

Hybrid Finishing Coatings Applied on Laminar Zinc Primers

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ABSTRACT: Hybrid finishing coatings were formulated with several film-forming materials and reinforcement fibers. In all cases, the same tri-pigmented epoxy-polyamide coating based on laminar zinc was used as primer. The results indicated that well-wetted fibers improved mechanical properties of finishing coating films, such as tensile strength, modulus of elasticity, hardness, adhesion, and impact resistance; on the other hand, elongation decreased according with type and level of reinforcement fibers selected. In addition, finishing coatings with semiconductive fibers displayed in salt spray (fog) apparatus, a high dissolution of metallic zinc of primer since these fibers would act as cathode in galvanic cells. According to IR spectrum analysis, chemical degradation was observed only in coatings with the binder susceptible to basic hydrolysis due to the action of hydroxyl ions formed on semiconductive fibers. Furthermore, nonconductive fibers included in finishing coatings displayed no changes in any film-forming material (even when alkyd resin was used) nor promoted excessive zinc dissolution of primer.

1. INTRODUCTION

The zinc-rich coatings and those formulated with extenders and corrosion inhibitors display higher anticorrosive efficiency than other types of coatings.^{1–5} Considering the sacrificial anode concept (cathodic protection), many coatings have been designed based on high purity zinc dust dispersed in organic and inorganic vehicles. These materials, when applied in film form, display a close contact between particles and with metallic substrate to be protected.^{6–8}

Primers formulated with metallic zinc usually need a finishing coating for controlling the metallic zinc dissolution (e.g., reaction with water, water vapor, oxygen, carbon dioxide, etc.) and binder degradation (e.g., action of ultraviolet radiation) during exposition to the environment; in many cases, a topcoat is also used for improving aesthetic appearance.

In recent years, the finishing coating is also applied to achieve films with great tensile strength and high modulus of elasticity (Young's modulus) and to control the propagation of cracks and checks formed by the volumetric shrinkage emergent of the degradation process and the lack of dimensional stability of substrate (e.g., thermal changes). To achieve the above-mentioned objectives, the formulation of topcoats for the trucking industry, agricultural machinery, aircraft, etc. could be based on hybrid structures with reinforcement fibrous material.

The objective of this research was to study the influence of content and the nature of reinforcement fibers as well as the type of film-forming material in finishing coatings applied on a tri-pigmented epoxy-polyamide primer based on laminar zinc.

2. FORMULATION AND MANUFACTURE OF COATINGS

2.1. Primer. The formulation was selected from previous studies.^{9–11} Pigmentation included laminar zinc (diameter 50/50, 10.5 μm ; purity, 99.5% w/w) as sacrificial anode, calcium silicate (diameter 50/50, 12.1 μm) as zinc particle spacer, and strontium wolframate (diameter 50/50, 3.0 μm) as inhibitor in 65/25/10 laminar zinc/spacer/corrosion inhibitor ratio v/v. Concerning film-forming material, it was based on an epoxy

resin (WPE, 450) and a polymeric curing agent (amine value, 210–220). The solvent mixture consisted in 42.7% xylene, 14.6% butanol, and 42.7% oxygenated hydrocarbon in weight. Several additives were used.

In turn, pigment volume concentration (PVC) was 40%; this value is slightly inferior to the critical one (CPVC, 44–46%), which was estimated on 75/80 μm thickness free films by the Gardner permeability test.¹²

Manufacture was carried out in a ball mill of 1.0 liter total capacity. Spacer and corrosion inhibitor were dispersed for 24 h; previous to primer application and with the purpose of avoiding a metallic zinc reaction with the humidity vestige from any component, laminar zinc was dispersed in high-speed agitation equipment for 180 s at 1400 rpm.

2.2. Finishing Coatings. **2.2.1. Pigmentation.** Pigment formulation included rutile titanium dioxide with surface treatment R1 (according Standard DIN 55912, a surface treatment up to 3% only with inorganic and organic substances) as opaque pigment and talc ($2\text{MgO}\cdot 4\text{SiO}_2\cdot \text{Mg}(\text{OH})_2$), barites (BaSO_4), and mica ($\text{K}_2\text{O}\cdot 2\text{Al}_2\text{O}_3\cdot 2\text{H}_2\text{O}$) in 2.5/2.5/1.0 w/w ratio as extenders. The opaque pigment/ extenders ratio was 15/85 w/w.

2.2.2. Film-Forming Material. The following materials were used:

- A pure acrylic resin (terpolymer of methyl methacrylate, normal butyl acrylate, and methacrylic acid) in spherical shape particles: 185 μm diameter D 50/50, 50 °C vitreous transition temperature T_g (DSC 20 °C/min), 60 000 average molecular weight, and 14 mg KHO/g acid value. Because of its high T_g , resin was plasticized with 54% chlorinated paraffin in 6/1 w/w ratio to give the mechanical properties of the film a suitable balance.

Solvesso 150/ethylene glycol acetate in 3.5/1.0 w/w ratio was used as solvent mixture.

