# Visual degradation of Zinc-surfaces in salt-spray tests: Black spots and White haze

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## ABSTRACT

Exposing samples to a neutral salt-spray in a corrosion climate chamber determines the corrosion resistance of passivated zinc or zinc alloy coatings. Clear surface finishes tend to produce black spots before the formation of voluminous white corrosion products, while black or dark finishes tend to form a white haze. This paper will try to reveal the mechanism of this corrosion mechanism that on many occasions confuses the outcome of corrosion testing. The black spots and white haze phenomena seem to be closely related.

## Introduction

Passivated zinc and zinc-alloy deposits provide a wide range of appealing surface finishes. The decorative surface aspects can range from bright to matte, from clear to black and a variety of interference colours such as blue-red, yellow-green or dark green-red iridescent. The passivation or the formation of a conversion coating on zinc enhances corrosion resistance. Neutral salt spray testing is at the moment the main test in use to verify corrosion resistance. The onset of voluminous white rust (zinc oxides) and red rust (iron oxides from the substrate) are the main criteria to evaluate corrosion resistant performance. [Fig. 1]



1. Corrosion inspection on threaded fasteners at Nedschroef Helmond BV- The Netherlands A passivation solution produces a complex gel-layer on a zinc (or zinc alloy) substrate by parallel chemical and electrochemical reactions.

Some typical (simplified) reactions to mention are:

Etching of the surface and local increase of pH:  $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ Precipitation of Chromium Hydroxide:  $Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+$ Formation of Chromium oligomers:  $2Cr(OH)_3 \rightarrow Cr_2O_2(OH)_2 + 2H_2O$ These oligomeric structures form the backbone of a trivalent chromium matrix. Many passivate solution constituents are build into the layer: oxo-anions such as sulfate, phosphate and

organic acids while halogens tend to be ion-

paired only on the outer side of the passivate. The single charge anions (fluoride, chloride) are good leaving groups and tend to be washed away or replaced easily from the conversion coatings. Metallic constituents tend to be mainly in the oxide form as a mixed zinc oxide / zinc hydroxide, but also iron, cobalt, calcium, magnesium oxides may be present as functional constituents or as contaminants.

Most of the coatings discussed are based on trivalent chromium passivation, the use of hexavalent chromium passivation is diminishing but not fully replaced yet because of the very specific economic and functional benefits. Hexavalent chromium salts are relatively low cost and provide excellent corrosion resistance. The electroplating industry is turning away from hexavalent chromium because of carcinogenic effects handling hexavalent chromium surfaces (and surely the risk of handling hexavalent passivate solutions). Global legislation and specifications in the automotive industry are restricting the use of hexavalent chromium in passivate solutions. Hexavalent passivation is enclosed in the discussion in order to complete the view presented on corrosion behaviour of passivated zinc.

From the decorative viewpoint the metallic/clear and jet-black finishes are favoured – especially for those applications focusing on the automotive industry. [Fig. 2]



2. Appealing finishes of passivated zinc & zinc alloy fasteners. Most popular are the black and metallic-clear finishes for the automotive industry.

### White haze

Essential to the proposed mechanism is to note that thin passivate coatings (100-250 nm) contain little water, are more compact and secure general conductivity by surface absorbed charges. Thick (-er) passivate coatings (250-500 nm) contain enclosed water which is essential for ion transport conductivity (and corrosion resistance) and tend to be more porous. The full coating will consist of a zinc (zinc-alloy) layer of determined thickness (typical 8 to12 micrometer), a monolayer of zinc oxides providing bonding to the subsequent passivate layer and lastly some adsorbed water molecules.

Zinc oxides have a strong bond with high covalent character. These oxides tend to have an excess of zinc ions creating a n-type semiconductor (conducting electrons)<sup>1</sup> On a zinc/zinc oxide interface the zinc will charge with electrons to compensate total charge in a dynamic equilibrium. The most reactive interface will be the zinc/zinc oxide barrier where oxygen will react directly with zinc to form new compact oxides. Oxygen penetrates the passivate layer and compact zinc oxides will start to grow on the metallic zinc-interface.

 $2Zn + O_2 \rightarrow 2ZnO$ 

The presence of humidity (salt spray from the corrosion cabinet or residual water in the passivate-gel) will hydrolyze the oxides to liberate hydroxides and zinc ions. At this stage passive eta-hydroxides are formed.<sup>2</sup>

 $ZnO + H_2O \rightarrow \epsilon - Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^{-1}$ 

This reaction proceeds in a very uniform way all over the zinc surface. From the moment that the zinc cations are neutralized by the negatively charged zinc metal interface, free hydroxides will diffuse towards the surface. The initial formation of compact oxides – bottom up from the zinc surface - is a visible phenomenon especially if these compact oxides (and some eta-hydroxides) are formed underneath a black passivate. We can see that underneath the passivate layer a white-



