Oil resistant Cr-free passivation coating for hot dip galvanised steel

One of the approaches to replace Cr-based passivation coatings with non-Cr is to use formulations based on sol-gel chemistry to provide a dense protection film on the metal substrate. However, as anti-rust oil is often applied on top of the passivation coating this usually deteriorates the corrosion protection performance of these coatings. Henkel has, therefore, developed a new anti-corrosive coating, BONDERITE O-TO 968, providing both outstanding oil resistance as well as baking and chemical resistance.

Passivation coating is widely used to protect hot dip galvanised (HDC) steel from corrosion. These passivation coatings are hybrid coatings whereby organic polymers act as a matrix with an inorganic phase dispersed within it. The inorganic part plays an important role in increasing the scratch resistance, durability and adhesion to metal substrate, whereas the organic part increases its flexibility, chemical resistance and compatibility with other organic systems. Traditionally, these coatings contain hexavalent chromium and provide outstanding corrosion performance mostly due to the self-healing properties of Cr. However, as hexavalent chromium is carcinogenic and environmental regulations are becoming stricter there is a need to develop a Cr-free solution.

One of the approaches to do this is based on sol-gel chemistry. The sol-gel process helps provide a dense protection film on the metal substrate which provides excellent corrosion protection. The process is based mainly on hydrolysis and condensation reactions of alkoxysilanes (such as teramethoxysilane TMOS), metal alkoxides (M(OR)n), alkoxides of cerium, titanium, zirconium, and organo-silanes.

Henkel has already launched its first range of products based on sol-gel chemistry for this application as an alternative of a Cr-based product. However, as anti-rust oil is often applied on top of the passivation coating, which usually deteriorates its performance, Henkel has developed a Cr-free passivation coating, BONDERITE O-TO 968, based on silane technology, specifically to cater for this need.

Table 1 Neutral salt spray test results

<table>
<thead>
<tr>
<th>Salt spray time</th>
<th>Corrosion area (%)</th>
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</thead>
<tbody>
<tr>
<td>Bonderite O-TO 968 coating</td>
<td></td>
</tr>
<tr>
<td>48h</td>
<td>0</td>
</tr>
<tr>
<td>72h</td>
<td>0</td>
</tr>
<tr>
<td>96h</td>
<td>0</td>
</tr>
<tr>
<td>120h</td>
<td>&lt;1</td>
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COATING PREPARATION AND PERFORMANCE

BONDERITE O-TO 968 is formulated with alkoxysilanes. One end of the alkoxysilane molecule contains hydrolysable end groups which are hydrolysed to silanol (Si-OH). The other end contains reactive end groups which react with other functional groups which exist in other inorganic or organic components or the metal substrate.

This product is based on functionalised polyurethane.
FORMING AND FINISHING PROCESSES

and polyacrylic hybrid resin. Zirconium and titanium based complexing agents are also added. In addition, we have used additives, such as de-foaming agents, levelling agents and wax to prepare a defect free, anti-friction film. It is believed that due to its unique molecular weight distribution and additives in the formulation, this product provides superior oil-resistant properties. Figure 1 shows a schematic film of BONDERITE O-TO 968 coating.

In order to get a passivation film with good properties, we recommend a coating weight of BONDERITE O-TO 968 film in the range of 0.8-1.2g/m². If the coating weight is too high, the film may perform better as regards corrosion resistance and alkaline resistance, but it may not dry sufficiently easily and may perform worse in baking resistance and stacking resistance tests. On the other hand, if the coating weight is lower than 0.8g/m², the film may not perform well in corrosion resistance, although it could have good baking or stacking resistance. Thus, the coating weight should be well controlled during application of this passivation product to the metal substrate.

Neutral salt spray test (NSST) results under ASTM B117 conditions (35°C, 5% NaCl, pH 6.5-7.2) are shown in Table 1. It shows the percentage of the corrosion area on HDG substrate with BONDERITE O-TO 968 passivation coating (1.0g/m²) as a function of the salt spray time. No corrosion was observed up to 96h. Even after 120h NSST, less than 1% corrosion area was found, which indicates good anti-corrosion performance.