- A vinyl resin based on a partially hydrolyzed vinyl chloride/vinyl acetate copolymer, in 87/13 w/w ratio. It has a white-yellowish fine dust aspect, 45 000 average molecular weight, and 0.1 mg KHO/g acid value. This resin was plasticized with 54% chlorinated paraffin in 5/1 w/w ratio. Cellosolve acetate/methyl isobutyl ketone/toluene in 4/1/1 w/w ratio was selected as the solvent mixture.
- A medium oil alkyd resin (45% w/w) in 50% w/w turpentine spirit solution, with Z-Z2 Gardner viscosity at 25 °C, color 5 Gardner (ASTM 1544), and 14 mg KHO/g acid value. The drying agents were 0.40% zirconium, 0.04% cobalt, and 0.10% calcium, expressed on resin nonvolatiles. To prevent superficial layer formation, 0.3% w/w methyl ethyl cetoxime on the formulation total was added. For coating manufacture, a low amount of toluene/glycol ether mixture was added for improving the stability of coatings.

2.2.3. Fibrous Material. Nowadays reinforcement fibers are used for improving several film properties.^{13–19} In this research, commercial fibers (graphite, silicon nitride, glass, or quartz) were included in the finishing coating formulations. The selected levels were 0.0, 1.0, and 2.0% w/w on coating solids; their characteristics are listed in Table 1.

Table 1. Main Characteristics of Reinforcement Fibers

fiber type	tensile strength, MPa	specific elongation	modulus of elasticity, GPa	density, g.cm ⁻³
graphite	12	1,50.10 ⁻³	8	1.73
silicon nitride	390	1,23.10 ⁻³	317	3.31
quartz	47	0,65.10 ⁻³	72	2.22
glass	53	0,82.10 ⁻³	65	2.23

Graphites are composites manufactured starting from a mixture of coke and pitch. The graphite used in the experiment behaves like a semiconductor²⁰ since it allows electric current to flow very strongly in one direction and very weakly in the opposite direction, Figure 1A.

Silicon nitride is a compound synthesized through several chemical reactions. This material is electrically insulating and dark gray to black in color. In this experiment, silicon nitride manufactured by reaction-bonded silicon nitride (RBSN) was selected,^{21,22} Figure 1B.

Glass is a hard material, normally fragile and transparent, and nonconductor of electricity. In this research, borosilicate glass fibers were employed, Figure 1C.

Vitreous silica is the generic term used to describe all types of silica glass; it is known as fused quartz or fused silica. The finished product is transparent and an insulating material from electrical viewpoint. In this experiment, fused silica was used in fiber form, Figure 1D.

2.2.4. Additives. A gel of castor oil at 15% w/w was prepared in a toluene/mineral spirits mixture (50/50 w/w ratio); it was added after finishing the pigment dispersion in 2% w/w for obtaining high-build products. A commercial blend of anionic and nonionic polymers was used as dispersing/stabilizing agent.

2.2.5. Pigment Volume Concentration. The PVC value selected was 20% for all finishing coatings. This small value ensures the presence of enough resin to get a shiny surface not

interrupted by excess pigment particles, except due to the possible presence of some reinforcement fibers.

2.2.6. Manufacture. In this study, hybrid coatings were made by ultrasonic dispersion (Hielscher–Ultrasound Technology; frequency, 20–24 kHz; ultrasonic power, 650 W adjustable). The efficiency of the fiber dispersion in the polymeric matrix was rheologically monitored (viscosity of the system, measured at 10⁻³ s⁻¹, decreased during the sonification process until reaching a stationary value: from 5 to 10 min according to the operating conditions); viscosity measurements corroborated the dispersion stability after 3 months in a can.

3. LABORATORY TESTS

3.1. Mechanical Properties of Finishing Coatings.

3.1.1. Tensile Strength and Elongation on Free Films. Topcoats were applied on a glass base by using a casting knife film applicator (Elcometer 3580), which allowed the adjustment of the film thickness in 10 μm steps from 0 to 6 mm by means of two integrated micrometric screws; the glass base was previously treated with polyvinyl alcohol to facilitate takeoff of the film after its formation was complete. In all cases, the dry film thickness was 180 ± 5 μm. The thickness was determined on a steel plate with reference patterns by using an electromagnetic induction thickness gauge (Elcometer 101). This is a nondestructive method to measure the thickness of nonmagnetic coatings.

Samples of suitable size were prepared; then, tensile strength and elongation were determined by using an Instron Testing Machine with 1 kg load and 2 cm·min⁻¹ speed, under the guidelines of ASTM D 2370. Modulus of elasticity (stiffness) was calculated starting from the linear region of the curve tensile strength vs specific elongation.

3.1.2. Buchholz Hardness. The topcoats were applied with the above-mentioned casting knife film applicator (180 ± 5 μm) on SAE 1010 steel panels previously sandblasted to confer roughness (R_{av} , 28 μm) and facilitating film adhesion; panels were prepared in duplicate.

Buchholz hardness, according DIN 53153, was determined as an average of five determinations on each panel. The test measures hardness of coatings using the indentation method (Elcometer 3095) with a bevelled disc indenting tool which is fitted into a stainless steel block exerting a constant test load of 500 g (17.6 oz). The gauge is placed on the coating for 30 s and the length of any subsequent indentation in the coating is measured using the graduated microscope.

