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Influence of Extender Type of Performance Of Modified Lamellar Zinc Primers

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The objective of this work was to gain a deeper insight into the behavior of zinc primer, containing either lamellar zinc alone or lamellar zinc mixed with an extender by means of accelerated tests in salt spray (fog) chamber and a 100% relative humidity cabinet. Mica, kaolin, and synthetic calcium silicate were used as extenders.

Several series of coatings were designed and manufactured employing the following binders: 20 cP chlorinated rubber, a vinyl copolymer, an unsaturated polymer, or an epoxy resin.

A simultaneous analysis of the experimental data was performed taking into account that the best performance is attained at pigment volume concentration (PVC) values equal to or slightly lower than the critical one (CPVC). Results indicate that for every lamellar zinc primer, it is possible to select an extender of high oil absorption as the spacer of the zinc particles attaining both very good blistering resistance and anticorrosive performance.

Keywords: Anticorrosive, primer, lamellar zinc, extenders, performance

Protective coatings are usually recognized as the most convenient method from a technical and economical viewpoint for protecting steel structures exposed to salt air and salt water spraying. Many coatings have been used to attain that objective; some of them, however, have been found to perform less satisfactorily than expected. Zinc-rich coatings and modified zinc coatings have been demonstrated to be more effective than other coating types. Their success is based on their particular ability to give cathodic protection (sacrificial action of the zinc)¹⁻³ and to act as a resistant barrier^{4,5} (zinc white corrosion products seal the protecting films). As mentioned, the anodic reaction corresponds to zinc particles dissolution and, on the other hand, the cathodic process involving the oxygen reduction is considered to take place at the steel surface.

As a result of these properties, zinc primers are very useful materials for preventing iron and steel corrosion.⁶ An easy laboratory experiment shows the protective action of a film based on metallic zinc. The electric current flows through a conductor between a painted panel and another panel without protection (both panels are placed inside an adequate electrolytic medium). After a period, the amperometer indicates that the current is very low and, therefore, galvanic action has clearly decreased. Nevertheless, the painted panel does not show signs of corrosion on the metallic substrate. This means that the film also protects the iron or steel after a galvanic period, pointing out that the pores are practically blocked. If an X-cut is made in the film on the substrate, a significant electrical current begins

to flow again because of the protective action of the metallic zinc. With other types of coatings no corrosion appears in the substrate under the zone adjacent to the X-cut. The useful life of the protective system depends on the zinc dissolution rate in a determined medium; it should be controlled to keep the surface cathodically protected.⁷

In atmospheric weathering, the rust-preventing mechanism of zinc-rich primers is dominated by the sealing action of zinc corrosion products on the paint surface.⁸ Under immersion conditions, the time of cathodic protection depends on the zinc content in the film. An optimum zinc content must be found for each formulation and exposition type on service.

A critical problem in zinc primers, particularly in those formulated in single-package form, could occur due to the highly reactive characteristic of the metallic zinc; in the presence of water, particularly at low pH, metallic zinc reacts and generates hydrogen gas in storage which could deform the can and even produce explosions.⁹ For primers based on acidic vehicles, the problem is more critical. As a result, the manufacturers usually prepare zinc primers in two packages and the zinc must be added to the vehicle prior to application.

Physicochemical properties, as well as the corrosion behavior of zinc primers, can be significantly affected by the shape of the zinc particle and pigment volume concentration (PVC). There is a critical value of PVC (CPVC) above which many of such dry film properties change abruptly, i.e., blistering and gloss decrease significantly whereas permeability and rusting increase dramatically.¹⁰

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Table 1—Metallic Zinc and Extender Characteristics

Pigment	Density, g.cm ⁻³	Diameter (50/50%), μm	Oil Absorption g/100 g
Spherical zinc	7.10	5.4	7
Lamellar zinc.....	7.10	10.5	14
Mica	2.82	33.1	61
Kaolin	2.58	1.2	51
Synthetic calcium silicate	2.26	12.1	280

Table 2—Modified Lamellar Zinc Primer Identification and Composition

Primer	Zinc/Extender Ratio, in Volume
A0, B0, C0, D0 ^a	100
A1, B1, C1, D1	80/20
A2, B2, C2, D2	70/30
A3, B3, C3, D3	60/40
A4, B4, C4, D4	50/50
A5, B5, C5, D5	40/60

(a) Note: primers designated A, B, C and D without numerical suffix contain spherical zinc as the sole pigment.

Several types of resins are suggested as binders to be used in the formulation of zinc-rich primers (usually based on spherical zinc particles) and modified zinc primers (lamellar zinc mixed with extenders). An important variable in the performance of zinc primers is the reciprocal action between the pigment and film forming material—the binder capacity for wetting the pigment particles modifies the CPVC value.¹¹

This work was aimed at gaining a deeper insight into the behavior of zinc primer, containing either lamellar zinc alone or lamellar zinc mixed with an extender, and resins of different chemical nature as binders by means of accelerated tests in a salt spray (fog) chamber and a 100% relative humidity cabinet.

PRIMERS FORMULATION AND MANUFACTURE

Pigments characteristics are shown in *Table 1*. They display different densities, particles sizes, and oil absorption.

