High-solids, one-coat paints based on aliphatic epoxy resin-siloxanes for steel protection

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A B S T R A C T

This research involved the design of high-solids, one-coat paints for the protection of metal structures with low maintenance requirements. The main paint components were: (i) an aliphatic epoxy resin cured with an aminosilane and chemically modified with alkoxysilanes as film-forming material, and (ii) rutile titanium dioxide as opaque pigment, a polysilicate strontium and zinc as corrosion inhibitor and, a synthetic calcium silicate and barites as extenders.

Some paints displayed excellent performance in salt spray apparatus (degree of rusting) and in 100% relative humidity cabinet (degree of blistering). Results indicate that as the aliphatic epoxy resin/alkoxide ratio increased, the degree of rusting improved while the degree of blistering worsened, in total agreement with film permeability. In addition, binders based on dimethyldiethoxysilane, methyltri-ethoxysilane and tetraethoxysilane, in that order, displayed an improved corrosion performance and a decreased blistering resistance. The reactivity of alkoxides and the chemical interaction with the metal substrate supports the obtained results.

Initial gloss and gloss and color retention improved as the alkoxide level increased; no significative differences were registered when the alkoxide type variable was considered.

In summary, the use of alkoxides as modifiers of an aliphatic epoxy resin allowed the formulation of hybrid paints with high anticorrosive and weathering resistance performance. The more suitable hybrid organic–inoganic paint must be selected according to the requirements of each structure in service.

1. Introduction

Silicon derivatives may form inorganic polymers with unique characteristics; that is why, they are being included in the formulation of protective coatings [1]. The alkoxysilanes, silicon derivatives and precursors of the polysiloxanes, are the most commonly used in this area because they have high strength chemical bonds of $\equiv$Si—O-type; this energy exceeds that of the —C—C— in the organic polymers (e.g. epoxy and polyurethane resins) [2] and enhances the film properties.

In general, alkoxysilanes used in paints are modified by the incorporation of hydrocarbon chains linked by covalent bonds to silicon (preferably aliphatic to prevent yellowing that generate the aromatic structures exposed to sunlight). The remaining covalent bonds link the silicon with oxygen atoms and through them with hydrogen or alkyl groups; the chain length of these groups must be less than five or six carbon atoms to facilitate the kinetic of the reactions included in the sol–gel process (polymerization of siloxanes by hydrolysis and condensation reactions). The presence of the hydrocarbon chain makes it more hydrophobic; the hydrophobicity increases with chain length.

It is appropriate to consider some aspects of alkoxides for carrying out their polymerization by sol–gel process: (i) they are soluble in alcohols and in both aromatic and aliphatic hydrocarbons, (ii) their reactivity increases with the number of groups —OH and —OC$_n$H$_{2n+2}$ in the structure since these allow obtaining macro-molecular networks, (iii) the pH plays an important role because values below to the isoelectric point of the silica produce polymeric gels while clearly alkaline values generate colloidal gels of lower density and specific area, and (iv) during aging process, volumetric shrinkage of network occurs spontaneous and irreversibly, with the expulsion of water and alcohol from the pores [3–5].

In paints based only on polysiloxanes, the cracking caused by the high surface tension during aging must be avoided (pressure difference increases as distance between the particles decreases).

The simplest solution is to allow the evaporation of the reaction products at a very low speed; this method, while effective, is not practical in many cases due to long drying times required (weeks or even months to form a dry system without cracking). The quoted period can be substantially lowered by incorporating chemical additives that modify the surface tension of the interstitial fluid, allowing the quick removal of the volatile components without cracking. It is appropriate to mention that when the polysiloxanes are used in combination with organic resins, cracks are not usually observed during film formation.

The aim of this research was the design of efficient high-solids, one-coat paints recommended for the protection of metal structures exposed to weathering, with low maintenance requirements; they were based mainly on an aliphatic epoxy resin stoichiometrically cured with an aminosilane and chemically modified in several degrees with alkoxysilanes.

