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Novel, one-step, chromate-free coatings containing anticorrosion pigments for metals—An overview and mechanistic study☆

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Abstract

The concept of superprimers, i.e., primers for metals with the conversion coating built in, has proven to be feasible. Such primers do not require a chromate (or other) conversion treatment of the metal and can be applied on any bare metal. The VOC content in the primer is kept low by using water-dispersed organic resins. Because of the high concentration of organofunctional silanes contained in the superprimer, its adhesion, both to the substrate and to overcoats, is excellent. The corrosion resistance of the primer can further be improved by adding corrosion-inhibiting pigments such as micronized zinc phosphate into the formulation. The corrosion protection performance of these coatings has been evaluated using performance tests and electrochemical methods. The primers have also been characterized with a variety of surface analytical methods. It will be shown that 2000 h of salt spray resistance has been obtained with the primers both on AA2024-T3 and HDG steel. This study will mainly present an overview of the chromate-free primers studied in our laboratory and will attempt to explain the mechanism by which one of the coatings, the epoxy–acrylate-based primer deposited onto aluminum, protects the metal from corrosion.

Keywords: Silane; Superprimer; Pigment; Chromate; Aluminum alloy

1. Introduction

Aluminum alloys and hot-dip galvanized (HDG) steel is often protected by a chromate containing pretreatment, a chromate containing primer and a topcoat, as shown in Fig. 1. It is, however, well known that the chromate in the pretreatment layer as well as in the primer layer is highly toxic and environmentally undesirable. Therefore, possibilities to replace the chromate in both layers are being explored all over the world. Another problem is the solvents used in the primer paints. These are usually solvents with a high content of volatile organic compounds (VOC). VOCs are also known to be environmentally harmful, because they can cause occupational hazards during production and when released in air, they can damage the protective atmospheric ozone layer.

This study solves the former problem by using non-chromate inhibitor pigments instead of chromate pigments in the primer. Further, the requirement of chromate conversion coatings (CCC) as a pretreatment can be eliminated in the presented system, because the use of silane coupling agents in the primer improves the adhesion and anti-corrosion performance of the primer on the metal to such an extent that a pretreatment is no longer necessary. The latter concern is addressed by the use of water-borne dispersions of binders and cross-linkers, in which water is the main solvent. The complete superprimer-containing coating system is shown in Fig. 1 on the right [1]. The name 'superprimer' originates from earlier studies in our laboratory, in which these direct-to-metal primer coatings were given the above-mentioned name.

The concept of superprimer is rather new [2–9]. Bis-silanes when mixed with conventional primers or binders have first been shown to impart excellent corrosion protection by van Ooij et al. [2]. The types of superprimers formulated and studied so far have been: (a) a room temperature (RT)-cured waterborne acrylate–epoxy–silane based superprimer for AA2024-T3 [3,4], (b) a RT-cured solvent-borne epoxy–isocyanate–silane-based superprimer for HDG steel [5,8], (c) a RT-cured waterborne

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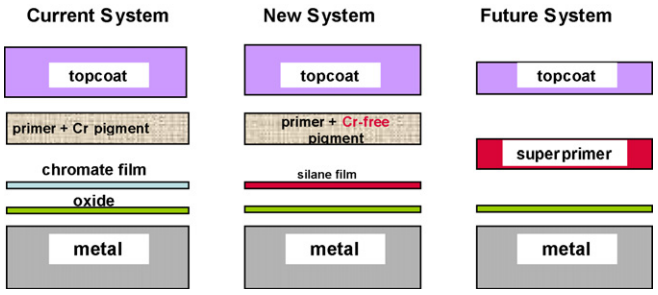

Fig. 1. Schematic of the superprimer coating system [1].

epoxy–silane system for AA2024-T3 [6] and a water-borne epoxy–silane system for HDG steel [9]. The use of silanes in coatings has also been studied by other groups but the applications are not necessarily for the corrosion protection of metals [10–13] or then the work falls more into the category of pretreatments or pre-paint treatments of metals [14–20].

A priority aim in our studies concerning the superprimers has been to investigate why and how the superprimer coatings protect the metals in corrosive environments. We have also characterized the resulting films as such (fresh) and as a function of curing time in order to understand which key reactions take place upon curing the films. An overview of the latest performance results concerning a family of four superprimers is reported in this paper and an explanation of how one of the superprimers is formed and how it protects the metal substrate from corrosion is also given. The mechanism of corrosion resistance of the primer chosen was evaluated mainly by scanning electron microscope in combination with X-ray dispersive analysis (SEM/EDX). The mechanisms of the other primer coatings are not quite identical to the one which will be presented here. The mechanisms of the others will be discussed elsewhere.

2. Experimental

2.1. Metals

AA2024-T3, AA7075-T6, AA6061 and HDG steel panels from ACT laboratories, Inc., Hillsdale, MI, and Stillwater Steel Supply, Stillwater, OK, were used in these studies.

2.2. Chemicals

Table 1 shows the family of superprimers based on different resin-crosslinker-silane-pigment combinations and Table 2 shows the type and producer of the resins and crosslinkers used in the superprimer formulations of Table 1. As shown in Table 2 the same EPI-KURE 6870-W-53 crosslinker and the NeoRez R-972 polyurethane resin are used in the novolac–epoxy–polyurethane formulation for AA2024-T3 as well as for the bisphenol A epoxy-based system on HDG steel.

The bis-sulfur silane, i.e., the bis[3-(triethoxysilyl) propyl] tetrasulfide and the bis-1,2-(triethoxysilyl) ethane (BTSE) silane were obtained from GE Silicones, Wilton, CT. The bis-benzene silane, i.e., the 1,4-bis(trimethoxysilylethyl)benzene, was obtained from Gelest Inc., Morrisville, PA. The chemical structures of the silanes used are shown in Fig. 2.