Metallic Zinc

Spherical zinc (also known as zinc dust) is prepared by the shock cooling of vaporized zinc dross and scrap, where

the electrical current can only be transferred tangentially between any two adjacent particles, and as a consequence, the opportunities for contact are limited.¹²

Spherical zinc is a dense pigment and usually provokes a fast sedimentation and strong agglomeration of particles in the can during storage which cannot be easily redispersed, even in the case of well-formulated coatings.¹³ Before application, spherical zinc-rich coatings must be adequately agitated to avoid undesired heterogeneities in the applied film, since in some zones the PVC/CPVC ratio is higher than one, which generates a coating with poor mechanical properties and high porosity. Likewise, in the neighboring areas with lower concentrations of zinc particles, the electrical contact appears to be insufficient to provide a satisfactory protective galvanic action to the underlying metallic structure. These considerations led us to examine the corrosion behavior of lamellar zinc in primers that are formulated to protect iron and steel substrates.¹⁴

Lamellar zinc exhibits a higher surface area/weight ratio than those of spherical form, which produces an effective electrical contact and low current density.^{15,16} Lamellar zinc allows for the formulation of zinc-rich primers with lower PVC (their CPVC values are less than those in spherical zinc-rich primers) and a reduction of settling in the can. However, experimental data indicate that lamellar zinc still provides an anode that is too plentiful at normal PVC to provide long-term protection. On these films, copious amounts of white zinc corrosion products are rapidly noted at the beginning of the exposure in the salt spray (fog) chamber¹⁷; its large galvanic action promotes osmotic phenomena and, as a consequence, film blistering.¹⁸

For the lamellar film manufactured,^{19,20} electrolytic zinc of high purity is employed. Fused zinc is pulverized in a cold chamber where it is converted into a solid form and then milled in a ball mill. Zinc particles are generally covered with a lubricant agent (carboxylic acid derivatives of long chains) to facilitate the manufacture.

Extenders

To improve the efficiency of lamellar zinc-rich primers, several modified primers were designed. Since the electrical contact of lamellar zinc particles is high, extenders of different characteristics were included as spacers to decrease the galvanic action (zinc consumption) as well as the costs.

Table 3—Spherical Zinc Rich Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117

Iron Corrosion	Hours	Primer	Pigment Volume Concentration, %													
			47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0	72.5	75.0	77.5	80.0
Scribed area	1000	A	*a	*	*	*	*	*	2	3-4	4-5	5	6-7	7-8	7-8	8
	800	B	*	*	2-3	4	5	6	7-8	8	8	8	*	*	*	*
	800	C	*	*	2	4-5	5	5-6	7-8	8	8	8	*	*	*	*
	600	D	4	5	6	7	7-8	7-8	8	8	*	*	*	*	*	*
Unscribed area	1000	A	*	*	*	*	*	*	2	2	2-3	4	5	6	8	6
	800	B	*	*	1	2-3	5	5-6	7-8	8	8	7	*	*	*	*
	800	C	*	*	1-2	2-3	4-5	6	7	8	7-8	6	*	*	*	*
	600	D	2-3	4	5	7	8	7-8	7	6	*	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 4—Spherical Zinc Rich Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247

Primer	Hours	Pigment Volume Concentration, %													
		47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0	72.5	75.0	77.5	80.0
A	500	*a	*	*	*	*	*	8-M	9-F	9-F	10	10	10	10	10
B	800	*	*	8-M	8-F	10	10	10	10	10	10	*	*	*	*
C	500	*	*	8-F	9-F	10	10	10	10	10	10	*	*	*	*
D	500	9-F	10	10	10	10	10	10	10	*	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Thus, the following extenders were considered:

MICA: From a chemical and mineralogy viewpoint, mica is an aluminum potassium silicate ($3\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and a ground Muscovite, respectively. Their crystals have a well-developed cleavage that allows the splitting into pigment particles.²¹

KAOLIN: Basically a hydrated aluminum silicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), kaolin is a fine grain crystallized clay that shows lamellar structure and repeats alumina-silica configurations. It is an inert pigment of little color and opacity obtained from the natural deposit of china clay, feldspar, kaolin, and similar materials.

SYNTHETIC CALCIUM SILICATE: Chemically known as $\text{CaSiO}_3 \cdot n\text{H}_2\text{O}$, this extender displays some dry hiding opacity but exhibits a very high oil absorption.

Film Forming Materials

CHLORINATED RUBBER (PRIMER A): 20-cP grade (viscosity in 25°C toluene solution at 20 wt%) was selected because it is adequate for brushing application. Chlorinated rubber films are hard and fragile without plastification; 42% chlorinated paraffin in a 70/30 resin/plasticizer weight ratio was employed to optimize film properties. An aromatic hydrocarbon of C9/white spirit (4/1 weight ratio) was used as the solvent mixture.

EPOXY BINDER (PRIMER B): The employed resin was constituted by a base with a weight per epoxide WPE of about 450 and a polyamine-amide hardener with an amine value in the range of 210-220. The solvent mixture, expressed in weight, was 42.7% xylene, 14.6% butanol, and 42.7% oxygenated hydrocarbon.

