Quelle/Publication: European Coatings Journal
Ausgabe/Issue: 09/2007
Seite/Page: 40

Shaped for performance

The combination of lamellar zinc and mica improves the efficiency of zinc-rich primers.
Lamellar zinc was investigated as a partial or complete replacement for spherical zinc in potassium-silicate based zinc-rich primers. Additionally, mica was examined as an extender for lamellar zinc. The best corrosion and blister resistance was obtained by using lamellar zinc combined with mica, at zinc addition levels well below those normally required in such primers.
Andrea M. Pereyra, Carlos A. Giudice.*
* Corresponding Author. Contact: Carlos A. Giudice, Cidepint, Calle 52/121 y 122 (1900), La Plata, Argentina, Tel. +54 221 4831142, Fax +54 221 4216214, cagiudice@yahoo.com

Primers based on dispersions with a high concentration of spherical zinc particles in organic and inorganic vehicles are well established, employing the sacrificial anode concept to provide corrosion protection [1-8]. In the zinc primer films, the pigment particles are in intimate contact with each other and also with the metallic substrate [9]. To ensure dense packing, the zinc content must be on the order of the CPVC (critical pigment volume concentration).

However, the spherical zinc dust carries the current between two adjacent particles in a tangential way because their mutual contact is limited [4, 10-12]. This problem has led to the study of other zinc particle shapes [13, 14]; thus for example, lamellar zinc exhibits high inter-particle contact, allowing zinc-rich formulations to be produced with lower PVC (the CPVC values are reduced, due to less dense packing and the higher surface to volume ratio).

The objective of this study was to determine the performance of zinc rich primers (using spherical or lamellar particle shapes) as well as lamellar zinc primers modified with mica as an extender, in accelerated laboratory tests (salt fog chamber and 100% relative humidity cabinet).

Experimental

Zinc and mica particles

Two types of zinc particles were used: spherical and lamellar [15, 16]. Both types were selected with a very low level of impurities (99.1% purity according to ASTM D 520 and ASTM D 521) [17, 18].

The particle size distribution was determined using a Micromeritics "Sedigraph". The experimental data showed an equivalent median spherical diameter D (50/50%) of 4.1 and 10.5 µm respectively for the spherical and lamellar particles.

The density was similar in both cases at 7.1 $g.cm^{-3}$ whereas the apparent density (bulk density) values were 2.4 and 1.0 $g \cdot cm^{-3}$ for spherical and lamellar particles, respectively. The oil absorptions were 8 and 15 g/100 g, respectively.

Two sizes of mica ($3\ Al_2O_3 \cdot K_2O \cdot 6\ SiO_2 \cdot 2\ H_2O$), with equivalent median spherical diameter D of 10.2 and 33.1 µm were selected [19]. The density for both sizes was 2.81 $g \cdot cm^{-3}$ while the bulk density values were respectively 0.42 and 0.28 $g \cdot cm^{-3}$. The oil absorption determined experimentally was 44 and 61 g/100 g for the small and large particle diameters respectively.

Test primer formulation

Two potassium silicates were prepared as film formers, with 4.0/1.0 and 4.5/1.0 silica/alkali molar ratio because of their excellent characteristics as film forming material [20]. The solids content was 30.0 % by weight; a surfactant was incorporated to improve wetting properties.

The paint samples were produced with a wide range of PVC values, increasing by 2.5% at each step. In the primers modified with mica, the mica was dispersed for 24 hours in a ball mill; in all cases the zinc dust was incorporated by agitation prior to application.

All primers were retained under laboratory conditions for 24 hours before application in order to provide for the partial oxidation of metallic zinc in the package, allowing the formation of alkaline zincates that would favour the important three-dimensional silicification of the film during the drying and curing stages [20]. Table 1 shows how the three series of zinc primers are identified.

Primer application, corrosion and fire resistance tests

Anticorrosive properties were tested by application to SAE 1010 steel panels of 100 x 150 x 1 mm (preparation to Sa 2½, SIS 05 59 00/67 standard); the maximum roughness Rm was 30 µm. For the primer application, only one coat was applied by brush to produce 75/80 µm dry film thickness [21, 22]. Panels were stored for seven days at 20 ± 2°C to complete their cure before beginning the tests.

The performance was evaluated by applying procedures ASTM B 117 (salt fog chamber, 1200 hours) and ASTM D 2247 (100% relative humidity cabinet, 500 hours) [23]. The panels were evaluated according to ASTM D 1654 and ASTM D 714 to assess the degree of blistering and degree of rusting respectively [24].