Several commercially available pigments have been screened for the substrates AA2024-T3, AA7075-T6, AA6061 and HDG steel. Promising candidates have been short-listed and the most typically used pigments in the superprimer-substrate combinations are shown in Table 1. The Alfa Aesar zinc phosphate was from Johnson Mathey, Ward Hill, MA and the calcium zinc molybdate (CZM) was from Molywhite Pigments Group, Cleveland, OH. The sodium metavanadate $NaVO_3$ for the HDG formulation was from Fluka in Switzerland and Corrostain 228,

Table 1
Family of superprimers

Substrate	For AA2024-T3 and AA7075-T6	For AA2024-T3	For AA2024-T3 and AA6061	For HDG steel
Resin system	Epoxy–acrylate	Novolac–epoxy–polyurethane	Polyurethane	Two epoxies + polyurethane
Crosslinker	Isocyanate silane	Amine adduct	None	Amine adduct
Silane	Bis-sulfur	Bis-sulfur	BTSE	Bis-sulfur or bis-benzene
Typical pigment	Zinc phosphate	Zinc phosphate	Calcium zinc molybdate (CZM)	$NaVO_3$ + Corrostain (Ca, Zn, P, Si and O)

Table 2
Resins and crosslinkers used in the different superprimer formulations

Product	Type of chemical	Company	For combination	Metal(s)
EPI-REZ WD510	Bisphenol A epoxy resin	Hexion Chemicals	Epoxy–acrylate	AA2024-T3, AA7075-T6
ECO-CRYL 9790	Acrylic resin	Hexion Chemicals	Epoxy–acrylate	AA2024-T3, AA7075-T6
A-Link 25	Crosslinker	GE Silicones	Epoxy–acrylate	AA2024-T3, AA7075-T6
EPI REZ 5003-W-55	Novolac–epoxy resin	Hexion Chemicals	Novolac–epoxy–polyurethane	AA2024-T3
EPI-KURE 6870-W-53	Crosslinker	Hexion Chemicals	Novolac–epoxy–polyurethane and two epoxies-polyurethane	AA2024-T3, HDG steel
NeoRez R-972	Polyurethane resin	DSM Neo-resins	Novolac–epoxy–polyurethane and two epoxies-polyurethane	AA2024-T3, HDG steel
NeoRez R-960	Polyurethane resin	DSM Neo-resins	Polyurethane	AA6061, AA2024-T3
Ancarez Ar 550	Bisphenol A epoxy resin	Air Products	Two epoxies–polyurethane	HDG steel
EPI-REZ 6520-WH-53	Bisphenol A epoxy resin	Hexion Chemicals	Two epoxies–polyurethane	HDG steel

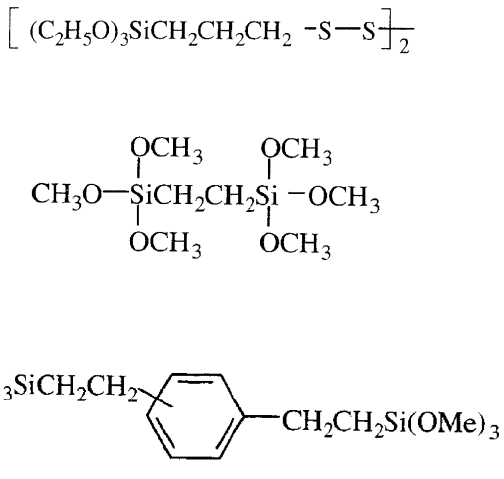

Fig. 2. Chemical structures of the silanes used (a) the bis[3-(triethoxysilyl) propyl]tetrasulfide (bis-sulfur silane), (b) bis-1,2-(triethoxysilyl)ethane (BTSE) and (c) 1,4-bis(trimethoxysilylethyl)benzene (bis-benzene silane).

a corrosion inhibitor pigment containing Ca, Zn, P, Si and O also used in the formulation for HDG steel was from Wayne Pigment Corp., Milwaukee, WI.

The chromate controls for both AA2024-T3 and HDG steel had been pretreated with chromate and were coated with a standard military high solids chromate-containing epoxy primer, (CA 7233 + CA 7233B, blended in a ratio 1:1), which was obtained from PPG Industries, Glendale, CA. This primer conforms to military specification MIL-PRF-23377 H of Type I and class C.

2.3. Sample preparation

The metal panels were thoroughly cleaned, rinsed with DI water and blow-dried. The formulation ingredients of each formulation shown in Table 1 were mixed together and high shear-blended. The formulations were applied onto panels by a draw-down bar. The primers coated onto aluminum alloys were cured at room temperature for 14 days and the epoxy-based primer for HDG steel was cured stepwise, viz., first 14 days at RT and then 30 min at 135 °C.

2.4. Properties and tests

The VOC contents of the superprimer formulations were calculated. The pot-lives of the formulations and the dry-to-touch times of the coatings were observed experimentally. The following ASTM standard tests were performed on the coating systems:

- ASTM B-117 salt spray test.
- ASTM D 714 3.5 wt.% NaCl solution immersion test.
- ASTM D 3359-97 tape adhesion test.
- ASTM D 3912 chemical resistance (6N HCl and 6N NaOH).
- ASTM D 4752 MEK double rub test.
- ASTM D 3363-00 pencil hardness test.

The corrosion resistance of the superprimed metals was also studied by electrochemical impedance spectroscopy (EIS). The experimental setup for EIS has been described elsewhere [21]. The EIS measurements were performed by using 3.5 wt.% NaCl and/or 0.5 M K_2SO_4 as the electrolyte medium.

2.5. Characterization methods

2.5.1. Overview of methods used

The superprimer liquid dispersions and/or the resulting coatings have been characterized by using the following methods, nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray reflection methods, scanning electron microscopy combined with energy dispersive X-ray analysis (SEM/EDX), time-of-flight secondary ion mass spectrometry (TOF-SIMS) and water/electrolyte uptake measurements. The results described in this study involve mainly the three latter methods, for which the instrumental descriptions are given here.

2.5.2. SEM/EDX

Scribes and cross-sections of scribes in panels exposed to the 30 day salt solution (3.5 wt.% NaCl) immersion test were examined in a Philips XL 30 environmental scanning electron microscope (ESEM). The back-scattered and secondary electron images were complemented by appropriate quantified chemical information from energy dispersive X-ray analysis (EDX) acquired as point and/or line scans. For EDX analysis small specimens of scribed panels were sputter-coated with Au–Pd film and analyzed. The cross-sectional samples were prepared in polished epoxy molds. The operating voltage used in the SEM analysis was 25 kV.