Table 5—Mica (33.1 μm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 1000 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %											
		37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	
Scribed area	A0	*a	*	*	9	9	9	9-10	10	10	10	10	9-10
	A1	*	*	*	9	9-10	10	10	10	10	8-9	7-8	8
	A2	*	*	9-10	10	10	10	10	8-9	8-9	8-9	8-9	*
	A3	*	10	10	10	10	10	9-10	8-9	8	*	*	*
	A4	9-10	10	10	10	10	9-10	8-9	8	*	*	*	*
	A5	7	9-10	10	10	10	9-10	9	8-9	*	*	*	*
Unscribed area	A0	*	*	*	9	9-10	9-10	9-10	10	10	10	10	9-10
	A1	*	*	*	9	10	10	10	10	10	7-8	7	6
	A2	*	*	10	9-10	10	9-10	10	8-9	7	6	6	*
	A3	*	10	10	9-10	10	10	8-9	7	6	*	*	*
	A4	10	9-10	10	10	10	9-10	7-8	6	*	*	*	*
	A5	7-8	10	9-10	10	10	7-8	7	5	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 6—Mica (33.1 μm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %										
	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5
A0	*a	*	*	2-D	4-D	4-MD	6-MD	6-MD	8-F	10	10
A1	*	*	*	4-MD	6-MD	6-MD	8-F	10	10	10	10
A2	*	*	4-D	6-MD	6-M	9-F	10	10	10	10	*
A3	*	4-D	8-MD	8-M	9-F	10	10	10	10	*	*
A4	6-D	6-MD	8-M	9-F	10	10	10	10	*	*	*
A5	6-M	8-F	9-F	10	10	10	10	10	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 7—Kaolin (1.2 µm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 1000 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %									
		42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
Scribed area	A0	*a	9	9	9	9-10	10	10	10	9-10	*
	A1	*	*	8-9	9-10	9-10	10	10	9	8-9	9
	A2	*	*	9-10	10	10	10	9	9-10	9	9-10
	A3	*	8-9	9-10	9-10	10	10	9	9-10	9	*
	A4	*	9-10	9-10	10	10	9-10	9	9	9	*
	A5	8-9	9	10	10	10	9	9-10	9	*	*
Unscribed area	A0	*	9	9-10	9-10	9-10	10	10	10	9-10	*
	A1	*	*	8	9-10	10	10	10	8	7-8	7
	A2	*	*	9-10	9-10	10	10	8	7	7	7
	A3	*	8	9	9-10	10	10	8-9	8	7	7
	A4	*	9	9-10	10	10	9-10	8-9	8	7-8	*
	A5	9	9-10	9-10	10	10	8	7-8	7	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 8—Kaolin (1.2 µm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %									
	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
A0	*a	2-D	4-D	4-MD	6-MD	6-MD	8-F	10	10	*
A1	*	*	4-MD	4-MD	6-M	8-F	10	10	10	10
A2	*	*	6-MD	6-M	8-F	10	10	10	10	10
A3	*	6-MD	6-M	8-F	10	10	10	10	10	*
A4	*	8-F	9-F	10	10	10	10	10	10	*
A5	4-MD	8-F	9-F	10	10	10	10	10	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 9—Synthetic Calcium Silicate (12.1 µm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 1000 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %													
		37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.5	67.5	
Scribed Area	A0	*	*	*	9	9	9	9-10	10	10	10	9-10	*	*	
		15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	
	A1	*	*	*	*	*	9-10	9-10	9-10	10	10	9	9	9-10	
	A2	*	*	*	8	9	10	10	10	9	9-10	9	*	*	
	A3	*	5	5	6-7	7-8	9	9	9	9	*	*	*	*	
	A4	4	4	4-5	4-5	6-7	6	6	5-6	*	*	*	*	*	
	A5	2	2	2-3	3	3-4	3-4	4	4	*	*	*	*	*	
	Unscribed Area	A0	*	*	*	9-10	9-10	9-10	10	10	10	10	9-10	*	*
			15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0
		A1	*	*	*	*	*	9	9-10	10	10	10	8	7-8	7
A2		*	*	*	7-8	9-10	10	10	10	9	8	7-8	*	*	
A3		*	4-5	5	6	7-8	9	8	7-8	7	*	*	*	*	
A4		3	3-4	4	4-5	6	5	4-5	4-5	*	*	*	*	*	
A5		1-2	2	2	3-4	3	3	2-3	2	*	*	*	*	*	

(a) * = untested; PVC too far from the critical value (CPVC).

VINYL COPOLYMER (PRIMER C): VAGH vinyl copolymer was used in this experiment. This resin is made up of 91% vinyl chloride and 3% vinyl acetate, with an HO⁻ ion from hydrolysis (6% vinyl alcohol). As chlorinated rubber, VAGH resin was also plasticized with 42% chlorinated rubber but a 4/1 weight ratio. Solvent mixture was 70.0% ethylene glycol acetate, 17.5% xylene, and 12.5% methyl isobutyl ketone in weight.

UNSATURATED POLYMER (PRIMER D): This resin was used as an unsaturated polymer based on phthalic acid and standard glycols, and was stabilized to the light and diluted in styrene. The selected resin shows clear color with a solid content of 63.5%, because the curing process of methyl ethyl ketone peroxide (MEKP) was employed.

Pigment Composition

Lamellar zinc primers were modified with an extender each time, in several percentage levels. For each PVC considered, the extender ranged from 20–60% in volume on the total pigment. Table 2 shows the primer identification of this experiment.

Pigment Volume Concentration

Samples were formulated in several PVC ranges according to the primer composition. In every case, partial increases of 2.5% were considered. Data from preliminary tests in the salt spray (fog) chamber, with the PVC ranging from 10–90% (given in 10% increments) for all the formulations, allowed one to define the PVC range more conveniently for studying in each case.

Pigment Dispersion

Extenders were first dispersed in their respective binders in a ball mill of 1.0-liter capacity for 24 hr. Rheological control allowed for the corroboration of both the efficiency and the stability of pigment dispersion. Then, high-speed agitation equipment was used for the metallic zinc dispersion (30 sec at 1400 rpm); in all cases, viscosity was adjusted for attaining a laminar flow. In the case of the epoxy primer and the unsaturated polymer before application, the hardener was added according to the manufacturers' suggested ratio. All the experimental primers were elaborated in duplicate.

EXPERIMENTAL METHOD

SAE 1010 steel plates measuring 100 × 150 × 1 mm were used as the metallic substrate. Metal surfaces were initially sandblasted to A Sa 2^{1/2} -3 grade, according to SIS 05 59 00/67, and degreased with vapor toluene. The maximum roughness was 40 μm.²²

The primer was applied by brushing (only one coat) and the thickness of the edges was reinforced by the immersion application of a sealer based on acrylic-styrene derivatives.

