Cost reduction and health, safety, and environmental issues are primary drivers of change in the coatings industry today. The users of all kinds of metal products are not only concerned that the products they buy will be long-lasting and the costs of maintenance minimal, but also that the materials used are damaging neither to human health nor the environment. The coatings manufacturer is thus continually faced with the need to provide coatings with ever-greater durability and protective properties to weathering and corrosion processes, without resorting to harmful substances.

Corrosion processes on metal surfaces can have a substantial influence on the economy due to the degradation and damage caused. The exact value of direct corrosion costs is hard to determine, but according to some sources, is estimated to be about 3% of the GDP.* This economic consideration is therefore a highly important aspect of new and improved anticorrosive technology.

The corrosion-inhibitive substances currently used in coatings are for the most part based upon species known to act as corrosion inhibitors for metals in aqueous solutions.1-3 Typical examples are chromates, molybdates, tungstates, vanadates, phosphates, phosphites, polyphosphates, borates, meteorites, nitrites, silicates, ferrites, and nitrothalates as their various metallic salts with polyvalent metals such as zinc, magnesium, calcium, strontium, barium, aluminum, and—more historically—lead. Pigments containing aluminum ions may reflect a salt with the corresponding anion, or may reflect the corresponding anion adsorbed or exchanged onto an alumina substrate. In some cases, multiphase pigments composed of more than one component have been developed. A stochiometric excess of the metallic component is also often employed, implying, for example, in the case of zinc-based compounds, the existence of zinc oxide or zinc hydroxide as a separate phase.

Metal oxides such as red lead and zinc oxide, as well as finely divided metals such as zinc, are widely known to promote the anticorrosive properties of coatings, as are laminar pigments such as micaceous iron oxides and aluminum flake.3 In alternative approaches, organic substances, such as succinic acid derivatives of mercaptobenzothiazole, have been developed as corrosion inhibitors for coatings. Ion-exchanged silicas, particularly those based on calcium ions, are also well known as inhibitive pigments.7

For many years, pigments based on chromate and lead have been regarded as toxic and have now either been replaced with chromate- and lead-free alternatives, or their continued use is coming under increasing scrutiny and regulation. However, many of the chromate- and lead-free alternatives are zinc-based compounds, and these are now also

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being subjected to closer scrutiny. This situation serves, of course, to underline a continued need for research into corrosion control by coatings and the development of effective heavy-metal-free and zinc-free inhibitive pigments as one approach to such corrosion control.

The present article is concerned with ion-exchanged silica (IES) anticorrosive pigments and, in particular, with recent developments in this field. IES pigments were originally developed and introduced in the 1980s9 as nonhazardous, environmentally compliant alternatives to traditional anticorrosive pigments, such as chromates and lead pigments, as well as the existing zinc phosphate anticorrosive pigments. In the intervening period, long-term outdoor exposure data has been obtained and considerable experience in their practical use has been gained.

After describing topical legislation pertaining to hazardous substances used in anticorrosion, such as chromates or Cr(VI) compounds and zinc-containing compounds, this article briefly reviews the nature of existing IES pigments and surveys corrosion control by coatings and inhibitors. This serves as background against which the mechanisms of action of IES pigments are discussed. Finally, new developments in the field of IES pigments are detailed.

**LEGISLATION**

Increasing concerns for the environment are leading to more and more legislative measures, essentially restricting the range of existing materials that can continue to be used. These measures in turn support the technological trend toward more environmentally friendly coating systems and the development of suitable raw materials to formulate these coatings. The pressure on the European coatings industry to introduce VOC-free and environmental health and safety (EHS)-compliant technologies significantly increased with the implementation of the EU VOC legislation which came into effect in 2007 and the ongoing EU chemical legislation, REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals), for which the preregistration phase was completed at the end of 2008.

One target of a common European registration under REACH is to ban all chemicals that may be considered hazardous. In the coatings industry, this amounts to approximately 20% of all chemicals used. As one consequence, alternatives to anticorrosive pigment materials based on Cr(VI) and Zn compounds are under evaluation.