2. Materials and methods

The experiments included the following steps: (i) the choice of the aliphatic epoxy resin, (ii) the selection of an aminosilane as curing agent and alkoxysilanes as co-binder, (iii) the design of the pigmentation, (iv) the formulation and manufacture of hybrid paints, and finally (v) the laboratory tests to establish the performance of painted panels.

2.1. Choice of the aliphatic epoxy resin

Epoxy paints are widely known and have achieved high commercial acceptance as protective and decorative paints for application on various substrates (steel, concrete, etc.). Nevertheless, they generally do not have good resistance to UV from sunlight when exposed for long periods [6]. Therefore, it became necessary to develop paints based on epoxy resin with better color and gloss retention. This was achieved by modifying the glycidic epoxy resins (prepared from bisphenol A and epichlorohydrin) with acrylic resins and also with melamine resins co-etherified with epoxy groups and epoxidized polyester resins. It is worth mentioning that the cited developments, although lead to better weathering resistance, simultaneously generate films with less resistance to corrosion than glycidic epoxy resins [7–10].

To improve performance against sunlight but without losing corrosion resistance, hybrid systems comprised of aliphatic epoxy resins and polysiloxanes are being studied as finishing paints [11–13]; aliphatic epoxy resins are generally liquid and therefore allow the paint formulation with low level of volatile components [14–16]. Accordingly, for this research, diglycidyl ether of 1,4-butanediol was selected (weight per epoxide WPE, 171).

2.2. Selection of silanes

The aminosilane for curing the aliphatic epoxy resin must be difunctional (two amine hydrogens) with the object of forming a lineal epoxy polymer with superior weatherability. The amino group gives alkalinity in aqueous solution and acts as catalyst of the hydrolysis and condensation reactions; in this way, a few large polymeric units (high molecular weight) are formed.

Taking into account the above mentioned, the aminopropyl methyldiethoxysilane was selected (chemical formula, $C_8H_{21}NO_2Si$; molecular weight, 191.3; equivalent weight, 95.7; appearance, clear liquid; density, $0.916\,g\,cm^{-3}$). The equivalent weight of aminosilane and the WPE of the aliphatic epoxy resin were used for the stoichiometric calculation of the amount of curing agent.

Polysiloxanes used as co-binder must have low molecular weight to produce high-solids paints. For this research, the following alkoxysilanes were selected: dimethyldiethoxysilane (formula, $C_6H_{16}O_2Si$; molecular weight, 148.3; aspect, clear liquid; density, $0.851\,g\,cm^{-3}$); methyltriethoxysilane (formula, $C_7H_{18}O_3Si$; molecular weight, 178.3; aspect, clear liquid; density, $0.895\,g\,cm^{-3}$) and, finally tetraethoxysilane (formula, $C_4H_{20}O_4Si$; molecular weight, 208.3; aspect, clear liquid; density, $0.934\,g\,cm^{-3}$). The binders included 30/70, 40/60, 50/50, 60/40 and 70/30 aliphatic epoxy resin/alkoxide (v/v) ratios.

2.3. Design of the pigmentation

The pigmentation included: (i) rutile titanium dioxide with R1 surface treatment according Standard DIN 55912 (density, $4.2\,g\,cm^{-3}$; oil absorption OA, 16) as opaque pigment, (ii) a commercial strontium zinc phosphosilicate of easy dispersion (density, $3.3\,g\,cm^{-3}$; OA, 34) as corrosion inhibitor and, (iii) a synthetic calcium silicate (density, $2.3\,g\,cm^{-3}$; OA, 280) and barites (density, $4.5\,g\,cm^{-3}$; OA, 9) in 3.0/3.0/1.0/1.5 (w/w) ratio as extenders.

2.4. Formulation and manufacture of hybrid paints

In this experiment, it was considered sufficient the water supply from the atmosphere and from components of the formulation having water absorbed. For this reason, no water was incorporated in the formulations to not affect the stability of hybrid paints in container.

2.4.1. Volatile organic compounds (VOC)
Aliphatic epoxy-siloxane systems do not require theoretically solvent in the formulation since both film-forming materials are liquids (i.e. 100% solids); nevertheless, it is not possible from a practical standpoint for pigmented systems due to their high viscosity (difficult application, poor film leveling, etc.). Consequently, the hybrid paints were formulated with 90% solids in volume including butyl acetate as solvent.

