

CURRENT METHODOLOGIES & CHEMISTRIES UTILIZED IN EFFECTIVE PASSIVATION PROCEDURES

by

Daryl Roll

Pharmaceutical Division Manager
Astro Pak Corporation

INTRODUCTION TO PASSIVATION THEORY

Chemical cleaning and passivation treatments on stainless steel tubing and equipment are an important aspect in the preparation of surfaces used in corrosive and critical environments. The formation of a higher chromium to iron (Cr/Fe) ratio in the passive layer will result in improved corrosion resistance and lowered rates of iron oxide formation (rouge). Clean process and transfer system surfaces are required to maintain purity of processes and products. A corrosion resistant surface insures continuous fluid quality with a lack of impurities generated at the stainless steel surface.

The importance of chemical cleaning and passivation of stainless steel has been documented by others in past publications.^{1,2} The formation of an inert surface is the goal for passivation techniques. Comparative results of various combined chelant processes in addition to nitric acid and electropolished surfaces will be presented. Stainless steel surfaces were treated and then tested with Electron Spectroscopy for Chemical Analysis ("ESCA") and Auger Electron Spectroscopy ("AES") procedures to determine improvements in surface chemistry.

Passivation results from the formation of a chemically inert surface, which maximizes corrosion resistance. The anodic oxide/hydroxide film is very thin (10 to 50 Angstroms "Å") and high in chromium oxide. Removal of contaminants is critical to the life of the passive layer and the reduction of corrosion. Thus, the benefits of the passivated surface are the increased corrosion protection and contaminant free surface leading to improved system life and purity of process fluids. There exist many physical parameters important in the measurement of a corrosion resistant surface including: surface area (roughness), oxide layer depth, chromium to iron ratio and surface contaminant inclusions. Periodic system inspections and performance of precision cleaning and passivation are required to insure maintenance of the passive layer.

Initial passivation of stainless systems is dictated by a need to repair the activated areas of all welds, as shown by recent research,³ and the need to insure an improved corrosion resistant surface throughout the system. Chemical cleaning and

passivation removes the adsorbed and included contaminants that provide sites for pitting corrosion as well as iron, which will evolve into rouge formation.

The oxygen concentration is highest near the surface and is vital to an effective passive layer. The measurement of the oxide thickness is important in the evaluation of the quality of the passive layer. The chromium content peaks in the 10 to 20 Å depth and is critical to the corrosion resistance of the surface. The iron concentration increases from the surface through the metal phase to the base or bulk alloy. Migration of iron toward the surface is a natural process and one of the sources of iron for the formation of rouge.

PHARMACEUTICAL MANUFACTURING APPLICATIONS

Critical water, product and process piping systems are candidates for chemical passivation of the tubing transfer and storage systems. Rouge will form and corrosion will occur under the conditions of use in typical Water for Injection ("WFI"), Reverse Osmosis ("RO"), Distilled Water ("DI"), Clean Steam ("CS"), Clean in Place ("CIP") and process piping systems. All of these systems are subject to precise quality controls and passivation requirements. This corrosion problem is intensified in systems using high temperatures, aggressive process chemicals and ultra pure water.

Operational conditions often lead to the formation of rouge deposits on the surface and will continue to self catalyze and attack into the base metal phase. This will begin to contaminate the process fluids with corrosion products (iron oxide, aluminum oxide and silicates). Surface smoothness degradation will escalate as corrosion increases. Proper chemical cleaning and passivation processes can complete the removal of these deposits, restoration of the passive surface.

Austenitic stainless steels are the most common utilized materials in the critical process applications. An analysis or compositional chart lists the minor components commonly found in the internal phase of the AISI 300 series and include carbon, manganese, phosphorus, sulfur and silicon.

Carbon delivers stabilization of the liquid melt and the formation of austenite. Carbon can form chromium carbides, which cause a chromium depletion zone nearby.

Manganese is a strong carbide and sulfide former which helps to eliminate chromium carbides and graphite formation.

Manganese and chromium both form carbides in weldment zones.

Phosphorus and sulfur stimulate carbide formation; however, they can both form sulfide inclusions on the surface.

Silicon is a graphite stabilizer but is neutralized by Manganese.

Aluminum is often found in trace amounts to reduce porosity and increase strength, but forms inclusions which result in pitting corrosion.

Stainless steel chemical concentrations change from the internal phase or bulk alloy, which is generally the specified alloy composition, up to the metal phase area (between 200 and 50 Angstroms below the surface), which is higher in chromium, molybdenum and nickel. The final surface, or passive layer (from 50 Å to the surface), consists of hydrolyzed or oxidized compounds high in chromium, carbon and oxygen, and is also lower in iron and nickel. The increased concentration of nickel and molybdenum in the metal phase stabilizes the high chromium oxide in the passive layer. The aluminum and sulfide inclusions are often found in the passive layer and require removal or will generate sites of pitting corrosion. These inclusions and contaminants are found in most stainless steels, since the source of base metal is recycled materials containing trace metals.