Considering REACH (2008, Annex XIV), the use of Cr(VI)-containing products will be subject to authorization in the near future. Other legislative measures relating to anticorrosive pigments include the ELV or “End of Life Vehicle” directive, which concerned a phase-out of lead pigments from 2003 and of Cr(VI) as a corrosion protection agent in primers and PT from 2007, together with the WEEE & RoHS directives (Waste Electrical and Electronic Equipment Directive, 2006), which restricted the use of Cr(VI) in white goods. Important too is the United States’ Occupational Safety and Health Administration (OSHA) regulation of 2006, which reduces employee permissible exposure limits (PEL) to Cr(VI) from 52 μg/m³ to 5 μg/m³.

Silica-based ion-exchanged pigments are generally regarded as nonhazardous substances and are thus not a matter of concern regarding any of these legislative measures.

**CORROSION CONTROL BY COATINGS AND INHIBITIVE PIGMENTS**

A principal function of any coating system applied to a metal substrate is to provide a barrier to prevent moisture, oxygen, and aggressive ions in the environment from reaching the metal surface and initiating the reactions that lead to corrosion. However, this barrier effect may degrade on aging in a corrosive environment or simply be impaired as a result of mechanical damage to the paint film exposing the underlying metal. In such cases, additional protective mechanisms are needed.

The corrosion-inhibiting properties of coatings have been widely studied, and inhibitive pigments as pigment extracts in aqueous solutions or from within a coating environment have also received considerable attention.10-16 Figure 1 provides a schematic representation of the main features of corrosion as applied to a coating containing an inhibitive pigment.

Water and ions permeate the coating and reach the metal surface, which is itself normally covered by an oxide or a chemical film as a result of surface pretreatment. An electrical potential becomes measurable as the metal surface is gradually wetted. This may reflect a passive state if the local ratio of available passivating to aggressive ions at the interface is high enough, if the available cathodic current is high enough to support passivation and the local pH is greater than the critical pH for passivation,17 where the latter generally increases as the local pH and the ratio of available passivating to aggressive ions at the interface decreases. The available cathodic current will depend, among other factors, on how fast oxygen can diffuse through the coating and other films that may be present at the interface.
Figure 1—The basic effect of anticorrosive coatings and inhibitive pigments in controlling corrosion of a metallic substrate.

Otherwise, and as aggressive ions become available at the metal surface, the manner in which the potential changes during the course of exposure is thought to signify the size of the anode and cathode areas and the electrical resistance existing between the active sites. In general, anode sites will develop at regions of oxide breakdown. The surrounding cathode areas are normally regarded as being larger than the anode area to an extent dependent on the potential drop between anode and cathode, as determined by the electrical resistance. If the local cathode potential is negative enough, hydrogen evolution will also contribute to the cathodic current, depending on the thermodynamic activity of water in the coating.

In this situation, the pigmented coating, which is not normally regarded as being structurally homogeneous, imposes an ionic resistance between developing anode and cathode sites, thereby restricting ionic movement. The inhomogeneity of the coating may arise from the existence of weaker polymer regions interdispersed in a stronger polymer continuum, by the presence of pigments and fillers, and by segregation of polymeric and coating species at surfaces and interfaces.

The ionic resistance, which may be a function of the resistivity of the coating and the electrochemically active area, normally controls the corrosion current under conditions where the coating is still protective to the substrate and adhesion of the coating to the substrate is being maintained. The weaker regions of a coating may grow at the expense of the stronger regions, as the latter degrade due to progressive uptake of water and ions with exposure time and the electrochemically active areas may grow due to the effect of the external environment and the corrosion reaction beneath the coating. The local generation of a high pH under the coating at cathodic sites in the presence of mobile cations such as sodium ions may eventually cause disbondment to occur. This may in turn lead to the appearance of second-generation anodic sites.