In all cases, the panels were prepared in duplicate and stored for seven days at 20 ± 2°C before beginning the tests. Dry film thickness (75/80 μm) was measured with an electromagnetic gauge employing bare sanded plates and standards of known thickness as reference.^{23,24}

The standardized procedures ASTM B 117 (salt spray chamber) and ASTM D 2247 (100% relative humidity cabinet) were performed on the painted steel samples.^{17,25} After finishing these tests, the painted panels were assessed with ASTM Standards D 1654 and D 714, in order to evaluate the degree of rusting and degree of blistering, respectively.²⁶

RESULTS AND DISCUSSION

The degree of rusting of the coated panels in the salt spray chamber (35 ± 1°C, pH 6.5–7.2, 5 ± 1% w/w NaCl and continuous spraying) shown in the odd-numbered Tables from 3–27.

The rate of failure at the X-cut (method A) is evaluated according to the representative mean creepage from the scribe. Value 10 defines a mean failure of 0 mm while 0 corresponds to 16 mm or more. On the unscribed area (method B), failure is measured by taking into account the percentage of surface corroded by the medium; the scale ranges from 10 (no failure) to 0 (over 75% of the failed area).^{27,28}

The degree of blistering of the experimental panels in a 100% relative humidity chamber is included in even numbered Tables from 4–28. The size of blistering is described in an arbitrary numerical scale from 10 to 0; in which 10 represents no blistering while the frequency is defined qualitatively, appointing D (dense), MD (medium dense), M (medium), and F (few).

Table 10—Synthetic Calcium Silicate (12.1 μm) Modified Lamellar Zinc/20 cP Chlorinated Rubber Primers. Degree of Blistering, ASTM D 714; Salt Spray (Fog) Testing, ASTM B 117, 500 hr

Primer	Pigment Volume Concentration, %												
	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.5	67.5
A0	*a	*	*	2-D	4-D	4-MD	6-MD	6-MD	8-F	10	10	*	*
	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0
A1	*	*	*	*	*	9-F	9-F	10	10	10	10	10	10
A2	*	*	*	8-F	10	10	10	10	10	10	10	*	*
A3	*	8-MD	8-F	8-F	9-F	10	10	10	10	*	*	*	*
A4	8-D	8-MD	8-M	9-F	10	10	10	10	*	*	*	*	*
A5	6-D	6-MD	8-F	10	10	10	10	10	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 11—Mica (33.1 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Rusting; ASTM D 1654 Salt Spray (Fog) Testing; ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %												
		30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0
Scribed area	B0	*a	*	*	*	*	9	9	9-10	10	8	7-8	8-9	8
	B1	*	*	9	9	9	9-10	10	10	9-10	9	*	*	*
	B2	*	9	9	9	9	10	10	10	9-10	*	*	*	*
	B3	*	9-10	8-9	8-9	9	10	10	10	10	*	*	*	*
	B4	6-7	9	9	9	9-10	9	9-10	10	*	*	*	*	*
	B5	5-6	6	7-8	9-10	9-10	9-10	10	9-10	*	*	*	*	*
Unscribed area	B0	*	*	*	*	*	8	8	8-9	8-9	8-9	5	5	4-5
	B1	*	*	8	8	8	8-9	8-9	9-10	9-10	8	*	*	*
	B2	*	8	8	8-9	8-9	8-9	9-10	9	8-9	*	*	*	*
	B3	*	9	8	8	8-9	10	8-9	9	7-8	*	*	*	*
	B4	6	8	8-9	9-10	9	8-9	7-8	8	*	*	*	*	*
	B5	5	6	7	9	9	8-9	7	7-8	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 12—Mica (33.1 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 800 hr

Primer	Pigment Volume Concentration, %													
	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	
B0	*a	*	*	*	*	6-MD	8-F	10	10	10	10	10	10	
B1	*	*	4-D	8-MD	9-F	10	10	10	10	10	*	*	*	
B2	*	6-MD	6-F	8-F	10	10	10	10	10	*	*	*	*	
B3	*	8-MD	8-F	9-F	10	10	10	10	10	*	*	*	*	
B4	8-MD	9-F	9-F	10	10	10	10	10	*	*	*	*	*	
B5	8-MD	9-F	10	10	10	10	10	10	*	*	*	*	*	

(a) * = untested; PVC too far from the critical value (CPVC).

Table 13—Kaolin (1.2 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %											
		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	
Scribed Area	B0	*a	*	*	9	9	9-10	10	8	7-8	8-9	8	
	B1	*	*	9	9	9-10	10	10	9-10	9	8	*	
	B2	*	*	9	9	9-10	10	9-10	9	9	8	*	
	B3	*	9	9-10	9-10	9-10	9	9	9	9	*	*	
	B4	*	9	9	9	9-10	9	8-9	8-9	9	*	*	
	B5	6	7-8	8	9	9	9	9	8	*	*	*	
Unscribed Area	B0	*	*	*	8	8	8-9	8-9	8-9	5	5	4-5	
	B1	*	*	8	8	8-9	8-9	7	7	6	5-6	*	
	B2	*	*	8	8-9	8-9	9	8	7	5-6	5-6	*	
	B3	*	8	8-9	8-9	8-9	8	7	6	5	*	*	
	B4	*	8	8	8-9	9	8	7	6	4-5	*	*	
	B5	5	6-7	7	8-9	9	9	8	8	*	*	*	

(a) * = untested; PVC too far from the critical value (CPVC).

