SHIELDEX®
Anti-Corrosive Pigments

Grace Materials Technologies
## SHIELDEX® Anti-Corrosive Pigments

### Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Company</td>
<td>3</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>The Products</td>
<td>4</td>
</tr>
<tr>
<td>Protection Mechanism</td>
<td>5</td>
</tr>
<tr>
<td>Detailed Protection Mechanism</td>
<td></td>
</tr>
<tr>
<td>Research &amp; Development</td>
<td>6</td>
</tr>
<tr>
<td>Technical Customer Service</td>
<td></td>
</tr>
<tr>
<td>Equipment of Application Development Laboratories</td>
<td></td>
</tr>
<tr>
<td>Test Capabilities</td>
<td></td>
</tr>
<tr>
<td>Packaging</td>
<td></td>
</tr>
<tr>
<td>Safety Issues</td>
<td>7</td>
</tr>
<tr>
<td>Total Quality Management</td>
<td></td>
</tr>
<tr>
<td>REACH</td>
<td></td>
</tr>
<tr>
<td>Global Scope</td>
<td></td>
</tr>
</tbody>
</table>

## Grace Product Range

- **SHIELDEX®**: Non-toxic Anti-corrosion Pigments
- **LUDOX®**: Colloidal Silica
- **SYLOID®**: Matting Agents for Coatings
- **SYLOJET®**: Pigments for Ink Jet Coatings
- **SYLOWHITE™**: Titanium Dioxide Extenders for Paints and Printing Inks
- **DURAFILL®**: Special Pigments and Fillers for the Paper and Pulp Industry
- **TRISYL®**: Silica Gel for Refining Edible Oil
- **DARACLAR®**: Beer Stabilizers
- **CRYOSIV®**: Desiccant for Refrigerant Drying
- **PHONOSORB®**: Beaded Adsorbents for Insulating Glass
- **SAFETYSORB®**: Desiccants for the Pharmaceutical and Diagnostic Applications
- **SYLOSIV®**: Molecular Sieve Powder for the Polyurethane Industry
- **SYLOBLANC®/SYLODENT®**: Abrasive and Thickening Agents for the Toothpaste Industry
- **PERKASIL®**: Reinforcing Agents for the Tire and Rubber Industry
- **SYLOBEAD®**: Molecular Sieve
- **SYLOBLOC®**: Antiblocking Agents

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**GRACE®, CRYOSIV®, DARACLAR®, LUDOX®, PHONOSORB®, SAFETYSORB®, SHIELDEX®, SYLOBLANC®, SYLODENT®, SYLOJET®, SYLOWHITE™, TRISYL® and ENRICHING LIVES, EVERYWHERE®** are trademarks, registered in the United States and/or other countries, of W. R. Grace & Co.-Conn.

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The Company

W. R. Grace & Co., one of the world’s leading specialty chemical companies, focused in silica and silica alumina technology.

We produce a wide spectrum of products, based primarily on synthetic amorphous silica gel, colloidal and precipitated silicas, zeolites and chromatographic materials.

Our broad material portfolio has contributed significantly to Grace’s position as a leading global supplier of silica, zeolite adsorbents and catalysts. Our specialty chemicals improve product performance and enhance manufacturing processes within an extensive range of industrial applications.

Our key strengths lie in the development of innovative technologies that improve product quality and application performance. Manufacturing flexibility, our global infrastructure and commitment to close customer relationships ensure a high level of customer satisfaction.

With manufacturing facilities, R&D centers and sales offices worldwide, we are well equipped to meet the challenges of today’s global marketplace. The structure of our business combines the strength of a global organization with the flexibility and adaptability of a regional partner.

With sales offices, marketing, and technical service located in all major countries, we can react swiftly to customers’ requirements.

Safety and environmental stewardship are priority issues for our company. Through the Responsible Care® Program, every Grace facility worldwide fulfills stringent health, safety and environmental requirements.

Material Safety Data Sheets and information regarding the compliance of Grace products with application related regulations are available on request. To ensure a constant high level of product quality, all Grace’s sites are ISO certified and practice Total Quality Management. Tailor-made products, on-time deliveries, expert technical assistance and reliable customer support make Grace the preferred industry supplier.