2.5.3. TOF-SIMS

Time-of-flight secondary ion mass spectrometry: SIMS spectra of the interfaces of the superprimer layers were acquired using an ION-TOF Model IV TOFSIMS instrument. The data were collected using $^{69}Ga^+$ as the primary ion source at 25 kV. The area analyzed was approximately 50 μm × 50 μm. A flood gun was used for charge neutralization. The mass resolution of the instrument ($m/\Delta m$) was 8000 at mass 28. This resolution enabled us to determine peak masses with better than 0.1 amu accuracy.

2.5.4. Water and electrolyte uptake measurements of superprimer coating

For this purpose two free standing films were cast. One film was prepared as the control sample which comprised of ECO CRYL 9790 acrylate, EPI-REZ WD-510 epoxy and DI water. The other sample termed L2 was the epoxy–acrylate formulation comprising of ECO CRYL 9790 acrylate, EPI-REZ WD-510 epoxy, bis-sulfur silane, A-Link 25 crosslinker and DI water. Free standing films were obtained by pouring the formulation mixture on a paraffin wax film by creating a mold using glass rods of 8 mm in diameter. The dimensions of the molds used were 24 cm × 2 cm × 0.8 cm. It was ensured that the dimensions of the mold were the same for both samples. The films were

left to dry in room temperature for 14 days. After curing, the set films were peeled off the paraffin and cut along the glass rods resulting in equally sized pieces. These pieces were further left to dry for 2 months before being exposed. From the above castings 2 cm × 2 cm × 0.8 cm pieces, two of each were cut and weighed with a high precision scale. One piece of each type of casting was immersed in 150 ml of DI water and 150 ml of 0.5 M K_2SO_4. The weight change of the sample during exposure was measured by weighing the samples every alternate day. The value calculated was the percentage change (gain) in the weight of the sample during immersion test for a period of 30 days.

3. Results and discussion

3.1. Test results

Table 3 shows the properties of the superprimer formulations and the test results of the coatings on the metals. In general the VOC content of a superprimer is about 40 g/l. The polyurethane formulation for AA6061 has a higher VOC content of 200 g/l, which is substantially higher compared to 40 g/l but still clearly lower than that of the chromate control, ∼340 g/l. The advantage of the polyurethane primer is that it can be formulated to a one-pack system with a shelf-life or in this case pot-life of 6 months. The typical pot-life of a superprimer is 3–4 h which is almost at the level of the chromate control (Table 3). Curing times of the coatings vary considerably. The epoxy-based system for HDG steel cures quickly to a dry-to-touch state (1–2 h) while the acrylate–epoxy is clearly the slowest in terms of curing (7–8 h).

All silane-containing primer systems scored 5B in the ASTM D 3359 adhesion test and all tested systems also passed the ASTM D 3912 chemical resistance test. The MEK double rub test value gives information of the extent of curing and crosslinking of the coating. The chromate control has a value of 300 rubs (Table 3). The step-cured (14 days RT + 30 min at 135 °C) epoxy-based system on HDG exceeds this value indicating that the coating is cured and crosslinked when keeping it a short time at an elevated temperature. For room temperature-cured primers on aluminum alloys a MEK value exceeding 50–60 rubs is acceptable. In this respect the other superprimers perform very well as their values are around 100. As shown in Table 3 the superprimer coatings have a pencil hardness varying from 2H to 4H. Only the polyurethane-based superprimer has a slightly lower value of 1H, which can probably be improved by adding a suitable crosslinker to the system. This addition would, however, convert the system automatically to a two-pack system, which then has a lower pot-life than the 6 months.

Fig. 3 shows the ASTM B-117 salt spray test results of the superprimer coatings on the various substrates. The systems were compared to chromate-containing control systems. Optimized coating systems all performed well over 2000 h in the test, which is usually a typical requirement in the coating industry. The polyurethane-based system on AA6061 even survived 4000 h in ASTM B-117 (Fig. 3d). This panel with its replica was tested by NAVAIR, China Lake, CA. Some of the panels shown in Fig. 3 were also tested in the ASTM D 714 3.5 wt.% NaCl solution immersion test and all of them performed very well for 30 days.

3.2. Characterization results

In order to understand the corrosion protection mechanism, surfaces and cross-sections of superprimer coatings on metal panels were investigated by SEM/EDX after 30 days of exposure in the salt water (3.5 wt.% NaCl) immersion test. Here we focus to report on results obtained for the first superprimer coating shown in Table 1, i.e., the epoxy–acrylate coating on aluminum. Fig. 4 shows SEM micrographs of a clean scribe and a scribe with precipitate of this coating on AA7075-T6. Fig. 5 presents the corresponding SEM/EDX analysis results of the area of the clean scribe shown in Fig. 4a and the precipitate in the scribe (Fig. 4b) on the epoxy–acrylate coating on AA7075-T6. The scribes of this system were mainly clean from precipitates and no pits or corrosion was detected in the scribes. As can be seen from Fig. 5a the SEM/EDX result shows mainly aluminum in the scribe, which originates from the substrate material. No actual protecting film could be observed in the scribes of the coating. Only a few precipitates were observed here and there in the scribes. The result of the analysis of the precipitate (Fig. 5b) shows high amounts of zinc, oxygen and phosphorus, which indicates that the zinc phosphate from the coating is able to leach out into the scribe to protect the scribe from corrosion during salt water immersion. There is also a fairly high amount of sodium in the precipitate, which apparently has precipitated from the 3.5 wt.% NaCl solution onto the scribe, when drying the sample.

The SEM cross-sections and the EDX cross-sectional analysis of the coating on the metal give information of the homogeneity of the system. The SEM cross-section of the epoxy–acrylate coating on AA7075-T6 after 30 days of salt immersion testing is presented in Fig. 6. As can be detected

Table 3
Properties of the superprimer formulations

Property	Chromate control	Acrylate–epoxy, Al-alloys	Novolac–epoxy–PU, AA2024-T3	Polyurethane, AA6061 and AA2024	Epoxy-based HDG steel
VOC (g/l)	∼340	∼40	∼30	∼200	∼40
Pot-life (h)	4–5	3–4	3–4	6 months	3
Dry-to-touch (h)	3–4	7–8	6	6	1–2
MEK double rub	300	98	90	>100	>300[a]
Pencil hardness	3H	3H	2H	1H	4H

[a] Step-cured; 14 days RT + 30 min 135 °C.

