Nanostructured Protective Coating Systems, Fireproof and Environmentally Friendly, Suitable for the Protection of Metallic Substrates

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The aim of this study was to formulate, develop, and determine the behavior of nanostructured protective coating systems, fireproof and environmentally friendly, suitable for the protection of metallic substrates. The results allowed concluding that the di- and tripigmented formulations based on laminar zinc, either alone or mixed with nanozinc, showed an excellent corrosion resistance when a nanostructured self-cured inorganic silicate (high silica/alkali ratio) was selected as the film forming material. Coating systems included a sealer of low permeability, which was based on the same film forming material that primers and on laminar pigments. Intumescent coatings were manufactured and then applied on the sealer; in this study, two types of products in an aqueous single package were formulated. The anticorrosive capacity was evaluated in a salt spraying (fog) chamber and in a 100% relative humidity cabinet while the performance against the fire action was determined by estimating the limiting oxygen index in the LOI cabinet, the flame advance in an inclined tunnel, and, finally, the thermal conductivity in a UL 94 flame chamber; in the last test, the degree of intumescence was also assessed. The results showed an excellent ability for corrosion controlling and, in addition, a good performance against the fire action of some of the non pollutant coating systems designed.

1. Introduction

All materials of construction are deteriorated by the action of fire; although iron and steel are usually considered totally immune, they demonstrated in many cases that after thermal action as a product of a conflagration their mechanical properties are noticeably diminished according to the elevation of temperature: thus, for example, from 250 to 500 °C, their mechanical resistance is reduced to 50% of the original value whereas up to 750 °C the diminution can reach 90%. On the basis of the previously mentioned information and in addition to the idea that iron and steel generally are susceptible to corrosion due to their high instability energy, it is necessary to design passive protective systems that simultaneously control the kinetics of the corrosive process to make it compatible with the estimated useful life of the structures and give resistance to them against the action of fire with the purpose of allowing the evacuation of people in civil and industrial facilities.

In the field of material protection, new approaches using nanoscale effects can be used to create coatings with significantly optimized or enhanced properties. Recent research on the incorporation of nanocomponents into conventional coatings has shown that nanosized materials can improve the physical and chemical properties of coating, i.e., it is now possible to formulate new kinds of coatings in which various nanomaterials are integrated into the microsystem in order to obtain unique and highly desirable properties. The final employment impact of nanoscience and nanotechnology in this discipline is seen in the development of new types of nanostructured systems with high technological importance.

Considering that both zinc-rich and modified coatings perform better than other anticorrosive ones and since their success is based on the particular capacity to generate cathodic protection (zinc particle acts like a sacrifice anode) and a resistant barrier, anticorrosive primers are frequently based on metallic zinc and on several film forming materials. Coating systems can include a sealer of low permeability, which is usually based on a compatible film forming material and on laminar pigments.

To ensure effective protection against fire, an intumescent coating is selected as the top coat. This type of coating provides the thermal insulation to steel structures and other substrates: the dried films, under the action of heat, first soften and then swell due to internal release of combustible gases that remain in part retained, reaching a thickness of more than 100 times the original. According to the above-mentioned information, the aim of this study was to formulate, develop, and determine the behavior of multilayer nanostructured coating systems, fireproof and environmentally friendly, suitable for the protection of metallic substrates.

2. Materials and Methods

2.1. Primer Formulation and Manufacture. In this paper, primers were formulated based on laminar zinc (10.5 µm average diameter; 99.5% purity in weigh; Figure 1) either alone or mixed with nanozinc (35 nm average diameter; 99.8% purity in weigh) as the inhibiting pigment (laminar shape in series A; mixture of laminar zinc and of nanozinc, 90/10 ratio v/v, in series B), calcium silicate (12.1 µm average diameter) as the spacer of zinc particles, and eventually zinc hydroxiphosphate (3.0 µm average diameter) as the complementary inhibiting pigment. A nanostructured self-cured inorganic silicate was manufactured as a film forming material, it started from a commercial sodium silicate solution (3.0/1.0 silica/alkali molar ratio) in an aqueous solution at 30% w/w and a colloidal silica solution of nanodimensions also at 30% w/w (0.32% sodium oxide content; 2.31 g cm−3 density); the final silica/alkali molar ratio was 5.5/1.0.

