class A                |
| 2.I        | 180           | 12/13            | Passed                | Class B                |
| 2.II       | >250          | 15/16            | Passed                | Class A                |
| 2.III      | 220           | 11/12            | Passed                | Class A                |
| 2.IV       | >250          | 15/16            | Passed                | Class A                |
| 2.V        | 190           | 12/13            | Passed                | Class B                |
| 2.VI       | >250          | 14/15            | Passed                | Class A                |
| Reference* | 2             | 0**              | Failed                | Class E                |

\* Commercial alkyd paint  
 \*\* No intumescence

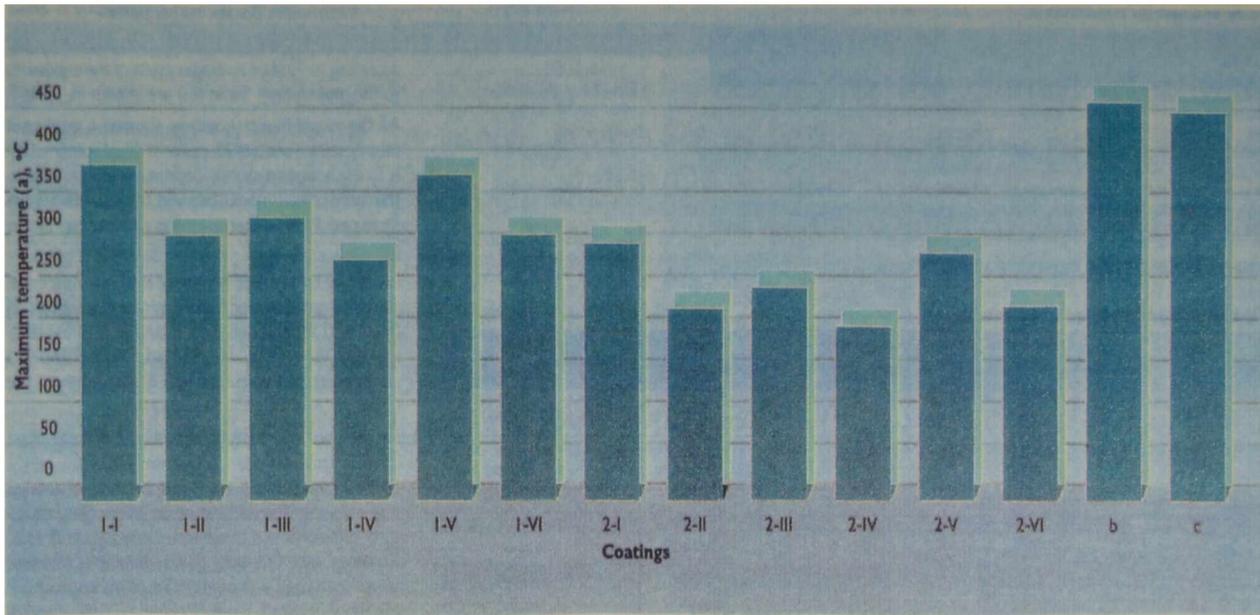


Fig. 11.- Thermal conductivity test.

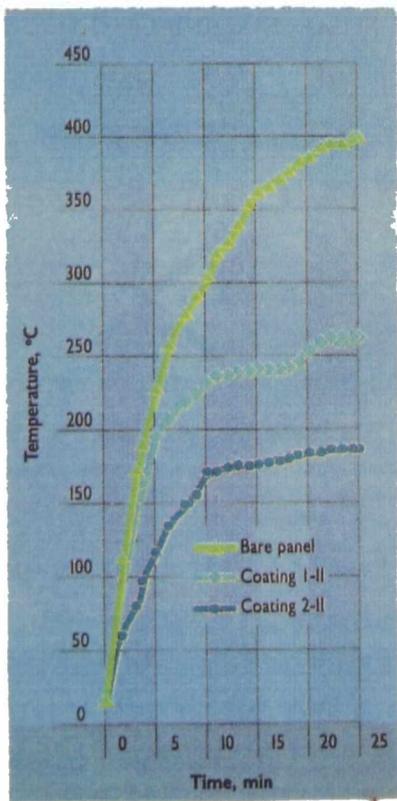


Fig. 12.- Influence of pigment volume concentration (PVC) on thermal conductivity.