3.1.3. Film Adhesion. Panels were prepared in a similar way as for Buchholz hardness; experiments were carried out by using an Elcometer model 106; to obtain the numerical values, each test dolly was bonded to the corresponding finishing coating by using an epoxy adhesive, and pulled off after curing. As this test has high dispersion of values, average values of ten determinations on each panel were calculated.

3.1.4. Impact Resistance. Panels were prepared as above-mentioned. To evaluate impact resistance of films to the effects of rapid deformation according ASTM D 2794, coatings were applied on 1 mm thick steel panels. A standard weight was dropped a distance to strike an indenter that deforms the coating and the substrate; the indentation was carried out on a coated face. By increasing the distance the weight drops at 1 in. (25.4 mm) at a time, the point at which failure occurred was determined using a magnifier (10× observation). At this test average values of five determinations on each panel were also calculated.

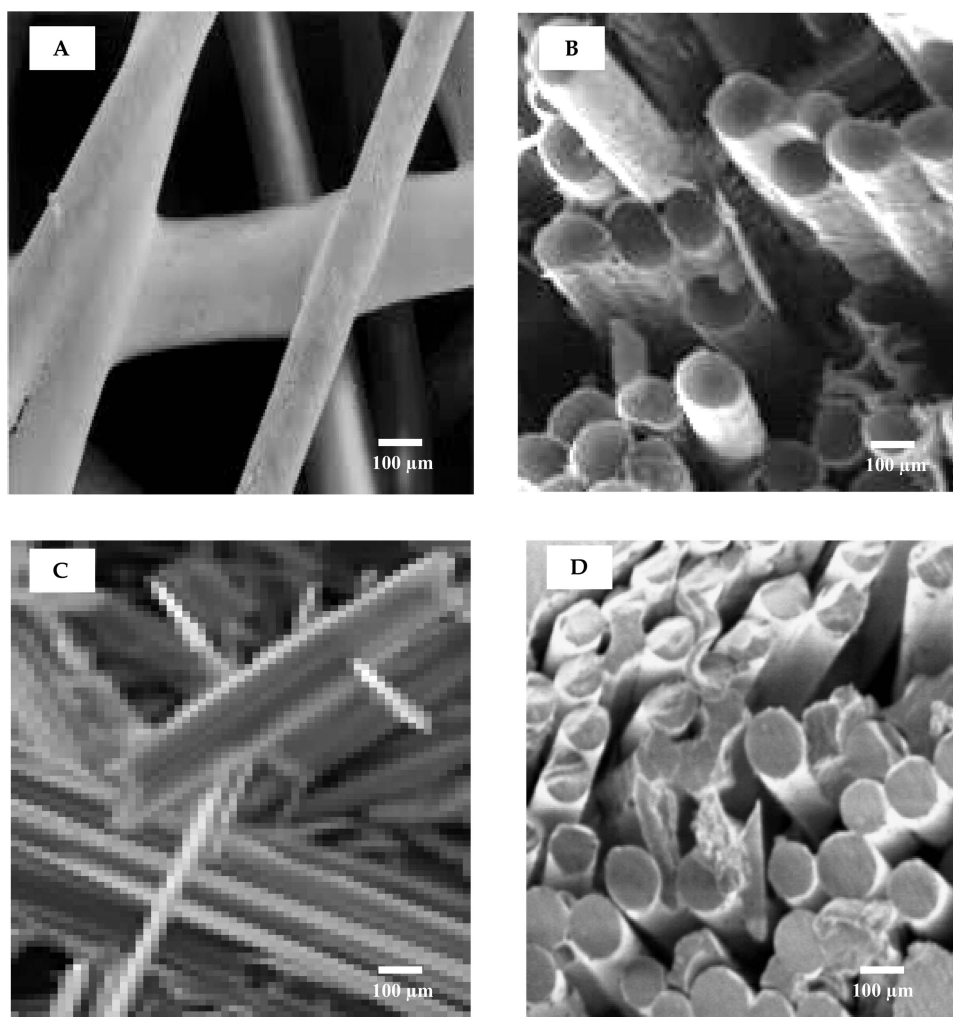


Figure 1. SEM micrograph of reinforcement fibers: (A) graphite, (B) silicon nitride, (C) glass, and (D) quartz.

3.2. Alkaline Resistance of Finishing Coatings. Glass panels were prepared in similar way than mentioned for other mechanical properties. In this test, they were partially immersed in 5% w/w sodium hydroxide solution at 25 °C for 24 h; partial immersion allowed the direct comparison of effect of alkaline solution on coating films under study.

After removing the panels from the solution, they were washed with distilled water and exposed in a laboratory environment for 24 h to dry.

Finally, they were examined by IR; for this assay, a Perkin-Elmer spectrometer was used (model Spectrum One), applying the attenuated total reflectance method (single rebound) and using zinc selenide viewer and diamond crystal as interface between the sample and infrared energy.

3.3. Aging of Coating Systems in Salt Spray (Fog) Apparatus and in 100% Relative Humidity Cabinet. SAE 1010 steel panels of $80 \times 160 \times 2 \text{ mm}^3$ were degreased with an oxygenated solvent (methyl isobutyl ketone, MIBK) in vapor phase and sandblasted to ASa 21/2 grade (SIS specification 05 S9 00/67) up to 25 μm maximum roughness R_m . Primer application was made in a single layer by brushing; panel edges were reinforced by dipping in a sealer based on a styrene-acrylic resin.