Table 14—Kaolin (1.2 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 800 hr

Primer	Pigment Volume Concentration, %											
	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	
B0	*a	*	*	6-MD	8-F	10	10	10	10	10	10	10
B1	*	*	8-MD	8-F	10	10	10	10	10	10	10	*
B2	*	*	6-F	8-F	10	10	10	10	10	10	10	*
B3	*	8-F	9-F	10	10	10	10	10	10	10	*	*
B4	*	9-F	9-F	10	10	10	10	10	10	10	*	*
B5	9-F	9-F	10	10	10	10	10	10	10	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 15—Synthetic Calcium Silicate (12.1 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %												
		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
Scribed Area	B0	*a	*	*	9	9	9-10	10	8	7-8	8-9	8	*	*
		10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0
	B1	*	*	*	*	*	9	9	9	10	10	9	9-10	10
	B2	*	*	*	6	6-7	7	8	8-9	9	9-10	9-10	*	*
	B3	*	*	4-5	5	6	6-7	7	7	7	6-7	*	*	*
Unscribed Area	B4	*	1	2	3	5	4-5	5	5	4-5	*	*	*	*
	B5	0	1	2	3	3	2	2	2	*	*	*	*	*
		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
	B0	*	*	*	8	8	8-9	8-9	8-9	5	5	4-5	*	*
		10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0
Unscribed Area	B1	*	*	*	*	*	8	7-8	8	9	9	8-9	8	8
	B2	*	*	*	5-6	5-6	6-7	7-8	8-9	8	7	7-8	*	*
	B3	*	*	4	5	5-6	6-7	6	5-6	5	5	*	*	*
	B4	*	1	1-2	2-3	4	3	2-3	2	2-3	*	*	*	*
	B5	0	0	1-2	2-3	3-4	3-4	3	2	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 16—Synthetic Calcium Silicate (12.1 µm) Modified Lamellar Zinc/Epoxy Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 800 hr

Primer	Pigment Volume Concentration, %												
	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
B0	*a	*	*	6-MD	8-F	10	10	10	10	10	10	*	*
	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0
B1	*	*	*	*	*	9-F	10	10	10	10	10	10	10
B2	*	*	*	8-F	9-F	9-F	10	10	10	10	10	*	*
B3	*	*	8-MD	8-M	9-F	10	10	10	10	10	*	*	*
B4	*	6-MD	8-MD	8-F	10	10	10	10	10	*	*	*	*
B5	4-D	6-MD	8-M	9-F	10	10	10	10	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 17—Mica (33.1 µm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %											
		30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5
Scribed area	C0	*a	*	*	*	8	8-9	9	9	9-10	9	9	8-9
	C1	*	*	8	8-9	8-9	9-10	9-10	9	9-10	9	*	*
	C2	*	8	8-9	8-9	9	10	10	9-10	9-10	*	*	*
	C3	*	8	8	8-9	9-10	9-10	9-10	9-10	10	*	*	*
	C4	7	8	9	9	9-10	9	9	9	*	*	*	*
	C5	4-5	6	7-8	8	10	9-10	9	9	*	*	*	*
Unscribed area	C0	*	*	*	*	7-8	7-8	8	8-9	9	7	7	6
	C1	*	*	7-8	8	8	9	9	7	6-7	6	*	*
	C2	*	7	7	8	9	9-10	8	7	6-7	*	*	*
	C3	*	7-8	7-8	8	9	9	8	6-7	6	*	*	*
	C4	5-6	7-8	7-8	9	9	8-9	7-8	7	*	*	*	*
	C5	5	6-7	7-8	8-9	9	8	7-8	7	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 18—Mica (33.1 µm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %											
	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5
C0	*a	*	*	*	6-D	6-MD	8-F	9-F	10	10	10	10
C1	*	*	6-MD	8-MD	9-F	10	10	10	10	10	*	*
C2	*	6-MD	8-MD	8-F	9-F	10	10	10	10	*	*	*
C3	*	6-MD	8-F	9-F	10	10	10	10	10	*	*	*
C4	8-M	9-F	9-F	10	10	10	10	10	*	*	*	*
C5	8-M	9-F	10	10	10	10	10	10	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 19—Kaolin (1.2 mm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %									
		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5
Scribed area	C0	*a	*	8	8-9	9	9	9-10	9	9	8-9
	C1	*	8	8	8-9	9-10	10	10	10	9-10	*
	C2	*	8	8	9	9	10	9-10	9	9	*
	C3	*	8	8-9	9	10	9-10	9	8-9	8	*
	C4	*	7-8	8	8-9	9-10	9	9	8-9	7-8	*
	C5	5-6	7-8	7-8	9	9	8-9	8	8	*	*
Unscribed area	C0	*	*	7-8	7-8	8	8-9	9	7	7	6
	C1	*	7-8	7-8	8	8-9	9	8	8	8	*
	C2	*	7-8	7-8	7-8	8	9	8	7-8	7	*
	C3	*	7-8	7-8	8	9	8	8	7	7	*
	C4	*	7-8	7-8	7-8	9	8	7	7-8	7-8	*
	C5	5	6	7-8	8	7	7	6	6	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 20—Kaolin (1.2 μm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM 2247, 500 hr

