Passivation is defined in MIL-STD-753 as a “...final treatment/cleaning process used to remove free iron or other anodic contaminants from the surfaces of corrosion-resistant steel parts such that uniform formation of a passive surface is obtained. This treatment induces a more noble (cathodic) potential onto the part, thus enhancing corrosion resistance.”

Stainless steel’s ability to resist corrosion is attributable to the formation of an insoluble, relatively unreactive chromium oxide-hydroxide enriched passive surface film that forms naturally in the presence of oxygen (self passivation).

The passive oxide layer can vary in thickness from a natural minimum of approximately 0.5 nm (5 Angstroms) to about 5.0 nm (50 Å) — i.e., approximately a one-molecule layer to tens of molecules in thickness. Ideally, the film is uniform, non-porous, and self-healing with the maximum chromium-to-iron ratio (Cr/Fe) possible to optimize corrosion protection.

Process Purpose
Stainless steel is rarely encountered under ideal conditions. Usually potentially corrosive surface impurities or contaminants as well as significant variations in the Cr/Fe ratio and passive film thickness are found. Consequently, industry has adopted the general practice of cleaning and passivating 316L stainless steel parts before placing them into service.

Thus, the purpose of cleaning and passivating is to:
• Provide a clean, non-rusting stainless steel surface.
• Optimize corrosion resistance by removal of surface contaminants — primarily iron, but also sodium, calcium, sulfate, phosphate, chloride, and other anodic impurities resulting from exposure to the environment and from processing.
• Maximize the Cr/Fe ratio in the protective oxide film.

The composition of 316L stainless steel listed in Figure 1 shows the chromium concentration to be 16 to 18 percent and iron at 61 to 69 percent. In the bulk alloy, the chromium concentration divided by the ion concentration — i.e., the Cr/Fe ratio — would typically be around 0.25.

As shown in the Figure 1 hypothetical cross section, a variety of contaminants are present in the top 10 Å. The chromium-enriched passive layers extend down to approximately 35 Å and the bulk alloy is reached at about 50 Å.

Auger Electron Spectroscopy
Only recently, with the development and application of Auger Electron Spectroscopy (AES) and Electron Spectroscopy for Chemical Analysis (ESCA), have the necessary analytical tools been available to characterize the elemental composition — including low levels of surface contaminants — and depth profile of the very thin passive layer.

With AES, a beam of electrons focused at the surface elicits the emission of Auger electrons that are then detected
and quantified for the elements of interest. By using an argon ion beam to sputter away metal, a quantitative depth profile at ~5 to 10 Å increments for these elements is obtained. In this way, the Cr/Fe ratio as a function of depth is calculated and plotted for an accurate picture of passivation process effectiveness.

The greater the numerical value of the Cr/Fe ratio, the more effective the removal of “rustable” iron and the more effective the passivation. A Cr/Fe value of 1.0 is considered minimal and 1.5 (or greater) the goal.

**Mechanical Polishing**

The purpose of mechanical polishing is to smooth a metal’s surface. It does not remove surface contaminants nor does it remove free iron to enhance the Cr/Fe ratio. The surface Cr/Fe ratio of mechanically-polished stainless steel has been found to be in the range of 0.25 to 0.4.

Precautions must be taken to ensure that any polishing grit (such as aluminum oxide or silicon carbide) is not embedded into and below the surface of the metal where it remains as a potential nucleation site for subsequent corrosion.

**Electropolishing**

The electropolishing (EP) process electromechanically removes metal (from 0.1 mil to 2.5 mils of surface) preferentially from the peaks or high points, thus smoothing or polishing the surface (see Figure 2).

EP can also remove carbon, free iron, and other surface contaminants. However, if specialized post-EP treatment is not performed, a film of strongly adherent and potentially corrosive phosphate salts may be left on the surface. Based on extensive testing and literature data, the chromium enrichment achieved by EP has typically resulted in a Cr/Fe ratio in the range of 0.4 to 1.0 or better. Additional treatment by chelant methods has always improved the Cr/Fe ratio while enhancing removal of residue contaminants.

**Mineral Acids**

Historically, mineral acids such as nitric acids per the ASTM A380 or QQP-35 procedures have been employed to passivate stainless steel. Nitric acid is described by the *Fire Protection Guide on Hazardous Materials* as a fuming, susflocating, and corrosive liquid.

Nitric acid fumes are very toxic and the liquid causes severe tissue burns. Thus, the exposure limit for nitric acid fumes is extremely low; the Time Weighted Average (TWA) is 2 ppm and...
the Short Term Exposure Limit (STEL) is 4 ppm. TWA and STEL are designations per the American Conference of Government Industrial Hygienists.

Nitric acid leaked or accidentally discharged during passivation and contacting either personnel or equipment can have very serious consequences.

**Chelant Passivation**

By contrast, chelants are safe, nontoxic (no Threshold Limit Values have been established), biodegradable, less corrosive, and much easier to handle and dispose of. The spent chelant passivation solution is normally approved for discharge directly into the local sanitary sewer system.

Chelating agents have been widely used for cleaning and passivating carbon steels and stainless steel for more than 30 years. Most recently, because of government concerns, safer and more effective chelant methods have been widely accepted by the pharmaceutical, cogeneration, and tubing manufacturing industries, among others.

Commonly used chelants are polyfunctional organic carboxylic acids, such as EDTA and citric acid, with salts containing hydroxyl and amine substituents.

The chelant’s acidic action increases the preferential dissolution of the unwanted material, while the strong complexing or sequestering action retains the “bad actors” in solution for subsequent removal and safe disposal. The reactive sites present on the chelating agents bond very strongly to the reactive site of the unwanted ion to form very stable and water-soluble structures.

