Introduction

Increasing environmental concerns and regulations to limit the use of chromate compounds in the last 25 years have resulted in widespread adoption of non-toxic anti-corrosive pigments in the coating industry to replace chromates in coil and general industrial primers. This trend has recently further accelerated with the introduction of REACH which is expected to eventually lead to a phase-out of Cr(VI) based products in the coatings industry.

To meet these environmental challenges to the industry, Grace developed the SHIELDEX® silica products, a range of highly effective, non-toxic, heavy metal free anti-corrosive ion exchange pigments. SHIELDEX® silica products are based on ion-exchanged amorphous silica and have been developed as a replacement for toxic anti-corrosive pigments like zinc chromate or strontium chromate as well as an alternative for heavy metal containing zinc phosphate based pigments. SHIELDEX® silica products have been successfully used in the marketplace for over 20 years and have an industry-established track record of delivering optimum anti-corrosion performance as a substitute to chromate based products.

The physical and chemical structure of SHIELDEX® ion exchanged porous silicas can be characterised in various ways. For the physical structure, this typically involves the pore size distribution, total porosity and the surface area. The surface chemistry may be characterised by the type and content of metal ion exchanged onto the silica and the resulting acid-base properties.

Changes in the chemistry and morphology of the ion exchanged silica particles can greatly influence the anti-corrosive efficiency of the pigments within a coating, therefore not all ion-exchanged silicas are equal in terms of anti-corrosive performance.

Grace’s core know-how of silica technology has enabled it to develop a new generation of SHIELDEX® ion-exchanged non-toxic anti-corrosive silica pigments, designed to meet the increasing demands for ever more efficient, environmentally friendly anti-corrosive pigments.

The newest edition to the product portfolio is the SHIELDEX® CS311 pigment, which has been designed to offer superior anti-corrosion efficiency and enhanced curing properties compared to existing ion exchanged silicas.

Key Features

SHIELDEX® CS311 silica is suggested for use primarily in coatings applied to galvanized steel and related substrates such as zinc alloy coated steels where the zinc alloy contains low amounts of aluminium or magnesium. Recommended application areas include coil coating primers, general industrial primers and primers for automotive coatings. SHIELDEX® CS311 silica is also suitable for use in single layer coatings applied over metal substrates and in the so-called primer-pretreatment coatings, designed to provide the function of both a primer and a metal pretreatment in a single layer. The use of SHIELDEX® CS311 silica can be particularly beneficial in coatings that cure under acidic conditions or that require acid catalysis to achieve adequate cure (e.g. acrylic and alkyd-melamine coatings). Other examples of successful and ongoing developments include the use of SHIELDEX® CS311 silica in radiation-curing (UV/EB) systems for coil coatings and in powder coating systems for general industrial applications.

Coil Coating Systems

SHIELDEX® ion-exchanged silica pigments have already become established as the leading non-toxic pigments in chrome-free coil coating systems. Essential to this success is their high performance and efficiency in even modern primer/topcoat systems as well as the promising results obtained in more than 10 years in outdoor weathering trials. SHIELDEX® CS311 silica is a next generation product, which further improves both anti-corrosion performance and allows for greater flexibility in the choice of the catalyst package.

Improved anti-corrosion efficiency

Strontium chromate pigments have been the standard benchmark in the coil coating industry in terms of anti-corrosion performance. SHIELDEX® CS311 silica was demonstrated to be an effective Cr(VI)-free alternative which allows the user to obtain similar anti-corrosion performance results to strontium chromate.

Salt spray testing

In salt spray testing, the SHIELDEX® CS311 silica was evaluated at two different addition levels against strontium chromate. Primers were applied over chromium-free pretreated galvanised steel at a dry film thickness of about 5µm and cured to a PMT* of 214-224°C. A polyester coil coating topcoat was subsequently applied at a dry film thickness of about 20µm with a further curing step to a PMT of 224-232°C completing the coating application. Test panels were prepared by introducing a cut edge, a scribe and a region of deformation formed under impact conditions. Salt spray testing was carried out for a period of 1000 hours and the results are displayed at pigment addition levels of 5% by weight (Fig. 1) and 11% by weight (Fig. 2).

SHIELDX® CS311 silica is based on a new ion-exchanged silica pigment technology and offers:
- Superior anti-corrosion efficiency
- Enhanced curing properties

*PMT = Peak Metal Temperature
Fig. 1: 1000 hour salt spray results for a polyester coil coating primer with topcoat, pigmented with either SHIELDEX® CS311 silica or strontium chromate, 5% by weight pigment addition level.

The SHIELDEX® CS311 silica thus shows optimized performances vs. existing SHIELDEX® silica products enabling the user to obtain the same anti-corrosion protection with lower total addition levels.

Curing Properties
The cure properties of the polyester high solids coil coating primer applied to chromium-free pretreated galvanised steel and pigmented with either SHIELDEX® CS311 silica or strontium chromate was evaluated after curing by means of MEK resistance expressed as the number of double rubs needed to remove the coating. Both the MEK resistance after curing of the primer and primer plus topcoat were assessed one day, three weeks, and six weeks after preparation of the wet paint. The results are given in Table 1.

Table 1: The effect of anti-corrosive pigmentation and wet paint ageing on the MEK resistance after curing of a high solids polyester coil coating system (11% addition level of active pigments).

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Storage Time (days)</th>
<th>Primer Only</th>
<th>Primer Topcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>SHIELDEX® CS311 Silica</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>SHIELDEX® C303 Silica</td>
<td></td>
<td>35</td>
<td>32</td>
</tr>
<tr>
<td>Strontium Chromate</td>
<td></td>
<td>65</td>
<td>nd</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td>54</td>
<td>60</td>
</tr>
</tbody>
</table>

SHIELDEX® CS311 pigments can allow the user to potentially achieve raw material savings through the optimizing of their existing primer formulas.

