Atmospheric Corrosion Behavior of Paint Systems Applied on Weathered Hot-Dip Galvanized Steel

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INTRODUCTION

The anticorrosive protection of steel with zinc coatings is a common procedure. Among these treatments, hot-dip galvanizing is a typical procedure for protecting steel structures which are to be exposed to the elements of the atmosphere.

A great number of galvanized steel structures have been exposed to the atmosphere for many years without any type of additional coating. As a consequence of such aggressive exposure, the thickness of the zinc layer decreases significantly and provides inadequate protection to the base steel, which may come to show evident signs of corrosion. This is especially the case in industrial or marine environments, which are very aggressive and promote a significant attack on the zinc coating.[1] In such situations the option exists to paint the structure—after conditioning the weathered surface—in order to prolong its service life and delay the degradation of the protective zinc coating.

On the other hand, the painting of new galvanized steel structures may occasionally be postponed to allow the zinc surface to be exposed for some time to the atmosphere. This was formerly common practice and was carried out intentionally in the belief that the weathering of galvanized steel led to better adhesion of the paint system.[2] Today this practice is advised against, since it has been seen in some situations that the risk of premature failure of a paint system is high when it is applied on galvanized steel weathered in the atmosphere.

The painting of galvanized steel has been the subject of many studies.[3-7] However, there is a relative scarcity of published information on the painting of weathered galvanized steel.

A determining factor of the success of the galvanized steel+paint system—also known as the duplex system—is the choice of an appropriate paint system for application on the zinc coating, since perfect compatibility between the two must be ensured. There is known to be a notable difference between painting galvanized steel and painting carbon steel. Certain paint systems, such as the case of alkyd paints and, in general, all oil-based paints, show good behavior when applied on steel, but are easily delaminated from the surface when applied on zinc substrates.

The durability of a paint coating applied on a galvanized steel surface which has been exposed for a certain time to the atmosphere depends on the aggressiveness of the atmosphere, the preparation of the weathered surface prior to painting, and the type of coating applied.

This work presents the results of an atmospheric corrosion study carried out over 11 years in three Spanish atmospheres of highly different degrees of aggressiveness (Madrid, Bilbao, and Tenerife), applying eight paint coatings on galvanized steel weathered in different conditions and using different methods to prepare the aged metallic surface prior to painting.

The behavior of the weathered galvanized steel / paint system will depend not only on the type of organic coating applied but also on the state of the zinc coating surface. In practice, a wide variety of surface conditions may be found, depending on the atmosphere to which the structure has been exposed and the exposure time, with different corrosion product layers and the presence or absence of soluble salts (chlorides, sulphates, etc.) among the corrosion products as a consequence of the reaction of atmospheric pollutants with the zinc surface, etc. The success of painting weathered galvanized steel will depend both on the choice of the appropriate paint system and the preparation of the zinc surface prior to painting.[8]

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Table 1—Hot-Dip Galvanized Steel. Surface Conditions Tested

Initial	Weathering	Surface Preparation
	—	Solvent Cleaning
	—	NH_3
	—	SSB
	OU	Solvent Cleaning
Fresh HDG Steel	HC	WB
	HC	SSB
	SF	WB
	SF	SSB
	SD	WB
	SD	SSB

OU: Outdoor exposure in an urban atmosphere.
HC: Exposure to humidity condensation cabinet.
SF: Exposure to salt fog cabinet.
SD: Exposure to moist sulphur dioxide cabinet.
WB: Wire brushing.
SSB: Sweep shot blasting.

The fundamental aim of this study is to analyze the influence of the surface condition of weathered galvanized steel before painting on the subsequent behavior of different paint systems when the latter are subsequently exposed to atmospheres of different degrees of aggressiveness.

EXPERIMENTAL

Test specimens of 5 × 10 cm were cut from a mild steel sheet of 1 mm thickness and subsequently submerged in a molten zinc bath to obtain a galvanized coating of 54 μm average thickness.

After degreasing with trichloroethylene they were weathered in different environments:

(a) Some specimens were exposed for 45 days to the low aggressive urban atmosphere of Madrid, corrosivity category C2 according to ISO 9223.[9] Given the insignificant amount of corrosion products formed during exposure, the subsequent conditioning of the weathered zinc surface was limited to simple rinsing with organic solvent in order to remove traces of dust.

(b) Other specimens were artificially weathered in the laboratory by exposure in a humidity condensation cabinet (ASTM D 4585,[10] eight days), salt fog cabinet (DIN 50021,[11] one day), or SO_2 cabinet (DIN 50018,[12] 14 days), respectively, simulating a rural atmosphere, a marine atmosphere, and an industrial atmosphere. In no case did corrosion products of the base steel appear. The weathered surfaces of the specimens were then prepared by brushing using a steel wire brush or by sweep blasting with a S23/S40 shot-abrasive mixture.

