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Hot-dip galvanized steel: surface structures and adhesion of paints

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The surface structures of as-received, pretreated and painted hot-dip galvanized steel are studied. The hardness of six different paint systems and their adhesion to selected types of zinc coating are investigated before and after accelerated ageing. Both hardness and adhesion depend on the pretreatment and the chosen combination of zinc coating and paint system.

1. Introduction

Hot-dip galvanizing of steel [1] is carried out by dipping the cleaned steel in molten zinc at ~450° C for approximately 10 min. During that time an iron–zinc alloy is formed and the surface is covered by a coating some hundreds of micrometres thick. If the steel is "Si-killed", i.e. contains $\gtrsim 0.2$ wt % Si, the surface will consist of grey iron–zinc. This consists of ζ-FeZn grains embedded in a matrix of pure zinc. If the steel is not Si-killed the reaction rate is lower and iron–zinc is formed only as an interphase between the steel and an outer layer of pure zinc. The surface is then bright and zinc crystal grains ranging in size from a few micrometres to several centimetres can be observed. Although both types of coating protect the steel against corrosion, a combination of hot-dip galvanizing and the right type of paint system can provide a life time approximately twice as long as the sum of the lifetimes provided by the zinc and the paint coating alone. The positive synergism occurs because the two coatings protect each other [2, 3]. When only primitive paints, such as oil-based lead carbonate or red lead, were available good adhesion was often obtained [4] as a result of the hot-dip galvanized surface developing a protective cover layer of corrosion products by reaction with air prior to the painting. Such products include oxides, hydroxides, and carbonates. Subsequently, thicker and denser paints were developed which prevented air from reaching the zinc coating. These paints did not require the zinc coating to be covered with such reaction products. Instead, it was found necessary to pretreat the zinc coating by cleaning and to roughen its surface either by etching or by sandblasting in order to get the paint to adhere to it [2].

An advantageous property of the painted hot-dip galvanized steel is that the paint layer should be coherent and the structure dense even after long-term use. A description of such properties is complex but it is believed that the hardness before and after exposure to a moist atmosphere can give useful information even if a high hardness in itself is not an indication for successful utilization. A well-known and useful performance property is the adhesion of the paint to the zinc coating also after exposure to a moist atmosphere. Adhesion depends on obtaining good chemical bonding to the zinc coating. Alkyds and fatty acids in the binder of the paint form a zinc soap which reduces the adhesion, especially after exposure to moisture. Oily contaminants on the zinc surface also reduce adhesion, while oxides, hydroxides, and carbonates improve it, as mentioned above [4, 5]. Surface roughening procedures which increase the actual surface area without penetrating right through the zinc coating increase the number of zinc/paint bonds. Hence precise control of the sandblasting used to roughen the zinc coating is important. A precondition for a paint system to be successful on hot-dip galvanized steel is that the zinc coating adheres well to the steel surface and remains free of crack even after long use. The size, orientation, and density of defects in the zinc crystals play a certain role in the ability of the coated structure to absorb movements by plastic deformation without the coating cracking and delaminating [6], but these aspects are not treated here. Rather, the present paper is a study of the surface structures and some properties of as-received, pretreated and painted hot-dip galvanized steels. In particular, a study is made of the adhesion and the hardness of certain paint systems applied to selected zinc coatings, both as prepared and after exposure to moist air.

2. Experimental procedure

Table I gives the compositions of the five steels used, together with the type and thickness of the zinc coating applied to each. Also listed in the table is the phase composition of each coating as determined by X-ray diffraction. In one series of experiments, oil-based calcium plumbate paint coatings were applied to all five hot-dip galvanized steels after they were sand-

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blasted with either natural hill sand or corundum grains ranging in size from 0.25 to 0.50 mm. Each square metre of the surface was exposed to sandblasting for approximately 7 min. In that time it accumulated 9 to 14 × 10^8 impacts of near normal incidence. The velocity of the grains ranged between 70 and 200 m $\sec^{-1}$. A second series of experiments was performed on steels 3 and 5 only, using five different paint systems: (i) vinyl resin/chlorinated rubber: (ii) latex: (iii) polyvinyl chloride acrylic resin; (iv) alkyd resin; and (v) chlorinated rubber. In this series the hot-dip galvanized steels were treated prior to painting by etching in 4 wt % H_3PO_4 at 20° C for 3 min or by sandblasting with the corundum grains under the same conditions as used in the first series of experiments.