In principle, pigments, fillers, and inhibitive pigments could contribute to anticorrosive properties by decreasing the permeability of the coating to oxygen under conditions where the electrical resistance is not high enough to control the corrosion current, by providing for a greater rate of diffusion of hydroxide ions away from the interface, or indeed by contributing to the electrical resistance of the coating through chemical or catalytic interaction with the polymer matrix during formation of the coating film. On the other hand, levels of pigmentation that are too high for a given pigmented polymer matrix may lead to local rupture of the continuous polymer as water is taken up during exposure, with a corresponding reduction in the electrical resistance and an increase in the corrosion current. This might eventually lead to a situation where oxygen reduction becomes rate-controlling.

Where electrochemically active pigments and inhibitors are present, restraint of the anode and cathode reactions over and above that provided by the coating may additionally be possible, whereby inhibitive species are released into the wet coating as a result of processes involving solubility, hydrolysis, and ion-exchange with transportation of those species to the metal surface. The exact manner of transportation is not always clear and may be a difficult process. It is often thought to involve pores in the coating or functional groups of the polymer acting as ion-exchange sites.

Many anions employed in inhibitive pigments are regarded as having anodic inhibition properties. The main function here is to prevent oxide breakdown and to carry out repair of the oxide where breakdown has occurred by insoluble compound formation. This leads to a reduction of the active anode area, but passivation itself is only likely under the restrictive conditions outlined above. Even the most efficient anodic inhibitors, such as lead azelate and chromates, are not capable of maintaining passivation where the concentration of aggressive ions such as chloride ions is greater than about 10−3 M. The solubility of many other pigments is often thought to be too low to enable passivation to take place even in environments that are not too aggressive. In practice, however, the solubility of a pigment may depend on complex formation with species present in the environment or in the coating.

It is also possible to control corrosion by reducing the rate of the cathode reaction. This is normally achieved by formation of films at cathode sites, where the function of the film is to restrict access of oxygen to an electroactive surface for oxygen reduction. This may involve the reduction of chromate to Cr(OH)₃ or, in other cases, involve the formation of insoluble salts such as phosphate,
molybdate, and silicate with zinc or calcium ions due to the prevailing alkaline conditions at the cathode. This mode of action is less likely to be effective under conditions where the electrical resistance of the coating controls the corrosion current and because the coating itself will restrict access of oxygen to the metal surface. The degree of cathodic inhibition imparted by the pigment would have to be greater than that imparted by the coating to result in a beneficial effect.

**REVIEW OF NONTOXIC ION-EXCHANGED SILICAS**

As previously mentioned, environmental concern related to the use of traditional chromate- and lead-based compounds in anticorrosion coating technology resulted in the introduction and use of IES pigments as environmental health and safety-compliant products, especially in the general industrial and coil coatings segment. The principal examples have been calcium IES anticorrosive pigments, which were introduced in the 1980s. This has been a continuous and slow process but has been gaining such momentum in the last few years that IES pigments are currently the leading nontoxic anticorrosive pigments used in chromate-free coil coating systems.

\[ M^{n+}/\text{silica} \]

where \( M^{n+} \) is a metal cation, such as calcium IES anticorrosive pigments, are nontoxic, heavy-metal-free, micronized, amorphous particles of controlled particle size distribution. The density of these pigments is about 1.8 g/cm\(^3\), which is quite low compared to conventional pigments. They also have a moderately alkaline reaction with water as indicated by the pH of an aqueous slurry which lies in the region of 9–10. The manufacturing process involves an ion-exchange reaction at the surface of silica between weakly acidic surface silanol groups and calcium hydroxide, as indicated in Figure 2.

During the manufacturing process, the surface area and porosity of the original silica are reduced, which helps to avoid excessively high oil absorption and pigment activity. For reasons of efficiency in use, the surface area, however, is still maintained at a comparatively high level with other types of inhibitive pigments. Typical surface areas for the standard Ca/silica pigments are around 60 m\(^2\)/g, for example. Calcium ions distribute themselves in the surface layers of the silica particles and the surface of particles can be represented, as in Figure 3, which shows how the calcium ions may be attached to the surface sites.