Introduction

Grace’s silica products have been used successfully for many years as performance enhancing additives for diverse coating applications. The silica material properties meet today’s requirements for highly sophisticated anti-corrosion and other coatings related applications.

Environmental concerns with the use of Cr(VI) compounds in anti-corrosion coatings technology have resulted in the introduction and use of EHS-compliant products.

By offering SHIELDEX® silica products as non-toxic anti-corrosive pigments, Grace enables the coatings manufacturer to meet current and future EHS* requirements.

*EHS = Environment, Health & Safety
The Products

SHIELDEX® anti-corrosive pigments are non-toxic, heavy metal free, micronized particles of controlled particle size distribution.

SHIELDEX® pigments are based on ion-exchanged synthetic amorphous silica and were developed as a replacement for toxic anti-corrosive pigments like red lead, zinc chromate or strontium chromate. SHIELDEX® products are also an alternative for heavy metal containing zinc phosphate based pigments.

SHIELDEX® anti-corrosive pigments are highly effective due to their density of about 1.8g/cm³ and high surface area. They possess neutralizing power due to the basic character of the pigment surface and can be used in a wide variety of resin systems.

High Effectiveness

SHIELDEX® anti-corrosive pigments are highly effective: typical addition levels are only 30%–50% compared to conventional anti-corrosive pigments (based on weight). Due to the low density of SHIELDEX® silica products compared to conventional anti-corrosive pigments, replacement with SHIELDEX® silica products should be done on a volume basis. Lower addition levels based on volume are sufficient for SHIELDEX® pigments as they possess a higher effectiveness due to their lower density compared with other conventional anti-corrosive pigments. Typical addition levels range from 2 – 8 vol. %.

Pigment Volume Concentration

Depending on the addition level of SHIELDEX® anti-corrosive pigments, the ratio of PVC to CPVC of the lacquer might be altered due to the relative high oil absorption level (ca. 60g/100g linseed oil or 116ml/100ml linseed oil), thus influencing the dry film properties.

This is most obvious for high PVC values. Depending on the type of binder, SHIELDEX® pigment products may improve the corrosion resistance and the toughness of the dry film, but like all pigments, it may reduce its flexibility. This can be overcome by adjusting the PVC, changing the filler combination or changing the cross-link density of the resin.

Basicity of SHIELDEX® Pigments

SHIELDEX® pigments exhibit a basic surface characteristic. Along with the neutralizing power this may lead to an increase in viscosity (as is possible for other basic pigments) if resins with acid functional groups are used. When amino-crosslinkers are used, the level of curing might be affected. Acid catalysts may lose some activity due to adsorption onto the SHIELDEX® silica surface during storage. This phenomenon can be controlled easily by suitable adjustment of the formulation. Reduction of the acidity can be achieved by neutralizing with amine compounds: other means of control include the use of non-ionic blocked catalysts or by the use of surface-active dispersing agents.

Grace has developed its new SHIELDEX® CS311 pigment which minimizes acid catalyst interaction during storage. This allows for better curing in acid catalyzed systems as well as providing the user more flexibility in their choice of catalyst package.

Fillers

Regarding fillers or pigments, there are no limitations when formulating with SHIELDEX® pigments. The combination with plate-like fillers like talc or acicular fillers like wollastonite can result in performance benefits. Combinations with other active anti-corrosive pigments are generally possible and may be advantageous in specific cases. For example, a combination of SHIELDEX® pigments with zinc oxide or zinc phosphate leads to a significant improvement of corrosion resistance when using alkyd resins.

SHIELDEX® pigments differ from other commonly used anti-corrosive pigments regarding their physical and chemical behavior, and can require adjustment of the existing formulation.
**Protection Mechanism**

The schematic representation below (Fig. 1) demonstrates how aggressive ions permeate the paint film. The release and subsequent migration of the cations lead to the formation of a protective layer on the surface of the metal substrate.

Thus, the anti-corrosive mechanism is two-fold: adsorption of aggressive ions and the formation of a protective layer on the substrate. Behind this simplistic overview, a complex electrochemical process takes place, which is described in more detail in Fig. 2.

![Schematic of Protection Mechanism](image)

**Detailed Protection Mechanism**

The electrochemical mechanism at the metal interface can be described as a local element. Metallic iron atoms are oxidized to ferrous ions (Fe\(^{2+}\)) \(^1\text{a}\) and can then be further oxidized to ferric ions (Fe\(^{3+}\)) at the anodic corrosion site.