After painting, all specimens were first stored for 4 weeks in laboratory air of 50 ± 5% r.h. at 23 ± 2° C. In addition, one-half of the second series of specimens were subsequently exposed at the same temperature to air of approximately 100% r.h. for 300 h. This procedure represented an attempt to simulate the normal ageing of paint in a humid atmosphere under accelerated conditions. Following these procedures, Vickers hardness measurements were made on some of the coatings, using a Leitz Miniload hardness tester and loads of 0.05 to 0.10 N were applied for 10 sec. For each load, five indentations were carried out. The adhesion of the coating was also measured. This was done by (i) milling a 12 mm internal diameter annulus down through the coating into the supporting steel substrate, (ii) gluing a 12 mm diameter cylinder on to the circular area of coating remaining inside the milled annulus, and (iii) measuring the tensile force required to pull the cylinder off within 90 sec. The glue used was strong enough to ensure that failure occurred neither through the glue nor at the glue/paint or glue/cylinder interfaces. Three determinations were carried out for each type and condition of coating. For coatings with the adhesion below 10 MPa the results varied typically within ± 5% with maximal 10%. The errors for results above 10 MPa are 2 to 3% with a maximum of 5%. For each of the cylinders the failure surface was examined in a binocular microscope to determine the percentage of the fracture in paint of the total area of the fracture surface. A grid in one of the oculars made it possible to estimate the different types of fracture areas.

In addition, some as-received and preheated hot-dip galvanized steel surfaces were examined in a scanning electron microscope fitted with an energy dispersive spectrometer, and some painted specimens were sectioned perpendicular to the surface and etched in 0.9% nital (0.9 wt % HNO_3 in ethyl alcohol).

3. Results and discussion

Figs 1 to 4 show the structure of as-received, sandblasted, etched and painted hot-dip galvanized steel surfaces, respectively. Fig. 1a shows a typical pure-zinc coating as-received. The surface consists of circular smooth areas linked by radial ridges. Grain boundaries are visible within the pattern of relief but are not related to it. In the case of an as-received iron–zinc surface, the pattern of relief is disturbed by angular grains of the iron-rich ζ-phase (Fig. 1b). The micrographs of the sandblasted surfaces (Fig. 2) show how the rounded natural hill sand forms hemispherical depressions ~ 100 μm diameter in a pure-zinc surface, while irregular grooves are formed when the harder, denser and more angular corundum sand is used. In Fig. 3, etched pure-zinc and iron–zinc surfaces are shown, together with an iron–zinc-coated surface which has been exposed to moist air. The latter contains oxides, hydroxides, and carbonates. The two chemically etched surfaces contain $Zn_3(PO_4)_2$ which on pure zinc appears as crystals and on iron–zinc as spheres containing small amounts of iron. In all three cases, it is observed that the surface created chemically is much rougher than the as-received surface; but it is neither clear now how well the reaction products adhere to the underlying material nor how well the paint will bond to them. The cross-sections through sandblasted and painted surfaces shown in Fig. 4 variously exhibit both relatively smooth and highly