![Figure 2](image1.png)

**Figure 2**—Diagrammatic representation of the ion-exchange reaction between silica and calcium ions.

![Figure 3](image2.png)

**Figure 3**—Representation of the surface of Ca/silica pigments.

It is worth noting that some coating formulations contain acidic substances, for example, in the form of resins bearing acidic groups or acid catalysts. In these cases, acid-base interactions can lead to viscosity instability or reduced cure rates according to the type of coating and application conditions. In many cases, this can be overcome by adjusting paint formulations with special additives, such as viscosity control additives, nonionic blocking of catalysts, use of co-catalysts, or use of pigments and inhibitive pigments having acidic surface sites.

Regarding the usage of Ca/silica pigments in anticorrosive coatings, it is noteworthy that addition levels are often about one-third to one-half that of conventional anticorrosive pigments in weight. This high efficiency is essentially a consequence of their low density of about 1.8, but also the comparatively high surface area, which affords a large contact area over which inhibitive species may be released during environmental exposure of the pigmented coating. Typical properties of Ca/silica pigments in relation to chromate and phosphate pigments are indicated in Table 1.

In general, when formulating with Ca/silica pigments, or alternatively, when replacing existing anticorrosive pigments with Ca/silica pigments, it

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Density (g/ml)</th>
<th>Oil Absorption (g/100 g)</th>
<th>pH</th>
<th>Surface Area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/SiO(_2)</td>
<td>1.8</td>
<td>60</td>
<td>9-10</td>
<td>60</td>
</tr>
<tr>
<td>SrCrO(_4)</td>
<td>3.6</td>
<td>32</td>
<td>7.5</td>
<td>–</td>
</tr>
<tr>
<td>ZnCrO(_4)</td>
<td>3.5</td>
<td>16</td>
<td>–7</td>
<td>–</td>
</tr>
<tr>
<td>Zn(_2)(PO(_4))(_4)</td>
<td>3.4</td>
<td>20</td>
<td>–7</td>
<td>–</td>
</tr>
</tbody>
</table>
is recommended that addition levels be worked out on a volume basis. However, addition levels expressed in weight on the total formulation for different paint systems often fall into the following ranges, and these can be seen as representing guideline addition levels:

- 1–4 wt% for water-based paints
- 3–6 wt% for solvent-based paints
- 3–9 wt% for reactive primers (e.g., coil coatings)

Three types of IES Ca/silica pigments have traditionally been offered that differ in silica particle morphology, particle size, and metal ion content, as shown in Table 2.

The standard Types A and B are available with average particle sizes of 5 µm and 3 µm, respectively, having a calcium ion content of 6% by weight expressed as a percentage of the total pigment. They are used in all types of solvent-borne and waterborne systems, two-component epoxy and polyurethane coatings, as well as in wash primers. Type C is primarily used in coil coatings but, like the other grades, is effective in most coatings used over galvanized and zinc-alloy coated steels.

As an example of performance, typical results obtained with Type A against zinc potassium chromate after 10 years’ outdoor weathering at an industrial site in a two-pack epoxy and a short-oil alkyd on sand-blasted steel (SA2.5) are shown in Figure 4. Test panels were exposed south facing at an angle of 45°.

The lower half of the panels show the primer-only result, and the top half shows the result for the primer/topcoat system, with the topcoat being a polyurethane or medium-oil alkyd, respectively. Corrosion inhibition at the scribe and adhesion properties are equivalent to the chromate references. Both primer and topcoat were applied to a dry film thickness of 50 µm.

Studies by other authors have confirmed the inhibitive properties of Ca/silica pigments in various types of primers and coatings.

Combinations of IES pigments such as Ca/silica pigments with other inhibitors and anticorrosive pigments, such as organic corrosion inhibitors or phosphate pigments, can provide synergic improvements in anticorrosive performance. Benefits in adhesion and anticorrosion performance of the coating system are also observed in specific instances when Ca/silica pigments are combined with adhesion-promoting substances such as organofunctional silane, titanate, and phosphate esters. Examples of these combinatorial possibilities can be seen in the published and technical literature.