Panels were prepared in duplicate and stored in the laboratory for three days at $25 \pm 2 \text{ }^\circ\text{C}$ before starting application of topcoats; in this lapse, the curing of epoxy-

polyamide film is only partial, which facilitates an appropriate adhesion between layers of the protective system.

Finishing coatings were also applied by brushing, in two layers, with 24 h interval between each layer; for the first layer, the surface tension was properly adjusted before application ($38/40 \text{ dina}\cdot\text{cm}^{-1}$) with the purpose for avoiding bubbles (removal of air and water vapor from inside the pores of primer film).

Finally, panels were kept in laboratory for 10 days at $25 \pm 2 \text{ }^\circ\text{C}$ until all layers were completely dried and cured.

The dry film thickness of each layer was determined by using a device consisting of a blade that cut the substrate, generating a discontinuity in V with an inclination angle of 45° . Subsequently, the distance in parallel plane to substrate was measured microscopically on an inclined face of the cut film (reading the device corrects the distance). The dry film thickness of primer ranged between 75 and 80 μm while that of the corresponding finishing coatings oscillated between 220 and 250 μm .

Panels were tested in a salt spray (fog) apparatus (1500 h) under the operating conditions specified in ASTM B 117. After finishing the test, an assessment of the degree of rusting was carried out according to ASTM D 1654.

Panels were also tested in a 100% relative humidity cabinet (500 h) under the operating conditions specified in ASTM B

2247. After finishing the test, assessment of the degree of blistering was carried out according to ASTM D 714.

4. RESULTS AND DISCUSSION

The factorial design included three binders for finishing coatings (pure acrylic resin, vinyl resin, and alkyd resin) by four types of reinforcement fibers (graphite, silicon nitride, glass and quartz) by three levels of reinforcement fibers in the dry layer (0.0%, 1.0%, and 2.0%); each topcoat was applied on the epoxy-polyamide primer based on laminar zinc/spacer/corrosion inhibitor. Thus, 36 finishing coatings were formulated and, in addition, manufactured in duplicate.

4.1. Mechanical Properties of Finishing Coatings.

Taking into account that the finishing coatings have a maximum of only 2% fibers, their presence in the hybrid structures produced significant changes in the mechanical properties considered as detailed in subsequent discussions.

4.1.1. Tensile Strength, Elongation, and Modulus of Elasticity of Free Films. As previously mentioned, values of tensile strength and specific elongation of coating films were initially determined, which allowed the subsequent calculation of the modulus of elasticity. The analysis of the results listed in Tables 1 and 2 enables the following conclusions:

(i) Reinforcement fibers: The graphite has the lowest tensile strength and the highest elongation while silicon nitride has the highest tensile strength and an elongation only lower than the graphite; quartz and glass fibers present comparable values of tensile strength and elongation.

(ii) Finishing coatings without reinforcement fibers: Polymeric materials were selected considering their film-forming properties (e.g., glass transition temperature T_g in the case of pure acrylic resin), chemical composition (type and level of oil in the alkyd resin), or the need of an external plasticization to achieve an appropriate balance of hardness/flexibility (e.g., the case of the vinyl resin); the three finishing coatings showed appropriate values of tensile strength and elongation to form film: those formulated with pure acrylic resin displayed the greatest tensile strength and the lowest elongation, whereas coatings with alkyd resin showed the lowest tensile strength and the highest elongation although the last ones with a performance just slightly higher than those with vinyl resin in their composition.

(iii) Hybrid finishing coatings: The obtained values both of the tensile strength and the elongation are based on the intrinsic properties of the fibers and of the coatings without reinforcement fibers as well as on the level of fibers incorporated to formulations.

In general, it is observed that all well-wetted fibers (silicon nitride, quartz, and graphite) increased both the tensile strength and the modulus of elasticity of films but decreased elongation in elastic deformation region.

All finishing coating with silicon nitride fibers, in the considered levels, displayed a greater increase both of the tensile strength and the modulus of elasticity than the coatings with quartz and graphite fibers, in that order; regarding elongation, silicon nitride fibers led to a reduction intermediate between those displayed by the quartz and graphite fibers.

Thus, for example, the acrylic finishing coating with 2% silicon nitride displayed the highest tensile strength (17.6 MPa) and a reduced elongation, although not the lowest of the experience (6%); on the other extreme, it was the alkyd coating finishing with 1% graphite, which presented only a slight improvement in tensile strength in relation to the coating