(c) Some nonweathered specimens were also prepared by cleaning with organic solvent or with NH_3 (a common practice in some galvanizing shops in order to improve the adhesion of the organic coating) or by blasting.

Table 1 lists the 10 surface conditions obtained and tested.

Eight paint systems were then applied following the suppliers' instructions. *Table* 2 shows the characteristics of the tested paint systems. All were applied by air spray, except for paint system 2 which was applied by brush. Only primer was applied on the lower half of the specimens, while both primer and topcoat layers were applied on their upper halves. In the case of the chlorinated rubber systems (systems 2 and 4) only topcoat was applied, one coat on the lower half of the specimens and two coats on their upper halves.

The painted specimens were stored in the laboratory for one month to ensure that they were fully cured before being subjected to the different tests.

Scribes were made on the right-hand side of the specimens to evaluate the degree of undercoating delamination from the scribe. The specimens were then exposed to atmospheres of different degrees of aggressiveness (Madrid, Bilbao, and Tenerife) (*Table* 3) and their state periodically evaluated, paying special attention to the degree of blistering according to ASTM D 714[13] and the delamination of the coatings.

Accelerated tests were also carried out in humidity condensation cabinets and salt fog cabinets, and measurements were taken of dry and wet adhesion.[14] Initial

Table 2—Characteristics of Paint Systems Applied on Weathered Hot-Dip Galvanized Steel

System Number	Primer	Finish	Total Average DFT (μm)
1	Vinyl chloride/isobutyl maleate copolymer (low molecular weight)	Acrylic aliphatic polyurethane	92
2	Chlorinated rubber pigmented with micaceous iron oxide (supplier 1) (1st coat)	Chlorinated rubber pigmented with micaceous iron oxide (supplier 1) (2nd coat)	113
3	Synthetic resin blend (substantially vinyl) inhibitive primer	High solids vinyl chloride/vinyl acetate copolymer	109
4	Chlorinated rubber pigmented with micaceous iron oxide (supplier 2) (1st coat)	Chlorinated rubber pigmented with micaceous iron oxide (supplier 2) (2nd coat)	133
5	Acrylic anionic emulsion of a methyl acrylate-based copolymer	Acrylic aliphatic polyurethane	77
6	Acrylic/titanium dioxide	Acrylic/titanium dioxide	88
7	Carboxylated vinyl chloride	Vinyl acrylic lacquer[a]	100
8(NR)[b]	Alkyd/zinc chromate	Alkyd	89

(a) Noncarboxylated vinyl chloride-vinyl acetate copolymer modified ([illegible]) with thermoplastic acrylic copolymer based on methyl and butyl methacrylates.
(b) NR = Not recommended.

Table 3—Characteristics of Performance Test

Location		Corrosion rate, (µm/year) Bare Steel	Bare Zinc	Corrosivity Category according to ISO 9223[9]
Open air, urban atmosphere	City of Madrid	39	0.65	C2
Open air, urban atmosphere	City of Bilbao	50.6	7.56	C4
Open air, marine atmosphere (very severe)	Tenerife Island	270	114	>C5

measurements were made using the cross-hatch or scribe and tape test and later measurements were taken using the scribe and tape test following immersion for 20 days in distilled water. The 0.04 in. (1 mm) wide scribe was made using an Erichsen punch, while in the cross-hatch test a lattice pattern (surface of cross-cut area) was made by cuts separated by 0.04 in. (1 mm).

RESULTS

In Tenerife, all the specimens were withdrawn after two years of exposure. In all cases the specimens exposed with only primer showed very significant damage, due to the great degree of aggressiveness of the atmosphere, which was appreciable and considerable from the first months of exposure. As for the complete systems (primer+topcoat), apart from some exceptions, practically all the specimens failed, with the acrylic and alkyd systems (systems 6 and 8) presenting the worst behavior. The strong degree of aggressiveness of this atmosphere was only tolerated during these first two years of exposure by some of the specimens protected by the other systems, specifically those that had not been previously weathered or were weathered in low aggressive atmospheres (urban atmosphere of Madrid or humidity condensation cabinet).[14]

Exposure continued for up to 11 years in the urban environments of Madrid and Bilbao. This paper refers to the results obtained in these two atmospheres, and the study focuses on the behavior of the different paint systems, the effect of weathering the galvanized coating in different conditions, and the different types of surface preparation prior to painting the weathered galvanized steel.

Without Weathering

Table 4 presents the results of the evaluation of the degree of blistering shown by the paint systems after different exposure times. Blister size and frequency values have been converted, according to ASTM D 714,[15] into numeric values using the Keane conversion table.[15] The vinyl/polyurethane system (system 1) and the chlorinated rubber system pigmented with micaceous iron oxide system (supplier 2) (system 4) offered the best behavior, since after 11 years of exposure the specimens exposed with complete paint systems (two coats in the case of system 4) did not show significant failure rates in either of the two atmospheres for any of the tested surface conditions. However, some specimens of the chlorinated rubber-micaceous iron oxide system (system 4) exposed to the Madrid atmosphere presented slight delamination of the paint system when only one coat had been applied.