SHIELDEX® CS311 silica provided excellent performance, comparable to that found with strontium chromate. It can also be seen that this performance level was already obtained with an addition level of SHIELDEX® CS311 of only about 5% by weight based on the primer formulation.

The new SHIELDEX® CS311 silica has been also compared to Grace’s existing SHIELDEX® C303 silica in a high-solid polyester-melamine coil coating primer with topcoat on Cr-free pre-treated galvanized steel panels at 1000 hours salt spray testing. As can be observed in Figure 3, panels with an addition rate of 5% by weight and 11% addition by weight of SHIELDEX® CS311 silica demonstrate higher anti-corrosion performance not only compared to panels with 5% addition weight of SHIELDEX® C303 silica, but also compared to panels where SHIELDEX® C303 silica has an 11% addition weight.

The SHIELDEX® CS311 silica thus shows optimized performances vs. existing SHIELDEX® silica products enabling the user to obtain the same anti-corrosion protection with lower total addition levels.
Catalyst Interaction

The SHIELDEX® CS311 pigment was tested for MEK resistance using different types of catalysts to evaluate interaction of the different SHIELDEX® silica products with the selected catalyst. Primers were again applied over chromium-free pretreated galvanised steel at a dry film thickness of about 5µm and cured to a PMT* of 214-224°C. A polyester coil coating topcoat was subsequently applied at a dry film thickness of about 20µm with a further curing step to a PMT* of 224-232°C completing the coating application. Catalysts utilized were Nacure® 5225, Epoxy blocked dodecylbenzene sulphonic acid (EDBSA), Nacure® X49-110, and Nacure® XC194. Tests were conducted at day 1, day 21, day 42 storage time, at temperatures of 20° and 50°C with and without an epoxy blocked phosphoric acid co-catalyst. In Figure 4, average MEK rub resistance averaged over the storage time, effects of co-catalyst and temperature are shown.

While overall differences exist between different catalysts, SHIELDEX® CS311 silica was shown to be suitable for use with any of the catalysts selected.

SHIELDEX® CS311 silica provides enhanced level of curing compared to commercially existing SHIELDEX® silica products using a wide range of catalysts.

SHIELDEX® CS311 silica was also tested to measure the influence on coating cure levels of the presence or absence of an epoxy blocked phosphoric acid co-catalyst (see Fig. 5).

Results indicate that SHIELDEX® CS311 silica can provide excellent levels of cure even without use of a co-catalyst.

SHIELDEX® CS311 silica can allow for simplification and more flexibility in the catalyst package during the curing phase.

Compared to strontium chromate, SHIELDEX® CS311 silica allows for good and stable levels of cure to be obtained.
**Rheological properties**
The viscosity as a function of shear rate of variously pigmented high solids coil coating primers was determined after incorporation of SHIELDEX® CS311 silica by a laboratory beadmill for varying times of dispersion to assess the effect of the intensity of pigment dispersion on the resulting rheological properties comparing these with commercially existing SHIELDEX® C303. Results are shown in Figures 6 and 7.

**Feature Effect Advantage for customer**

- **Outstanding Anti-Corrosion Resistance**
  - Lower A/C pigment addition levels vs. existing IES pigments
  - Comparable A/C performance to SrCr
  - Raw Material cost savings
  - Cr-free alternative to strontium chromate

- **Enhanced Curing Stability**
  - Lower interaction with catalysts
  - Reduced need for synergists
  - Flexibility in choice of catalyst package
  - Simplification of primer formulation

- **Optimal Rheological Properties**
  - Low sensitivity to prolonged dispersion time
  - Good application properties

SHIELDEX® CS311 silica like SHIELDEX® C303 silica is not very sensitive to prolonged dispersion times within the time-scales investigated regarding the viscosity of the final paint. There is a slight increase in the low shear rate viscosity as can be seen in Figure 7, but this rapidly drops off with increasing shear rate allowing good coating application properties.
Research & Development
Technical Customer Service

Grace has assembled a global coatings Technical Customer Service (TCS) group, dedicated to developing worldwide technical partnerships with our customers in the effective use of SHIELDEX® anti-corrosive pigments. The group consists of experienced coatings professionals whose primary objective is to ensure customer satisfaction regarding application and product performance related issues. Working closely with our global sales organisation, the coatings TCS group strives to exceed customer expectations.

The main support activities are:

- Customer consultation through site visits, video-conferencing and other forms of telecommunication.

- TCS projects, which involve Grace application development laboratories, undertaking investigative laboratory work on behalf of the customer, using their defined coating system. This is often performed under secrecy or confidentiality agreements.

The TCS coatings group is centrally managed and regionally based, offering both local knowledge and worldwide support.

Laboratory facilities are available in the following locations:

- USA – Baltimore, MD, supporting North America and Canada
- Germany – Worms, supporting Europe, Middle East and Africa
- Malaysia – Kuantan, supporting Asia-Pacific
- Japan – Atsugi, supporting Asia-Pacific
- China – Shanghai, supporting China
- Brazil – Sorocaba, supporting Latin America

Wherever you are located, you can always expect the same high quality level of technical advice and support, which are a pre-requisite for developing technical cooperation and successful business partnerships in the future.

Grace is a leading global supplier of catalysts; engineered and packaging materials; and, specialty construction chemicals and building materials. The company’s three industry-leading business segments – Grace Catalysts Technologies, Grace Materials Technologies and Grace Construction Products – provide innovative products, technologies and services that enhance the quality of life. Grace employs approximately 6,500 people in over 40 countries.

Grace SHIELDEX® products meet all current REACH requirements.*