The Development of Water Based Shop Primers

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International | Marine, Protective, Yacht and Aerospace Coatings | AKZO NOBEL
Shop Primers

• Thin (15-20 μm) coating applied to protect steel during ship construction.
• Applied on a dedicated production line.
• Key requirements:
  – Rapid drying ( < 2 minutes).
  – Compatible with modern cutting, welding and shipbuilding processes.
  – Mechanically strong.
  – Up to 6+ months corrosion protection.
  – Overcoatable with final coating scheme (anticorrosive etc)
• Shop Primer market dominated by organic solvent based zinc silicates.
  – High VOC content (~650g/l)
  – In an estimated shop primer market of 40m litres this gives 30m litres/annum of solvent emissions.
Shop Primers - The Shop Primer line

- Volatile Cabinet
- Automatic Paint Spraying Machines
- Line Controls
- Pre-Heater
- Shot-Blaster
- Air-Knife
- Conveyors
Shop Primers - The Shop Primer line

- Shop primer is used to protect the steel during ship construction.
- Main anticorrosive coating is applied later at ‘block’ stage.

- Steel is also bought in by shipyard pre-coated with shop primer. The shop primer is coated at a ‘trade coater’ using the same procedure.
Shop Primers - Product requirements
Shop Primers - Product requirements

Excellent Anticorrosive Properties

Corrosion – Failure of the Shop Primer
Reducing VOC’s

• Shipyards are under increasing pressure to reduce solvent emissions
  – US EPA issued a ‘Maximum Achievable Control Technology’ rule (MACT) for application of coatings in shipyards (December 1995).
  – EU Solvent Emission Directive (full compliance by October 2007)
  – FE Some countries now looking to reduce VOC’s

• Two options are available to shipyards;
  – Installation of abatement equipment - i.e. burn the solvent emissions
  – Use waterborne coatings
Reducing VOC’s - Abatement option

Thermal Oxidation Abatement
Reducing VOC’s - Abatement option

- ~ €500k installation costs (per line)
- ~ €50k / annum maintenance and running costs.
- Operation uses up natural resources - gas, oil.
- And results in CO$_2$, CO, SO$_x$ emissions to environment.
- For 100K Litres of a typical solvent based Shop Primer ~ 250 tonnes CO$_2$ is emitted into the atmosphere.
Reducing VOC’s – 1st generation water based coatings

• Water based Shop Primers have been available since 1930’s
  – All based on inorganic alkali silicate compounds $\text{SiO}_2 : M_2\text{O}$.
    $(M = \text{Na or K})$

• These coatings provide many of the required shop primer performance attributes, **but have one inherent flaw:**
  – The residual salts that remain on the alkali silicate shop primer causes osmotic blistering when overcoated with anticorrosive.

Immersion of full anticorrosive system in sea water for 1 month
Reducing VOC’s – 1st generation water based coatings

- Osmotic blistering in the anticorrosive scheme was caused by a high water soluble salt content in the traditional alkali silicate binders.

\[ 2 \text{Si-O-K} + \text{Zn}^{2+} \rightarrow \text{Si-O-Zn-O-Si} + \text{KOH} / \text{K}_2\text{CO}_3 \]

- For a coating based on a 3.9 : 1 \( \text{SiO}_2 : \text{K}_2\text{O} \) binder the theoretical water soluble salt content is \~ x10 the recommended maximum salt contamination level for safe overcoating in modern shipbuilding yards.

- These traditional (1st generation) alkali silicate waterbased shop primers were (and still are) unsuitable for the major shop primer market.
Alternative water based technologies

- To avoid the potential for blistering a new binder system was needed.
  - compatible with modern welding, cutting and fairing processes
  - therefore inorganic.

- A range of alternative technologies were assessed:
  - Silicon based binders:
    - Lithium and ammonium silicates
    - Silicate-siliconate hybrids (patented)
    - Silica sols → Low soluble salt content but poor film properties
  - Inorganic binders:
  - Alternatives to shop primers concept
    - Chemical pre-treatments
Alternative water based technologies

The higher the salt content, the increased likelihood of osmotic blistering.
Alternative water based technologies

- Zinc containing silica sol based coatings have a very low soluble salt content.
- However the film properties (hardness, early water resistance) are poor.  
  - This leads to increased blistering susceptibility.
- A route to improve coating film properties was needed.
- If the size of the sol is reduced (<10nm) and the coating exposed to humid conditions (50%+) excellent film properties can be achieved.
- The film properties improve via the "Gel Reinforcement Mechanism"
‘Gel Reinforcement’ Mechanism

- Process a variant on technology used for silica gel reinforcement

In the can
Stabilised colloidal dispersion of silica in water

Immediately after application and drying
Strong attraction between spherical silica particles

Gel reinforcement by contact with humidity
3 dimensional silicate network
Alternative water based technologies

- Reducing the sol size produced coatings with excellent film properties.