The considered values of pigment volume concentration (PVC) were selected starting from the critical values (CPVC); these were estimated in the corrosion test (salt spraying chamber, Figure 1) and in the measures of permeability carried out on
permeability to oxygen, water, and water vapor.\(^{37,38}\) The mean diameter specified of the micaceous iron oxide particles;\(^{38}\) the variation was estimated in 50/52\% for the formulations with zinc/extender/inhibitor ratio.

### Table 1. Pigment Composition of Primers

| Sample | Metallic Pigment\(^{a}\)/Extender/inhibitor ratio (v/v) | PVC, % | CPVC, % |
|--------|-----------------------------------------------------|--------|---------|
| I.1    | 80.0/20.00/0.0                                         | 47.5   | 46/48   |
| I.2    | 80.0/20.00/0.0                                         | 45.0   | 46/48   |
| I.3    | 80.0/20.00/0.0                                         | 42.5   | 46/48   |
| I.4    | 80.0/20.00/0.0                                         | 40.0   | 46/48   |
| II.1   | 65.0/25.0/10.0                                         | 45.0   | 44/46   |
| II.2   | 65.0/25.0/10.0                                         | 42.5   | 44/46   |
| II.3   | 65.0/25.0/10.0                                         | 40.0   | 44/46   |
| II.4   | 65.0/25.0/10.0                                         | 37.5   | 44/46   |

\(^{a}\)Metallic pigment: series A, lamellar zinc (100\%); series B, lamellar zinc/nanozinc (90/10 ratio v/v).

free films (75/80 \(\mu\)m dry film thickness) by applying the Gardner method.\(^{33}\) Values of PVC ranged from 42.5\% to 50.0\% (CPVC was estimated in 50/52\% for the formulations with zinc/extender and in 48/50\% for tripigmented compositions); the variation between consecutive samples was 2.5\%, Table 1.

Compositions were prepared in double packages with the purpose of avoiding the reaction between the metallic zinc and the water which would lead to the formation of hydrogen gas in the can. Consequently, previous to the application of primers and in a high speed mixer, the laminar zinc was dispersed;\(^{34-36}\) then, according with the formulation, zinc nanopowder was incorporated.

### 2.2. Sealer Formulation and Manufacture.

In this case, the above-mentioned sodium silicate solution (silica/alkali 5.5/1.0 molar ratio) was used as a film forming material. With respect to pigmentation, micaceous iron oxide (Fe\(_2\)O\(_3\): 16.5 \(\mu\)m average diameter; 87.2\% purity in weight) and mica (3Al\(_2\)O\(_3\)+K\(_2\)O+6SiO\(_2\)+2H\(_2\)O; 10.2 \(\mu\)m average diameter), in a 50/50 ratio v/v, were selected. The quantitative relationship between the pigment and the binder, expressed in terms of PVC, was 25.0\% with the purpose of designing a film of low permeability to oxygen, water, and water vapor.\(^{37,38}\)

The manufacture of sealer S involved, in one first stage, the dispersion of extender (mica) in the vehicle. Although the micaceous iron oxide displays a high chemical inertia, with the purpose of giving to the system prolonged stability in the package, the incorporation of this pigment was performed previous to the application of sealer.

The dispersion time was fit, according to the operative conditions of the equipment, with the purpose of reaching the mean diameter specified of the micaceous iron oxide particles; the determination was microscopically made.\(^{37,38}\)

### 2.3. Intumescent Coating Formulation and Manufacture.

To ensure effective protection against fire, the top coats selected were two intumescent coatings.\(^{39-43}\) Between the active pigment, pentaerythritol was used as a supplier of carbon (water solubility at 20 °C, 6.05 g/100 mL); ammonium polyphosphate as a catalyzing agent (white powder; 30.2\% phosphorus and 14.5\% nitrogen; low water solubility at 20 °C, 0.18 g/100 mL) and melamine as a gas generator (decomposition temperature, approximately 130 °C; water solubility at 20 °C, 0.32 g/100 mL).