Table 2. Tensile Strength, Specific Elongation, and Modulus of Elasticity of Free Films of Finishing Coatings

fiber type	fiber level, %	tensile strength, MPa	specific elongation	modulus of elasticity, MPa
Pure Acryl Resin Coating				
no fiber	0.0	5.5	1.20	4.6
graphite	1.0	6.2	1.26	4.9
graphite	2.0	6.9	1.28	5.4
silicon nitride	1.0	13.2	1.13	11.6
silicon nitride	2.0	17.6	1.06	16.6
glass	1.0	5.6	1.17	4.8
glass	2.0	5.9	1.16	5.1
quartz	1.0	8.2	1.08	7.6
quartz	2.0	11.0	1.01	10.9
Vinyl Resin Coating				
no fiber	0.0	4.8	1.26	3.8
graphite	1.0	5.5	1.22	4.5
graphite	2.0	6.0	1.18	5.1
silicon nitride	1.0	11.6	1.21	9.6
silicon nitride	2.0	15.5	1.11	14.0
glass	1.0	4.9	1.20	4.1
glass	2.0	5.1	1.19	4.3
quartz	1.0	7.2	1.12	6.4
quartz	2.0	9.7	1.06	9.1
Alkyd Resin Coating				
no fiber	0.0	4.7	1.27	3.7
graphite	1.0	5.2	1.21	4.3
graphite	2.0	6.1	1.17	5.2
silicon nitride	1.0	6.3	1.21	5.2
silicon nitride	2.0	15.5	1.12	13.9
glass	1.0	4.9	1.20	4.1
glass	2.0	5.0	1.19	4.2
quartz	1.0	6.3	1.12	5.6
quartz	2.0	9.4	1.05	8.9

without fibers (5.2 and 4.7 MPa, respectively) but retained a high elongation (21%).

On the other hand, glass fibers showed the smallest efficiency for the three polymeric materials: tensile strength, elongation, and modulus of elasticity suffered no significant changes in relation to coatings without reinforcement fibers. This results because the surface of the glass fibers did not allow the suitable transference of tensile strength from the polymeric matrix. The above-mentioned would be attributable to the different surface tensions of mill base and fibers (poor wetting of glass fibers during dispersion, which was confirmed by microscopic observation); probably with the use of a suitable surfactant leading to a surface tension of the mill base similar (or better, only slightly lower to reach a good stability in the can) to that of glass fibers on their surface, an adequate wetting of the fibers could be reached with the consequent improvement in mechanical properties of the films.

The topcoats manufactured with the three film-forming materials (pure acrylic resin, plasticized vinyl resin, and alkyd resin) displayed similar percent changes in their film mechanical properties when modified with fibers; for example, the relationship between the values of tensile strength of films

with and without 2% silicon nitride oscillated between 3.2 and 3.3.

In summary, the research indicates that it is possible to obtain pairs of values of tensile strength and elongation for each type of film-forming material and type and level of reinforcing fiber to incorporate in the formulation, in function of the requirements to which the painted substrates will be subjected in service: well-wetted reinforcing fibers would be responsible of absorbing the tensile strength to which the films are subjected in service (e.g., cracks and checks produced during aging and weathering, expansion and shrinkage of the substrate mainly due to thermal changes, etc.).

4.1.2. Buchholz Hardness. The Buchholz hardness values for coatings based on pure acrylic resin, vinyl resin, and alkyd resin, without reinforcement fibers in their composition, are listed in Table 3.

Table 3. Buchholz Hardness, Film Adhesion, and Impact Resistance of Free Films of Finishing Coatings with 2% Fiber Level

fiber type	Buchholz hardness	film adhesion, kg·cm ⁻²	impact resistance, inch-pounds (N·m)
Pure Acryl Resin Coating			
no fiber	93	16	15 (1.65)
graphite	99	16	17 (1.87)
silicon nitride	111	19	20 (2.20)
glass	94	16	15 (1.65)
quartz	102	17	18 (1.98)
Vinyl Resin Coating			
no fiber	83	15	14 (1.54)
graphite	91	16	16 (1.76)
silicon nitride	104	19	18 (1.98)
glass	84	16	14 (1.54)
quartz	93	17	16 (1.76)
Alkyd Resin Coating			
no fiber	71	15	13 (1.43)
graphite	76	16	14 (1.54)
silicon nitride	87	19	16 (1.76)
glass	72	15	13 (1.43)
quartz	79	17	14 (1.54)

Fibers of silicon nitride, quartz and graphite, in the two levels considered, improved film hardness: the highest percent increase was observed with the addition of silicon nitride, followed by quartz and, finally by graphite, in this order.

Concerning glass reinforcement fibers, no significant differences were observed in film hardness for the finishing coatings based on the three considered binders (in all cases, the increase in film hardness was inferior to 2%). As mentioned in the analysis of results corresponding to tensile strength and elongation on free films, this behavior occurred because the surface of the glass fibers did not allow the suitable transfer of tensile stress from the polymeric matrix.

4.1.3. Film Adhesion. No significant differences in average values of film adhesion were attained for coatings based on pure acrylic resin, vinyl resin, and alkyd resin, without reinforcement fibers in their composition (Table 3). Inspection of the dolly faces determined that the failure mode was in all cases a combination of about 50% between proper adhesion (interface metal-coating film) and cohesive (film body).

In this test, all fiber types (except glass), in the two levels considered, also improved film property: an increase of film adhesion was observed with the addition of silicon nitride, followed by quartz, and finally by graphite, in this order.

Although the results did not show significant differences between the three film-forming materials considered, in all cases it was found that the failure changed to totally proper adhesive, which indicates that the fibers improved the mechanical behavior in the film body. This would suggest that the roughness profile should be increased for applications on service in relation to that used in this experiment.