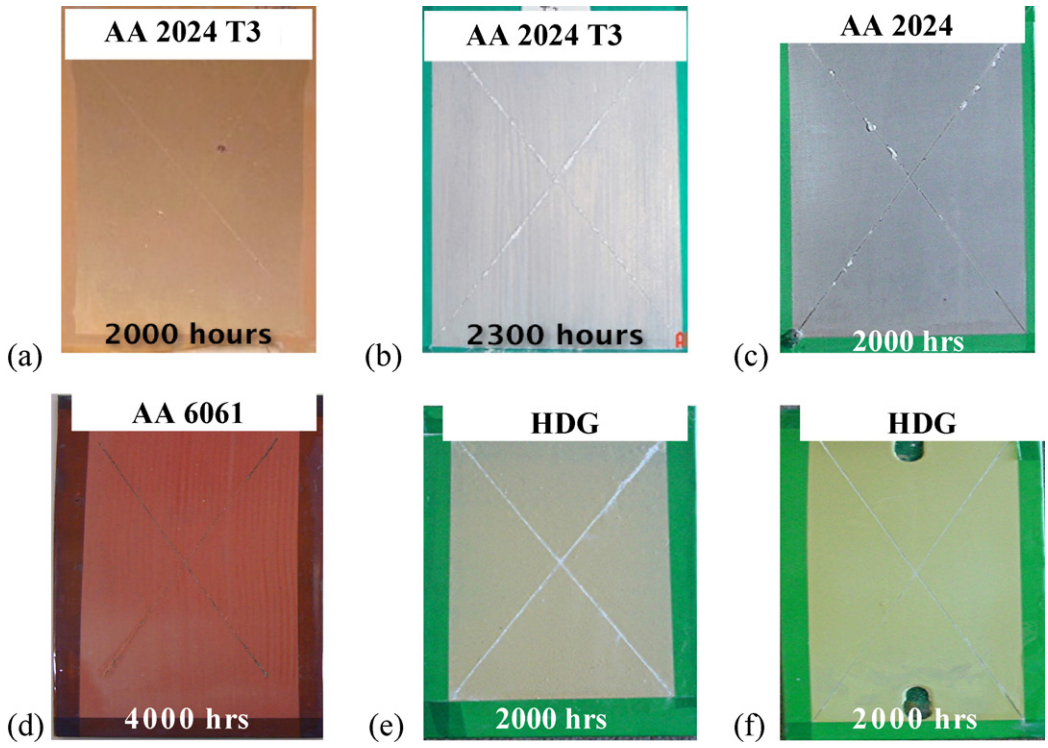

Fig. 3. ASTM B-117 salt spray test results of (a) the chromate control on AA2024-T3, (b) the acrylate–epoxy based system on AA2024-T3, (c) the novolac–epoxy–polyurethane based coating on AA2024-T3, (d) the polyurethane based coating on AA6061, (e) the epoxy based system on HDG and (f) the chromate control on HDG.

from the figure the coating shows different layers. EDX point scans were taken on several different points in these regions. The EDX results of the thinnest layer very close and slightly further away from the AA7075-75 metal are presented in Fig. 7a and b. Examples of point scans of (a) the particles in the middle layer, (b) the bulk of the middle layer and (c) the bulk of the upper layer are shown in Fig. 8. The EDX scan very close to AA7075-T6 is rich in aluminum, carbon and sulfur (Fig. 7a). Oxygen, zinc, phosphorus and silicon are also detected very close to the metal. The spot slightly further away from the metal contains mainly carbon and oxygen, but also sulfur, silicon and zinc are detected in minor amounts (Fig. 7b). Thus, the EDX scans indicate that very close to the primer-metal interface there is a region rich in bis-sulfur silane.

Therefore, our first conclusion was that this superprimer probably bonds primarily through silanol groups to the AA7075-T6 surface, but then TOF-SIMS analysis was performed on this epoxy–acrylate coating that was carefully removed from the AA7075-T6 surface without contaminating the side of the surface that had been bonded to the metal. The TOF-SIMS result revealed that the outmost interface of the primer was rich in acrylic groups, which originate from the ECO-CRYL 9790 acrylic dispersion. Thus, the epoxy–acrylate coating bonds to the aluminum surface through acrylic groups and very close to the primer metal interface there is a very thin layer rich in bis-sulfur silane. The elemental analysis result in the vicinity of the metal-primer interface is, however, so rich in carbon and oxygen (Fig. 7b) that it is unlikely that the bis-sulfur silane

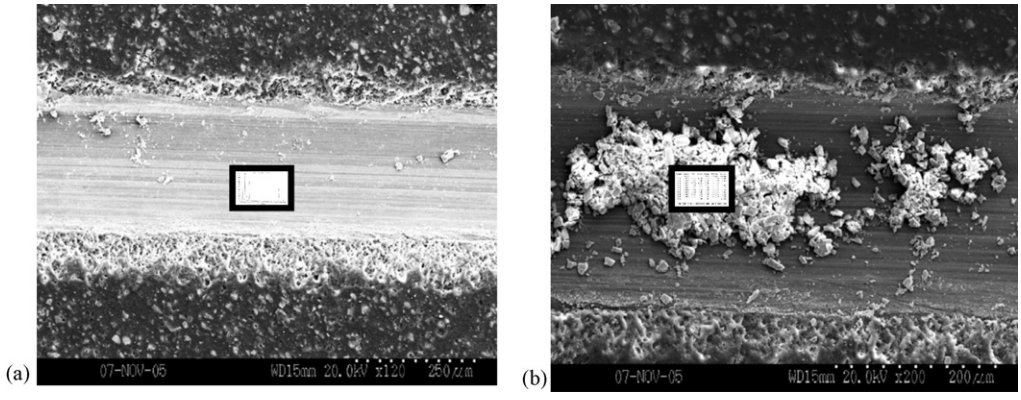

Fig. 4. SEM micrographs of (a) a clean scribe and (b) a scribe with a local precipitate on the epoxy–acrylate coating on AA7075-T6 after 30 days of salt immersion testing.