In contrast, the alkyd system (system 8) showed the worst behavior, as was to be expected for a system that is not recommended for this situation, and a significant level or even complete detachment of the paint system was observed with almost all the tested specimens (*Figure* 1). This occurred both with specimens where only the primer was applied and those where the complete system was applied, and was appreciable after six years of exposure.

The rest of the systems showed intermediate behavior, with some occasional failures in certain conditions and atmospheres, though, in general, their behavior was fairly good, especially in those cases where the complete system was applied.

Specimens Weathered In Low Aggressive Conditions

Table 5 presents the results of evaluation of the degree of blistering. The best behavior again was shown by the vinyl/polyurethane system (system 1) and the chlorinated rubber system pigmented with micaceous iron oxide (supplier 2) (system 4), since no significant symptoms of deterioration were detected for any of the tested conditions on the specimens exposed with the complete systems. However, as in the previous case, the chlorinated rubber-micaceous iron oxide system presented delamination problems on the lower half of the specimens where only one coat had been applied. These systems, together with the other chlorinated rubber-micaceous iron oxide system (supplier 1) (system 2), seemed to perfectly tolerate exposure up to 11 years in both atmospheres after weathering prior to painting, provided that the surface was prepared with organic solvent in the case of weathering outdoors or by brushing or blasting in the case of weathering in the humidity condensation cabinet.

The alkyd system (system 8) again showed the worst behavior, with considerable delamination on all the specimens, while the rest of the systems presented intermediate behavior.

For the case of weathering in the humidity condensation cabinet, better behavior was generally observed for the specimens prepared by brushing than those prepared by blasting.

Specimens Weathered In High Aggressive Conditions

Table 6 presents the results of the evaluation of the degree of blistering. All the complete systems tested (1, 2, 3, 4, and 8) seemed to tolerate perfectly well weathering in the salt fog cabinet when the surface was subsequently prepared by blasting before application of the paint system. Brushing, however, was not suitable for most of the

Table 4—Degree of Blistering, after Different Atmospheric Exposure Times, for Specimens Painted on Nonweathered Hot-Dip Galvanized Steel

NON-WEATHERED HDG STEEL — PRIMER

System (Table 2)	Test Site	Organic Solvent 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.	NH3 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.	Sweep shot blasting 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.
1	Madrid	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	10	10								10	10	10	8	7	7	7
	Tenerife	7	8	5	4				10	9	9	9				5	4	3	5			
2	Madrid	7	7	7	7	7	7	7														
	Bilbao	10	10	10	10	10	10	10														
	Tenerife	8	4	2	2																	
3	Madrid	10	10	10	10	10	10	d10	10	10	10	10	10	10	d10	10	10	10	10	10	10	10
	Bilbao	10	10	10	9	9	9	9	10	10	10	10	9	9	9	10	10	10	9	9	5	8
	Tenerife	10	8	9	2				7	7	7	7				5	4	4	2			
4	Madrid	10	10	10	9	9	9	d10	10	10	10	9	8	8	d10	7	7	7	7	7	7	d10
	Bilbao	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Tenerife	8	6	7	2				6	4	5	3				8	4	2	2			
5	Madrid	10	10	10	10	10	10	9	10	10	10	10	10	10	10	7	7	7	7	7	7	7
	Bilbao	8	8	6	8	6	7	7	10	10	10	10	10	9	7	7	7	7	7	7	6	5
	Tenerife	7	5	2	2				7	8	5	2				7	5	4	2			
6	Madrid	10	10	10	10	10	10	9	10	10	10	10	10	10	9	10	10	10	10	10	10	9
	Bilbao	10	10	10	10	10	8	8	10	10	10	10	10	7	6	10	10	10	10	8	5	4
	Tenerife	4	3	3	2				4	2	2	2				5	4	4	2			
7	Madrid	10	10	10	8	7	7	7	10	10	10	10	10	10	8	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	8	5	10	10	10	10	8	9	7	10	10	10	10	10	9	9
	Tenerife	8	4	2	2				6	4	2	2				8	2	2	2			
8	Madrid	10	10	10	8	9	d25		10	10	10	10	d100			10	10	10	8	5	dNG	
	Bilbao	10	10	10	10	9	5	5	10	10	10	10	10	10	9							
	Tenerife	7	7	6	3				10	10	5	3				7	6	4	2			