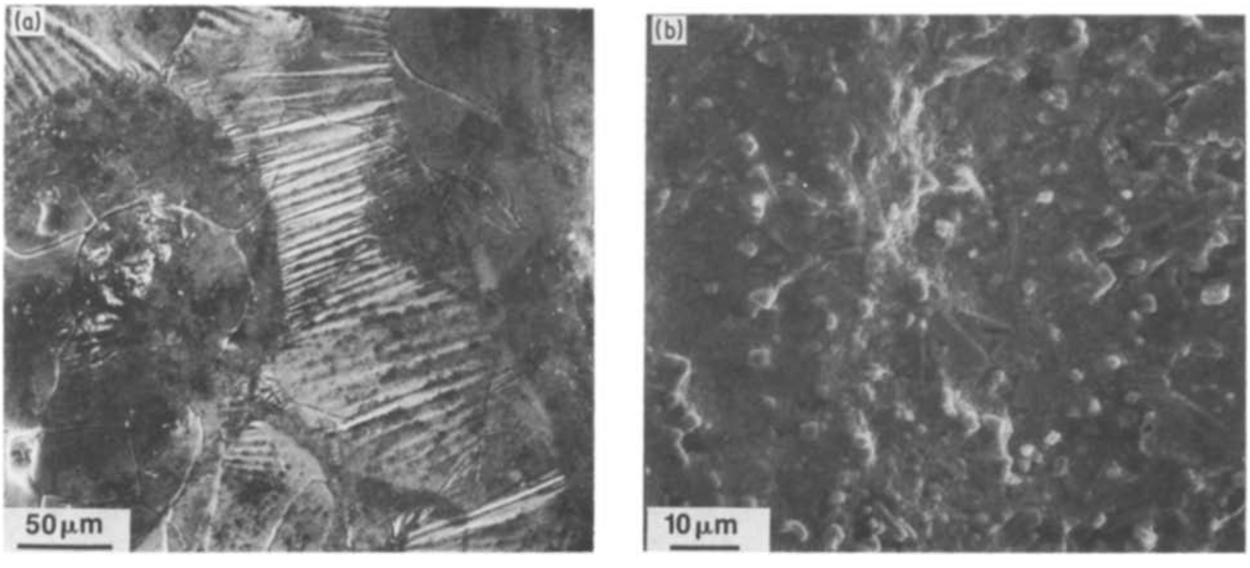


Figure 1 Surfaces of hot-dip galvanized steel. (a) A typical pure-zinc surface showing grain boundaries between zinc crystals and circular smooth areas linked by radial ridges; (b) an iron–zinc surface showing angular grains of the ζ-phase.

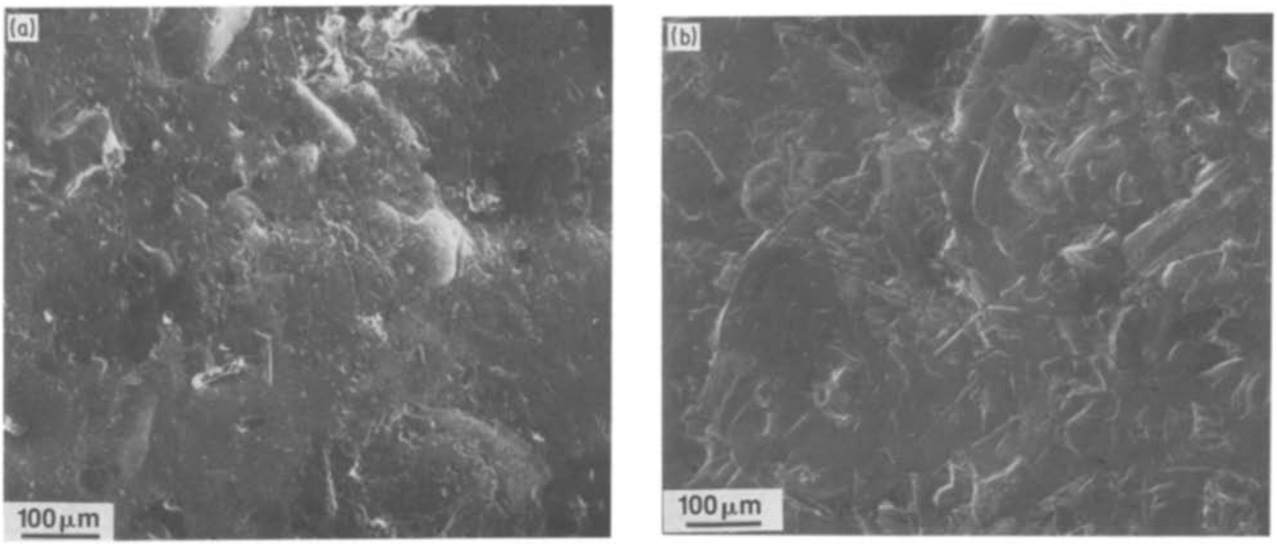
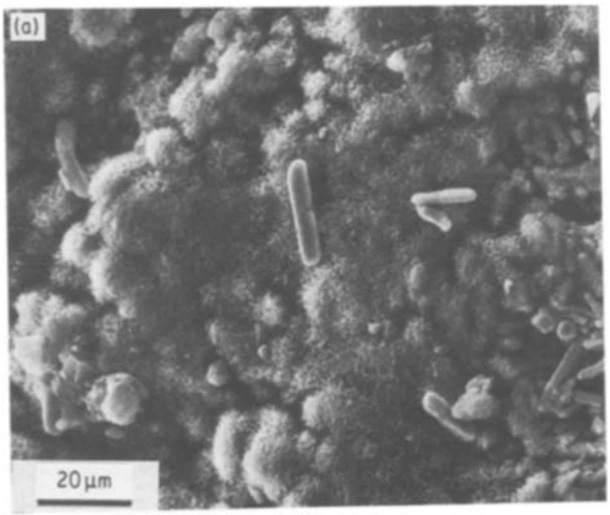