PASSIVATION - THE PROCESS

Surface cleanliness is important to product purity and passivation processing.⁴ Clean stainless steel surfaces during start-up of newly constructed systems are critical for the purity of products and processes. The following requirements can assure a clean and passive surface:

- The surfaces need to be free of oil, marks and organic films. The degreasing of the system can be completed with an alkaline detergent solution and tested with the water break test as described in ASTM A-380.
- All surfaces need to be free of iron contamination and inclusions. Removal of free iron and iron compounds can be accomplished with the use of passivation solutions. The inclusions will require special treatment, or the use of chelants. The Ferroxyl test (ASTM A-380) is very sensitive at identifying free iron on the surface.
- Secure closure of all openings after cleanliness is attained. Ensure there is an absence of non-compatible metal components in the system and no dead legs present.
- Welding is to be free of significant heat tint and smeared layers from wire brushing. Compliance to be verified with borescope and visual inspection for all of the above requirements.⁵

The chemical passivation process can be performed by many techniques including the use of mineral acids or citric-based chelant systems. Nitric acid and other mineral acids are effective on removal of iron; however, they will not remove many of the inclusions or other surface metal contaminants.

Citric acid together with other chelants dissolves surface contaminants and iron compounds. They also continue to keep the dissolved ion attached to the chelant so that precipitation or deposition of the contaminant will not occur, allowing complete flushing of the contaminants from the system with rinse waters. These chelants are generally of similar chemical structure and contain multiple acid groups, which are subject to pH and ionic strength effects. They can be effective on different compounds under various conditions. EDTA (Ethylene diamine tetra acetic acid) is another example of a chelant that can be utilized under various conditions to specifically dissolve and remove certain metal and non-metal contaminants particularly aluminum, sulfides, calcium, manganese silica, carbon and silt).

A series of studies were performed to establish optimum techniques in the chelant passivation treatment of electropolished and non-electropolished surfaces. Citric acid and a series of chelants can be used to dissolve the iron, residual metal and organic contaminants. The mineral acids dissolve the iron and then the ions are free to precipitate if conditions change. ESCA results of the chromium to iron ratio (Cr/Fe) for various test conditions on 316L samples are listed in Figure 1.

Electropolishing is an electrochemical process, which removes surface material to produce a smoother passivated and corrosion resistant oxide film. It removes hydrocarbon contaminants and flattens the morphology of the surface by removing the peaks, cracks and crevices. This process removes contaminants, stress and strain that often result in pitting and stress corrosion.⁵

Electropolishing yields a surface condition with a carbon level of 40 to 50% atomic percent. The Cr/Fe ratio is generally between 1.3 and 1.6, an oxide layer depth of 15 to 25 Å and an improved smoothness. The surface smoothness can be improved by a factor of 2. The Cr/Fe for the surface is increased with chemical passivation techniques.

WELDING AND THE HEAT AFFECTED ZONE

The welding process will generate a significant change in the chemistry of the surface elements from the weld bead area through the heat-affected zone. The corrosion resistance is dramatically reduced throughout most of the weld area. Recent studies show the chromium concentration is less than 10% in the weld bead area and less than 15% in the HAZ (Heat Affected Zone).³ With the resultant Cr/Fe ratios less than 1, these areas will generate iron oxide rouge under nearly all conditions. The low chromium content of the weldment area is present with a higher concentration of

manganese, peaking at the heat tint band. These areas have been reported as susceptible areas for corrosion. This presents a significant reason for post weld passivation.

The formation of oxides and heat tint compounds were found to depths below 100 Å. Passivation processes are generally considered to affect a depth of only 50 Å and are relatively transparent. This indicates that passivation processes alone will not remove the heat tint discoloration. Therefore heat tint may still be present after passivation, even though the surface will contain a passive layer and be corrosion resistant.

Citric chelant passivation treatments resulted in the restoration of uniform chromium enriched passive layer with a chromium to iron ratio of approximately 2.0. This meets typical industrial specifications for the establishment of a corrosion resistant passive layer. After the chelant passivation treatment, the chromium concentration is generally 20 atomic percent and an iron concentration of approximately 10 atomic percent.³

EVALUATIONS, RESULTS AND COMPARISONS

Performance evaluation and quality control techniques are a vital part of the passivation process. The monitoring of the chemical passivation process is provided through the use of a spectrophotometer for the evaluation of the iron removal rate. This is the common verification technique used in field operations to determine the establishment of a passive layer with the removal of iron. The FerroxyI test (ASTM A-380) is a second requirement for the establishment of the verification of free iron removal from the surface. Conductivity of the rinse fluids is monitored for determination of effective flushing and removal of all residual chemicals. AES and ESCA quality control testing of representative samples may also be utilized in new facility construction projects and passivation process analysis.