Primer	Pigment Volume Concentration, %												
	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5			
C0	*a	*	6-D	6-MD	8-F	9-F	10	10	10	10	10	10	10
C1	*	6-MD	8-MD	8-F	9-F	10	10	10	10	10	10	10	*
C2	*	6-MD	6-M	8-F	10	10	10	10	10	10	10	10	*
C3	*	8-F	9-F	10	10	10	10	10	10	10	10	10	*
C4	*	9-F	9-F	10	10	10	10	10	10	10	10	10	*
C5	8-F	9-F	10	10	10	10	10	10	10	10	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 21—Synthetic Calcium Silicate (12.1 μm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 800 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %												
		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
C0		*a	*	8	8-9	9	9	9-10	9	9	8-9	*	*	*
		10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0
Scribed Area	C1	*	*	*	*	*	8-9	9	9	10	9	9	9	9
	C2	*	*	*	5-6	6-7	7	7	8-9	8-9	9	9	*	*
	C3	*	*	4	5	5-6	5-6	6	7-8	7-8	8	*	*	*
	C4	*	2	3-4	4	4-5	5	5-6	5-6	6	*	*	*	*
	C5	0	1	2-3	3	3	3	3	3-4	*	*	*	*	*
C0		35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0
		*	*	7-8	7-8	8	8-9	9	7	7	6	*	*	*
Unscribed Area	C1	*	*	*	*	*	8	8	8	9	8-9	8	8	7-8
	C2	*	*	*	5	5-6	6-7	7	8	8	8	7-8	*	*
	C3	*	*	3-4	4	4-5	5	5-6	7	6	5	*	*	*
	C4	*	1-2	3	3-4	4	5	4	4	4	4	*	*	*
	C5	0	0	2	3	3-4	3	3	3	3	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 22—Synthetic Calcium Silicate (12.1 μm) Modified Lamellar Zinc/VAGH Vinyl Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %													
	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	
C0	*a	*	6-D	6-MD	8-F	9-F	10	10	10	10	10	*	*	*
	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	
C1	*	*	*	*	*	10	10	10	10	10	10	10	10	10
C2	*	*	*	8-MD	9-F	10	10	10	10	10	10	10	*	*
C3	*	*	8-MD	9-F	9-F	10	10	10	10	10	10	*	*	*
C4	*	6-MD	8-M	8-F	10	10	10	10	10	10	*	*	*	*
C5	6-D	6-MD	8-M	9-F	10	10	10	10	10	*	*	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 23—Mica (33.1 µm) Modified Lamellar Zinc/Unsaturated Polymer Primer. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 600 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %										
		27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
Scribed area	D0	*a	*	*	7-8	8	8	9	9-10	8-9	8	7-8
	D1	*	8	8	8	9	9-10	9-10	10	10	*	*
	D2	*	8	8	9	9-10	10	9-10	9	9-10	*	*
	D3	8	7-8	8	9	10	9-10	9	8-9	*	*	*
	D4	5	6	8-9	10	9-10	10	9	8	*	*	*
	D5	4	5-6	7	9-10	9-10	8-9	8-9	8-9	*	*	*
Unscribed area	D0	*	*	*	6	7	7	8-9	8-9	8	6-7	6
	D1	*	7	7	7-8	8-9	8-9	8-9	7-8	7-8	*	*
	D2	*	7	7	8-9	8-9	9	8	7	6	*	*
	D3	7-8	7	7	8	9	9	8	7	*	*	*
	D4	4-5	5	8	9	8-9	8	7	7	*	*	*
	D5	4	4-5	6-7	9	8-9	8	8	7-8	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 24—Mica (33.1 µm) Modified Lamellar Zinc/Unsaturated Polymer Primer. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %										
	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
D0	*a	*	*	6-MD	8-MD	9-F	10	10	10	10	10
D1	*	6-MD	6-F	8-F	10	10	10	10	10	*	*
D2	*	8-F	8-F	10	10	10	10	10	10	*	*
D3	6-MD	8-F	8-F	10	10	10	10	10	*	*	*
D4	8-F	9-F	10	10	10	10	10	10	*	*	*
D5	9-F	9-F	10	10	10	10	10	10	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 25—Kaolin (1.2 µm) Modified Lamellar Zinc/Unsaturated Polymer Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 600 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %									
		30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
Scribed Area	D0	*a	*	7-8	8	8	9	9-10	8-9	8	7-8
	D1	7	8	8	8-9	9-10	9	9	9	*	*
	D2	6-7	8	8	8-9	9-10	9	9-10	10	*	*
	D3	7	8	8	8	9	9	9	9	*	*
	D4	7	7-8	8	8	9-10	9	9	9	*	*
	D5	5-6	6	7-8	9-10	9-10	9-10	10	9-10	*	*
Unscribed Area	D0	*	*	6	7	7	8-9	8-9	8	6-7	6
	D1	6	7	7-8	8	8-9	8	7	6	*	*
	D2	6	7-8	7-8	7-8	9	7-8	7	7	*	*
	D3	6	7-8	8	8	8-9	7	7	6	*	*
	D4	6	7	7-8	7-8	8	8	7	6	*	*
	D5	5	6	7	8	8	8-9	7	7-8	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 26—Kaolin (1.2 µm) Modified Lamellar Zinc/Unsaturated Polymer Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %									
	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
D0	*a	*	6-MD	8-MD	9-F	10	10	10	10	10
D1	6-MD	6-F	8-F	10	10	10	10	10	*	*
D2	6-MD	8-F	8-F	10	10	10	10	10	*	*
D3	8-MD	8-F	8-F	10	10	10	10	10	*	*
D4	8-MD	8-F	9-F	10	10	10	10	10	*	*
D5	8-M	9-F	9-F	10	10	10	10	10	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Table 27—Synthetic Calcium Silicate (12.1 µm) Modified Lamellar Zinc/Unsaturated Polymer Primers. Degree of Rusting, ASTM D 1654; Salt Spray (Fog) Testing, ASTM B 117, 600 hr