2.4.2. Pigment volume concentration (PVC)
Preliminary paints were formulated in a wide range of pigment volume concentrations for estimating the critical pigment volume concentration (CPVC). The preparation of the paints and panels was performed as indicated below (surface tension was adjusted in all cases to 40 dynes cm^{-1}).

The CPVC values obtained in previous tests of degree of rusting (salt spray apparatus) and degree of blistering (100% relative humidity cabinet) varied in a narrow range between 32 and 35% for all samples and for dry film thickness between 220 and 230 μm; the low CPVC values are attributable to high OA of synthetic calcium silicate. According to the above, the PVC selected was 32.0%.

It is worth mentioning that the CPVC values, estimated theoretically for all samples through equation $CPVC = (100/\rho)/[(OA/0.935) + (100/\rho)]$ o $CPVC = 1/(1 + OA\,\rho/93.5)$, are placed in the range determined in the quoted previous laboratory tests (ρ is the pigment density).

2.4.3. Manufacture
The pigments were dispersed in the vehicle based on the aliphatic epoxy resin solubilized in butyl acetate. The process was conducted in a high-speed disperser for approximately 25–30 min (7–8 Hegman gauge) and then, the corresponding siloxane was added.

Aliphatic epoxy resin-siloxane paints were prepared in two moisture free containers; one of them with the dispersed pigments and the second with the aminosilane. Prior to the paint application,

the components of both packages were mixed (the pot life ranged between 5 and 7 h at 20 °C, requiring no induction time).
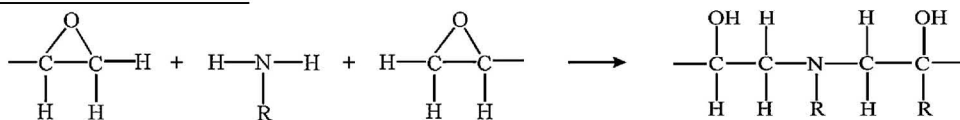
2.4.4. Reference paint

As mentioned, epoxy coatings based on bisphenol A are the most used for the protection of several substrates. For this reason, the quoted film-forming material was selected for preparing the Reference paint. This was based on the same pigmentation than hybrid paints under study and diethylenetriamine in stoichiometric amount as curing agent at room temperature. Because its equivalent weight is 20.6 (MW, 103.0; amount of H$^+$, 5), to polymerize 100.0 g of epoxy resin of WPE equal to 500, 4.1 g of curing agent (20.6 × 100/500) was required. Manufacture was performed similarly to the mentioned for hybrid paints.

2.5. Laboratory tests

The following tests were carried out in duplicate:

2.5.1. Performance related to anticorrosive properties
2.5.1.1. Water vapor permeability.
This test was conducted on dry paint films under DIN 52615 guidelines. The following glass filters were used: 60 mm in diameter, 4.5 mm thickness and 3 porosity; dry film thickness ranged between 220 and 230 μm. The filters, with the painted side up, were introduced into a vessel

$$\underset{\underset{H}{\overset{|}{C}}}{\overset{O}{\overset{\triangle}{C}}}\!-\!C\!-\!H \;+\; H\!-\!\underset{R}{\overset{|}{N}}\!-\!H \;+\; H\!-\!\underset{\underset{H}{\overset{|}{C}}}{\overset{O}{\overset{\triangle}{C}}}\!-\!C\!- \quad\longrightarrow\quad \text{—C—C—N—C—C—}$$

of about 60 mm in diameter, inside which was disposed distilled water without direct contact with the filters; then, it was sealed the annular space between the filter and the interior of the test vessel. Subsequently, it was determined the reference weight.

The specimens were placed in a convection oven under controlled conditions of humidity and temperature (50% and 23 °C, respectively). It was assessed the amount of vapor that circulated at steady state (constant weight at intervals of 24 h).

Firstly, it was calculated the flux density of water vapor diffusion (DDV) in g m^{-2} day^{-1} and then, the air thickness equivalent to the diffusion of water vapor (Sd, air layer that has the same resistance to the water vapor diffusion that the paint film thickness considered). For this purpose, it was used the expression Sd = 20/DDV indicated in DIN 52615.

