Providing beauty and durability

Zinc and degassing-friendly powder combination protects steel.

Kris Buysens.

Galvanised steel fencing should look attractive and stay attractive. A degassing-friendly powder coating with the right rheological behaviour allows a smooth, attractive coating to be achieved without pinholes/air bubbles on different types of galvanised steel without the need to pre-heat the substrate. An optimal protection is achieved when all steps of the process typical for a duplex system - galvanisation, pre-treatment and powder coating - are correctly done. The degassing-friendly powder coating described in this paper offers the desired protection in terms of corrosion and UV resistance when used in a duplex system. It has been proven in practice that the positive synergy between zinc and a powder coating, correctly applied on to a steel substrate, provides optimal protection for the steel against wind, rain and UV radiation.

\[ D_{\text{duplex}} = 1.3 \times D_{\text{galvanised steel}} + D_{\text{coating}} \] (D = Life expectancy)

At points where both the coating and the zinc layer are damaged, the steel is protected by the cathodic effect of zinc. Under the influence of an aggressive atmosphere (such as acid rain or salts) an unprotected zinc layer is attacked and reduces in thickness. A powder coating layer prevents this degradation in a duplex system.

The process is key to a good result

A prerequisite for an optimal result is that all the steps of the process - galvanisation, pre-treatment and coating - are done in the correct way and are geared to one another. The chemical/mechanical pre-treatment is an essential step. The subsequent application of a defect-free, homogeneous coating is of high importance as well.

The combination of porosity and thickness of the zinc layer, in the case of hot-dip galvanising or zinc-spraying, can lead to the formation of pinholes and/or air bubbles in the final powder coating. It is at these weak spots that corrosion can take place. One possibility to reduce the degassing is the pre-heating, in combination with warm spraying, of the galvanised substrate. The addition of a degassing agent to the formulated powder prior to its application may help as well. However, both techniques have their drawbacks and therefore the use of a specially developed powder coating is recommended (Table 1).

The TGIC-free “PRO 100” range from Flanders Powder (Table 2) enables pinhole-free coatings to be obtained on various types of galvanised steel without the need to preheat. Formulated with an ideal rheological behaviour, the coating offers good protection against humidity (corrosion) and UV radiation. Recently, the “EXT 42” system has been approved by GSB for use on hot-dip galvanised steel building components.

Good pre-treatment is important in a duplex system

For optimal performance, the adhesion between the zinc-treated substrate and the powder coating is of major importance. A good pre-treatment of the zinc layer provides this as can be seen from some of the possibilities and their typical characteristics (Table 3). Every chemical process leading to the formation of a conversion layer should be preceded by a cleaning and etching step in order to remove grease, impurities and oxide deposits from the substrate. In the case of zinc-spraying, the powder is applied on to a dust-free zinc layer that has been applied on the steel substrate shortly before.

Powder contains non-mutagenic hardener

The powder coating system described in this paper is based on a saturated polyester resin and a non-mutagenic hardener. This is in contrast to TGIC (triglycidyl isocyanurate)-containing powders that were formerly used and makes this new type of powder safer and more acceptable in use. The high tribo-chargeability guarantees a high transfer efficiency both with corona and tribo guns. As there is no need to add an external degassing agent to obtain the degassing properties the powder can be recycled without any problem. Like any other conventional powder coating, this degassing-friendly powder should be stored in a dry place below 25°C. In order to obtain a smooth surface (hiding irregularities of the substrate), it is recommended that a minimum layer thickness of 80µm is applied. A coating thickness of 80µm also provides a better protection of the substrate underneath.

Correct curing gives the best results

Curing the coating correctly is the basis for the best result. Properties such as impact, water and UV resistance only fully develop when the polymerisation of the film is sufficient. Curing according to a point between the two curves (Figure 1) leads to the desired result. Time and temperature of each point refer to the effective metal temperature.