Iron Corrosion	Primer	Pigment Volume Concentration, %										
		27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
Scribed Area	D0	*a	*	*	7-8	8	8	9	9-10	8-9	8	7-8
		10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0
	D1	*	*	*	6	7-8	8-9	9	9	9	9	9
	D2	*	*	5	5-6	7	7-8	8-9	9	9	9	*
	D3	*	*	4-5	5	5-6	7	6	6	6	6-7	*
	D4	*	2-3	3-4	4	4-5	4	4	4-5	4-5	*	*
D5	0	0	1	1-2	3-4	3	3	2-3	*	*	*	
Unscribed Area	D0	*	*	*	6	7	7	8-9	8-9	8	6-7	6
		10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0
	D1	*	*	*	5-6	7	8	8	8	8-9	8	7-8
	D2	*	*	4-5	5	6-7	7	8	7-8	7	7	*
	D3	*	*	4	4-5	5	6	7	6-7	6	6	*
	D4	*	1-2	2	3-4	4-5	5	5	5	5-6	*	*
D5	0	0	1	1	3	2-3	2	2	*	*	*	

(a) * = untested; PVC too far from the critical value (CPVC).

Table 28—Synthetic Calcium Silicate (12.1 µm) Modified Lamellar Zinc/Unsaturated Polymer Primers. Degree of Blistering, ASTM D 714; 100% Relative Humidity Chamber, ASTM D 2247, 500 hr

Primer	Pigment Volume Concentration, %										
	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5
D0	*a	*	*	6-MD	8-MD	9-F	10	10	10	10	10
	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0
D1	*	*	*	8-MD	8-F	9-F	10	10	10	10	10
D2	*	*	6-MD	8-MD	8-F	10	10	10	10	10	*
D3	*	*	6-MD	8-F	10	10	10	10	10	10	*
D4	*	6-MD	8-MD	9-F	10	10	10	10	10	*	*
D5	2-D	4-MD	8-MD	10	10	10	10	10	*	*	*

(a) * = untested; PVC too far from the critical value (CPVC).

Test results in the salt spray chamber and the 100% relative humidity cabinet follow:

BINDER AND EFFICIENCY: Salt spray tests were performed until one of the samples began to show signs of corrosion. The longest period of testing corresponded to the primers based on 20-cP chlorinated rubber/42% chlorinated paraf-

Table 29—Sum Values of Degree of Rusting and of Degree of Blistering. Lamellar Zinc Modified Chlorinated Rubber Primers

Primer	Extender		
	Mica	Kaolin	Calcium Silicate
A0	65.7	65.7	65.7
A1	66.0	65.5	77.5
A2	67.8	66.8	79.2
A3	69.8	71.8	61.6
A4	74.3	74.8	48.8
A5	75.5	75.0	33.8

Table 30—Sum Values of Degree of Rusting and of Degree of Blistering. Lamellar Zinc Modified Epoxy Primers

Primer	Extender		
	Mica	Kaolin	Calcium Silicate
B0	67.2	67.2	67.2
B1	68.8	68.2	75.8
B2	69.8	70.2	65.5
B3	71.2	71.5	51.5
B4	72.0	71.5	36.2
B5	70.0	65.2	26.0

Table 31—Sum Values of Degree of Rusting and of Degree of Blistering. Lamellar Zinc Modified Vinyl Primers

Primer	Extender		
	Mica	Kaolin	Calcium Silicate
C0	64.7	64.7	64.7
C1	66.2	65.7	74.8
C2	67.8	67.2	66.2
C3	70.5	69.8	59.6
C4	70.8	69.0	42.8
C5	69.7	64.0	27.8

Table 32—Sum Values of Degree of Rusting and of Degree of Blistering. Lamellar Zinc Modified Unsaturated Polymer Primers

Primer	Extender		
	Mica	Kaolin	Calcium Silicate
D0	66.2	66.2	66.2
D1	67.5	67.0	68.8
D2	68.2	68.2	60.5
D3	68.2	68.0	52.8
D4	63.5	67.5	40.8
D5	61.5	66.8	21.8

fin (70/30 resin/plasticizer ratio W/W) (1000 hr), then the epoxy and vinyl primers (800 hr), and finally the unsaturated polymer primers (600 hr); the latter was the binder that showed the lowest efficiency in the salt spray chamber.

A similar criterium was chosen for the 100% relative humidity cabinet tests but this related to the development of blisters; 800 hr were selected for the primers based on epoxy binders and 500 hr for the others.

TYPE OF BINDER AND ESTIMATED CPVC: Each CPVC was estimated considering the degree of rusting and degree of blistering results and, in particular, the adhesion tension of the dry and/or cured films not aged yet in the accelerated tests (Elcometer Tester Model 106, ASTM D 4541).

At the CPVC value, the adhesion tension was maximum and, from a qualitative viewpoint, the fracture was totally adhesive (failure at the interface substrate-film). PVC values higher or lower than the CPVC bring failures of the cohesive/adhesive type, which means a partial breaking at the interface as well as inside the film.²⁹

Approximately 10 determinations were made on each panel, which were prepared in duplicate due to the high dispersion of the values and the type of failure at the break observed on this kind of test.

An important feature of binders is their pigment particle wetting capacity. Effective wetting was observed with the chlorinated rubber binder, since a small quantity of it was enough to attain the CPVC value. Considering the same pigment content for both zinc-rich primers and the modified ones, that is, considering the four selected binders, those with chlorinated rubber (polar) showed the highest values of CPVC. This intensive reciprocal action between pigment and binder occurs due to absorption or possible chemisorption. On the other hand, the unsaturated polymer (nonpolar binder) showed a minimum of this reciprocal action with the pigment since a great quantity of binder was necessary to attain the corresponding CPVC (the lowest values of all the experimental compositions were attained with this binder). Between both extremes, an intermediate wetting was achieved when vinyl and epoxy resins were selected as binders (partially polar).