Due to the permeability of the organic coatings to oxygen and water, these are present at the coatings/metal interface where reduction of oxygen to OH\(^-\) ions \(^1\text{b}\) takes place as the cathodic reaction.

Depending on the alkalinity in the coatings, silica can dissolve as silicate ions \(^2\text{a}\). This soluble fraction of the pigment can react with ferric ions \(^3\text{a}\) at the coatings/metal interface. This results in the formation of a protective layer \(^4\text{a}\).

Parallel to this reaction, cations on the silica surface are released \(^2\text{b}\) and – by reaction with the soluble silica \(^3\text{b}\) – can form a silicate film in alkaline regions on the metal surface. This together with the iron silicate helps to reinforce the protective layer by formation of a mixed oxide layer on the metal surface \(^4\text{b}\).

**Environment** (containing moisture H\(_2\)O, oxygen O\(_2\) and aggressive ions e.g. H\(^+\))

Coating containing SHIELDEX® particles

- Fe\(^{2+}\) → Fe\(^{3+}\) + e\(^-\)
- Fe\(^{2+}\) → Fe\(^{2+}\) + 2e\(^-\)

- SiO\(_3^{2-}\) + H\(_2\)O → SiO\(_2\) + 2OH\(^-\)

- 2e\(^-\) + H\(_2\)O + 1/2O\(_2\) → 2OH\(^-\)

**Anode**

- Fe\(^{2+}\) → Fe\(^{3+}\) + e\(^-\)

**Metal Substrate**

e\(^-\)

**Cathode**

- 2e\(^-\) + H\(_2\)O + 1/2O\(_2\) → 2OH\(^-\)
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.

Equipment Application of Development Laboratories

1. coil coating oven
2. UV curing equipment
3. convection ovens
4. drying recorder
5. gloss measurement equipment

Test Capabilities

1. salt spray cabinet (usually run to ASTM B117)
2. humidity cabinet (usually run to DIN 50017)
3. tanks for immersion tests e.g. water, special salt solutions
4. electrochemical test equipment (dc measurements, ac impedance, electrochemical noise, operating on 8 channels)
5. bohlin rheometer
6. coil coating oven
7. facilities for mechanical and physical testing of coatings
8. reaction vessels for preparing pigments and inhibitors
9. various analytical techniques including electron and optical microscopy and elemental determination
10. light scattering particle size measurement
11. measurement of coating film thickness on ferrous and non-ferrous metals

Packaging

We offer a wide range of flexible packaging options for our SHIELDEX® pigment products, including:

- specialised multilayer palletised valve bags
- customized big bag options
- silo trucks for bulk deliveries

The prompt delivery of SHIELDEX® anti-corrosive pigments around the world is assured through our global supply chain.
Safety Issues

Safety is a priority at Grace. SHIELDLEX® anti-corrosive pigments are non-toxic products based on synthetic amorphous silica. For further information our EH&S (Environment, Health & Safety) department are ready to offer assistance.

Total Quality Management

We at Grace are committed to Total Quality Management and to continuously improving our processes. To maintain our high standards, we employ Grace’s Six Sigma® philosophy of process optimization designed to continually investigate and optimize process parameters in order to achieve the highest efficiencies.

Our Six Sigma® program initiative involves the improvement of product consistency, production flexibility and capacity, employing advanced statistical methods and evaluation procedures for the benefit of our customers.

Global Scope

Our sites are all ISO 9001 or 9002 certified. External and internal audits are conducted on a regular basis as an important component of our efforts to improve our capabilities, products and services.

REACH

As a premier specialty chemicals company, it is one of Grace’s utmost priorities to comply with all relevant legislation, including REACH. Therefore, in November of 2008 we undertook extensive efforts to achieve compliance of all our products, substances and formulations. Since the beginning of 2010, our main products, including synthetic amorphous silica, zeolites and synthetic amorphous silicates, are all registered under REACH. Regardless of which product you buy from us in the EU, you can be assured that all necessary steps have been taken to ensure continuous and smooth supply of your products.
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 6,000 people in over 40 countries.

Grace products meet all current REACH requirements.*

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