Regarding glass reinforcement fibers, in the two levels considered, no significant differences were observed in film adhesion for the finishing coatings based on the three considered binders (in all cases, the increase was only in the order of standard deviation as maximum). As mentioned, this behavior occurred because the surface of the glass fibers was not adequately wetted by the polymeric matrix during coating manufacture and was not due to the intrinsic characteristics of the fibers themselves.

4.1.4. Impact Resistance. Finishing coatings without reinforcement fibers displayed on the impact area just slight cracking and nondetachment of films; the values are listed in Table 3.

On the other hand, all the films with reinforcement fibers at both levels showed significant superior impact resistance; average values indicate a better behavior when a 2% reinforcement fiber was used. The highest ones corresponded to coatings formulated with pure acrylic resin followed by those with vinyl resin and, finally by coatings based on alkyd resin. In all cases, nondetachment was determined.

It was observed that impact resistance values decreased with silicon nitride, quartz, graphite, and finally with glass, which practically did not modify the impact resistance in any finishing coating, perhaps because of the aforementioned lack of wetting.

In summary, results displayed that the use of adequate reinforcement fibers according with the type of film-forming material improves the film impact resistance, similarly to that observed in Buchholz hardness and adhesion.

4.2. Alkaline Resistance of Finishing Coatings. On the basis of IR analysis, it was concluded that coatings based on pure acrylic resin and vinyl resin displayed satisfactory resistance to 5% sodium hydroxide solution, which was corroborated by visual observation (the film properties did not exhibit changes such as softening, chalking, or loss of adhesion). Thus, Figure 2 shows the IR spectrum of the finishing coating based on pure acrylic resin with 2% silicon nitride: it is observed that there was no difference in characteristic peaks between the original panel and that immersed in alkaline solution. In addition, the spectrum displays characteristic peaks of pure acrylic resin at 600–800 cm⁻¹ (C–C); 1000–1200 cm⁻¹ (C–O); 1720–1740 cm⁻¹ (C=O carboxyl group); and 2700–2900 cm⁻¹ (C–H).

With respect to finishing coatings formulated with alkyd resin, a noticeable structural modification due to alkaline hydrolysis was determined; in this case, softening, chalking, and loss of adhesion of films were visually observed. Accordingly, Figure 3 displays the IR spectrum of finishing coating based on alkyd resin with 2% silicon nitride. For panels immersed in alkaline solution, significant changes were determined at 1640–1650 cm⁻¹ (C=O ester) and 1000–1200 cm⁻¹ (C–O–C ester) as well as the apparition of new peaks at 3000–3600 cm⁻¹ (O–H) and 2800–2900 cm⁻¹ (C–H, adjacent to ester);

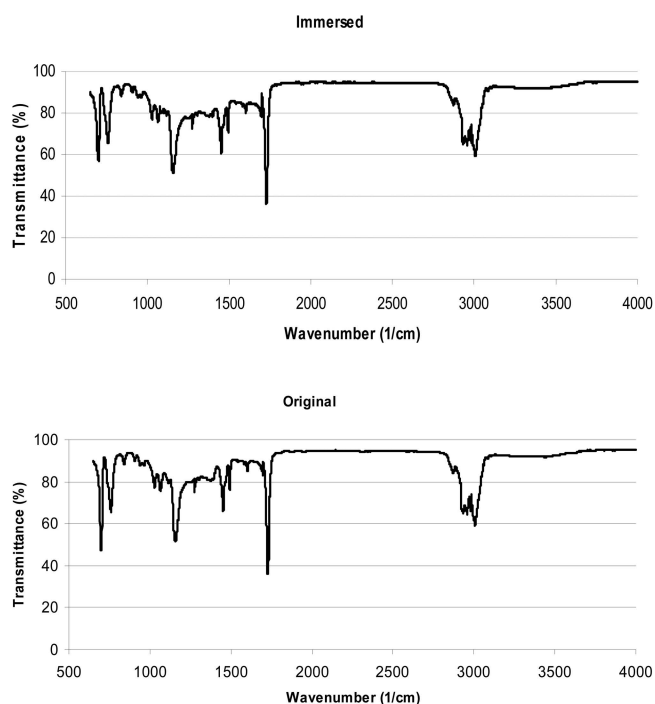


Figure 2. FT-IR spectrum of finishing coatings based on pure acrylic resin reinforced with 2% silicon nitride: original panel (lower) and immersed in alkaline solution (upper).