Figure 5 shows the excellent wet adhesion obtainable in a typical wash primer for-

Table 2—A Comparison of Typical Properties of the Different Grades of IES Pigments\(^*\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Type A</th>
<th>Type B</th>
<th>Type C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>White powder</td>
<td>White powder</td>
<td>White powder</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.8</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Oil absorption (g/100 g)</td>
<td>60</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>Calcium content (%)</td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^*\)IES pigments Types A, B, and C are available commercially under the following tradenames: IES Type A = Shieldex AC5; IES Type B = Shieldex AC3; and IES Type C = Shieldex C303. Shieldex is a registered trademark of W.R. Grace & Co.–Conn.

Figure 4—IES Type A vs zinc chromate in a two-pack epoxy and a short-oil alkyd after 10 years of outdoor weathering.

Figure 5—The effect of IES Type B in combination with Silane A187 on wet adhesion of a wash primer formulation with topcoat on aluminum (Al/Mg Alloy) after water soaking at 40°C for 240 hours.
mulation based on polyvinylbutyral, containing a small amount of phosphoric acid, when IES Type B is combined with the epoxy-capped Silane A187 (3-glycidoxypropyltrimethoxy silane).

Exposure conditions were two weeks at 40°C in distilled water, and the top half of the panels were overcoated with an acrylic/isocyanate topcoat at a dry film thickness of 40 µm. The panels were dabbed dry upon removal from the water bath. Crosshatch and sticky tape removal adhesion tests were carried out immediately thereafter. No signs of adhesion loss or blistering were evident in the case of the primer containing both Type B and Silane A187, whether tested as primer only or as a full system with topcoat.

In view of VOC issues, waterborne coatings are currently of great interest. Figure 6 provides an example of IES Type A in combination with a second organic corrosion inhibitor (Alcophor® 827, * a zinc salt of nitrophthalate) in a waterborne alkyd applied over cold-rolled steel. After salt spray testing, significant improvements in scribe adhesion were seen for the combination compared to the individual inhibitors. Underfilm corrosion was evident in the case of the uninhibited coating.

For the purpose of these tests, primers were applied at 40 µm dry film thickness to degreased cold-rolled steel panels, and after seven days of air-drying, submitted to hot salt spray (ASTM B117) for a period of seven days.

Ion-exchanged pigments having a lower calcium content may be desirable to help minimize the basicity of the pigment surface, while at the same time maintaining anticorrosive performance. IES Type C Ca/silica pigment was developed for this purpose. It has an average particle size of 3 µm, but a calcium content of 3%, and offers high performance in coil coatings, powder coatings, and acid-curing systems, particularly on galvanized steels.

Figure 7 refers to electrochemical impedance testing of a polyester primer/topcoat coil coating system applied over Bonder 1303 treated galvanized steel immersed in 3.5% NaCl solution for up to 3000 hr. The primer was pigmented with either strontium chromate, Type C IES, or titanium dioxide serving as a blank. The primer was applied to a dry film thickness of 5–7 µm at a PMT of 216–224°C, the topcoat being applied at 20–22 µm with a PMT of 224–232°C. Impedance values were obtained on unscribed coated metal as a function of frequency over the range 10^3 Hz to 10^6 Hz in a standard three-electrode set-up. The graphs show capacitance and resistance of the working electrode assembly as a function of exposure time.

*Alcophor is a registered trademark of Cognis IP Management GmbH.

**Resydrol is a registered trademark of Cytec Surface Specialties Austria GmbH.

Figure 6—The effect of the combination of Type A with an organic inhibitor in a waterborne alkyd (Resydrol® 436W) on salt spray performance over degreased cold-rolled steel (seven days ASTM B117 at 40 µm).

It can be seen that there is only a slight increase in capacitance of the coatings containing strontium chromate or Type C IES, implying little uptake of water in comparison with the blank, where capacitance changes are substantial. Similarly, the resistance values decrease only slightly for the coatings containing inhibitive pigments compared to the blank, and resistance values above 10^6 ohms.cm² are maintained, implying little breakdown of the coating.