Figure 2 Sandblasted pure-zinc coating formed on steel by hot-dip galvanizing. (a) Surface eroded with natural hill sand which forms semispherical depressions and leaves some quartz and feldspare grains embedded in the surface. (b) Surface eroded with corundum sand which forms irregular grooves, leading to a very rough surface. Only very few corundum grains remain embedded in the surface.

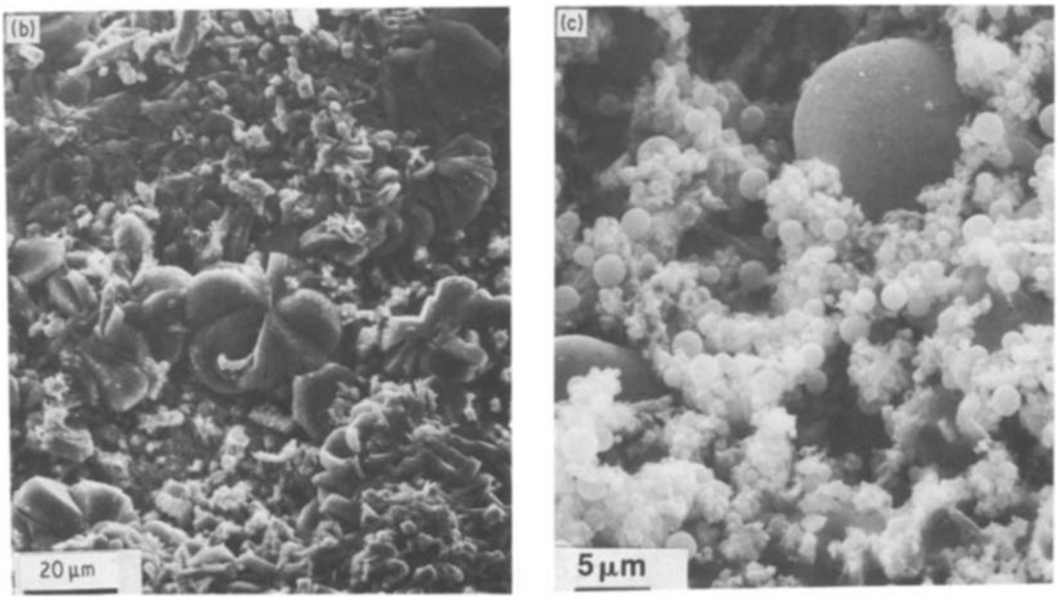
convoluted boundaries between the zinc coating and the paint. Evidently, the ductile pure zinc was partly removed and extensively plastically deformed during the sandblasting (Fig. 4b); and where the underlying brittle, columnar ζ-phase grains were exposed they broke up with little or no plastic deformation.