Compliance requirements and procedural verification are critical in the performance of chemical treatments in the high technology and industries falling under federal regulations. The certification and validation package for passivation processes is of special importance. It should contain specific procedural documentation, certificate of passivation and acceptance, quality control testing logs, chemical batch records, certificates of chemical analysis and a detailed scope of included systems and designations of treated equipment.

The material performance and quality can be measured with the analysis techniques of ESCA, AES, and SEM (Scanning Electron Microscopy). These analytical techniques illustrate the elemental composition of the surface and the chemistry of the stainless steel with depth in the outer 100 Angstroms. These results will show the quality of the passive layer and its expected resistance to corrosion.

AES profile test results are shown in Figure 2. Sample C is a graph of a sample that has been electropolished and subsequently passivated with a citric/chelant process. Sample A is a sample that has been electropolished with no further chemical treatment. These graphs illustrate the incremental improvement in the Cr/Fe ratio with the citric/chelant passivation technique.

Comparative experimental testing of mineral acid passivation techniques and a citric based chelant treatments provided clear evidence that citric acid systems were more effective and provided a higher Cr/Fe ratio. Corrosive environments testing indicated significant improvement in reduced rouging tendencies with the citric/chelant systems.

The first set of results is for electropolished samples with/and without chemical passivation treatments. The nitric acid passivated stainless sample is shown with a 1.8 Cr/Fe ratio, which is higher than the natural 2B surface of 1.7. Results of ESCA testing for citric acid based passivation systems show an improvement to an advantageous 2.0 to 2.5 Cr/Fe ratio. The second set of results is for Non-Electropolished samples. The control sample with no chemical treatment has a Cr/Fe ratio of 1.5. The citric/chelant systems show improved ratios of 2.0 to 2.2.

Further testing with the addition of a chemical intensifier during the passivation treatment and the use of an oxidizing solution treatment after passivation resulted in similar improvements in the Cr/Fe ratio from base conditions. These results are shown in figure 5-8. Improved oxide depth and carbon removal is shown in these samples with the AES testing.

LOOKING AHEAD

Environmental considerations are important when designing and utilizing chemical cleaning and passivation treatment systems. Nitric and other mineral acids are hazardous chemicals and present distinct safety, waste and environmental hazards. Citric acid based systems use non-hazardous food grade materials that pose very few environmental concerns. Personnel safety, risk of hazardous material spills and waste disposal alternatives are important liability considerations in the choice of a passivation treatment.

Maintenance of critical systems and their state of passivity is crucial to their long-term condition and effect on product quality. Systems should be inspected routinely to ensure that rouge or corrosion products are not building up or leading into the system. Regular inspection and record keeping practices can assist in the evaluation of water treatment quality, the process piping condition and the need for precision cleaning and passivation. Removal of rouge deposits is important in the preparation of a system to produce highest quality products and for the subsequent passivation of the surface.

CONCLUSIONS

The basic method of natural passivation is exposure of the stainless steel surface to air. The 2B finish is uniform, clean and durable. Nitric acid passivation treatment removes excess iron and some adherent contamination; however, it does not remove aluminum inclusions. Electropolishing removes material in a controlled manner while smoothing the surface. Mechanical cleaning methods leave a smeared surface layer of lower corrosion resistance. Passivation processes are required after any mechanical surface treatment or welding. Pickling is a chemical process, which aggressively removes surface material and generally results in a rougher surface. Heat tint is a potential source of rouging and batch process contamination.

Improved surface finish treatments are available including advanced citric/chelant passivation techniques that result in improved corrosion resistance. The chelant passivation processes were tested for Cr/Fe ratios. Significant improvements in these ratios were cited in the results and resultant higher corrosion resistance has been shown to follow.

ESCA Analysis and Results

ELECTROPOLISHED SAMPLES:

<u>SYSTEM</u>	<u>CHROMIUM/IRON RATIO</u> (Cr/Fe)	<u>OXIDE RATIO</u> (CrO/FeO)	<u>OXIDE THICKNESS</u>
No Chemical Treatment - Sample A	1.7	2.3	26 Å
Nitric Acid - Sample B	1.8	2.9	22 Å
Citric/Chelant - Sample C	2.4	3.2	30 Å
Citric/Chelant - Sample D	2.5	3.6	32 Å
Citric/Chelant - Sample E	2.0	3.0	24 Å
Citric/Chelant - Sample F	2.0	2.6	25 Å

NON-ELECTROPOLISHED SAMPLES:

<u>SYSTEM</u>	<u>CHROMIUM/IRON RATIO</u> (Cr/Fe)	<u>OXIDE RATIO</u> (CrO/FeO)	<u>OXIDE THICKNESS</u>
No Chemical Treatment - Sample G	1.5	2.2	21 Å
Citric/Chelant - Sample H	2.2	3.5	24 Å
Citric/Chelant - Sample I	2.0	3.0	31 Å
Citric/Chelant - Sample J	2.2	3.2	28 Å

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