Maintenance of high impedance values for chromate-free coil coatings applied over galvanized steel were also observed by Zin et al. In this case, the authors were concerned with resistance to corrosion at the cut-edge under acid rain conditions, and good levels of inhibition were observed for combinations of ion-exchanged pigments with molybdate/phosphate pigments. Good performance was also observed by Deflorian et al. for coil coatings pigmented with calcium/silica and applied over galvanized steel.

According to one model of impedance of a painted metal system, the measured impedance less the resistance between the paint surface and a reference electrode that would be used in a three-electrode experimental set-up is composed of the capacitance of the intact part of the coating in parallel with the interfacial impedances at the anode and cathode regions, each in series with the coating resistances over the anode and cathode. Normally, the anode interface impedance will be composed of the impedance, due to the anode reaction operating in parallel with the double layer capacitance and, similarly, a double layer capacitance will operate in parallel with the impedance of the cathode reaction. The cathode impedance will, in general, be composed of the hydrogen evolution reaction in parallel with the impedance for oxygen reduction.

If either the anode or cathode has a much higher impedance than the other, the corrosion current will be determined by this higher impedance, but the measured impedance will be that associ-
ated with the lower impedance branch. The model would then reduce to the one commonly used in studies of coated metals where corrosion is considered to occur at the base of pores in the coating or at the base of low resistance regions in the coating.

The interfacial impedances are in general inversely proportional to the active anode area \( a_a \) and cathode area \( a_c \) so that maintenance of the high impedance reflected in Figure 6 can be explained in terms of maintenance of a low defective area, assuming that \( a_a \) and \( a_c \) are mutually exclusive,

\[
a_a + a_c = A_d / A_g
\]

where \( A_d \) is the defective area of the coating and \( A_g \) is the total apparent area of the coating. This in turn implies the operation of some mechanism serving to restrict the growth of electrochemically active areas under the coating.

**MECHANISMS OF ACTION OF ION-EXCHANGE PIGMENTS**

In light of the previous discussion, the mechanism of action by which IES pigments are believed to contribute to the protective function provided by a coating is indicated in Figure 8. This diagram refers to ferrous substrates, although excellent protection is also found over galvanized steel and aluminum substrates, as described.

Briefly, water and aggressive ions permeating the coating encourage release of metal ions and soluble silica as inhibitive species, which diffuse and migrate to the interface, where anode and cathode sites are beginning to develop on the metal surface as a result of ingress of the corrosive environment. At these sites, the inhibitive species form protective films of calcium silicate in the case of Ca/silica pigments and other metal silicate

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Figure 7—Capacitance and resistance of the coating assembly vs immersion time in 3.5% NaCl for coil coatings applied to pretreated galvanized steel.

Figure 8—Diagrammatic representation of the mechanism of action of IES pigments shown for the case of calcium/silica on ferrous substrates.

Environment (containing \( H_2O, O_2 \) and aggressive ions, e.g., \( H^+, \text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-} \))

Coating containing IES Particles

\( Ca_{2+} \)

\( SiO_2^{-/-}\text{Si(OH)}_2^{-/+} \)

\( CaSiO_2 \)

\( SiO_2^{-/-}\text{Si(OH)}_2^{-/+} \text{+CaSiO}_2 \)

\( SiO_2^{-/-}\text{Si(OH)}_2^{-/+} \text{+CaSiO}_2 \)

\( M \rightarrow M^{2+} + 2 e^- \) Anode

\( \text{O}_2 + 2H^+ + 4 e^- \rightarrow 2H_2O \) Cathode

Metal substrate (e.g., Fe, Zn)

Dissolution of silica restricts pH increase at the cathode.

Note: particle sizes of the IES pigment might typically be about 3µm.
compounds according to the nature of the metal being protected, providing anodic and cathodic protection. These processes of film and compound formation result in effective suppression of the corrosion reaction.