In this paper, trihydrated alumina (aspect, granulated crystalline powder; 0.65 \(\mu\)m average diameter; loss of weight in burning at 800 °C, about 35.5\% w/w) and well-dispersed magnesium hydroxide nanopowder (97.5\% MgO purity w/w; 78 nm average diameter; loss of weight in burning at 800 °C, about 15\% w/w) were used as flame retardants pigments; both inorganic compounds contain an important percentage of hydration water. In addition, rutile titanium dioxide (aspect, very fine white powder; 0.25 \(\mu\)m average diameter) was used as an opaque pigment.

Two thermoplastic materials were selected as binders: a pure acrylic latex (copolymer of methyl methacrylate and of normal butyl acrylate; minimum temperature of film formation, 13 °C; water absorption after 24 h immersion, 12% w/w) modified with nanosilica (acrylic latex/nanosilica solution ratio, 3/1 solids in volume) and a styrenated acrylic latex as reference (copolymer of the normal butyl acrylate and of styrene; minimum temperature of film formation, 20 °C; water absorption after 24 h immersion, 8% w/w); in both cases, the solid concentration in weight was of 50\%.\(^{44}\)

For the present experiment, although in one case the latex was used in conjunction with nanosilica, it was decided to formulate both intumescent coatings with 75\% PVC that is approximately a 15\% superior to the critical value;\(^{45}\) the values of the CPVC were also estimated in a previous way.\(^{33}\) This last one is based on fires which have a major effect on the interiors of civil and industrial workplaces. The formulation of intumescent coatings is indicated in Table 2.

The manufacture was carried out in a discontinuous mill of high-speed stirring provided by one double jacket to control the system temperature during the pigment dispersion.

### 2.4. Preparation of Panels.

The identification of the test panels is shown in Table 3. The metallic substrates (SAE 1010 steel plates) displayed an initial degree A; they were previously degreased with solvent in the vapor phase and then sanded to the degree Sa 2 1/2 (SIS specification 05 59 00/67; maximum roughness \(R_m\), 35 \(\mu\)m).

All the panels were initially protected with formulated primers. The application of primers was performed in only one layer (75/80 \(\mu\)m dry film thickness); in all cases, the panels were prepared in duplicate and stored for 7 days at 20 ± 2 °C. The sealer application was carried out in a single layer, with a...
The inorganic matrix polymer was characterized by applying X-ray (the diffraction pattern of each sample in a glass holder was obtained at room temperature with Cu K radiation in a Philips 3020 diffractometer); diffraction intensities were measured at small angles between 0.6° and 4.0° with a step of 0.02° for 10 s per point.

The XRD studies showed an interatomic distance between Si and O about 1.62 Å, and besides that, each oxygen is linked to two silicon atoms or to one silicon and one metal atom. The structure of glasses has a Si and O random arrangement with cations placed into holes in the network.

3.2. Coatings Systems Behavior. The factorial design for series A and B included 1 alkaline silicate (primer) × 2 pigmentsation (primer) × 4 PVC values (primer) × 1 sealer × 2 intumescent coatings; therefore, the design led to a total of 16 anticorrosive/fireproofing systems for both series A and B.

To study the variables considered (main effects), a statistical interpretation was carried out. First, the variance was calculated, and later, the Fisher F test was carried out. The results indicated that all the mentioned variables displayed an important influence on the performance of the protective systems.

Results of series A and B corresponding to DR, degree of rusting; DB, degree of blistering; LOI, limiting oxygen index; AL, flame advance, and CT, thermal conductivity of anticorrosive–fire retardant coating systems are shown respectively in Tables 4 and 5.
3.2.1. Anticorrosive Performance. With the purpose of establishing the efficiency of each protective system from an anticorrosive point of view, the values of the degree of rusting corresponding to the areas without cutting and of the degree of blistering were averaged. With respect to this last aspect, initially the mean value corresponding to the size and the frequency was calculated; to quantify the frequency, the following numerical values were assigned: no blisters, 10.0; F (few), 7.5; M (medium), 5.0; MD (medium dense), 2.5 and D (dense), 0.0.