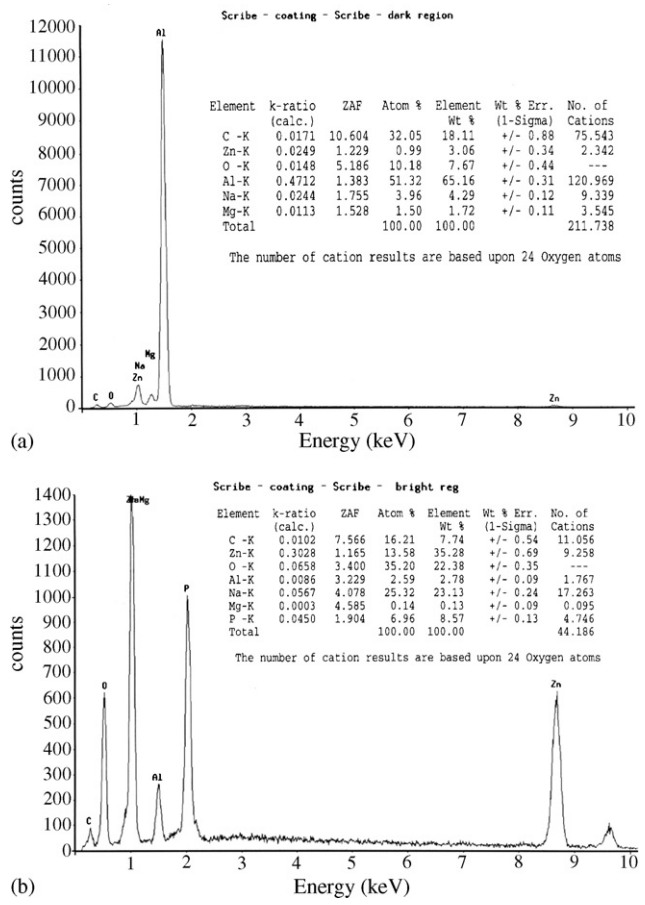

Fig. 5. The SEM/EDX analysis results of the area of (a) the clean scribe and (b) the precipitate in the scribe on the epoxy–acrylate coating on AA7075-T6 after 30 days of salt immersion testing.

is the only component near the interface. According to the results it is more likely that the acrylate resin and the bis-sulfur silane have interacted with each other and the primer coating is built up by this network in which the pigment particles are incorporated.

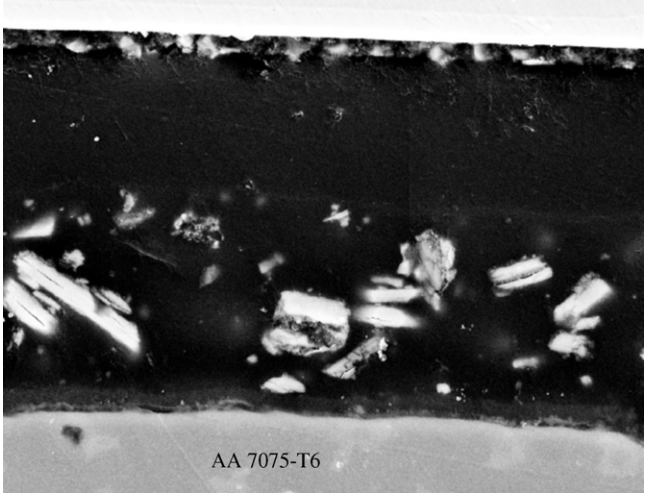

Fig. 6. The SEM cross-sections of the epoxy–acrylate coating on AA7075-T6 after 30 days of salt immersion testing.

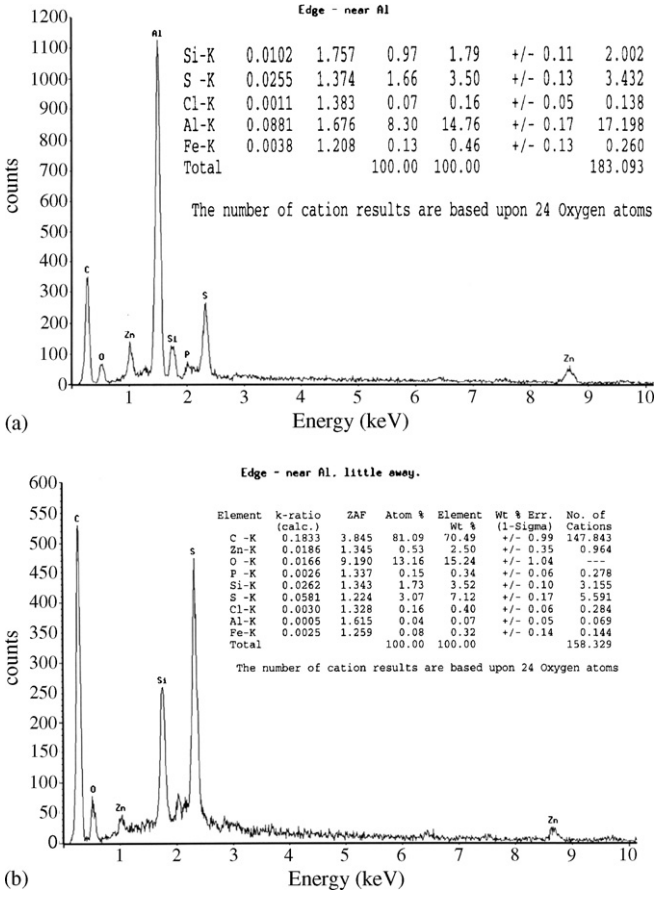

Fig. 7. The SEM/EDX results of the interface between the metal and the actual superprimer layer, scan (a) is taken very near and (b) slightly further away from the metal AA7075-T6.