The iron–zinc coating was also partly removed and at some places broken up by sandblasting (Figs 4c and d). Note the small volume fraction of zinc matrix visible between the iron–zinc phase grains.

The last part of Table I shows results of the adhesion and hardness measurements carried out on calcium plumbate paint. There is a clear tendency for the paint to adhere better to iron–zinc than to pure zinc, probably because a zinc soap forms on the latter even in laboratory air. At the same time there is evidence of hardening of the paint on the pure-zinc surface. The hardness of the paint on the pure-zinc surface was approximately twice that on the iron–zinc surface. This hardening is believed to be due to an

Figure 3 Surfaces of variously pretreated hot-dip galvanized steel. (a) A sandblasted iron–zinc surface after exposure to air of ~ 100% r.h. for 2 d at room temperature. The original iron–zinc surface is completely covered with oxides, hydroxides, and carbonates. (b) A pure-zinc surface chemically pretreated with H_3PO_4 for 3 min. The reaction product is $Zn_3(PO_4)_2$. (c) An iron-zinc surface chemically pretreated in the same way. The spherical reaction product is $Zn_3(PO_4)_2$ containing small amounts of iron.



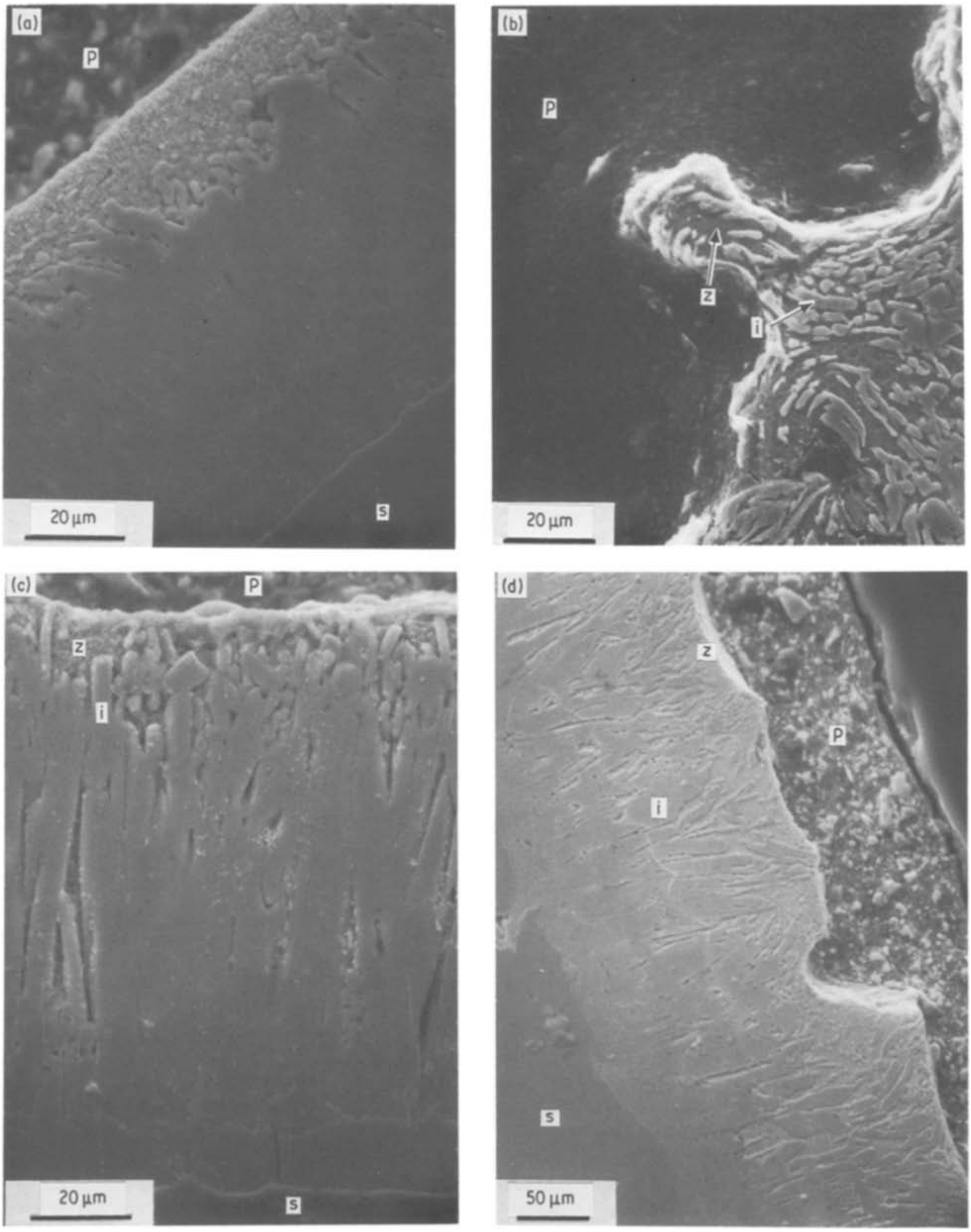


Figure 4 Hot-dip galvanized steel which has been sandblasted with corundum grains and painted. Pure-zinc coatings are shown in (a) and (b) and iron–zinc coatings in (c) and (d). (a) The pure-zinc surface is partly removed by erosion. (b) The coating is deformed during the sand blasting while some columnar ζ-phase grains are broken up in a brittle manner. (c) The ζ-phase is partly broken up at the surface in a brittle manner. The pure-zinc matrix is visible between the ζ-phase grains. (d) The rough surface created by sand blasting. P = paint, z = pure zinc, i = iron–zinc, and s = steel.