The alkaline pH of the pigments and their buffering properties may also contribute to the protective action by preventing the pH of the corrosive environment within the coating and in the vicinity of the interface from becoming too acidic, an aspect that is dependent on both the nature of the coating and the external environment. Similarly, the silica nature of the pigments may further aid anticorrosive properties by reducing pH rises that tend to occur at cathodic sites by reaction with hydroxyl ions formed by the cathodic reaction.

In this description, the meaning of soluble silica might be questioned. Figure 9 displays the molar concentration of silica found to be dissolved in water as a function of pH, following Iler.\(^4\)

It is apparent that there is a background concentration of silica as silicic acid of about 2 \(\text{m moles}\) (corresponding to about 100 ppm), independent of pH in the near neutral to alkaline pH range. As a pH of 9 is approached though (a typical pH found for ion-exchange pigments), increasingly more silica is converted to soluble silicate. Of course, it is important that the solubility does not become too high, since a pigment having high solubility in water can increase the water sensitivity of a coating.

Further evidence for the release and transportation of metal ions and silica species from within a coating environment comes from XPS studies of the interfacial region of coated metals after exposure to aqueous media. Typical results from these studies are shown in Tables 3 and 4, which show the elemental analysis of the metal surface averaged over the depth normally sampled by the XPS method of a few nm’s after removal of the coating containing a calcium/silica pigment and following exposure.

Table 3 refers to the case of a model polystyrene pigmented with a calcium ion-exchanged pigment applied over steel and immersed in either distilled water or 3.5% sodium chloride solution. Figure 9 displays results obtained for an alkyd coating applied over steel, similarly pigmented and exposed to humidity (BS3900) or salt spray (ASTM B117) conditions.

It should be noted that the technique samples an area, typically on the order of 1 cm\(^2\), and the results obtained therefore represent an average over this area. It is evident that increasing amounts of both calcium and silicon are found at the metal surface after exposure, implying an enrichment, the greatest amounts being found after exposure to saline conditions. The decreasing iron signal with increases in the calcium and silicon signal, particularly observed with the polystyrene coating, is indicative of film formation over the metal surface. From the elemental ratios and the averaged nature of the concentrations found, it is difficult to be precise about the actual compounds present, but compound and film formation at the metal surface is believed to involve metal silicates, as mentioned earlier.

Granzio et al.\(^4\) also used XPS to study steel surfaces after exposure to extracts of calcium/silica in 0.5M \(\text{Na}_2\text{SO}_4\) solution, finding evidence for an enrichment at the surface of calcium and silicate species, implying again the formation of
silicate films. Similar conclusions were drawn by Armstrong\(^4^3\) and Romagnoli et al.\(^4^4\).

NEW DEVELOPMENTS IN ION-EXCHANGED PIGMENTS

IES porous silica pigments have a complex structure ultimately composed of small primary particles. The structure of the silica pigments can be varied by controlling the size of the primary particles and the degree and geometry of aggregation and agglomeration of primary and secondary structures within a particle,\(^4^5\) where the final particle size might typically be around 3 µm. The surface chemistry of IES porous silicas can be varied by controlling the type of exchanging metal cation and the percentage conversion with respect to the available silanol group concentration.

Both the physical and chemical structure of IES porous silicas can be characterized in various ways. For the physical structure, this typically involves the pore size distribution, total porosity, and the surface area. Porosity and surface area typically fall in the range of 0.1 to 3 ml/g and 10 m\(^2\)/g to 1000 m\(^2\)/g respectively.\(^4^6^-^4^8\) Figure 10 shows an SEM micrograph of a typical porous silica falling within this range. The surface chemistry may be characterized by the type and content of metal ion exchanged onto the silica and the resulting acid-base properties: metal ions could, for example, be Ca\(^2^+\), Mg\(^2^+\), Sr\(^2^+\) or Ce\(^3^+\)/Ce\(^4^+\).\(^4^9^-^5^0\)

As can be appreciated from the previous discussion concerning the anticorrosive mechanism of action, changes in the chemistry and morphology of the IES particles can greatly influence the anticorrosive efficiency of the pigments within a coating, so it is true to say that not all silicas and IES silicas are equal in terms of anticorrosive performance. Realization of this has resulted in the development of a new generation of ion-exchanged nontoxic anticorrosive silica pigments, developed to meet the increasing demands for ever more efficient, environmentally safe anticorrosive pigments. One particular grade from this development, known as IES Type D, is being commercialized under the name of Shieldex CS311. Typical properties of this grade are given in Table 5.