A two foot long flame tunnel as specified in ASTM D 3806 was used to determine the flame spread value (FSV = Ls-La, where Ls and La are respectively the spread of flame observed on the coated panels and on a naked steel panel selected as reference).

Lamellar zinc alone is too active

Tables 2-4 show the results of the corrosion tests in the salt spray and 100% humidity cabinet. An analysis of the data on primers using spherical and lamellar zinc was carried out, which indicated that the best performance was reached with PVC values near the CPVC or just below this value. As the content of lamellar zinc increased, the CPVC decreased from approximately 60/65% for primer 1.1 to 50/55% for primer 1.5, falling by 3-4% for each primer in the series.

Primers based mainly on spherical zinc and formulated with a PVC below the CPVC showed an abrupt diminution of the anticorrosive performance, whereas those primers that included lamellar zinc, in spite of being prepared at a PVC well below to the CPVC, maintained their efficiency.

These results suggest that the corrosion products of spherical particles could not only increase the electrical resistance of the protective system but also that they could reduce the amount of zinc available. This could be attributed to the electrical isolation of the centre of the particles, which would eliminate effective contact between them and with the substrate.

Visual observations showed that primers based on lamellar particles were covered with more white corrosion products than those formulated with spherical zinc. This indicates that lamellar zinc generates an anode which is too active even at PVC values very inferior to the CPVC; additionally, the anode could be depleted unnecessarily, as shown in Figure 1.

The results corresponding to the degree of blistering showed a greater tendency to blister formation in those compositions with lamellar zinc as the only pigment, particularly at a PVC only slightly below the CPVC. The

Quelle/Publication: **European Coatings Journal**
Ausgabe/Issue: **09/2007**
Seite/Page: **40**

formation of soluble corrosion products could be the apparent cause of the low resistance to blister formation (at PVC values below the CPVC) shown in the 100% relative humidity cabinet (osmotic blistering).
As the spherical zinc/lamellar zinc ratio increased the blister resistance also increased; blistering was not observed for pigment levels near to or greater than the corresponding CPVC. The pure spherical zinc primers 1.1 showed elevated blistering resistance. If the corrosion resistance of lamellar zinc could be retained and if its blistering tendency could be eliminated at PVC values below the CPVC, some technical and economic advantages would be obtained from the use of this type of pigment.

Mica plus lamellar zinc gives best performance

An analysis of the degree of rusting and the degree of blistering corresponding to the series studied allowed the estimation of the CPVC values. In general, the use of mica led to a reduction of the CPVC and therefore for PVC/CPVC ratios equal to unity the PVC of the modified zinc primers was lower.
Some primers of Series 2 and 3 showed excellent performance in the salt fog chamber and the 100 % relative humidity cabinet across wide levels of PVC below the estimated CPVC. Thus, those primers based on 10.2 and 33.1 µm diameter mica showed exceptional results for PVC values from 35.0 to 45.0 and 32.5 to 42.5, respectively.
Primer 2.4 exhibited, from a technical-economic point of view, the best performance of all the primers across a 10 % range of PVC in both the accelerated tests; as a consequence, slight heterogeneities that could ultimately appear in these primers after completing the zinc dust incorporation and prior to coating application would not have a significant effect on the corrosion inhibiting capacity and blistering resistance.
The results in the flame spread test showed the highest rating, a value of 0, in all cases, which implies that the behaviour was similar to that displayed for the bare steel panel used as reference. These results could have been expected due to the totally inorganic character of the compositions.

Effective primers at lower PVC

Self-curing metallic silicates (with a high silica/alkali ratio) act as excellent film forming materials. These inorganic silicates allow the formulation of efficient zinc lamellar primers modified by using mica to space the zinc particles. This controls the high galvanic activity of lamellar zinc that leads to blister formation by osmotic phenomena in the applied films.
For the best samples, the lowest lamellar zinc content in the dry film, calculated at the corresponding estimated CPVC values, is approximately 20% by volume or even slightly lower. The mica, particularly that with 33.1 µm diameter, showed a good ability to reduce the CPVC without affecting the optimum performance for the two accelerated tests considered, and also to reduce the cost of the primer.
Several zinc rich primers (100% spherical zinc, 75/25 spherical zinc/lamellar zinc ratio and 50/50 spherical zinc/lamellar zinc ratio) also exhibited very good performance and would be considered as acceptable alternatives.
All coatings formulated offered excellent resistance to the fire test, which would allow their use as primers in a multicoat system for anticorrosive/non-flammable protection of metallic structures.
A further advantage of the alkaline silicates used for the treatment of substrates against the action of the fire, in addition to their overall non-flammability, is the small amount of smoke given off during burning, with no toxicity for living beings; their low cost is also advantageous. In terms of their most important disadvantages, it is necessary to mention the high alkalinity of the solutions, which demands special care in handling.