3. White haze, compact oxides developing under the passivate layer (cracks are caused by dehydratation in vacuum)

grey layer is formed. We recognize this type of interfacial oxidation as "white haze" On clear surfaces it is more difficult to see this effect especially when the parts retrieved from the climate chamber are still wet. The structural integrity of the passivate layer will avoid these oxides from breaking through. If for some reason the passivate loses the gel-like properties due to dehydratation (over-heating a thick passivate layer) the oxides break through the surface and form amorphous hydroxides<sup>2</sup>: the corrosion reaction runs out of hand developing voluminous white rust. [Fig 3-4 White haze and voluminous white rust] Passivate coatings incorporating differing metal ions with strong hydrogen bonds (Ca, Mg or even Si) will contain oxide/hydroxide formation

under the passivate layer as long as the

passivate is not broken down (chloride tearing up de Cr(III) matrix by cleaving the oxygen bonds) or structural damage is limited (being mechanical or by dehydratation).



*4. White corrosion products, beta oxides Breaking through a black passivation layer* 

development of white rust are not related.

Without any surface anomalies the overall reaction of a white haze surface resembles a huge cathode with the overall reaction:  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2 \text{ OH}^-$  as long the zinc metal can provide the extra electrons to keep the zinc/n-zinc oxide interface neutral. Typically trivalent and hexavalent black passivation show white haze development on zinc alloys (you will need an alloying metal to create black oxides) in an early stage in neutral salt spray testing. This confuses the determination of the onset of true (voluminous) white corrosion. A practical way to overcome this problem is to evaluate the parts when still wet (after a short rinse), only voluminous white rust will show. The start of white haze and the

On many occasions one may observe excellent corrosion resistance even when white haze develops in an early stage. The effect of white haze formation is even more pronounced when using a sealant. The free hydroxides are trapped between passivate and seal (some sealants can become white opalescent in contact with these hydroxides). Again this effect has no relation to the breakthrough of voluminous white corrosion products.

## **Black Spots**

One of the mysteries of zinc plated parts placed in the salt spray cabinet is that quite rapidly black circular spots appear in a seemingly random fashion on clear /metallic surfaces. The initial spot-diameter is in general between 100 micrometer and 1 mm. Surely they will also exist on black surfaces but the black defects are difficult to spot on such a surface. Only when voluminous white rust breaks through the black/grey areas expand to corroded bands and streaks. On sealed surfaces we could observe the appearance of black spots at 48h neutral salt spray exposure but the form and number remained constant until at 820h the first onset of white corrosion products becomes visible.



5. Black spot developed in last (circular) stage just before onset of voluminous white rust: a grey disk, black ring, and a matte buffer zone. A streak of white corrosion products is running down vertically

[Fig. 5] The black spot nature can be best observed just before voluminous white rust occurs. If the spot is large enough one could observe a grey disk in the middle consisting mainly in substrate material (steel, iron). On many occasions when voluminous white rust is developed the center of the black spot will be the first to form red corrosion (red rust) as soon as the cathodic protection of zinc fails. Initial black spots only show a deep black center with a matte dull band. A typical phenomenon is "cratering" - the spot is a location where zinc ions are removed from surface of the zinc layer. The typical black colour is a bit of a mystery. The largest contribution to the black colour seems to be cratering and increased

roughness (due to selective zinc removal). Most zinc oxides provide white or colourless crystals – only if you have an iron-group element (Fe,Co,Ni) present or some of the trivalent Cr-salts, black oxyde deposits can be formed. It is unlikely that iron from the substrate diffuses towards the surface to create a black deposit when the initial zinc deposit thickness is sufficiently thick (> 2 micrometer). On the otherhand the black pits seem to show anodic behaviour. It is not unlikely that intermediate peroxozinc salts are formed:  $Zn + O_2 \rightarrow ZnO_2$ . Surface analysis shows that a black spot is the only region that retains the chloride (from salt spraying)<sup>3</sup> on the surface if the sample is thougoughly rinsed. This could mean that chloride fixates as zinc peroxychloride,

ZnOCl, which is fairly stable in mild anodic environment. By direct oxidation of zinc chloride or hydratation of the oxychloride Simonkolleite,  $Zn_5(OH)_8Cl_2.H_2O$ , is formed in the final stage<sup>4</sup>. All named compounds do not have a black aspect – but we cannot exclude that intermediate salts formed with trivalent chromium in the passivate reacts to a black oxide product.

Zinc appears to be selectively dissolved from a single locality. The semiconductor behaviour of zinc oxides provides an answer. The zinc oxides are present between the metal and the passivate layer. Local variations in crystal structure and dopants (mainly  $Zn^{2+}$ ) from the passivate process, induce a positive charge in the oxide layer by means of interstitial zinc-ions. This positive charge is balanced by a negative charge of the metal side. [Fig. 6]



6. Formation of anodic zones: These layers are not to scale: the passivation layer(green), zinc oxide (yellow), zinc (blue), steel/substrate (grey).