Fig. 8a shows an example of a point scan on one of the particles, which are clearly visible in the cross-section SEM micrograph (Fig. 6). This scan (Fig. 8a) is rich in carbon, zinc, oxygen and phosphorus, which clearly indicate that the particles are in fact the zinc phosphate pigment particles. Of interest is what the middle layer between the particles consists of? As expected there is carbon and oxygen and minor amounts of silicon and sulfur. C and O originate from the resin or resins and the bis-sulfur incorporated in the layer. So far the amounts of chlorine have been very low, of the order of less than 0.40 elemental wt.%, but as we move up to the scan of the upper layer (Fig. 8c) we observe that the amount of chlorine slightly increases up to 1.5 wt.%. The upper layer is very rich in carbon and oxygen, but hardly any zinc, phosphorus, silicon or sulfur can be detected in this layer, which indicates that there is virtually no bis-sulfur or zinc phosphate in this layer. The chlorine could have come from the 3.5 wt.% NaCl solution, but a cross-section of the same coating was also analyzed before exposure to the salt water immersion test and the upper layer of the unexposed coating contained even more chlorine than the exposed coating. This meant that the chlorine in the upper layer originated more likely from one of the ingredients of the formulation rather than the NaCl electrolyte. In the epoxy–acrylate superprimer the only component that can contain chlorine or residues of chlorine is the EPI-REZ WD510 epoxy resin, which is a typical DGEBA

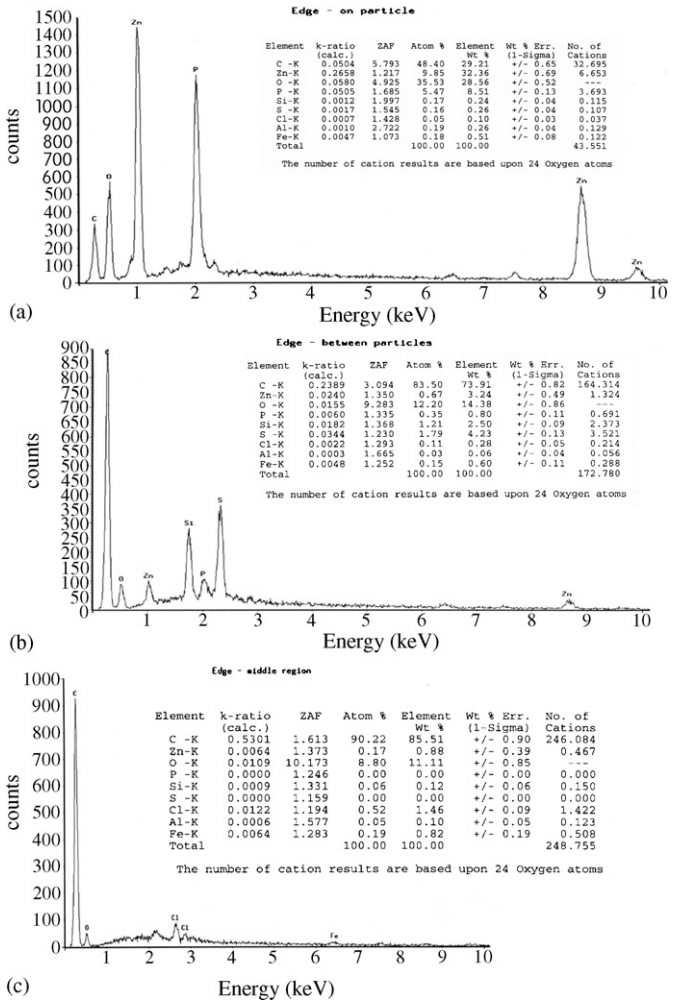

Fig. 8. SEM/EDX elemental analysis result of the different layers/regions of the epoxy–acrylate superprimer on AA7075-T6, (a) one of the particles in the lower layer, (b) the bulk of the lower layer and (c) the upper layer.

type of epoxy resin, produced from epichlorohydrin and bisphenol A. Since the upper layer primarily contained C, O and Cl and hardly any Zn, P, Si or S could be detected in it, we suspected that the layer is mainly an epoxy layer. This conclusion meant that the middle layer would be an acrylate–siloxane–zinc phosphate layer which is rich in siloxane near the primer-metal interface but ultimately bonds to the aluminum through the acrylic groups.

3.3. Water and electrolyte uptake results

In Figs. 9 and 10 the water and electrolyte (K_2SO_4) absorption characteristics of the epoxy–acrylate superprimer are shown. Fig. 9 presents the weight increase of the free-standing films. The water uptake is compared for the primer films with (sample L2) and without (control sample) the silane + crosslinker addition. Two conclusions can be drawn from this figure. First, the uptake of pure water is about twice as much as for the electrolyte solution for both types of films. Secondly, both in water and in electrolyte, the water uptake is faster for the two films containing the silane + crosslinker than for the films without silane + crosslinker. However, eventually, i.e., after 3–4 weeks,

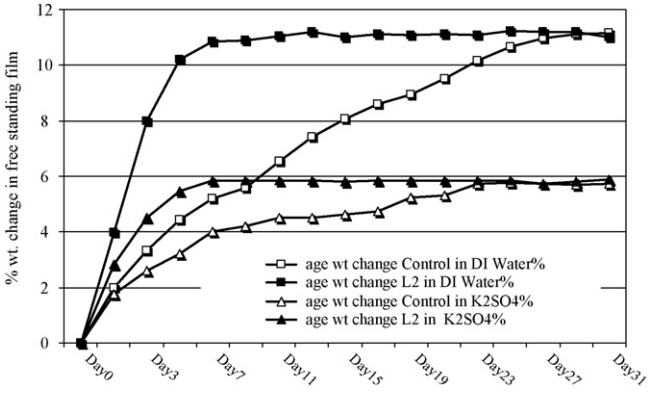

Fig. 9. Water and electrolyte (K_2SO_4) uptake results of the epoxy–acrylate superprimer free standing films with (sample L2) and without (control sample) silane and crosslinker as a function of time.

the water uptake reaches the same level of saturation, with or without silane and crosslinker.

These observations are counter-intuitive, but on close investigation of the samples, the underlying reason for this trend becomes clear. We know that the epoxy and the acrylate phases do not mix but phase separate into two layers. During water immersion the film curled up with more expansion on the acrylate side than on the epoxy side of the film. This implies that the water has a greater affinity for the acrylate phase, both with and without silane. The reason why the silane initially accelerated the water uptake may be sought in the fact that the silane was neat, i.e., not hydrolyzed. Thus, the silane attracts water or electrolyte into the film and the water hydrolyzes the silane to a certain extent, thus accelerating the water ingress.