Quantifying the values and considering, as reference, the CPVC of the samples based on vinyl and epoxy binders, those primers formulated with chlorinated rubber showed values about 20% higher; moreover, when the unsaturated polymer resin was employed, CPVC values were approximately 10% lower.

PIGMENTATION AND CPVC: A simultaneous analysis of the experimental data was conducted taking into account that the best performance is attained at PVC values equal to or slightly lower than the corresponding CPVC.

For all the studied binders, lamellar zinc-rich primers showed CPVC values that were significantly lower than those enhanced with spherical zinc. This decrease ranged between 15 and 20% according to the type of binder.

Lamellar zinc has a higher oil absorption value (higher specific area) in comparison to spherical zinc. This concept justifies the estimated CPVC values in this study.

On the scribed and unscribed areas, primers based mainly on spherical zinc and formulated with a PVC lower than CPVC showed an abrupt falling-off of the anticorrosive performance, while those primers, including lamellar zinc, that were manufactured at PVC that was greatly lower than CPVC maintained their quality.

These results could have happened because zinc corrosion products on spherical particles may not only increase the electrical resistance of the protective system but may also decrease the amount of effective available zinc since the center of the particles could be electrically isolated (polarizing effect) between them as well as with the metallic base.

According to visual observations during the testing, particularly in the zone nearest to the scribe, primers based on lamellar particles became more covered with white zinc corrosion products than those based on spherical ones. The last concept and the degree of rusting data suggest that the lamellar zinc provides an anode that is too plentiful inclusive at PVC values very inferior to the estimated critical value; therefore, the anode could be unnecessarily wasted.

Concerning the degree of blistering, results corresponding to the coated panels showed an apparent greater tendency to blister in the compositions in which lamellar zinc was used as sole pigment for all the samples (different binders), particularly at PVC values slightly less than the critical value. The greater tendency to form soluble corrosion products from lamellar zinc primer may be responsible for the apparent decrease in blistering resistance (at PVC less than CPVC) shown in the 100% relative humidity testing (osmotic blistering).

However, it seems that if both the corrosion resistance of the zinc in the lamellar form could be maintained and the blistering tendency could be eliminated at PVC values less than CPVC, some technical and economical advantages might be gained from the use of lamellar zinc pigment. Certainly, the performance of the zinc-rich primers gives incentive for studying the formulations modified with several extenders.

TYPE OF EXTENDER AND EFFICIENCY: In general, the use of extenders resulted in a CPVC reduction. Consequently, when a PVC/CPVC ratio was equal to one or slightly less, a decrease of the adequate PVC values for the modified zinc primers was determined. The amount of the decrease depended on the extender type (CPVC decreased as oil absorption of the extender increased) and also on the level of lamellar zinc replaced (less lamellar zinc/extender ratio in the composition led to a greater loss).

Result analysis included the estimated CPVC and the three consecutive inferior values that represent a PVC range of 7.5%. All of them are noted in the corresponding tables of degree of rusting and degree of blistering.

To establish the performance of each primer, the value of the degree of rusting corresponding to scribed and unscribed areas was averaged in the first step. Then, the value of the degree of blistering obtaining in this form was added and called the efficiency index of each primer. Finally, to define the primer A, B, C, or D (and each type of extender) that presents the best behavior in a wide

range of PVC, the sum value of the respective efficiency index for the formulated primers at the CPVC and its three consecutive inferior values was calculated.³⁰

For blistering resistance, an average value was first calculated for each PVC corresponding to the size and the following numerical values assigned to the frequency: no blistering—10.0; F (few)—7.5; M (medium)—5.0; MD (medium dense)—2.5 and D (dense)—0.0.

These results are included in *Tables 29–32*. The highest values correspond to better performances in the salt spray cabinet and in the 100% relative humidity chamber.

CONCLUSIONS

It is possible, in principle, for each binder and lamellar zinc to select an extender of high oil absorption as a spacer for the zinc particles, but it is very important to carefully define the PVC and the pigment composition (lamellar zinc/extender ratio) to obtain the best performance. For example, for 20-cP chlorinated rubber primers (1000 hr in salt spray and 500 hr in the relative humidity chamber) and employing mica (oil absorption, 61) as the extender, the best result was obtained with the sample A5 (PVC from 40.0–47.5%, lamellar zinc/extender 40/60 ratio in volume) with a sum value of 75.5.

When synthetic calcium silicate (oil absorption, 280) was employed, the best efficiency was obtained with the sample A2 (PVC from 25.0–32.5%, lamellar zinc/extender 70/30 ratio in volume) with a sum value of 79.2. This sum value corresponded to the best performance for all the samples tested taking into account both accelerated tests. For these excellent samples, the lowest zinc content in the dry film, calculated at the corresponding estimated CPVC values, was approximately 20% by volume. This level seems to be enough to achieve an optimum performance for the two accelerated tests considered, that is to obtain an effective cathodic protection of the substrate and also a controlled galvanic action that will avoid the appearance of great quantities of zinc soluble products that promote, via osmosis, the film blistering.

The extender selection must consider not only the economical viewpoint but also the optimum CPVC value (and consequently the PVC) of the formulation for each particular case since it affects several important properties of the film (adhesion, hardness, abrasion resistance, etc.).^{31–33}

Data indicate that some modified lamellar zinc primers are very versatile since they can be formulated at a wider range of PVC without modifying their performance. Slight heterogeneities in these primers, before application, might be repaired and do not generate areas of different corrosion-inhibitive capacity and/or blistering resistance.

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