When the zinc layer becomes locally thinner free electrons can be drained to the steel electron sink. Interstitial zinc ions are not bound by the counter charge and can diffuse to the surface. A local anodic channel is created that can transport zinc-ions through the passivate layer. As soon as iron is exposed to the salt spray / oxygen environment the cathodic protection of zinc takes over to keep iron in a metal / atomic state. It is not a surprise that black spots occur by preference on locations where the zinc layer is less thick or the crystal structure of zinc is distorted (cleaning- and rinsing- failure before plating), or when the substrate contains crystal seeds with more Silicon, Carbon or Manganese inclusions.

The anodic channel acts as a zinc-ion pump towards the surface. The electrochemical halfreaction is the same for sacrificial corrosion protection:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-1}$ 

If the steel is not exposed to air the excess electrons are drained to substrate.

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The morphology of black spots is easily recognized by formation of a crater with sharp edge with micro-roughened zinc & zinc salts on the bottom. [Fig. 7a-b]



7a. Crater Rim (black spot located at the bottom) 250x

7b. Same Crater Rim enlarged 1000x- notice the micro- roughness inside the black spot

## Putting black and white together

Independent of the type of passivate white haze and black holes are formed in the same time period – unfortunately black holes are (nearly) not visible on black passivate surfaces and white haze is difficult to observe on clear finishes. The white haze forms part of a controlled mechanism to form compact oxides on the metal surface while the black spots provide the counter charge by releasing zinc ions. If we put the half-reaction from white haze formation and the half-reaction from the black spots together we obtain:

 $\frac{1}{2}O_2 + Zn + H_2O \rightarrow 2(OH)^2 + Zn^{2+}$ 

Both reaction products are transported to the surface and can form white corrosion products. I did omit the possibility free hydroxide and zinc reacting with carbon dioxide with the formation of Hydrozincite,  $Zn_5(CO_3)(OH)_6$ , as a self-protecting patina formed in outdoor exposition. The described observations are made on coatings exposed to salt spray testing in climate cabinets. The relationship with neutral salts spray (NSS) testing and an outdoor exposure test is very controversial. The black spots seem to occur exclusively in NSS testing- and most probably related to the constant exposure to high chloride containing solution.

Visual observation of voluminous white corrosion shows often that the underlying passivate layer is intact (and even reflect an undamaged zinc surface through these corrosion "veils").

Anodic and cathodic zones are separated by neutral oxides comparable to a pn-junction in a semiconductor – this explains why we have electron transfer through the Zinc/substrate layer and ion transport above the passivate layer. Close examination of black spots show a matte/white ring where "neutral" zincoxides provide a barrier to overcome a shortcircuit of the electrochemical battery. This way the black spot can provide sacrificial protection to sustain the formation of compact oxides in white haze areas. [Fig. 8]



[Fig. 9]The proposed mechanism gives also some explanation to observed corrosion phenomena: On horizontal exposed surfaces black spots seen to be the center of voluminous white rust.



The diffusion of hydroxide is much faster than the free zinc ions. With no solution flow, the white corrosion products form on top of the black spot as white haystack. Removing the white corrosion products will show that the black spot is still there intact.

9. Horizontally corroding black spot fully covered with voluminous white rust (collecting free hydroxides)



10. Voluminous hydroxides breaking through the (black) passivate layer due to wrong packaging / drying and water condensation.

[Fig.10] The occurrence of white spots on black passivated parts is sometimes observed when the final curing of the passivate is not completed. The excess water molecules can dissolve acids from the plating line (airborne HCl fumes from etching & activation). Formation of condensation droplets in closed (plastic) package can also weaken the passivate matrix by leaching salts from the passivate generating localised corrosion attack.

[Fig. 11] A more typical effect is seen with parts that are mounted in the corrosion cabinet without shielding the unplated contact points. Cathodic protection will generate zinc-ions being washed down with the salt spray solution. Formation of white corrosion products starts when the zinc ions are intercepted by the very mobile hydroxide anions.



11. White corrosion products running over the surface. The attachment points provide the free zinc ions (little or no zinc in the top hole, plating contact point) while hydroxides move in from the sides.

### Conclusion

White haze and black spots are essential side effects of the corrosion protection mechanism provided by passivated zinc coatings when exposed to neutral salts pray corrosion testing. Both phenomena are not linked to the required or specified corrosion performance of the coating. White haze and black spots can remain unaffected for a long period as long as the formation of amorphous zinc hydroxide is not initiated. In order to make a correct observation of the start of voluminous white rust it is best to examine the parts leaving the corrosion cabinet when still wet.

Seals and carbon dioxide can provide a fixation of the surface ions – it will extend the corrosion performance but tends to result in a stronger visual degradation of the surface before the voluminous white corrosion starts.

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