IES Type D 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 aluminum or magnesium. Recommended application areas include coil coating primers, general industrial primers, and primers for automotive coatings. IES Type D 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 this product 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 IES Type D in radiation-curing (UV/EB) systems for coil coatings and in powder coating systems for general industrial applications.

In addition to the determination of the anticorrosive properties conferred to a coating by IES Type D by means of salt spray testing, the rheological and curing properties of coatings containing this pigment have been evaluated, since they are also important factors in the design of anticorrosive primers. An example is given in the following in which the use of IES Type D in a high-solids acid catalyzed polyester-melamine coil coating primer is described.

Salt Spray Testing

For salt spray testing, the pigment was evaluated at two different addition levels against strontium chromate. Primers were applied over chromium-free pretreated galvanized steel at a dry film thickness of about 5 µm and cured to a PMT of 214–224°C. A polyester coil coating topcoat was subsequently applied at a dry film thickness of about 20 µm, 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 hr and the results are displayed in Figure 11.

It is apparent that IES Type D provided excellent performance comparable to that found with strontium chromate. It can also be seen that there was little benefit to increasing the addition level of IES Type D beyond about 5–6% by weight, based on the primer formulation.

Curing Properties

The cure properties of the polyester high-solids coil coating primer applied to chromium-free pretreated galvanized steel and pigmented with either IES Type D 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 and two weeks after preparation of the wet paint. The results are given in Table 6.

Compared to strontium chromate and the blank, IES Type D clearly allows good and stable levels of cure to be obtained.

RHEOLOGICAL PROPERTIES

The viscosity as a function of shear rate of the variously pigmented high-solids coil coating primers was determined after incorporation of the pigments by a laboratory beadmill for varying times of dispersion to assess the effect of the intensity of pigment dispersion on the resulting rheological properties. These results are shown in Figures 12 and 13.
anticorrosive performance under accelerated testing compared to the established and traditional pigment types, providing motivation to perform longer-term outdoor exposure trials. One particular grade from this development—IES Type D—is being commercialized. It is expected that new developments in IES technology will continue to support high standards of corrosion inhibition in environmentally friendly anticorrosive coating systems.

**SUMMARY AND CONCLUSIONS**

Legislative pressure is driving the trend to more environmental friendly coating systems. It is expected that ion-exchanged silica pigments will be turned to more and more as the preferred nontoxic method of corrosion control in all types of coatings, as the desire to couple high anticorrosive performance with environmental awareness intensifies.

IES pigments have already become established as the leading nontoxic pigments in chromate-free coil coating systems. Essential to this success is their high performance and efficiency in even modern primer/topcoat systems, as well the promising results obtained over more than 10 years of outdoor weathering trials. Ion-exchanged silica technology now has a long track record of successful use in coil coatings as a nontoxic alternative to strontium chromate.

Inhibitive mechanisms of action of these pigments involve the formation of protective films at anode and cathode sites. The effectiveness of this mechanism can, in turn, be influenced by the silica structure, the type of cation, and the proportion of conversion of the available silanol groups existing at the silica surface.

New developments in ion-exchanged silica technology have been shown to provide improved anticorrosive properties under accelerated testing compared to the established and traditional pigment types, providing motivation to perform longer-term outdoor exposure trials. One particular grade from this development—IES Type D—is being commercialized. It is expected that new developments in IES technology will continue to support high standards of corrosion inhibition in environmentally friendly anticorrosive coating systems.

**References**


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