The results are displayed in Table 6; the highest mean value of the degree of rusting and of the degree of blistering were averaged. With respect to this last aspect, initially the mean value corresponding to the size and the frequency was calculated; to quantify the frequency, the following numerical values were assigned: no blisters, 10.0; F (few), 7.5; M (medium), 5.0; MD (medium dense), 2.5 and D (dense), 0.0.

The results are displayed in Table 7; they range from 0 to 10. For example, for the limiting oxygen index, the values 0 and 10 were assigned for 555 and 0 mm, respectively; and for flame advance, the values 0 and 10 were assigned for 555 and 0 mm, respectively; and finally for thermal conductivity, 0 and 10 were assigned for 500 and ≤200 °C, respectively. In all cases, intermediate values were considered (linear scales between the quoted extremes values). Later, the mean values of the realized tests were calculated, Table 7.

The determination of LOI index was carried out with a flow rate of 3.2 cm·s⁻¹. Experimental results corresponding to both intumescent coatings showed a self-extinguishing capability since their limiting oxygen index was higher than that corresponding to the experimental accepted limit for this type of charred LOI 28%. As a consequence, this test did not allow to establish a strong influence of the formulation variables considered in this study since both intumescent coatings displayed a very good performance: 42 and 48% for RI (fire-retardant coating based on styrenated acrylic emulsion) and RII (fire-retardant coating based on pure acrylic emulsion modified with nanosilica solution), respectively.

The equation ΔL = Ls − La allowed the calculation of the flame advance ΔL assessed in the inclined tunnel, where Ls and La are the averages of the three flame advances observed respectively on the coated panels and on a bare cement asbestos panel selected as reference (distance due to the reflection of the flame, 55 mm); the average of the three consecutive highest values of the flame advance was calculated, which were measured at intervals of 15 s.

Although both intumescent coatings showed very good performance, results indicate a marked difference among the
efficiency of both intumescent coatings. Protective systems with RII as the finishing coat showed an enhanced performance with regard to the panels with RI: the average values were 6 and 22 mm, respectively, beyond the flame advance registered on the panel of asbestos-cement.

As mentioned in the thermal conductivity test, panels protected with coatings systems under study were placed in the UL 94 flame chamber for avoiding airflows. A panel of bare steel, placed in a horizontal position, was selected as reference. A thermocouple as the measurement system was set to the face superior of the panel. A Bunsen burner, facing toward the face inferior to the panel, was located at a distance of 15 mm; the intensity of the flame was regulated so as to reach on the other side a temperature of 500 °C after 25 min. The coated panels were tested in a similar way, evaluating the temperature through the aforementioned thermocouple during the experiment.

The following criteria for qualifying as successful the formulated intumescent was applied: the temperature registered by the thermocouple at the back face of the painted panels should not exceed 200 °C during the test.

Results indicate that in both coatings the thermal insulation due to the charred coat formed after testing at the front of the panels led to temperatures at the back face inferior to the fixed limit: a maximum temperature of 181 and 195 °C were reached at the back face after finishing the test respectively for coatings RII and RI which corroborates in this test a superior performance of RII with respect to RI.

The excellent thermal insulation could be explain since both coatings showed a significant intumescence and a quite uniform development; only in a few cases was a slight depression attributable to the flame pressure observed. The insulating layers remained firmly adhered to the substrate in all panels. Referring to the average height of the intumescence, values ranged between 22 and 25 mm for coating RI and between 28 and 30 mm for coating RII, Figure 4.

In addition, the effect of both endothermic filler should reduce the rate of temperature rise at the back face of metallic substrates: trihydrated alumina and well-dispersed magnesium hydroxide nanopowder counterbalanced the natural exothermic heat of decomposition produced during intumescence in the pyrolysis zone.