The reason why the electrolyte does not penetrate the films to the same degree as the pure water, is not known yet, but it could be speculated that the groups that attract the water into the polyacrylate part of the film are the carboxylic acid groups. The polyacrylate used in this study was a co-polymer of an acrylate and acrylic acid. Once a sufficient amount of potassium has migrated into the film, the carboxylic acid groups have been

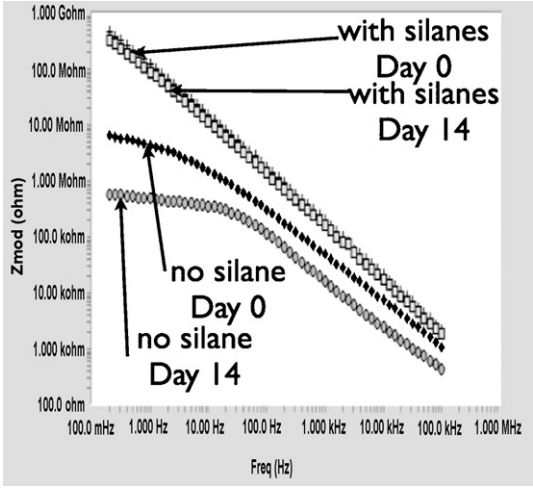

Fig. 10. EIS results with K_2SO_4 electrolyte for the epoxy–acrylate coatings with (sample superprimer) and without (sample control) silane and crosslinker on AA2024-T3 metal substrates as a function of time.

converted to potassium carboxylate groups, which are no longer strongly hydrophilic. The observation that the rates of water and electrolyte uptake are almost the same, during the first 2 days, but then begin to separate, supports this view.

In Fig. 10 the EIS results are presented for the same two types of films, but now deposited onto a metal substrate. Only the K_2SO_4 electrolyte was used here, not pure water. The results are very remarkable, as they show a trend opposite to the one shown in Fig. 9. The impedance of the film with the silane remains almost constant for the entire exposure period of 14 days. The film without silane is different in three respects: (i) it has a higher film capacitance C, as the intercept at a frequency $f = 0.16$ Hz is lower; this intercept is numerically equal to $1/C$; (ii) it has a lower overall resistance (impedance at low frequency); (iii) it absorbs the electrolyte considerably faster than the film with the silane and crosslinker, as is concluded from the drop in low-frequency amplitude with time. Since it is known that the acrylate film is at the metal interface and the epoxy film is on top (see Fig. 6), these results indicate that the electrolyte ingress into the epoxy films is actually reduced when the film is prepared with the non-hydrolyzed silane and the crosslinker, whereas it was increased for the polyacrylate film, as we concluded from the results shown in Fig. 9.

The mechanism behind the reduction of the permeability of the epoxy, whereas that of the acrylate is increased, may lie in the fact that the crosslinker can actually react with the epoxy, but may not react with the acrylate [7]. The silane interacts with the acrylate and also attracts water for hydrolysis to this phase, but may not crosslink the acrylate completely. Evidence for epoxy crosslinking by the crosslinker has been seen in our NMR data of these systems [7]. Also, the lower capacitance of the film with the silane and crosslinker, as compared with the film without silane and crosslinker, suggest a crosslinking reaction, as the other factors which have an effect on the film capacitance, surface area and film thickness were the same for both types of film. Films with higher crosslink density, which cannot swell as much as films with lower crosslink density, tend to have a lower dielectric constant.

Overall, the combined results indicate a vastly superior performance of the film containing the silane and the crosslinker in protecting a metal substrate. Its stability in exposure to electrolyte has been greatly increased. On the other hand, the water uptake of the lower layer, the polyacrylate, is increased by the silane. This phenomenon has a positive effect on the release of anti-corrosion corrosion pigments, as discussed in the next section.

4. Corrosion protection mechanism of the epoxy–acrylate superprimer on Al

Before explaining the corrosion inhibiting mechanism of the epoxy–acrylate superprimer coating on aluminum, it should be explained how this coating is formed, which is shown schematically in Fig. 11. Fig. 11a presents the coating right after application, when the formulation components, the ECO-CRYL 9790 acrylate, the EPI-REZ WD510 epoxy, the bis-sulfur silane, the A-link 25 isocyanate silane crosslinker and the zinc phosphate have not fully interacted with each other. As the water evaporates the dispersion components are forced closer to each other. The superprimer dispersions have been characterized by liquid state ^{13}C NMR [7] and the resulting films by solid state ^{13}C NMR and RAIR. These results have shown that the acrylate interacts with the silane forming an acrylate–silane layer in the middle of the coating, where also the zinc phosphate particles are incorporated (Fig. 11b). The epoxy, however, does not interact much with the other ingredients except for the crosslinker. Therefore, the epoxy forms virtually a layer of its own on top of the crosslinked acrylate–silane–zinc phosphate layer. The epoxy–crosslinker reaction involves the OH groups of the epoxy, which react with the isocyanate groups of the crosslinker forming a small amount of urethane groups, which