2.5.1.2. Degree of rusting.
SAE 1010 steel panels were used to prepare test specimens; they were previously degreased with solvent in vapor phase and sanded to Sa 2½ degree (SIS Specification 05 59 00/67) with 25 μm maximum roughness (Rm). Dry film thickness ranged between 220 and 230 μm. In all cases, to ensure the complete drying/curing of films, the specimens were kept in controlled laboratory conditions for ten days before beginning tests (25 ± 2 °C and 65 ± 5% relative humidity).

The specimens were exposed for 2500 h in salt spray apparatus under operating conditions defined in ASTM B117. It was assessed the degree of rusting in the whole panel (Method B) and from X-cut made with a sharp instrument up to the base (Method A), according to ASTM D610.

2.5.1.3. Degree of blistering.
Specimens were prepared in similar way to those above-described; tests were performed in a 100% relative humidity cabinet for 2500 h, under the guidelines of ASTM D2247. The resistance to osmotic process was evaluated using ASTM D714.

2.5.2. Performance related to weathering exposure
The accelerated aging of specimens was conducted in a Xenon Arc Light Apparatus, according to Cycle 1 of ASTM G155 (filter, daylight; irradiance, 0.35 W/m^2 mm; wavelength, 340 nm; cycle, 102 min light at 63 °C black panel temperature and 18 min of light and distilled water spraying) for 300 h.

2.5.2.1. Initial gloss and gloss retention.
Gloss was assessed with a BYK Gardner apparatus, applying an angle of incidence and reflection of 60°. The gloss retention was expressed as percentage of initial gloss.

2.5.2.2. Color retention.
The color determination (CIELAB system) was performed with a BYK Gardner apparatus, by using the D65 source (it represents the average sunlight including UV) with 45°/0° light rays. The calculation of color retention was carried out using the equation: $\Delta E = (\Delta a^2 + \Delta b^2 + \Delta L^2)^{1/2}$, where Δa and Δb represent the increase or decrease in levels of chromaticity and ΔL the luminosity difference.
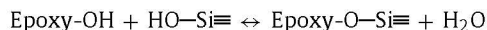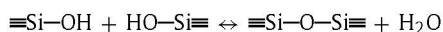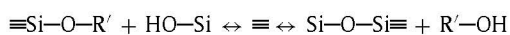
3. Results and discussion

3.1. Chemical reactions

As known, the polymerization of the epoxy resin with amines takes place at room temperature according to following reaction:

where R corresponds in these experiments to silane of aminosilane.

Regarding hydrolysis and condensation reactions of metal–organic precursors, the reactions would be as follows:

$$\equiv\text{Si—O—R}' + H_2O \leftrightarrow \;\equiv\text{Si—OH} + R'\text{—OH}$$

$$\equiv\text{Si—O—R}' + \text{HO—Si} \leftrightarrow \;\equiv\; \leftrightarrow \; \text{Si—O—Si}\equiv + R'\text{—OH}$$

$$\equiv\text{Si—OH} + \text{HO—Si}\equiv \;\leftrightarrow\; \equiv\text{Si—O—Si}\equiv + H_2O$$

$$\text{Epoxy-OH} + \text{HO—Si}\equiv \;\leftrightarrow\; \text{Epoxy-O—Si}\equiv + H_2O$$

where R$'$ corresponds to the alkyl of ethoxy and the epoxy-OH to the epoxy cured according to the above equation.

In summary, the film-formation of the hybrid paints would involve: (i) the addition reaction of oxirane functional groups, i.e. the reaction between ethylene oxides disposed at the end of linear chain of the aliphatic epoxy resin and the reactive hydrogens of aminosilane used as curing agent, and (ii) hydrolysis and condensation reactions between the alkoxysilanes used as co-binder and the cured aliphatic epoxy resin.

Thereby, it is formed a completely crosslinked epoxy-polysiloxane polymer, i.e. a genuine hybrid structure since inorganic and organic components are mutually linked through chemical bonds (non-interpenetrating structure).