Modifying rheology prevents degassing problems

How a degassing problem during the lacquering of hot-dipped galvanised or zinc-sprayed steel may occur has already been discussed. The most effective way to negate this type of problem is by the use of a powder with modified rheological behaviour.

Rheology is the study of the flow of materials. It is obvious that the final properties of a powder coating surface (such as levelling or blisters/pinholes caused by degassing) are mostly influenced by the rheological behaviour during the melting/curing phase. During this phase, the material transforms from a pure viscous mass into a pure elastic gel. It is principally the melt or viscous phase that is of importance here: the lower the viscosity and the longer it takes before polymerisation starts, the better the resulting levelling and degassing (of substrate and coating).

To understand the influence of powder composition on flow and degassing behaviour, plate-plate rheological studies (constant frequency and constant strain oscillation measurements) were performed on the degassing-friendly material and a conventional Qualicoat certified powder coating. Measurements were conducted with a “Stresstech” Rheometer (from Cytac Surface Specialties) at heating rates of 5°C/min and 20°C/min (Figures 2 and 3).

At both heating rates, the viscosity minimum of the degassing-friendly powder lies significantly below and is shifted to the right, (enclosed gasses have more time to escape) compared with the standard Qualicoat material. This is the ideal scenario for obtaining a smooth coating without pinholes or air bubbles on degassing substrates.

Comparison of Figure 2 and Figure 3 clearly indicates that the viscosity minimum also depends on the selected heating rate [1]. A faster heat-up rate will result in a further improvement of flow.
Durability differs for different duplex systems
Practical experience shows that the combination of zinc and powder coating for the finishing of steel fencing, construction elements etc., guarantees optimal and long outdoor protection. How long exactly this protection lasts strongly depends on the environmental conditions to which the object is exposed. An overview is given of the different corrosion categories (Table 4). The criterion for this classification is the corrosion rate of zinc expressed in microns per year. For each class, an expected lifetime can be proposed for different types of duplex systems [2].

For a duplex system composed of a zinc layer and an outdoor durable powder coating layer chromatisation is expected to give the longest protection, namely more than 15 years in corrosion class C4. In the case of zinc phosphate or shot-blasting, the expected lifetimes in this class are 5-15 years and 2-5 years respectively, while in C2 and C3 environments more than 15 years of protection is expected from both of these systems.

A two-layer powder coating system, composed of an epoxy primer and an outdoor durable layer, applied on galvanised steel, offers extra protection: from 5-15 years in the case of zinc phosphate and more than 15 years with a chromate conversion layer in very aggressive conditions (C5). Accelerated durability tests give a good indication of how certain coating systems will behave under real conditions. Therefore, the degassing-friendly powder coating was put through a number of tests.

Chromate conversion layer gives best salt spray results
The neutral salt spray test was carried out as below:
- Test method: ISO 7253 (5% NaCl solution, 35 °C)
- Scribe: 0.5mm (DIN 53 167)
- Delamination + corrosion around the scribe (with sharp knife) (ISO/DIS 4628-8, draft)
- Degree of blistering (ISO 4628-2)
- Test performed on RAL 6009 formulation

The results are given in Table 5. As expected, a chromate conversion layer gives the best result in an accelerated salt spray test. The other types of pre-treatment should give sufficient protection for long term use in climate classes C2 and C3.

Zinc-spraying carried out correctly guarantees an excellent corrosion protection as well, even in relatively aggressive conditions.

Kesternich test shows SO2 resistance
The presence of sulphur dioxide (SO2, acid rain) is typical for industrial environments. The corrosion rate of zinc increases linearly with the increase of sulphur dioxide concentration in the air. Therefore, a Kesternich test can provide interesting results. The concentration of SO2 that was used in the test described below is very high, giving a very good indication of how this special powder coating will resist corrosion in a strongly polluted, industrial environment.