ACKNOWLEDGEMENTS

The authors are grateful to CONICET (the Argentine National Council for Science and Technology), to UTN-FRLP (Universidad Tecnológica Nacional Facultad Regional La Plata) and to CICPBA (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) for their sponsorship of this research.

REFERENCES

[1] L. D. Vincent, Materials Performance, 39 (5), 38, 2000
[2] S. Mukherjee, Paintindia, 49 (7), 31, 1999
[3] G. Parashar, D. Srivastava, P. Kumar, Progress in Organic Coatings, 42 (1-2), 1, 2001
[4] C. H. Hare, Jnl Prot Coatings & Linings, 15 (4), 17, 1998
[5] J. Vilche, E. Bucharsky, C. Giudice, Corrosion Science, 44, 1287, 2002
[6] G. Chapman, Pitture e Vernici, 75 (17) 27, 1999
[7] E. Phifer, Jnl Prot Coatings & Linings, 2 (2) 46, 1992
[8] G. Gettwert, W. Rieber, J. Bonarius, Surface Coatings International, 81 (12) 596, 1998
[9] R. Mudd, Jnl Prot Coatings & Linings, 12 (10), 51, 1995
[10] C. Giudice, J. Benitez, M. Morcillo, Surface Coatings International, 80 (6) 279, 1997
[11] E. Cavalcanti, O. Ferraz, Progress in Organic Coatings, 23, 185, 1993
[12] C. Hare, Paintindia, 48 (4) 31, 1999
[13] H. Marchebois, S. Joiret, C. Savall, J. Bernard, S. Touzain, Surface Coatings Technology, 157, 151, 2002
[14] H. Marchebois, S. Touzain, S. Joiret, J. Bernard, C. Savall, Progress in Organic Coatings, 45 (4), 415, 2002
[15] Benda-Lutz Werke, Technical Brochures, Traismauer, Austria (1991).
[16] K. Zimmermann, European Coatings Journal, 1 (1), 14, 1999
[17] ASTM D 520- 84, Specification for zinc dust pigment, 1993
[18] ASTM D 521-90, Tests methods for chemical analysis of zinc dust (metallic zinc powder), 1994
[19] J. B. Preston, Pigment Handbook, Vol. I, Ed. Patton, Wiley, N.Y., USA, p.249, 1973
[20] C. Giudice, A. Pereyra, Soluble metallic silicates in the anticorrosive inorganic coating formulation with non-flammable properties, Pitture e Vernice, 2007 (in press)
[21] C. Giudice, J. Benitez, Corrosion Reviews, 13 (2-4), 81, 1995
[22] C. Giudice, D. del Amo, Corrosion Control Prevention, 43 (1), 15, 1996
[23] M. Frizzi, E. Aragon, Jnl Prot Coatings & Linings, 19 (9) 58, 2002
[24] L. Ketter, W. Julius, D. Weldon, Materials Performance, 31 (8), 35, 1992

Results at a glance

- The performance of zinc-rich anticorrosive primers based on inorganic potassium silicate and containing pure spherical zinc, pure lamellar zinc and mixtures at different ratios was compared across a range of PVC contents.
- Primers containing only lamellar zinc showed good corrosion resistance but poor resistance to osmotic blistering in a high humidity test.
- Mixing the lamellar filler mica with lamellar zinc gave improved corrosion and blistering resistance as well as lower costs.

Quelle/Publication: **European Coatings Journal**
Ausgabe/Issue: **09/2007**
Seite/Page: **40**

- Lamellar zinc gave a lower CPVC than spherical zinc and required less pigment for effective protection. These levels were further reduced by adding mica.
- Best performance can be obtained by using mixtures of lamellar zinc with either spherical zinc or mica.
- All samples achieved the highest rating (flame spread value FSV=0) in a surface spread of flame test.