In addition, tests of abrasion resistance carried out in this research (ASTM D968 and Taber Rotary Platform Abrasion Tester) indicate that the curing reaction of the epoxy resin has a kinetic significantly lower than the reactions of hydrolysis and condensation of alkoxides; this explains the formation of the cited hybrid structures and also justifies the no incorporation of water in the formulation of paints.

On the other hand, the literature indicates that molecules of alkoxides, after the hydrolysis leading to the formation of silanols,

Table 1
Results of tests related to anticorrosive properties.

Alkoxide type	Epoxy resin/alkoxide ratio	Sd, m	Degree of rusting	Degree of blistering
Dimethyldiethoxysilane	30/70	0.03	4–5	10
	40/60	0.05	6	10
	50/50	0.07	7	10
	60/40	0.11	8–9	8-MD
	70/30	0.20	9–10	7-MD
Methyltriethoxysilane	30/70	0.04	6–7	10
	40/60	0.06	7	10
	50/50	0.08	8	9-F
	60/40	0.17	9	7-MD
	70/30	0.24	10	6-D
Tetraethoxysilane	30/70	0.05	8	10
	40/60	0.08	9	9-F
	50/50	0.09	9	8-F
	60/40	0.21	10	7-MD
	70/30	0.37	10	5-D
Reference paint	–	0.67	10	4-D

also establish covalent bonds with iron substrate: silanol groups are readily adsorbed onto the metal surface via formation of hydrogen bonds with surface hydroxyl groups (Metal—OH). In a subsequent stage, such bonds convert to stable metalosiloxane bonds ($\equiv$Si—O—Metal) at interface by releasing water [17–19].

The mentioned reactivity at interface would contribute to the results discussed below (degree of rusting in salt spray apparatus and degree of blistering in 100% relative humidity cabinet).

3.2. Performance related to anticorrosive properties

3.2.1.1. Water vapor permeability

The air thickness Sd generally increased (less vapor diffusional flow) with the decreasing of the alkoxysilane content in the film-forming material. Sd values are indicated in Table 1 (standard deviations ranged between 0.01 and 0.03). In addition, by extrapolating Sd values to 100% epoxy resin in the binder, the results display that the paint based on aliphatic epoxy resin would have higher Sd value than those with the three alkoxysilanes selected.

The results also indicate that the corresponding Sd values increased for paints based on dimethyldiethoxysilane, methyltriethoxysilane and tetraethoxysilane, in the quoted order. The increasing reactivity of the alkoxides (higher number of hydrolyzable and condensable groups) would lead to a more compact polymer structure and therefore to films with more resistance to vapor diffusional flow.

On the other hand, Reference paint showed the highest Sd value: 0.67 m (standard deviation, 0.03), i.e. the lowest value of flux density of water vapor diffusion DDV.

3.2.1.2. Degree of rusting

For all paints, Table 1 indicates that the corrosion resistance improved as the aliphatic epoxy resin/alkoxide ratio increased, in total agreement with Sd and degree of blistering.

Furthermore, the corrosion performance improved for binders based on dimethyldiethoxysilane (2 ethoxy groups), methyltriethoxysilane (3 ethoxy groups) and tetraethoxysilane (4 ethoxy groups), in that order: for similar permeability (particularly for small Sd values), degree of rusting improved as the reactivity of the alkoxides increased.

These results would be attributable to the capacity of alkoxides to form film-forming materials strongly polimerized as well as covalent bonds with the metal. The high chemical interaction with metal substrate would lead to the formation of high dimensional stability products at interface: the metalosiloxanes do not produce significant changes in volume by gain or loss of water molecules as

they do iron oxides (this generates shear stresses at the interface leading to adhesion loss).

On the other hand, results allow mention that the paint based on aliphatic epoxy resin would present the highest value of degree of rusting, 10 (by extrapolating the values, the corrosion resistance increased with the epoxy resin content in the binder). Finally, the Reference paint displayed the highest value of degree of rusting (the corrosion resistance is in total agreement with the Sd).