BONDERITE O-TO 968 shows excellent oil resistant performance, and is certificated by key customers in China. To evaluate film performance, we conducted a number of tests in an aggressive testing environment. Bonderite O-TO 968 and a commercially available passivation product were compared. The NSST results are shown in Figure 2. Figure 3 shows the SEM image of the cross-section of BONDERITE O-TO 968 coating applied on metal substrate, and the element distribution (atomic %) as a function of distance to the substrate. Figure 4 shows the cross-cut NSST of BONDERITE O-TO 968 coating on HDG panels: a) Morphology, b) SEM image of cross-cut area.

Fig 2 Comparison of 72h NSST of: a) BONDERITE O-TO 968 film, b) other commercial film

Fig 3 a) SEM image of cross-section of BONDERITE O-TO 968 coating applied on metal substrate, b) element distribution (atomic %) as a function of distance to the substrate

Fig 4 72h cross-cut NSST of BONDERITE O-TO 968 coating on HDG panels: a) Morphology, b) SEM image of cross-cut area
applied on HDG substrate (coating weight is around 1.0g/m²) and were dried at room temperature for five minutes. Then a thin layer of anti-rust oil was applied on the surface. It is expected the anti-rust oil can penetrate the film easily because it was still not fully cured. The panels were tested for 72 hours under NSST conditions described above.

*Figure 2* shows a comparison of oil resistance performance between BONDERITE O-TO 968 and the other commercial passivation product. No white rust was observed on the panels coated with BONDERITE O-TO 968 (see *Figure 2a*), whereas the other product showed a white corrosion layer (see *Figure 2b*).

We used cross-section SEM-EDX to analyse the passivation coating. In *Figure 3a*, a homogenous and dense passivation film was observed with a thickness of about 1µm. In *Figure 3b*, distribution of the main elements in BONDERITE O-TO 968 coating is shown. Carbon is present on the surface of passivation film, while silicon tends to be close to substrate. It is hypothesised that this distribution is achieved because of good hydrolysis and condensation of silanes, and such a distribution provides improved paintability and adhesion properties to the passivation coating.

*Figure 4a* shows the overall morphology of the cross-cut HDG steel coated with BONDERITE O-TO 968 coatings after 72h NSST. All panel surfaces and even the cross-cut area is free of white corrosion products. The SEM image of the cross-cut area is shown in *Figure 4b*, and which indicates no corrosion reaction had commenced even at the edge of the cross-cut part.

In cases of corrosion damage or any defect in the film, metal under the coating acts as a cathode and the damaged area acts as an anode. In this situation, it is hypothesised that BONDERITE O-TO 968 releases a corrosion inhibitor.
containing high valent metal compounds. This corrosion inhibitor reaches the defect site and forms a barrier film which prevents the further corrosion damage. This mechanism of corrosion protection is known as self-healing effect. A schematic representation of the self-healing effect of the passivation coating is shown in Figure 5.

We have studied other properties of BONDERITE O-TO 968 coating. Various test results are shown in Figure 6.

- 6a: Alkali resistance (dip coated panels in 2% FC-363G, 50°C for 2 min, and then 48h NSST)
- 6b: Baking resistance (bake coated panels in 240°C for 20 min, and test the colour change ∆E)
- 6c: Solvent resistance (rub coated panels with 80% EtOH/MEK for 30 times/20 times back and forth, and test the colour change ∆E)
- 6d: Paintability (powder paint (Akzo Nobel EA05BH), DFT 40-60µ, cross-hatch, 5J impact)

The results demonstrated that this passivation coating performed well not only in its oil resistant property, but also in corrosion protection, heat resistance, chemical resistance and good adhesion to top coatings.

CONCLUSIONS

BONDERITE O-TO 968 is a new organic-inorganic hybrid chrome-free passivation coating that provides a homogenous and dense film to protect HDG substrate from corrosion. This newly developed anti-corrosive coating shows outstanding oil resistance as well as baking and chemical resistance. Additionally, it also provides good paintability. BONDERITE O-TO 968 addresses environmental and sustainability concerns associated with Cr based coatings and it is expected that it will provide some additional benefits, such as oil resistance properties to customers, not available with current passivation products in the market.

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