NON-WEATHERED HDG STEEL — PRIMER + FINISH

System (Table 2)	Test Site	Organic Solvent 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.	NH3 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.	Sweep shot blasting 5 m.	9 m.	1 y.	2 y.	4 y.	6 y.	11 y.
1	Madrid	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	9	9	10	10	10	10	8	8	9	10	10	10	10	8	9	9
	Tenerife	10	10	10	10				10	9	9	9				8	7	7	5			
2	Madrid	10	10	10	10	9	8	8	10	10	10	10	10	10	10	10	10	9	9	9	9	9
	Bilbao	10	10	10	10	10	9	9	10	10	10	10	10	9	8	9	8	7	7	7	7	7
	Tenerife	10	10	10	9				7	9	5	2				9	2	3	4			
3	Madrid	10	10	10	10	9	9	9	10	10	10	10	10	10	d30	10	10	10	10	10	10	8
	Bilbao	10	10	10	10	10	8	9	10	10	10	10	8	9	9	10	10	10	10	8	9	8
	Tenerife	10	10	10	9				7	6	5	2				10	10	10	6			
4	Madrid	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	8
	Bilbao	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	9
	Tenerife	10	10	10	5				10	10	6	5				10	10	6	5			
5	Madrid	10	10	10	10	10	10	9	10	10	10	10	10	10	10	10	10	10	8	7	7	7
	Bilbao	10	10	10	10	9	8	9	10	10	10	10	10	10	10	7	7	7	7	7	7	7
	Tenerife	10	10	10	9				10	10	10	9				10	9	8	8			
6	Madrid	10	10	10	10	10	10	8	10	10	10	10	6	9	8	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	10	9	10	10	10	10	7	7	6	10	10	10	10	10	10	10
	Tenerife	5	5	4	2				7	5	4	2				3	5	4	3			
7	Madrid	10	10	10	10	8	9	9	10	10	10	10	10	8	9	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	10	7	10	10	10	10	8	8	7	10	10	10	10	10	10	9
	Tenerife	10	10	7	4				10	10	6	6				8	8	4	2			
8	Madrid	10	10	10	10	9	9	d90	10	10	10	10	10	10	d100	10	10	10	9	8	d40	
	Bilbao	10	10	10	10	10	d50		10	10	10	10	9	d100								
	Tenerife	10	10	10	8				10	10	10	8				10	10	7	6			

delamination, % of the surface.
: Not tested.

m: months.
y: years.

systems, except for the chlorinated rubber system pigmented with micaceous iron oxide (supplier 2) (system 4), which showed the best behavior.

The duplex systems (galvanized+painted) were observed to be especially sensitive to the presence of sulphate ions at the metal/paint interface. All the complete systems tested (1, 2, 3, 4, and 8) showed some type of failure in one or both of the two stations where the study was carried out in the two surface conditions tested. The chlorinated rubber-micaceous iron oxide system (supplier 1) (system 2) weathered in a SO_2 cabinet and blasted was the only system which did not show failure in either of the two atmospheres. In general, better behavior was observed for blasted specimens than for brushed specimens.

Adhesion Results

Table 7 shows the results of the adhesion test performed under both dry and wet conditions. Since the scribe and tape test is a "go-no go" method, there is no difficulty in differentiating between good and bad adhesion. Paint systems 1 and 3 present the best general adhesion. At the other end of the scale are systems 4, 6, 7, and 8 (not recommended). In general terms, the scribe test (dry) is less critical than the cross-hatch test (dry). The scribe test (wet) is the most critical of the three.

The following overview may be drafted from the adhesion results: generally, coatings adhere badly to fresh galvanized steel. In this situation, a slight attack on the zinc surface by weathering in a nonpolluted atmosphere, or by slight blasting, may improve adhesion by facilitating anchorage (mechanical interlocking) of the paint to the metallic substrate. On the other hand, if weathering of the zinc surface is carried out in atmospheres polluted with SO_2 or NaCl, the formation of soluble zinc corrosion products would favor the delamination of the paint coating in moist environments. In these cases, it is necessary to eliminate the zinc corrosion products by effective surface preparation.

DISCUSSION

After 11 years of atmospheric exposure in the rural atmospheres of Madrid and Bilbao, the two tested chlorinated rubber-micaceous iron oxide systems and the vinyl/acrylic system do not present significant symptoms of deterioration when applied on a galvanized steel surface which has not been previously weathered or has been slightly weathered outdoors or in a humidity cabinet, irrespective of the surface preparation method used. With the rest of the systems, better behavior is generally observed with brushed specimens than with blasted specimens. Blasting caused greater deterioration of the protective zinc layer, even leaving the base steel partly uncovered—as is observed in the EDAX analysis carried out on the metallic surface after blasting (*Figure* 2). This conditioning is therefore both harmful and unnecessary, since no saline pollution (soluble salts) is found in the weathered zinc coating.