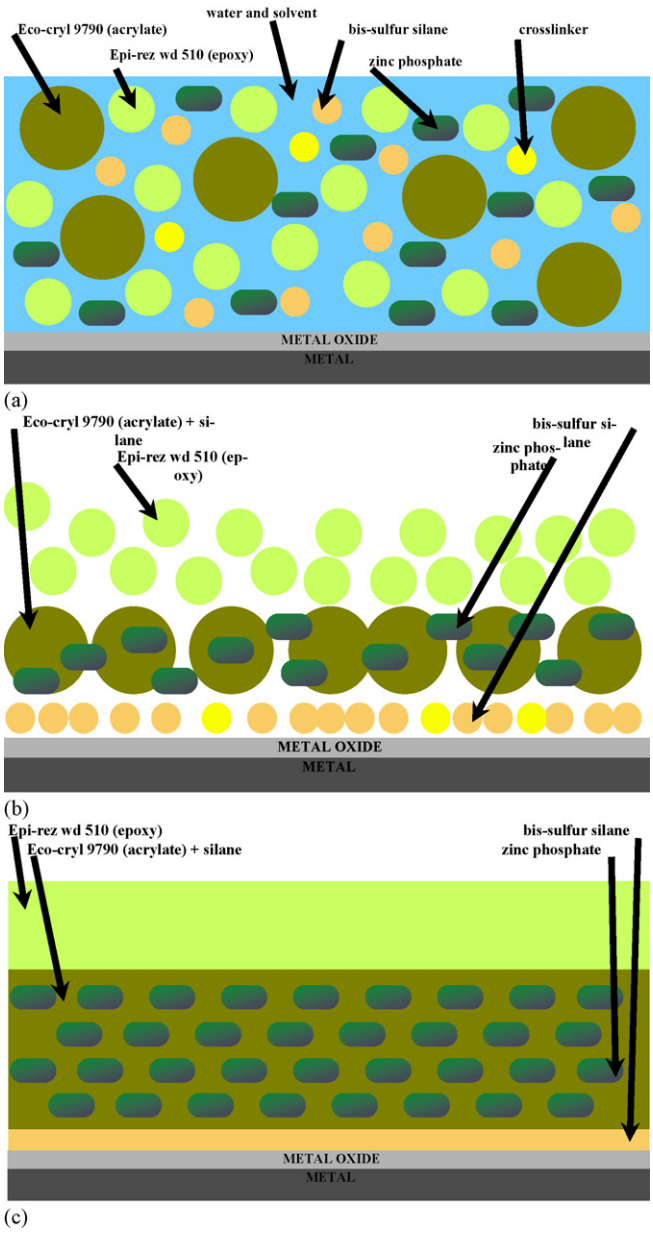

Fig. 11. Formation of the epoxy–acrylate coating on aluminum during curing, (a) right after application, (b) as water evaporates and the components interact and (c) final coating.

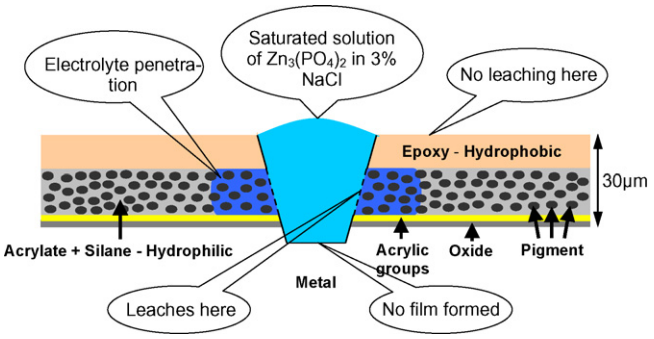

Fig. 12. Principle of the corrosion inhibiting mechanism of the acrylate–epoxy–silane superprimer containing the zinc phosphate pigments, which protect the metal on-demand.

branch these two chemicals together. The amount of crosslinker in the formulation is, however, so small that traces of the crosslinker are not detected in the SEM/EDX scan of the layer. The reaction was, however, verified by FTIR when the chemistry of the epoxy and the isocyanate silane was studied separately. A schematic of the final self-assembled epoxy–acrylate coating is presented in Fig. 11c, which naturally resembles the SEM micrograph of the actual cross-section of the coating shown in Fig. 6.

The water and electrolyte uptake results showed that the epoxy layer of the coating is hydrophobic and the acrylate–silane layer is hydrophilic. There is, however, good interfacial adhesion between these two layers due to the silane present in the acrylate–silane layer. The lower layer is rich in bis-sulfur silane, which forms a layer close to the metal. When the entire coating on aluminum is scribed and immersed in the 3.5 wt.% NaCl solution, the ions of the solution Na^+, Cl^-, OH^- and H^+ start to attack all layers of the coated metal. As the epoxy layer is hydrophobic hardly any water or electrolyte will be able to penetrate into this layer of the coating, but as the acrylate–silane layer is hydrophilic the water including the ions are able to penetrate into the middle layer of the coating. As this happens the zinc phosphate pigment particles of the acrylate–silane layer are able to actively leach out into the salt water that surrounds the scribe. The phenomena described are presented schematically in Fig. 12. As shown in Fig. 12 the zinc phosphate leached out into the scribe forms a saturated solution of $Zn_3(PO_4)_2$ in the 3.5 wt.% NaCl solution and thereby prevents any further ingress of electrolyte into the coating. The bis-sulfur silane film close to the metal protects the metal from the electrolyte by forming a hydrophobic network of polysiloxane as the unhydrolyzed ethoxy groups of the silane are able to hydrolyze in the presence of water and react with each other forming a protective film of siloxane, Si–O–Si, close to the metal. If the water in the scribe is removed, no film is formed in the scribe, as most of the zinc phosphate along with the sodium and chlorine is washed away from the scribe.

The corrosion protection mechanism of the epoxy–acrylate coating, which is self-assembled into layers after depositing it from a water-borne dispersion is unique, as the chemistry of the coating facilitates the leaching of the zinc phosphate on-demand, when the coating is scribed and attacked by an electrolyte. The chemistry of the coating allows the zinc phosphate to act like chromate ions (in a regular coating), when the coating is exposed to salt water. The chromate ions are well known to leach out only on demand, when a polymer coating is exposed to a corrosive environment [22]. The zinc phosphate pigments have been known to have low leachabilities in polymer coatings deposited from solvent-borne dispersions, which have lead to the impression that they are not able to function as active corrosion protective pigments [22]. This study proves this perception to be inadequate for zinc phosphate in water-based systems. Zinc phosphate will work as an active corrosion inhibitor in coatings that are sufficiently hydrophilic.

As a final comment it should perhaps be mentioned that the other coating systems presented in the overview of this paper do not work in the same way as the presented epoxy–acrylate coating, as they do not possess the hydrophobic top layer, shown in Fig. 12. The stratification of layers is only observed in the epoxy–acrylate coating. The other systems contain a more hydrophilic type of epoxy, which enables the dispersion of the pigments into the entire coating and the release of them when immersed in water or electrolyte.

5. Conclusions

A set of superprimers has been developed, which have been put through performance tests and characterized with a variety of methods. An overview of the latest performance test results of the primers has been given here along with a mechanistic study of how one of the well-performing superprimers protects the metal from corrosion. The performance test results reveal that

- Silane-containing chromate-free low-VOC superprimers can be developed for aluminum alloys and also for a more demanding substrate such as HDG steel.
- The primers deposited onto the metals without a conversion coating perform very well in the performance tests. They are comparable to the chromate controls containing chromate both in the pretreatment as well as in the primer layer.

An extensive case study of the epoxy–acrylate primer (the first coating in Table 1) demonstrated that zinc phosphate pigment particles can in fact function as active “on-demand” corrosion inhibitors in this coating that has been formed from a water-borne polymer dispersion. In this particular coating the zinc phosphate is able to leach out only from the hydrophilic acrylate–silane–zinc phosphate layer, creating a reservoir of saturated zinc phosphate in the surrounding salt solution while the hydrophobic epoxy layer protects the acrylate containing layer and thereby the rest of the coated metal.

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