improved oxidation of the binder caused by a higher zinc content, as diffusion of zinc into the paint occurs parallel with saponification [5]. Table I also shows that there is the same or better adhesion when corundum is used to blast the surface instead of natural sand, probably because a rougher surface is created by the corundum grains.

Table II reports measurements of the adhesion of selected paints to variously pretreated pure-zinc and iron–zinc surfaces before and after exposure to moisture. The latex paint followed calcium plumbate in bonding better to sandblasted iron–zinc than pure zinc even in atmospheric air, probably because a zinc soap was formed in the paint/substrate interface. This

TABLE I Chemical analysis of the steel substrates, characterization of the hot-dip galvanized zinc coatings applied to them, adhesion of calcium plumbate paint to sandblasted surfaces after storage in laboratory air (23 ± 2° C, 50 ± 5% r.h.) for 4 weeks, and Vickers hardness of the same surface

		Steel number				
		1	2	3	4	5
Chemical analysis of steels (wt %)	C	0.04	0.03	0.15	0.28	0.07
	Si	0.18	0.001	0.03	0.27	0.21
	Mn	0.42	0.29	0.05	0.57	0.40
	Fe	98.74	99.42	99.0	97.4	98.5
Hot-dip galvanized coating	(μm)	Pure zinc 62 ± 4	Pure zinc 61 ± 2	Pure zinc 100 ± 20	Iron zinc 93 ± 6	Iron zinc 120 ± 9
X-ray signal*	Zn	+++	+++	++	++	++
	ζ-phase	++	++	++	+++	+++
	ZnO	+	+	+	−	+
Adhesion of paint (MPa)[†]: (N)		6.8	5.0	8.4	11.3	9.6
(C)		9.3	4.4	10.0	13.8	11.4
Vickers hardness of paint (MPa): (N)		140 ± 10	170 ± 10	150 ± 10	75 ± 5	90 ± 5