- Test method: ISO 3231; 8h; 1l SO2, 40°C, 16h aeration, 25°C
- Test performed on RAL3002, RAL5008 and RAL6029 formulations applied on hot-dip galvanised steel with chromate conversion layer. In these drastic conditions, the colour change is relatively small (Figure 4). No blistering was observed on completion of the test. This is a good indication of the coating’s resistance to a strongly polluted atmosphere.

New system gives similar UV protection to that of conventional coatings
A QUVB (313nm lamp) test gives an accelerated indication of the UV resistance of a coating. The degassing-friendly system was compared in this type of test with a conventional, Qualicoat (Class 1) certified powder coating (REF in Figure 5):
- Test method: ISO 11507:1197; UV-B 313nm (FS40 lamp); 4h UV, 60°C, 4h condensation, 40°C
- Test performed on RAL6029 and RAL5008 formulation

For both gloss and colour retention, the new system seems to give comparable results to those of the Qualicoat certified system. For that reason it is expected that the system will also fulfill the expectations in real outdoor conditions.

Possibilities with degassing epoxy primer and zinc-rich primer
The combination of a degassing epoxy primer (applied at 60-80µm) with an outdoor durable top layer (80-120µm) on galvanised steel results in further improvement of corrosion resistance. The expected lifetime of such a two-layer system is very high: more than 15 years even in a C5 climate (with chromate conversion layer).

An interesting alternative for a duplex system (zinc + 1 powder layer) is a 2-layer powder system applied directly on to correctly shot-blasted steel. Preliminary salt spray tests have shown that such a system gives comparable results to those of a duplex system, using zinc phosphate as pre-treatment, in terms of corrosion resistance. Both the epoxy- and the zinc-rich primer are available in the "Pro 100" product range.

A detailed study comparing the corrosion resistance of different types of systems, applied on galvanised and sand-blasted steel is still in progress and further reports will follow in the future.

References
[2] GSB quality label or building components of coated hot-dip galvanised steel (GSB International : Gütegemeinschaft für die Stückbeschichtung von Bauteilen e.V.; www.gsb-international.de) and ISO 12911-1.

Results at a glance
- A duplex system consisting of zinc and a powder coating system based on a saturated polyester resin and a non-mutagenic hardener has been developed.
- The viscosity minimum of the degassing-friendly powder is lower than the standard "Qualicoat" material, which is the ideal scenario for obtaining a smooth coating without pinholes or air bubbles on degassing substrates.
- A chromate conversion layer gives the best result in an accelerated salt spray test but the other types of pre-treatment, in terms of corrosion resistance. Both the epoxy- and the zinc-rich primer are available in the "Pro 100" product range.
- Possibilities with degassing epoxy primer and zinc-rich primer
- For both gloss and colour retention, the new system seems to give comparable results to those of the Qualicoat certified system. Recently, the system has been approved by GSB for use on hot-dip galvanised steel.

The author:
-> Kris Buysens graduated with a PhD in chemistry from the University of Leuven/Belgium in 1996. In that same year he joined UCB Chemicals. Before he became responsible for the technical service and development of powder coatings resins in 2001 he was project leader for UV curable powder coatings. At the start of 2004 he joined the R&D team of Flanders Powder/Belgium.
Figure 1: Cure profile for the degassing-friendly powder (nominal 10 min at 200°C metal temperature required)

Figure 2: Rheology, 5°C/min

Figure 3: Rheology, 20°C/min
Figure 4: Kesternich-SO₂ test: colour retention

Figure 5: Accelerated QUVB test: gloss retention
Table 1: Possible ways to reduce the degassing problem