When weathering has taken place in the salt fog cabinet, the blasting of the surface prior to application of the paint system favors a better subsequent behavior of the coating. Simple brushing is not sufficient since it does not achieve effective removal of the saline pollutants present in the weathered zinc coating. This can be seen in the Cl-peaks of the EDAX analyses carried out on weathered galvanized steel surfaces after brushing (*Figure* 3a) and after blasting (*Figure* 3b). The systems that offer the best behavior are again the chlorinated rubber systems and system 3 (vinyl/vinyl copolymer).

When weathering is carried out in the SO_2 cabinet, none of the tested systems seem to perfectly tolerate the presence of sulphate ions at the interface after brushing or blasting, though, in general, better behavior is offered by the blasted specimens. As in the case of weathering in the salt fog cabinet, greater removal of saline pollutants is achieved, as can be observed in the S peaks of the corresponding EDAX analyses (*Figure* 4). Once again, the best behavior is offered by the chlorinated rubber systems.

Both for nonweathered surfaces and with the different types of weathering, the best behavior is provided by the chlorinated rubber systems pigmented with micaceous iron oxide and by the vinyl/polyurethane system. However, with the chlorinated rubber-micaceous iron oxide systems, it is necessary to assure a sufficient coating thick-

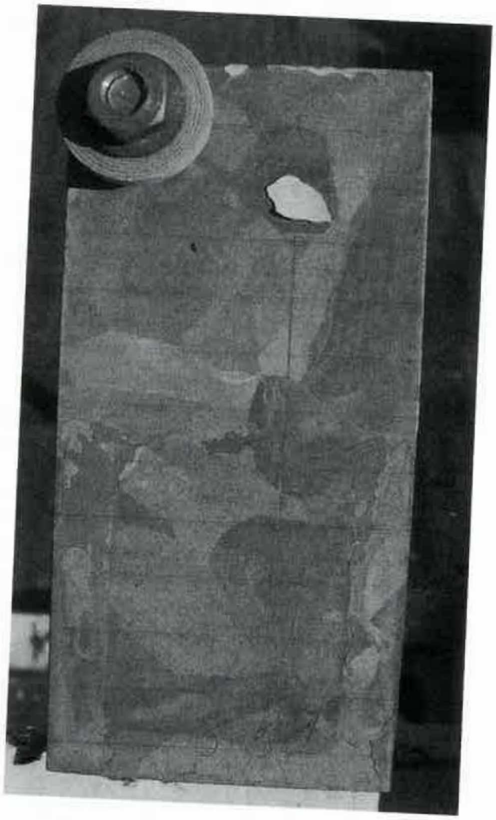

Figure 1—Photograph of the sample corresponding to system 8 (alkyd, not recommended) applied on hot-dip galvanized steel weathered for 45 days in an urban atmosphere, after 11 years of exposure in the Madrid atmosphere. Almost complete disappearance of the coating is observed, except in some small zones.

Table 5—Degree of Blistering, after Different Exposure Times, for Specimens Painted on Hot-Dip Galvanized Steel Weathered in Low Aggressiveness Conditions: Outdoor Exposure in an Urban Atmosphere and Exposure to Humidity Condensation Cabinet

System (Table 2)	Test Site	OUTDOOR EXPOSURE														CONDENSING HUMIDITY CHAMBER																											
		PRIMER							PRIMER+FINISH							PRIMER														PRIMER + FINISH													
		Organic Solvent							Organic Solvent							Wire Brushing							Sweep shot blasting							Wire Brushing							Sweep shot blasting						
		5m	9m	1y	2y	4y	8y	11y	5m	9m	1y	2y	4y	8y	11y	5m	9m	1y	2y	4y	8y	11y	5m	9m	1y	2y	4y	8y	11y	5m	9m	1y	2y	4y	8y	11y	8m	9m	1y	2y	4y	8y	11y
1	Madrid	10	10	10	10	10	10	9	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao								10	10	10	9	9	9	8								10	10	10	10	10	9	9								10	10	10	10	10	10	8
	Tenerife	8	9	6	2				9	2	9	8				6	4	2	2				6	4	2	2				10	10	8	6				10	10	8	8			
2	Madrid								10	10	10	10	10	10	10															10	10	10	10	10	10	10	9	8	8	8	9	6	9
	Bilbao								10	10	10	10	10	8	9															10	10	10	10	10	10	8	10	10	10	8	8	7	7
	Tenerife								10	10	10	10																		10	10	10	5				10	10	7	5			
3	Madrid	10	10	10	10	10	10	d30	10	10	10	10	10	10	d10	10	10	10	10	8	6	d75	10	5	7	7	7	7	d75	10	10	10	10	10	10	6	10	8	7	7	7	7	7
	Bilbao	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	7	8	5								10	10	10	10	10	10	10							
	Tenerife	7	7	5	3				10	10	10	10				10	10	8	6											10	10	10	10										
4	Madrid	10	10	10	10	10	10	d25	10	10	10	10	10	10	10	10	10	10	10	4	d20		10	10	10	10	7	6	d10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Tenerife	4	4	2	2				10	8	9	8				8	5	4	2				8	4	4	2				10	10	10	0				10	10	8	8			
5	Madrid															10	10	10	9	7	7	7	10	10	10	8	7	7	7	10	10	10	8	7	7	7	10	10	10	10	10	10	10
	Bilbao															10	10	10	10	10	10	10	10	8	7	6	6	5	5	10	10	10	10	10	10	10	10	10	10	9	9	9	9
	Tenerife															6	6	4	2				6	6	4	2				10	10	10	10				10	10	10	5			
6	Madrid															10	10	10	10	10	10	10	7	7	7	7	7	7	7	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao															10	10	10	10	10	8	6	10	10	10	10	10	8	6	10	10	10	10	10	6	7	10	10	10	10	10	10	8
	Tenerife															4	2	2	2				4	2	2	2				7	7	5	2				6	5	3	3			
7	Madrid	10	6	5	5	5	5	6	10	6	5	5	5	5	6	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	8	8	6	10	10	10	10	10	10	10
	Bilbao															10	10	10	10	10	10	10	10	10	10	10	10	6	7	10	10	10	10	10	10	10	10	10	10	10	10	10	8
	Tenerife	7	4	2	2				10	10	3	2				7	4	2	2				6	2	2	2				10	10	10	2				10	10	8	4			
8	Madrid	10	10	10	10		d100		10	10	10	8	9	8	d100	10	10	10	10	10	d25		10	10	10	10	9	d25		10	10	10	10	10	d90		15	10	10	8	9	9	d[illegible]
	Bilbao																																										
	Tenerife	7	5	3	2				9	6	6	8				10	10	8	8				5	4	2	2				10	10	10	7				7	8	5	3			