The authors:
-> Andrea M. Pereyra studied chemical engineering at the National Technological University of Argentina and obtained her PhD in fire retardant coatings at La Plata National University in 2006. At present she is a professor at the National Technological University.
-> Carlos A. Giudice obtained his degree in chemical engineering at La Plata National University in 1973 with a PhD in antifouling paints. He is now a member of Argentina's National Council for Scientific and Technical Research (CONICET), carrying out studies on paints and a professor at the National Technological University.

Quelle/Publication: **European Coatings Journal**
Ausgabe/Issue: **09/2007**
Seite/Page: **40**

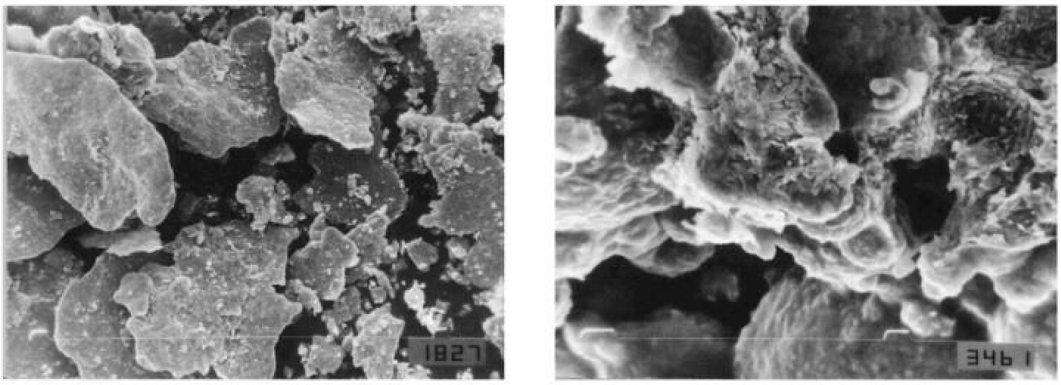

Figure 1: Left: Lamellar zinc dust (SEM, 1000x); Right: lamellar zinc primer film (SEM 7500x; 1200 hr salt fog chamber)

Quelle/Publication: European Coatings Journal
Ausgabe/Issue: 09/2007
Seite/Page: 40

VINCENTZ

Table 1:
Sample identification (ratios are by volume)

Series 1. Zinc-rich primers	
1.1	spherical zinc, 100%
1.2	75/25 spherical zinc/lamellar zinc
1.3	50/50 spherical zinc/lamellar zinc
1.4	25/75 spherical zinc/lamellar zinc
1.5	lamellar zinc, 100%
Series 2. Lamellar zinc primers modified with mica (10.2 µm)	
2.1	80/20 zinc/mica
2.2	70/30 zinc/mica
2.3	60/40 zinc/mica
2.4	50/50 zinc/mica
2.5	40/60 zinc/mica
Series 3. As Series 2 but using 33.1 µm mica	
3.1.	80/20 zinc/mica
3.2	70/30 zinc/mica
3.3	60/40 zinc/mica
3.4	50/50 zinc/mica
3.5	40/60 zinc/mica

Quelle/Publication: **European Coatings Journal**
Ausgabe/Issue: **09/2007**
Seite/Page: **40**

Table 2: Degree of rusting on X-scribed area of panels (ASTM D 1654, Method A)

Primer series	PVC % (in bold) and test results**											
	42.5	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**	**60.0**	**62.5**	**65.0**	**67.5**	
1.1	*	*	*	1	2	4	4–5	6–7	7–8	8	7–8	
1.2	*	*	5	6–7	6	7–8	7–8	9–10	9–10	9	*	
1.3	*	7–8	7–8	8	8	8–9	9–10	9	8–9	*	*	
1.4	7–8	7–8	8–9	8–9	8–9	9	9	8–9	*	*	*	
1.5	8–9	9	9–10	9–10	9–10	9–10	7–8	7–8	*	*	*	
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
2.1	*	*	*	*	9	9–10	9–10	10	10	9	8–9	8–9
2.2	*	*	*	9–10	10	10	10	10	8–9	8–9	8	*
2.3	*	*	9–10	9–10	9–10	10	9	9	9	9	*	*
2.4	*	9	9–10	10	10	10	9	7–8	8	*	*	*
2.5	6	8	8–9	9–10	9–10	9	9	8–9	*	*	*	*
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
3.1	*	*	*	*	9	9–10	10	10	9	8–9	7–8	8
3.2	*	*	*	9–10	10	10	10	10	8–9	8–9	8	*
3.3	*	*	10	10	10	10	9–10	8–9	7–8	7–8	*	*
3.4	*	9	10	10	10	9	8–9	8	8	*	*	*
3.5	6	8	9	10	9–10	9	8–9	8	*	*	*	*