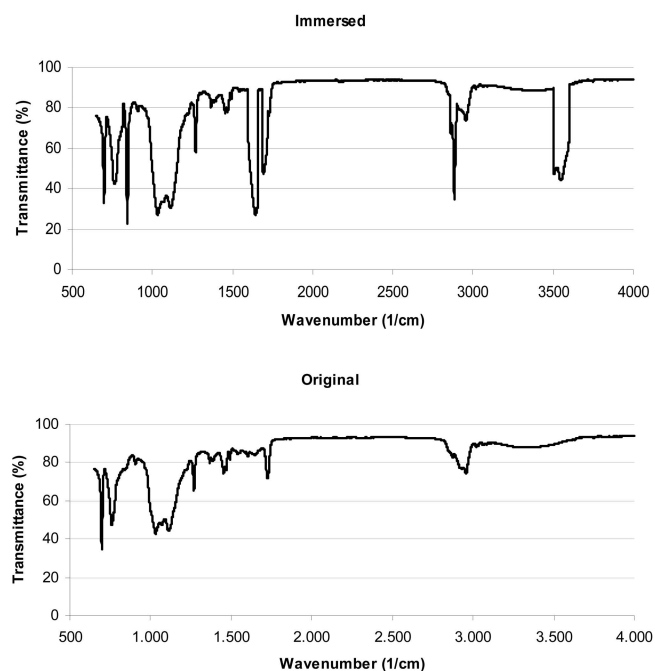


Figure 3. FT-IR spectrum of finishing coatings based on alkyd resin reinforced with 2% silicon nitride: original panel (lower) and immersed in alkaline solution (upper).

at 800 cm^{-1} the C–C stretching vibration is markedly different due to alkaline hydrolysis leading to a different degree of esterification adjacent to C–C.

4.3. Aging of Coating Systems in Salt Spray (Fog) Apparatus and in 100% Relative Humidity Cabinet. As mentioned, the primer formulation used in this experiment was selected from a previous study⁹ in which tests in salt spray (fog) apparatus (1500 h) and 100% relative humidity cabinet (500 h)

were performed; this unique primer was selected to study the influence of variables considered in this experiment: content and nature of reinforcement fibers as well as type of film-forming material in finishing coatings. The results of this study that included coating systems (the above-mentioned primer with different finishing coatings) confirmed the excellent performance displayed by the primer alone in the previous study. Thus, for example, degree of rusting of all coated panels exposed to salt spray (fog) apparatus showed a value 10 for 1500 h: 0 mm of advance from the X-cut, Method A and 0% of failed area, Method B; in all cases, delamination from X-cut and undercutting corrosion were not observed. On the other hand, degree of blistering of all experimental panels exposed to 100% relative humidity cabinet displayed the value 10 for 500 h: absence of blisters.

Nevertheless, the anticorrosive capacity of primer/finishing coating systems allowed establishing significant differences in the performance between hybrid coatings with semiconductive and nonconductive fibers in their composition.

In coating systems with hybrid coating films based on semiconductive fibers (graphite), excessive galvanic activity (high amount of zinc soluble salts) was visually observed, particularly in the X-cut. In addition, significant degradation was found on films based on alkyd resin; the corresponding IR spectrum displays very similar changes to that obtained in alkaline resistance tests. It is noteworthy that this was not detected in the epoxy-polyamide primer or in the finishing films with pure acrylic resin and vinyl resin in their composition.

These results suggest that semiconductive fibers included in the hybrid coatings led to the laminar zinc dissolution of primer (typical anodic reaction) since these fibers would act like cathodes of galvanic cells; the mentioned zinc dissolution due to the cathodic behavior of semiconductive fibers is undesirable since it reduces the anticorrosive efficiency of the primer (less useful life) in which zinc must act as a sacrificial anode but just to protect the steel base (cathode in galvanic cell). As alkyd resin is susceptible to basic hydrolysis, the hydroxyl ions formed on semiconductive fibers would be responsible for producing the degradation of its chemical structure.

It is worth mentioning that in those systems where the finishing coating was made with nonconductive fibers, no change was detected in the film-forming materials, even when alkyd resin was used. In the last case, the IR spectrum correlates well with that obtained from the panel not submerged in alkaline solution.

5. CONCLUSIONS

The results indicate that fiber type must be selected with the highest possible values both of tensile strength (in all cases superior to dry coating film) and of elongation (similar or only slightly inferior to coating dry film). This would allow the formulation of finishing coatings with high a modulus of elasticity (high tensile strength) but without reducing the elasticity of the resin itself or that achieved by the incorporation of external plasticizers.

The results of this investigation display the importance of properly selecting both specific surfactants and dispersing technology for each type of reinforcing fiber, mainly considering the chemical nature of the surface treatment. The case of the glass fibers used in the experiment is a clear example of the above, since as mentioned probably with the use of a suitable surfactant these fibers could have also led to an improvement of the mechanical properties of films as observed

with the other fibers (adhesion, hardness, and impact resistance).

The protective systems based on primer with laminar zinc and topcoat with semiconductive fibers displayed a high galvanic activity of zinc, which occurs because the fibers act as cathode in corrosion cells (hydroxyl ions are formed on semiconductive fibers); in addition, a significant degradation was found in the film-forming material susceptible to basic hydrolysis (alkyd resin in topcoat). On the other hand, finishing coatings made with nonconductive fibers displayed no changes in any film-forming material, even when alkyd resin was used.