- However <10nm sols leads to a short pot life (<30 minutes).
  - $Zn^{2+}$ ions destabilise the silica sol

- Modification to the surface of the sol with alumina ions improved pot life.
  - Alumina modified sols have improved stability to metal ions.

- Alumina modified 7nm sols allows a pot life of approximately 4hrs. Further developments will see this extended.
2nd generation water based shop primers

- 2nd generation water based shop primers have been developed using the silica sol technology.

- Protected by 5 patents and overcomes the limitations of 1st generation coatings based on alkali silicate binders.

- Comprises a novel silica sol with a much higher SiO$_2$:$K_2$O mole ratio (>45:1) than 1st generation products.

- The theoretical water soluble salt content for this new binder system is significantly lower and safe for overcoating and immersion.
# 2nd generation water based shop primers

<table>
<thead>
<tr>
<th>Attribute</th>
<th>2nd generation WB SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC</td>
<td>Zero</td>
</tr>
<tr>
<td>Volume Solids</td>
<td>36%</td>
</tr>
<tr>
<td>Pot Life</td>
<td>4 hrs</td>
</tr>
<tr>
<td>Application</td>
<td>Standard Airless Spray</td>
</tr>
<tr>
<td>Drying characteristics</td>
<td>&lt;2mins (~solvent based)</td>
</tr>
<tr>
<td>H&amp;S position</td>
<td>All materials registered</td>
</tr>
<tr>
<td></td>
<td>- EINECS (Europe)</td>
</tr>
<tr>
<td></td>
<td>- TSCA (US)</td>
</tr>
<tr>
<td></td>
<td>No known H&amp;S issues</td>
</tr>
</tbody>
</table>

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# 2nd generation water based shop primers

<table>
<thead>
<tr>
<th>Generic Type</th>
<th>VOC g/l</th>
<th>Protection (months)</th>
<th>Weldability (solid wire)</th>
<th>Cutability</th>
<th>Heat resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc ethyl silicate</td>
<td>609</td>
<td>18</td>
<td>Fair</td>
<td>Fair</td>
<td>N/A</td>
</tr>
<tr>
<td>Weldable and heat resistant zinc silicate</td>
<td>628</td>
<td>6</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Very Good</td>
</tr>
<tr>
<td>High speed weldable and heat resistant zinc silicate</td>
<td>636</td>
<td>&gt;12</td>
<td>Very Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>2nd generation WB SP based silica sol binder</td>
<td>0</td>
<td>&gt;6</td>
<td>Very Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
2nd generation water based shop primers - Application
2nd generation water based shop primers – Cut-ability

Excellent air plasma cutting
2nd generation water based shop primers - Weldability

Excellent one sided butt welding

Upper side

Under side
2nd generation water based shop primers - Weldability

Compatible with typical fabrication processes
Anticorrosive Performance

2nd generation WB SP @ 15 μm DFT

Front Back

Front Back

12 months in Geoje, Korea

After heating to 800°C

6 months in Felling, UK

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Anticorrosive performance - Overcoating Compatibility

- 2nd generation WB SP can be directly overcoated with anticorrosive system:

  - Alkali Silicate 1 months immersion
  - 2nd generation WB SP 12 months immersion
  - Solvent Based Shop Primer 12 months immersion
Eco Efficiency Analysis

- Eco Efficiency Analysis assesses the cost structure and ecological impact of competing products and processes from a value chain perspective.

- Analysis was carried out with and without abatement costs
### Eco Efficiency Analysis – Comparative system costs

#### System costs/m²

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Raw materials</th>
<th>Manufacturing</th>
<th>Margin</th>
<th>Coating including abatement costs</th>
<th>OEM</th>
<th>Use</th>
<th>Disposal</th>
<th>Total costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weldable &amp; Heat resistant zinc silicate</td>
<td>1.17</td>
<td>1.35</td>
<td>x</td>
<td>0.19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.71 + x</td>
</tr>
<tr>
<td>High Speed Weldable &amp; Heat resistant zinc silicate</td>
<td>2.03</td>
<td>1.13</td>
<td>x</td>
<td>0.19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.35 + x</td>
</tr>
<tr>
<td>Competitors Weldable &amp; Heat resistant zinc silicate</td>
<td>1.17</td>
<td>1.35</td>
<td>x</td>
<td>0.19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.71 + x</td>
</tr>
<tr>
<td>2nd gen Water based SP based on silica sol binder</td>
<td>1</td>
<td>1</td>
<td>x</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2 + x</td>
</tr>
</tbody>
</table>