*+++ = strong, + = weak, ++ = medium, − = absent.
[†](N), hot-dip galvanized surface blasted with natural sand.
(C), hot-dip galvanized surface blasted with corundum.

is confirmed by the mode of fracture, as almost all the fracture occurred in the interface. A similar tendency is found for the alkyd resin but the saponification was first completed after exposure to moisture as the figures for the mode of fracture show: specimens not exposed to moisture failed in the paint layer, whereas those exposed to moisture failed at the paint–zinc interface, supposedly in the saponification zone. There is a tendency to improved adhesion after exposure to moisture for the two chlorinated rubbers and polyvinyl chloride acrylic resin paints, which do not saponify, as the chemical reaction process in the binders seems to be enhanced by the presence of water vapour. This is supported by the figures for mode at fracture because a major part of the fracture (at least for the sandblasted specimens) occurs in the paint layer. A significantly better adhesion after exposure to moisture for polyvinyl chloride acrylic resin and chlorinated rubber on sandblasted iron–zinc is followed by a significant increase in the hardness of the coatings. Again, both of them fail mainly in the paint layer and it is believed that the increased chemical reaction process in the binders is responsible for the increase of both adhesion and hardness. Sandblasting instead

TABLE II Properties of five paint systems on variously pretreated pure-zinc and iron–zinc surfaces after storage for 4 weeks and after subsequent exposure to water saturated air for 300 h. Extent of fracture in paint is percentage of the total area of the fracture surface formed by failure in the paint film rather than along the paint/substrate insurface

Paint system		Treatment after painting							
		Stored				Stored and Exposed to ~100% Relative Humidity for 300 Hours			
		Chemical		Blasted		Chemical		Blasted	
		Zn	Fe–Zn	Zn	Fe–Zn	Zn	Fe–Zn	Zn	Fe–Zn
Vinyl resin/ chlorinated rubber	Adhesion (MPa)	4.8	8.2	10.2	11.8	11.6	11.6	14.8	12.6
	Extent of fracture in paint (%)	0 ± 0	18 ± 5	100 ± 0	33 ± 8	36 ± 12	60 ± 10	86 ± 8	84 ± 8
	Vickers hardness (MPa)				70 ± 5				70 ± 4
Latex	Adhesion (MPa)	7.6	8.0	10.2	14.4	5.2	10.2	13.8	17.0
	Extent of fracture in paint (%)	14 ± 6	0 ± 0	12 ± 4	5 ± 1	11 ± 5	11 ± 4	75 ± 8	84 ± 3
	Vickers hardness (MPa)				50 ± 4				50 ± 5
PVC acrylic resin	Adhesion (MPa)	4.4	4.8	2.8	2.6	6.8	9.6	7.8	9.4
	Extent of fracture in paint (%)	81 ± 5	90 ± 4	100 ± 0	100 ± 0	56 ± 12	30 ± 10	100 ± 0	89 ± 5
	Vickers hardness (MPa)				17 ± 2				32 ± 4
Alkyd resin	Adhesion (MPa)	6.6	5.6	6.4	8.0	4.0	6.2	3.8	4.6
	Extent of fracture in paint (%)	80 ± 8	90 ± 6	100 ± 0	85 ± 7	39 ± 12	50 ± 10	0 ± 0	6 ± 1
	Vickers hardness (MPa)				90 ± 6				90 ± 7
Chlorinated rubber	Adhesion (MPa)	4.8	4.8	5.8	3.8	7.6	8.4	9.2	8.4
	Extent of fracture in paint (%)	100 ± 0	100 ± 0	0 ± 0	0 ± 0	100 ± 0	100 ± 0	89 ± 10	84 ± 7
	Vickers hardness (MPa)				30 ± 4				93 ± 8

of etching generally improved adhesion significantly only in the case of latex and vinyl resin/chlorinated rubber paints probably because of weak bonding between the etching products and the binder in the paint.

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