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Notes

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■ REFERENCES

- (1) Pereyra, A. M.; Giudice, C. A. Shaped for performance: the combination of lamellar zinc and mica improves the efficiency of zinc-rich primers. *Eur. Coat. J.* **2007**, *9*, 40.
- (2) Díaz, L.; Chico, B.; De La Fuente, D.; Simancas, J.; Vega, J. M.; Morcillo, M. Corrosion resistance of new epoxy-siloxane hybrid coatings. A laboratory study. *Prog. Org. Coat.* **2010**, *69*, 278.
- (3) Vilche, J. R.; Bucharsky, E. C.; Giudice, C. A. Application of EIS and SEM to evaluate the influence of pigment shape and content in ZPR formulations on the corrosion prevention of naval steel. *Corros. Sci.* **2002**, *44*, 1287.
- (4) Bastos, A. C.; Zheludkevich, M. L.; Klüppel, I.; Grundmeier, G.; Ferreira, M. G. S. Modification of zinc powder to improve the corrosion resistance of weldable primers. *Prog. Org. Coat.* **2010**, *69*, 184.
- (5) Gergely, A.; Pfeifer, E.; Bertóti, L.; Török, T.; Kálmán, E. Corrosion protection of cold-rolled steel by zinc-rich epoxy paint coatings loaded with nano-size alumina supported polypyrrole. *Corros. Sci.* **2011**, *53*, 3486.
- (6) Giudice, C. A.; Benítez, J. C.; Pereyra, A. M. One coat system for metallic protection against corrosion and fire spreading. *Pittura Vernici Eur. Coat.* **2005**, *81*, 33.
- (7) Giudice, C. A.; Pereyra, A. M. Tecnología de pinturas y recubrimientos. *Componentes, Formulación, Manufactura Y Control De Calidad*; Editorial edUTecNe: Argentina, 2009.
- (8) Arianpouya, N.; Shishesaz, M.; Ashrafi, A. Analysis of synergistic effect of nanozinc/nanoclay additives on the corrosion performance of zinc-rich polyurethane nanocomposite coatings. *Polym. Compos.* **2012**, *33*, 1395.
- (9) Pereyra, A. M.; Giudice, C. A.; Herrera, L.; Echeverría, F.; Castaño, J. Tri-pigmented anticorrosive coatings based on metallic zinc as inhibitor. *Surf. Coat. Int.* **2006**, *89*, 245.
- (10) Pereyra, A. M.; Canosa, G.; Giudice, C. A. Nanostructured protective coating systems, fireproof and environmentally friendly, suitable for the protection of metallic substrates. *Ind. Eng. Chem. Res.* **2010**, *49*, 2740.
- (11) Canosa, G.; Alfieri, P. V.; Giudice, C. A. Hybrid intumescent coatings for wood protection against the fire action. *Ind. Eng. Chem. Res.* **2011**, *50*, 11897.
- (12) Gardner, H.; Sward, G. *Paint Testing Manual, ASTM STP 500*; ASTM: West Conshohocken, PA, 1972; Chapter 6.1.

(13) Mao, Y.; Jia, M. Application of glass flakes in novolac-epoxy vinyl ester resin anticorrosive coatings. *Beijing Huagong Daxue Xuebao (Ziran Kexueban)*. *J. Beijing Univ. Chem. Technol. (Nat. Sci. Ed.)* **2007**, *34*, 145.

(14) ALMaadeed, M. A.; Kahraman, R.; Noorunnisa Khanam, P.; Madi, N. Date palm wood flour/glass fiber reinforced hybrid composites of recycled polypropylene: Mechanical and thermal properties. *Mater. Des.* **2012**, *42*, 289.

(15) Kouloumbi, N.; Ghivalos, L. G.; Pantazopoulou, P. Effect of quartz filler on epoxy coatings behavior. *J. Mater. Eng. Perf.* **2003**, *12*, 135.

(16) Caicedo, J. C.; Ipaz, L.; Vanegas, O.; Aperador, W.; Cundar, A. Y.; Delvasto, S. Diseño y caracterización de un compuesto fibrorreforzado de matriz polimérica y fibra de carbono como modelo en la implementación de cascos para ciclismo. *Supl. Rev. Latinoam. Metal. Mater.* **2009**, *S1*, 1127.

(17) Gómez, A. M.; Alzate, C. C.; Márquez, A.; Restrepo, J. W.; Jaramillo, F. Efecto de la temperatura sobre la resistencia a la tracción de algunos refuerzos de fibras para matrices cerámicas o poliméricas. *Rev. EIA* **2009**, *11*, 65.

(18) Kunal, D.; Ray, D.; Banerjee, C.; Bandyopadhyay, N. R.; Sahoo, S.; Mohanty, A. K.; Misra, M. Physicomechanical and Thermal Properties of Jute-Nanofiber-Reinforced Biocopolyester Composites. *Ind. Eng. Chem. Res.* **2010**, *49*, 2775.

(19) El-Nemr, K. F.; Ali, M. A.; Hassan, M. M. Waste newsprint fibers for the reinforcement of radiation-cured (styrene-butadiene rubber)-based composites. Part II characterization and thermal properties. *J. Vinyl Addit. Technol.* **2012**, *18*, 228.

(20) Breusing, M.; Ropers, C.; Elsaesser, T. Ultrafast Carrier Dynamics in Graphite. *Phys. Rev. Lett.* **2009**, *102*, 1.

(21) Porz, F.; Thümmel, F. Oxidation mechanism of porous silicon nitride. *J. Mater. Sci.* **1984**, *19*, 1283.

(22) Riley, F. L. Silicon Nitride and Related Materials. *J. Am. Ceram. Soc.* **2004**, *83*, 245.