d: delamination, % of the surface. m: months.
▇: Not tested. y: years.

Table 6—Degree of Blistering, after Different Exposure Times, for Specimens Painted on Hot-Dip Galvanized Steel Weathered In Highly Aggressive Conditions

SALT FOG CHAMBER

System (Table 2)	Test Site	PRIMER – Wire Brushing 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER – Sweep shot blasting 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER+FINISH – Wire Brushing 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER+FINISH – Sweep shot blasting 6m.	9m.	1y.	2y.	4y.	6y.	11y.
1	Madrid	10	10	10	10	5	5	5	10	10	10	10	8	8	9	10	10	10	7	7	7	7	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	6	6	6								10	10	10	8	8	7	7							
	Tenerife	6	6	7	7				6	4	4	3				8	8	8	4				10	5	7	4			
2	Madrid															10	10	10	10	10	10	10	10	10	10	10	9	8	8
	Bilbao															10	10	10	10	10	7	7	10	10	10	10	10	6	6
	Tenerife															7	7	6	2				8	6	7	6			
3	Madrid	10	10	10	8	6	5	d[illegible]	10	10	10	10	9	8	d10	10	10	10	10	8	8	7	10	10	10	10	10	10	5
	Bilbao	10	10	10	10	10	7	7	10	10	10	10	10	10	9	10	10	10	10	10	8	8	10	10	10	10	10	10	10
	Tenerife	8	6	3	3				4	4	4	4				7	7	7	6				6	8	8	8			
4	Madrid	10	10	10	8	7	6	d10	10	10	10	8	7	d50		10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Tenerife	6	4	4	2				6	4	4	6				10	5	7	5				9	8	8	4			
5	Madrid																												
	Bilbao																												
	Tenerife																												
6	Madrid																												
	Bilbao																												
	Tenerife																												
7	Madrid																												
	Bilbao																												
	Tenerife																												
8	Madrid	10	10	10	8	6	6	6	10	10	10	10	10	10	9	10	10	10	9	7	7	d20	10	10	10	10	10	10	8
	Bilbao																												
	Tenerife	4	3	3	3				8	7	5	7				5	4	3	3				8	8	7	4			