Finally, the analysis of results suggests that although both intumescent coatings showed very good performance, the coating based on pure acrylic emulsion modified with nanosilica displayed a noticeable major resistance against the fire action than the one with the styrenated acrylic emulsion in its composition, perhaps due to the presence of a binder partially mineralized in its composition.

### 3.3. Simultaneous Analysis of Anticorrosive and Fireproofing Efficiency.

In the last stage of the statistical interpretation, all results were averaged to reflect simultaneously both the anticorrosive capacity and the resistance to the fire action. Thus, the mean values corresponding to the variables considered in this study (main effects) were obtained. In this case, the highest mean value indicates the best overall performance as well.

**Table 7. Statistical Results: Performance against Fire of Coating Systems**

| sample | LOI, % | AL, mm | CT, °C |
|--------|--------|--------|--------|
| RI     | 42     | 22     | 198    |
| RII    | 48     | 6      | 178    |
| R      |        |        | 500    |

*LOI, limiting oxygen index; AL, flame advance; CT, thermal conductivity, and R, bare panel as reference.*
The nanostructured materials offer interesting properties to study in the field of coating technology; in this paper, the following nanomaterials were successfully used:

- Nanosilica solution allowed the preparation of the efficient water-based primers and a sealer, with fireproof properties for steel protection, based on a nanostructured self-cured inorganic silicate (high silica/alkali ratio) as a film forming material.
- Well-dispersed nanozinc solution as the main inhibitor improved the anticorrosive capacity when it was mixed with laminar zinc to formulate primers based on nonpolluting pigments of the environment.
- Magnesium hydroxide nanopowder, in conjunction with microtrihydrated alumina, as flame-retardant pigments, and nanosilica solution as co-binder of pure acrylic resin led to the design of water-based intumescent coatings with very good performance against fire.

Results of Table 8, which includes simultaneous statistical analysis of all variables studied in the coating systems, support the conclusions reached from Table 6 in relation to the influence of the composition of the pigment and to those corresponding to Table 7 where the mean performance of intumescent coatings is included.

For example, Table 8 indicates that (i) with respect to the influence of the composition of pigment in primers, higher performance was achieved with a zinc/extender/inhibitor, 80/20 ratio v/v/65/25/10 ratio v/v (mean value 8.4) than that with the ratio zinc/extender 80/20 ratio v/v (mean value 7.2); (ii) in relation to the influence of nanosilica pigments, zinc/extender, series B (zinc laminar/nanozinc 90/10 ratio v/v, mean value 8.6) performed in a markedly superior way to series B (zinc laminar/nanozinc 90/10 ratio v/v, mean value 8.6) performed in a markedly superior way to series A (100% zinc laminar, mean value 7.1); and finally (iii) concerning the influence of the binder type in intumescent coatings, the pure acrylic emulsion modified with nanosilica solution showed a better efficiency (mean value 9.8) than the styrenated acrylic emulsion (mean value 9.1).

In summary, the simultaneous analysis of all variables indicates that among the nanostructured protective coating systems studied, fireproof and environmentally friendly, the most suitable one for the protection of metallic substrates is that defined as B.10.

4. General Conclusions

The nanostructured materials offer interesting properties to study in the field of coating technology; in this paper, the following nanomaterials were successfully used:

- Nanosilica solution allowed the preparation of the efficient water-based primers and a sealer, with fireproof properties for

| Table 8. General Statistical Results |
|--------------------------------------|
| Influence of Pigmentation Type       |
| pigment composition | zinc/extender, 80/20 ratio v/v | zinc/extender/inhibitor, 65/25/10 ratio v/v |
| series A (laminar zinc) | 6.8 | 7.4 |
| series B (laminar zinc/nanozinc) | 7.6 | 9.5 |
| general | 7.2 | 8.4 |

| Influence of Nanozinc in Primers |
|----------------------------------|
| series A | series B |
| 7.1 | 8.6 |

| Influence of Binder Type in Fire-Retardant Coating |
|--------------------------------------------------|
| styrenated acrylic emulsion | pure acrylic emulsion modified with nanosilica solution |
| 9.1 | 9.8 |

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