3.2.1.3. Degree of blistering

Values of Table 1 indicate that the decreasing amount of alkoxide in the film-forming material (higher epoxy/alkoxide ratio) led to an increasing blistering.

Furthermore, blistering resistance decreased in paint films based on dimethyldiethoxysilane, methyltriethoxysilane and tetraethoxysilane, in that order. Results indicate that the increasing Sd with the reactivity of alkoxides led to more blistering, despite the increased adhesion to the substrate by chemical interaction (Metal—O—Si$\equiv$ bonds).

In addition, the results obtained by extrapolating values indicate that paints based only on aliphatic epoxy resin would display more blistering than those with the three alkoxysilanes in their composition (the resistance to blistering decreased with the epoxy resin content in the binder). Finally, it is important to mention that the Reference paint displayed the lowest value of degree of blistering (4-D), which is consistent with the value of Sd (the highest of all tested paints).

3.3. Performance related to weathering exposure

3.3.1.1. Initial gloss and gloss retention

Table 2 displays the initial gloss and the gloss retention for each epoxy resin/alkoxide ratio, since the very low standard deviation indicates the no significant influence of the alkoxide type on the gloss of the hybrid films.

Table 2
Results of tests related to weathering exposure.

Epoxy resin/alkoxide ratio	Gloss		Color retention, ΔE
	Initial	Retention, %	
30/70	72.7 (0.9)	91.3 (0.8)	1.1 (0.1)
40/60	70.5 (0.8)	90.6 (1.0)	1.4 (0.2)
50/50	69.7 (1.2)	89.1 (0.7)	1.8 (0.3)
60/40	67.3 (1.1)	85.7 (1.3)	2.3 (0.3)
70/30	63.1 (0.8)	73.2 (0.9)	4.0 (0.3)
Reference paint	62.0 (1.0)	2.3 (0.7)	22.4 (0.5)

Results allows to conclude that the average values of initial gloss and gloss retention for the three alkoxide types were increasing with the decrease of the aliphatic epoxy resin/alkoxide ratio, which means that the incorporation of one of any three alkoxides improved the initial gloss and the gloss retention. For example, paint based on 30/70 epoxy resin/alkoxide ratio showed high values of initial gloss, 72.7 (0.9) and of gloss retention, 91.3% (0.8). The latter is comparable to those values usually presented by efficient finishing paints (e.g. acrylic-aliphatic polyurethane as binder).

It is worth mentioning that for the bisphenol A epoxy paint used as reference, the initial gloss was 62.0 (1.0), which is inferior to those presented by all hybrid paints. Concerning the gloss retention, this was only 2.3% (0.7), which confirms that Reference paint is easily degraded by sunlight action.

3.3.1.2. Color retention

In this test, the alkoxide type also displayed no significant influence (Table 2, very low standard deviation). The excellent color stability is reflected by ΔE; the improved stability (low ΔE) was obtained with the increasing alkoxide content in the film-forming material. For example, the value 1.1 (0.1), for paint based on 30/70 epoxy resin/alkoxide ratio, is highly satisfactory for efficient finishing paints.

In summary, the increasing level of polysiloxane in the binder (lower aliphatic epoxy resin/alkoxide ratio) led to films of better weathering resistance; from this point of view, the more suitable hybrid organic–inoganic paint must be selected according to the service requirements.

Regarding the behavior of Reference paint, the ΔE of 22.4 (0.5) indicates a strong degradation of the organic polymeric material, which significantly contrasts with the high stability of hybrid paints.

3.4. Global efficiency of high solids, hybrid paints

With the purpose of establishing the global efficiency of each paint, the following considerations were made: (i) the values of degree of rusting corresponding to the areas with and without cutting were initially averaged; (ii) the values of degree of blistering were carried to the scale from 0 to 10 averaging the size and the frequency; 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; (iii) the initial gloss and the gloss retention values were also carried to the scale from 0 to 10 and then averaged; for this, both values, varying from 0 to 100, were proportionally expressed in the scale 0–10; (iv) the color retention values were also carried to the scale from 0 to 10; for ΔE inferior to 10, the qualification was done by calculating the difference to 10 while for values of 10 or more, it was considered 0 and, finally, (v) the sum values S of (i), (ii), (iii) and (iv) were calculated; the quoted values were expressed as efficiency E, i.e. as a percentual fraction of maximum S (alkoxide type, 200 and aliphatic epoxy resin/alkoxide ratio, 120), Table 3.