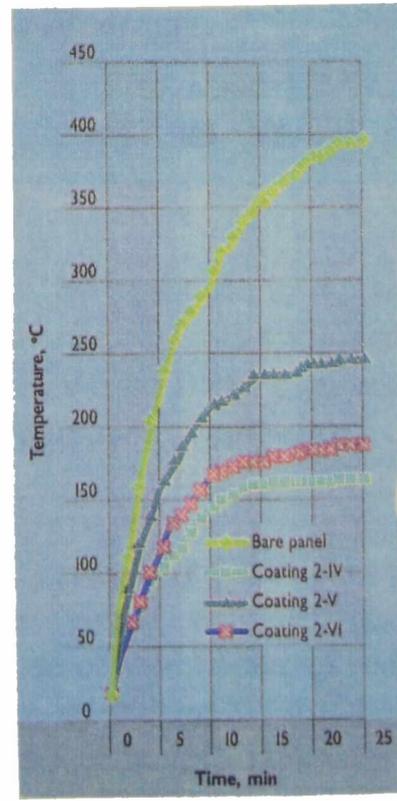


Fig. 13.- Influence of catalyst and filler types on thermal conductivity.



All coatings were classified as Class A or B and their performances were better than the commercial alkyd paint selected as reference: Class E, Fig. 10.

Without any doubt, an important consideration in the performance of the thermal protection coating is the ability to maintain their properties during exposure to the aggressive humidity or water. Film degradation due to leaching or extraction of the intumescent agent by water usually alters the expansion process, thereby destroying the thermal effectiveness of intumescent coatings. In spite of the similar properties of both dehydrating agents employed in this study, the very low water solubility of catalyst C2 compared to C1 makes it the preferred material for formulating coatings that must provide serviceability under humid or wet conditions.

However, the higher thermal stability of the ammonium polyphosphate C2 generates a thicker insulating layer and hence a more effective protection.

### **Thermal conductivity test**

The following criteria for qualifying as successful the formulated intumescent was applied: the temperature registered by the thermocouple at the backface of the painted panels must not exceed 200 °C during the test (25 minutes). Results are displayed in Fig. 11, which indicates that in all cases the thermal insulation due to the charred coat formed after testing at the front of the panels led to temperatures at backface lower than those attained both with the bare material and the reference paint under the same conditions of testing.

From above mentioned viewpoint, some coatings with significant mean height of intumescence (Table V) fulfilled the requirement since they showed a maximum temperature at backside inferior to the fixed limit (200 °C).

The values obtained in these experiences corroborate the conclusions reached in the intermittent Bunsen burner flame test in relation with the influence of PVC and catalyst type. Fig. 12 indicates a better insulating behavior of coating 2.II (PVC 65.0 %) than coating 1.II (PVC 60.0 %) while Fig. 13 shows that the coating 2.VI (ammonium polyphosphate C2) had a higher efficiency than coating 2.V (catalyst C1).

Moreover, this test allowed to attain conclusions regarding the influence of fillers incorporated by partial replacement of titanium dioxide. Some coatings showed an improvement of the thermal protection by introducing into those compositions an endothermic filler like hydrated aluminium oxide; this pigment counter-balanced the natural exothermic heat of decomposition produced during intumescence in the pyrolysis zone. Coatings with hydrated aluminium oxide showed the best behavior in this experiment: the effect of endothermic filler should reduce the rate of the backface temperature rise of metallic substrates. On the other hand, no significant differences were observed in samples either with titanium dioxide or with titanium dioxide/modified barium metaborate as pigment: time-temperature data were not altered with this filler.

## CONCLUSIONS

1. The performance of an intumescent coating depends on the ability to maintain their physical properties during exposure to humidity or water. The environment can deteriorate the film and besides leaches or extracts some components and consequently decrease the thermal effectiveness.

2. Laboratory tests demonstrated the effect of pigment volume concentration on fire retardancy. Results on intumescent coatings in which PVC was varied indicated that efficiency is higher at PVC 65.0 % than 60.0 %. Other PVC values above of the critical one were not considered since its influence on some key service properties of the coating is important.

3. Hydrated aluminium oxide has demonstrated an improved thermal control of a metallic substrate when exposed to fire action. Differential thermal analysis of this filler displays an endothermic behavior. On the other hand, modified barium metaborate used as filler did not show an altering in the thermal profile at least in the desired temperature region.

4. Owing to the highest thermal stability and the lowest water solubility, ammonium polyphosphate C2 is the preferred compound as catalyst.

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