<table>
<thead>
<tr>
<th>Pre-heating</th>
<th>And/or warm spraying</th>
<th>Degassing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Drawbacks</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Reduced productivity</td>
<td>- Difficult to control coating thickness and degree of cure</td>
<td>- Inaccurate dosing can lead to gloss variations</td>
</tr>
<tr>
<td>- Higher energy consumption</td>
<td>- Risk of sagging</td>
<td>- Wavy surface and a gloss level that is difficult to control</td>
</tr>
<tr>
<td>- Risk of degradation of the chemical conversion layer</td>
<td>- Most of the time, degassing is incomplete</td>
<td>- Problem to recycle the powder</td>
</tr>
<tr>
<td>- Fast oxidation of the zinc layer</td>
<td></td>
<td>- Reduced outdoor durability when overdosing</td>
</tr>
<tr>
<td>(in the case of sand-blasting as the pre-treatment)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: The "PRO 100" powder coating range for steel applications

- Degassing-friendly epoxy primer
- Zinc-rich primer
- Degassing-friendly, outdoor durable, TGIC-free powder (= "EXT 42")
### Table 3: Pre-treatment methods for galvanised steel and the properties that they impart

<table>
<thead>
<tr>
<th>Chemical methods</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromatisation (Cr⁶⁺)</td>
<td>- excellent protection against corrosion (also in aggressive environments),</td>
</tr>
<tr>
<td></td>
<td>- broad applicability</td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>- slightly reduced corrosion protection compared to chromatisation (in aggressive environments)</td>
</tr>
<tr>
<td></td>
<td>- improved thermal stability compared to chromatisation-quality depends on zinc layer (presence of lead)</td>
</tr>
<tr>
<td>Zirconisation</td>
<td>- environmentally-friendly, chrome-free alternative</td>
</tr>
</tbody>
</table>

**Mechanical methods**

| Shot-blasting            | - removal of impurities and corrosion products                             |
|                          | - creating a rough surface to improve adhesion                             |
### Table 4: Corrosion classes and their effects on zinc

<table>
<thead>
<tr>
<th>Code</th>
<th>Corrosivity category</th>
<th>Corrosion rate of zinc (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>Dry rural areas. Low level of pollution</td>
<td>0.1-0.7</td>
</tr>
<tr>
<td>C3</td>
<td>Urban and industrial areas (inland) with low level of SO₂-pollution or maritime climate with low levels of salt</td>
<td>0.7-2</td>
</tr>
<tr>
<td>C4</td>
<td>Industrial climate and maritime areas with moderate salt level</td>
<td>2-4</td>
</tr>
<tr>
<td>C5</td>
<td>Industrial area with high humidity or maritime area with high salt level</td>
<td>4-8</td>
</tr>
</tbody>
</table>
### Table 5: Results of the neutral salt spray test on different coating systems

<table>
<thead>
<tr>
<th></th>
<th>Blisters¹ after 500/1000h</th>
<th>Delamination² after 500/1000h</th>
<th>Corrosion³ after 500/1000h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-dip galvanised</td>
<td>None / None</td>
<td>1.2 mm / 2 mm</td>
<td>0.8 mm / 1.8 mm</td>
</tr>
<tr>
<td>+ shot-blasting</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot-dip galvanised</td>
<td>None / None</td>
<td>0 mm / 0 mm</td>
<td>0 mm / 0 mm</td>
</tr>
<tr>
<td>+ chromatisation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot-dip galvanised</td>
<td>None / 1(S2)</td>
<td>1.1 mm / 1.3 mm</td>
<td>0.5 mm / 1.5 mm</td>
</tr>
<tr>
<td>+ zirconisation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc-spraying (85 Zn 15 Al)</td>
<td>None / None</td>
<td>0 mm / 0 mm</td>
<td>0 mm / 0 mm</td>
</tr>
</tbody>
</table>

¹ Density of blisters: 0: None; 5: Dense; Size of blisters: S: small; S: big
² Delamination: remove the loose coating using a knife blade held at an angle, in the manner of an eraser. Determine the overall width, in millimetres, of the zone of delamination (arithmetic mean measured at 6 points). Deduct the width of the original scribe from the average overall width of delamination and divide by 2.
³ Infiltration/corrosion: same procedure as for delamination but now measure the zone of corrosion.