MOIST SO_2 CHAMBER

System (Table 2)	Test Site	PRIMER – Wire Brushing 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER – Sweep shot blasting 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER+FINISH – Wire Brushing 6m.	9m.	1y.	2y.	4y.	6y.	11y.	PRIMER+FINISH – Sweep shot blasting 6m.	9m.	1y.	2y.	4y.	6y.	11y.
1	Madrid	7	7	7	7	7	7	8	8	8	8	8	5	5	5	7	7	7	7	3	3	3	10	9	8	7	3	3	3
	Bilbao	8	5	5	8	8	8	8	8	8	8	7	7	6	6	8	8	8	8	8	8	7	7	7	7	7	8	8	4
	Tenerife	7	0	8	1				6	4	3	2				8	8	8	7				10	8	8	7			
2	Madrid															10	10	10	10	9	9	d50	10	10	10	8	8	6	6
	Bilbao															10	10	10	10	10	10	8	10	10	10	10	10	6	8
	Tenerife															10	10	10	6				10	10	10	10			
3	Madrid	d100							8	8	5	5	8	d50		d100							8	8	8	8	5	5	d10
	Bilbao	10	10	10	10	10	7	d5	10	10	10	10	10	7	d5	10	10	10	8	8	7	7	10	10	10	10	10	10	8
	Tenerife	4	4	2	3				3	4	4	2				5	4	4	2				10	10	10	7			
4	Madrid	d50							10	10	10	10	d50			10	10	10	8	7	7	d15	10	10	10	10	10	10	10
	Bilbao	10	10	10	10	10	d50		10	10	8	8	8	d20		10	10	10	10	10	10	10	10	10	8	8	7	7	7
	Tenerife	4	4	2	2				4	4	2	2				10	8	8	4				10	10	9	8			
5	Madrid																												
	Bilbao																												
	Tenerife																												
6	Madrid																												
	Bilbao																												
	Tenerife																												
7	Madrid																												
	Bilbao																												
	Tenerife																												
8	Madrid	10	10	10	10	d100			10	10	10	10	d50			d100							10	10	10	8	7	7	d50
	Bilbao																												
	Tenerife	4	2	2	2				3	2	2	2				8	4	5	7				5	5	7	2			

d: delamination, % of the surface.
▨: Not tested.

m: months.
y: years.

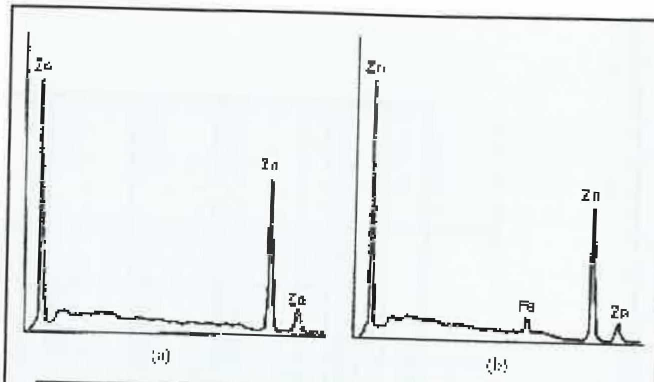

Figure 2—EDAX spectra of the zinc surface after weathering in the humidity condensation cabinet and then cleaning by wire brushing (a) or sweep shot blasting (b). The presence of Fe in the case of sweep shot blasting shows that this cleaning method causes some damage to the zinc coating, leaving the base steel partially uncovered.

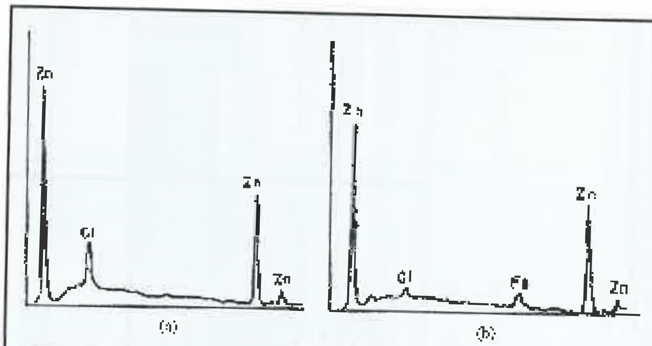

Figure 3—EDAX spectra of the zinc surface after weathering in the salt fog cabinet and then cleaning by wire brushing (a) or sweep shot blasting (b). It is seen that cleaning by sweep shot blasting is more effective for removing chlorides, though part of the base steel is left uncovered.

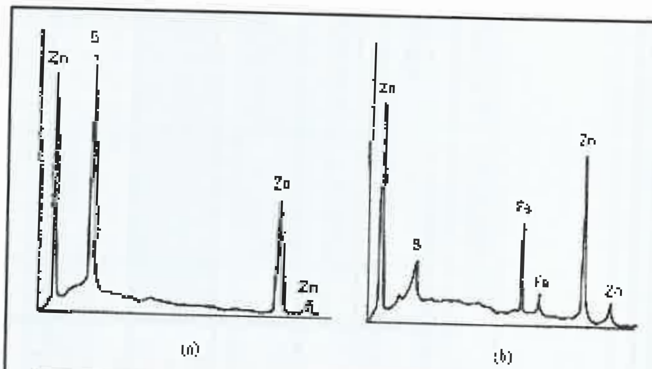

Figure 4—EDAX spectra of the zinc surface after weathering in the moist sulphur dioxide cabinet and then cleaning by wire brushing (a) or sweep shot blasting (b). As in the case of chlorides, sweep shot blasting is seen to be more effective for removing sulphates, though part of the base steel is left uncovered.