**Costs (normalized)**

Mean: 2.69 corresponds to 1

1.4

1.0

0.6
Eco Efficiency Analysis – Ecological impact

- Ecological impact was more challenging

- 6 ecological dimensions were used;
  - Energy use
  - Material use
  - Toxicity
  - Hazard potential
  - Emissions to air, water and land
  - Land use or biodiversity
## Eco Efficiency Analysis – e.g. Toxicity dimension

<table>
<thead>
<tr>
<th>Grams/functional unit</th>
<th>W &amp; H ZnSi</th>
<th>HS W &amp; H Zn Si</th>
<th>Competitors W &amp; H ZnSi</th>
<th>2nd gen WB Zn SP based on silica sol binder</th>
<th>Toxicity Potential Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent 1</td>
<td>0</td>
<td>6.07</td>
<td>10.21</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Solvent 2</td>
<td>25.86</td>
<td>15.22</td>
<td>48.61</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Raw Material 1</td>
<td>0</td>
<td>0.29</td>
<td>0</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Solvent 3</td>
<td>0</td>
<td>8.99</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>Solvent 4</td>
<td>0</td>
<td>14.42</td>
<td>0</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Raw Material 2</td>
<td>13.05</td>
<td>8.11</td>
<td>8.66</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Solvent 5</td>
<td>8.29</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>Solvent 6</td>
<td>0</td>
<td>0</td>
<td>11.86</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Total</td>
<td>2480.6</td>
<td>3151.3</td>
<td>3788.2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

### Indicators (normalized)
- Max: 3788.2 corresponds to 1

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### Eco Efficiency Analysis – Ecological impact

<table>
<thead>
<tr>
<th></th>
<th>W &amp; H ZnSi</th>
<th>HS W &amp; H Zn Si</th>
<th>Competitors W &amp; H ZnSi</th>
<th>2nd gen WB SP based on silica sol binder</th>
<th>Calculation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions (waste)</td>
<td>0.47</td>
<td>0.74</td>
<td>0.67</td>
<td>1.00</td>
<td>10%</td>
</tr>
<tr>
<td>Emissions (POCP)</td>
<td>0.41</td>
<td>0.69</td>
<td>1</td>
<td>0.00</td>
<td>0%</td>
</tr>
<tr>
<td>Material</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0%</td>
</tr>
<tr>
<td>Energy</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>15%</td>
</tr>
<tr>
<td>Toxicity</td>
<td>0.65</td>
<td>0.83</td>
<td>1</td>
<td>0.00</td>
<td>60%</td>
</tr>
<tr>
<td>Hazard</td>
<td>0.65</td>
<td>0.57</td>
<td>1</td>
<td>0.00</td>
<td>15%</td>
</tr>
<tr>
<td>Land use</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0%</td>
</tr>
<tr>
<td>Total</td>
<td><strong>0.69</strong></td>
<td><strong>0.81</strong></td>
<td><strong>0.97</strong></td>
<td><strong>0.10</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Environmental Footprint (normalised)**

**Mean: 0.65 corresponds to 1**

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Eco-Efficiency Analysis

- Ecological impact and systems costs

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Weldable and heat resistant zinc silicate</td>
</tr>
<tr>
<td>2.</td>
<td>High speed weldable and heat resistant zinc silicate</td>
</tr>
<tr>
<td>3.</td>
<td>Competitor solvent based weldable and heat resistant zinc silicate</td>
</tr>
<tr>
<td>4.</td>
<td>2nd generation WB SP based on silica sol binder</td>
</tr>
</tbody>
</table>

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Summary

- Shop primers are used to protect steel during ship construction
- Thin film which can be left on as part of final anticorrosive system
- Shop primers are low volume solids
- Solvent based shop primers are very high VOC
- 1st generation (alkali silicate) water based shop primers were not compatible with modern shipyard requirements
- 2nd generation of products using patented silica sol technology solves residual soluble salt problem
- Performance of 2nd generation water based shop primer is equivalent to solvent based shop primers
- Compatibility with shipyard practises
- The product is also IMO PSPC compliant!!! (DNV B1)