**Results and Discussion**

The AES depth profile data for the chelant processes compared to EP, nitric acid, and mechanical polishing treatment of 316L stainless steel are plotted in Figure 3 and presented in Tables 1 and 2. It is readily apparent that the chelant procedure gave significantly greater chromium enrichment at the surface and higher values at the peak depth.

Based on the data in Table 2B, the lower Cr/Fe surface values for the EP technique may be indicative of the strongly adherent surface contaminants such as the previously mentioned phosphate or sulfate salts, which are significantly reduced by chelant passivation. ESCA data in Table 2C show significant improvement by the chelant process.

For precision-polished flow control components to be used in corrosive environments, both effective passivation and retention of surface finish are critical. Figure 4 presents one typical Auger Cr/Fe ratio depth profile for a precision-lapped valve part that was mechanically polished followed by chelant passivation. Inset beneath the curve is a summary of the profilometer data obtained before and after passivation. A Cr/Fe peak value of 1.55 was achieved with no finish degradation.

Experience has shown that passivation results in terms of Cr/Fe ratios can vary depending on the stainless steel supplier, heat treatment, milling operations, surface smoothness, grain size, minor variations in elemental composition, and other factors. However, chelant passivation is consistent with providing the cleanest surfaces while routinely approaching or exceeding the target Cr/Fe ratio of 1.5.

**About the Authors**

Kenneth B. Balmer, founder and president of Cal-Chem Corp. (South El Monte, CA), has been a leader in the development of technology for precision cleaning and passivation for the pharmaceutical, biotechnology, food, aerospace, power, and other industries. Martin Larter is the lead chemist in Cal-Chem’s R&D laboratories.

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**Table 1**

<table>
<thead>
<tr>
<th>PASSIVATION PROCESS</th>
<th>SURFACE</th>
<th>IMPROVEMENT (%) BY CHELANT</th>
<th>PEAK</th>
<th>IMPROVEMENT (%) BY CHELANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electropolished (EP)</td>
<td>0.50</td>
<td>176</td>
<td>0.85</td>
<td>95.3</td>
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<tr>
<td>EP Plus Phosphoric Acid</td>
<td>0.89</td>
<td>55.1</td>
<td>1.14</td>
<td>45.6</td>
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<tr>
<td>EP Plus Nitric Acid (70°F)</td>
<td>0.81</td>
<td>67.9</td>
<td>1.24</td>
<td>33.9</td>
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<tr>
<td>EP Plus Nitric Acid (140°F)</td>
<td>0.79</td>
<td>72.2</td>
<td>1.06</td>
<td>56.6</td>
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<tr>
<td>EP Plus Chelant</td>
<td>1.38</td>
<td>—</td>
<td>1.43</td>
<td>—</td>
</tr>
<tr>
<td>EP Plus Chelant</td>
<td>1.36</td>
<td>—</td>
<td>1.66</td>
<td>—</td>
</tr>
<tr>
<td>180 Grit Mechanically</td>
<td>0.43</td>
<td>428</td>
<td>0.43</td>
<td>428</td>
</tr>
<tr>
<td>Polished (MP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP Plus Chelant</td>
<td>2.27</td>
<td>—</td>
<td>2.27</td>
<td>—</td>
</tr>
<tr>
<td>MP Plus Chelant</td>
<td>1.8</td>
<td>—</td>
<td>2.0</td>
<td>—</td>
</tr>
<tr>
<td>Heat-Affected Zone of Weld</td>
<td>0.27</td>
<td>270</td>
<td>0.85</td>
<td>17.6</td>
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<tr>
<td>with EP (HAZ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAZ of Weld with</td>
<td>1.0</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>EP Plus Chelant</td>
<td></td>
<td></td>
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<td></td>
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</table>

**Table 2**

**A. Auger Cr/Fe Ratio by Depth Profile Technique**

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>SURFACE</th>
<th>MAXIMUM</th>
<th>SURFACE</th>
<th>MAXIMUM</th>
<th>PERCENTAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35</td>
<td>1.5</td>
<td>1.2</td>
<td>1.6</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>0.85</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>60</td>
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<tr>
<td>3</td>
<td>1.7</td>
<td>2.1</td>
<td>1.8</td>
<td>2.7</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>N/A</td>
<td>1.5</td>
<td>N/A</td>
<td>2.1</td>
<td>45</td>
</tr>
</tbody>
</table>

**B. Auger Surface Contaminants (Approximate Atomic %) by Surface Survey Technique**

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>PHOSPHOROUS</th>
<th>SULFUR</th>
<th>PHOSPHOROUS</th>
<th>SULFUR</th>
<th>PHOSPHOROUS</th>
<th>SULFUR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>86</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>0.3</td>
<td>0.4</td>
<td>0.2</td>
<td>84</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>0.5</td>
<td>0.8</td>
<td>0.5</td>
<td>75</td>
<td>—</td>
</tr>
</tbody>
</table>

**C. ESCA Cr/Fe and Oxide Ratios**

<table>
<thead>
<tr>
<th></th>
<th>ELECTROPOLISHED ALONE</th>
<th>ELECTROPOLISHED PLUS CHELANT</th>
<th>IMPROVEMENT (%) BY CHELANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr/Fe</td>
<td>1.6, 1.9</td>
<td>4.0</td>
<td>120</td>
</tr>
<tr>
<td>Cr Oxide/Fe Oxide</td>
<td>3.5, 3.8</td>
<td>7.9</td>
<td>120</td>
</tr>
</tbody>
</table>