Table 7—Adhesion Results Under Both Dry (Scribe Test and Cross-Hatched Test) and Wet (Scribe Test) Conditions

System (Table 2)	Non-Weathered						Outdoor Exposure			Condensing Humidity Chamber						Salt Fog Chamber						Moist SO_2 Chamber					
	Organic Solvent			Sweep Shot Blasting			Organic Solvent			Wire Brush			Sweep Shot Blasting			Wire Brush			Sweep Shot Blasting			Wire Brush			Sweep Shot Blasting		
	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)	C(d)	S(d)	S(w)
1	○	○	○	○	○	○	●	○	●	○	○	○	●	○	○	●	○	●	○	○	○	●	○	●	●	○	●
2	●	●	●	●	○	○	●	○	○	●	●	●	●	○	○	●	●	●	●	●	○	●	●	●	●	●	●
3	●	●	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	●	○	●	●	○	●
4	●	●	●	●	●	●	○	●	●	●	●	●	○	●	●	●	●	●	○	○	○	●	●	●	●	●	●
5	○	○	●	○	○	○	■	■	■	○	○	○	●	●	●	■	■	■	■	■	■	■	■	■	■	■	■
6	●	○	●	●	○	●	■	■	■	●	○	●	●	○	●	■	■	■	■	■	■	■	■	■	■	■	■
7	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	■	■	■	■	■	■	■	■	■	■	■
8	●	●	●	●	○	●	●	○	●	●	○	●	●	○	●	●	●	●	●	●	●	●	●	●	●	●	●

C(d): Cross-hatch (dry)
● Bad behaviour
○ Good behaviour
■ : Not-tested
S(d): Scribe (dry)
S(w): Scribe (wet)

Figure 5—Photograph of the sample corresponding to system 4 (chlorinated rubber pigmented with micaceous iron oxide (supplier 2) applied on hot-dip galvanized steel weathered in the humidity condensation cabinet and cleaned by wire brushing, after 11 years of exposure in the Madrid atmosphere. Small zones without coating on the lower half of the specimen, where only one coat was applied, are observed.

ness. If the thickness is not sufficient, small zones can appear without coating together with brown color stains, originating in the pigment (micaceous iron oxide), probably due to the selective eroding of the vehicle of the paint (*Figure* 5), something that the authors of this work had already observed in this type of system in a previous study.[26]

The worst behavior is offered by the acrylic systems and the alkyd system, especially the latter, which shows significant delaminations in all the conditions tested both weathered and nonweathered. This is something that was expected and well known, since this system is not recommended for application on galvanized steel. Alkyd paints, and, in general, all oil-based paints, delaminate easily from the zinc substrate by reacting with it to form soaps (soluble salts) which degrade adhesion at the metal/paint interface.

Intermediate behavior can be found with the rest of the systems.

There is very good correspondence between the results of accelerated tests in the humidity cabinet and salt fog cabinet[14] and those obtained in the atmospheric exposure test. This is observed with regard to both the possible classification of the tested paint systems as a function of their anticorrosive behavior and, on the other hand, the greater efficiency of blasting compared with brushing when saline pollutants are present and the greater efficiency of brushing when such pollutants are absent.

However, as was mentioned in an earlier paper by the authors,[14] the measurement of both dry and wet adhesion of the paint film is not a good method for predicting coating behavior on weathered galvanized steel. Some cases have been reported of bad adhesion under dry or wet conditions alongside good in-service behavior, such as the chlorinated rubber system pigmented with micaceous iron oxide (supplier 2). Certainly a correlation between loss of adhesion and corrosion protection does not always appear to exist.

CONCLUSIONS

The chlorinated rubber systems pigmented with micaceous iron oxide and the vinyl/polyurethane system offer the best behavior when they are applied with an adequate thickness, on weathered galvanized steel surfaces.

These systems seem to perfectly tolerate weathering prior to painting when this is performed in environments of a low degree of aggressiveness (rural or urban atmosphere). In the case of weathering in the presence of chloride ions (marine atmosphere) they also present good behavior when the surface is prepared by blasting. As for weathering in the presence of SO_2 (a strong industrial atmosphere), no system seems to tolerate this perfectly, though better behavior is observed in general for specimens prepared by blasting.

The worst behavior is offered by the acrylic/acrylic system and the alkyd system, especially the latter, which presents great delamination in almost all the tested conditions.

In general, better behavior is observed for the systems applied on surfaces prepared by brushing when weathering is performed in the absence of saline pollutants. In contrast, blasting seems to be the best solution for surface preparation prior to painting when weathering causes the presence of saline pollutants among the zinc corrosion products.

ACKNOWLEDGMENTS

The authors of this work wish to express their gratitude to Industrias Duero Madrid for the preparation of the galvanized specimens and to the companies Amercoat, Euroquímica, Bruguer, Glasurit, Hempel, Jallut, and Sigma Coatings for the supply of the paint systems used in the research. They also thank LABEIN and UNELCO for the facilities provided for the performance of atmospheric exposure tests.

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