The analysis of the results included in Table 3 indicates that:

- *Influence of alkoxide type:* values are only slightly different; the highest value was obtained by tetraethoxysilane ($S = 157.3$; $E = 78.6\%$), followed by methyltriethoxysilane (154.5; 77.2%) and finally, by dimethyldiethoxysilane (153.5; 76.8%).

Consequently, it was considered appropriate to conduct a separate analysis of results of the properties related to the anticorrosive performance and weathering resistance. Thus, a statistical interpretation was carried out; first, the variance was calculated, and later, the Fisher F test was performed.

It is concluded that this variable influenced significantly on the anticorrosive properties and not on the weathering resistance.

Table 3
Global performance of hybrid paints.

Alkoxide type	Sum value, S^a
Dimethyldiethoxysilane	153.5 ($E = 76.8\%$)
Methyltriethoxysilane	154.5 ($E = 77.2\%$)
Tetraethoxysilane	157.3 ($E = 78.6\%$)
Epoxy resin/alkoxide ratio	Sum value, S^b
30/70	100.3 ($E = 83.6\%$)
40/60	100.3 ($E = 83.6\%$)
50/50	98.3 ($E = 81.9\%$)
60/40	82.2 ($E = 73.5\%$)
70/30	78.1 ($E = 65.1\%$)

[a] 20 elements, with a value of 10 each (maximum sum value, 200).
[b] 12 elements, with a value of 10 each (maximum sum value, 120).

This made that the influence of the alkoxide type is attenuated in the global efficiency. Then, to select the alkoxide type, only the results of tests related to anticorrosive properties were considered, Table 1. The analysis of the results allows to visualize that the best performance was reached with tetraethoxysilane, methyltriethoxysilane and dimethyldiethoxysilane, in that order.
- *Influence of aliphatic epoxy resin/alkoxide ratio:* the two inferior ratios (30/70 and 40/60) displayed the best performance ($S = 100.3$; $E = 83.6\%$), which was decreasing with the increasing of the aliphatic epoxy resin in the composition, Table 3.

In summary, the analysis of all variables indicates that the most suitable paint for the anticorrosive protection of metals exposed to the weathering is based on tetraethoxysilane in the two superior levels (30/70 and 40/60 aliphatic epoxy resin/alkoxide ratios), followed very closely by the 50/50 ratio. The final selection among the hybrid paints studied should be done by carrying out technical-economic studies.

The above results are based on that the synthetic calcium silicate, due to its high OA, allowed reaching a low CPVC and therefore, selecting a reduced PVC for hybrid films of 220–230 μm dry film thickness. In spite of the reduced PVC, it allowed the formulation of paints with suitable anticorrosive performance (advisable for primers, which are usually formulated with high PVC/CPVC ratios) and with adequate gloss and color retention (appropiate for finishing paints, which are always formulated with low pigmentation levels).

Finally, it is important to mention that hybrid paints showed excellent stability in laboratory for 12 months (confirmed through viscosity measurements at low shear rate) and that no thinning was required for application in spite of they were formulated with approximately 90% solids in volume (fulfilling with the most exigent international environmental regulations).

4. Conclusions

- The high anticorrosive efficiency of some hybrid paints is based on that they can be formulated in a wide range of film permeability according to the composition of the film-forming material (alkoxide type and aliphatic epoxy resin/alkoxide ratio), the pigmentation (mainly by the synthetic calcium silicate of extremely high oil absorption used as extender) and the PVC considered (equal or slightly less than the reduced CPVC).
- The excellent weathering resistance of some hybrid paints is based on that the aliphatic epoxy resin is not easily degradable by sunlight as conventional glycidic epoxy resins and on the use of a curing agent and a co-binder of inorganic nature. Although the type of alkoxide showed no significant influence on initial gloss and gloss and color retention, the increasing level of alcoxide improved significantly the weathering resistance.

Acknowledgements

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