* No sample prepared, because the PVC was far from the critical value
** Rating of failure was evaluated according to the advancement from the cut zone: 10 corresponds to 0 mm, whilst 0 indicates 16 mm or more

Quelle/Publication: European Coatings Journal
Ausgabe/Issue: 09/2007
Seite/Page: 40

Table 3: Degree of rusting on unscribed areas of panels (ASTM D 1654, Method B)

Primer series	PVC % (in bold) and test results**											
	42.5	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**	**60.0**	**62.5**	**65.0**	**67.5**	
1.1	*	*	*	3–4	4	5	6–7	8–9	8–9	8–9	8	
1.2	*	*	6	7	8	8–9	9	9–10	8–9	5	*	
1.3	*	7–8	8	9	10	9–10	8–9	8–9	5	*	*	
1.4	8	8–9	8–9	8–9	10	9–10	9	5	*	*	*	
1.5	8	9	9–10	10	10	9	5	5	*	*	*	
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
2.1	*	*	*	*	9	9	8–9	10	10	8–9	7–8	6–7
2.2	*	*	*	9	10	10	10	10	8	7–8	6–7	*
2.3	*	*	9	9–10	9–10	10	10	8–9	7–8	7	*	*
2.4	*	8	9	10	10	9–10	8	7	6	*	*	*
2.5	6	6–7	8	9	9–10	9	8	7	*	*	*	*
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
3.1	*	*	*	*	9–10	10	9–10	10	10	7–8	5–6	5
3.2	*	*	*	9–10	10	10	10	10	8	6–7	6	*
3.3	*	*	9–10	10	10	10	8	6–7	4–5	4	*	*
3.4	*	9	9	10	10	9	7	4–5	4	*	*	*
3.5	6	6–7	8–9	10	9–10	8	6	6	*	*	*	*

* No sample prepared, because the PVC was far from the critical value
** Rating of failure was measured taking into account the percentage of the surface area corroded by the medium, from 10 (no failure) to 0 (over 75% failure)

Quelle/Publication: European Coatings Journal
Ausgabe/Issue: 09/2007
Seite/Page: 40

VINCENTZ

Table 4: Degree of blistering in humidity test (ASTM D 714)

Primer series	PVC % (in bold) and test results**										
	42.5	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**	**60.0**	**62.5**	**65.0**	**67.5**
1.1	*	*	*	9–F	10	10	10	10	10	10	10
1.2	*	*	6–F	9–F	10	10	10	10	10	10	*
1.3	*	8–MD	8–M	9–F	9–F	10	10	10	10	*	*
1.4	4–MD	6–M	6–F	8–F	10	10	10	10	*	*	*
1.5	4–MD	6–M	8–M	8–F	10	10	10	10	*	*	*
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
2.1	*	*	*	*	4–MD	6–MD	8–MD	9–F	9–F	10	10	10
2.2	*	*	*	6–MD	8–MD	8–F	9–F	10	10	10	10	*
2.3	*	*	8–M	8–M	9–F	10	10	10	10	10	*	*
2.4	*	8–F	9–F	10	10	10	10	10	10	*	*	*
2.5	8–F	9–F	10	10	10	10	10	10	*	*	*	*
	30.0	**32.5**	**35.0**	**37.5**	**40.0**	**42.5**	**45.0**	**47.5**	**50.0**	**52.5**	**55.0**	**57.5**
3.1	*	*	*	*	4–MD	6–MD	8–M	9–F	10	10	10	10
3.2	*	*	*	8–M	8–F	9–F	9–F	10	10	10	10	*
3.3	*	*	8–F	9–F	10	10	10	10	10	10	*	*
3.4	*	10	10	10	10	10	10	10	10	*	*	*
3.5	9–F	9–F	10	10	10	10	10	10	*	*	*	*

* No sample prepared, because the PVC was far from the critical value

** The size of the blisters is described on a numeric, arbitrary scale from 0 to 10, where the last value represents an absence of blisters, whilst the blister frequency is defined qualitatively: D (dense), MD (medium dense), M (medium) and F (few)