

Developing an Effective Passivation Process to Maintain Laser Mark Integrity for Medical Device Components

Daryl L. Roll, P.E. and Rod Webb, J.D.

Introduction

Laser marking is commonly used for medical device identification and as an alignment aid for surgical tools, stents, tubing, dental products, orthopedic products and many others. The mark is conspicuous and permanent and will sustain repeated use and sterilization. Many medical devices are made from stainless steel material because of its natural corrosion resistance and relatively chemical inert surface. However, laser marking of stainless steel alters the surface composition and degrades the natural passive layer resulting in a mark that is susceptible to corrosion. To restore the passive layer, the mark should be passivated using nitric or citric acid but the process must be thoroughly developed in order to prevent over-etching the mark beyond readability.

Industry passivation specifications such as AMS QQ-P-35, ASTM A380 and ASTM A967-05 provide a relatively comprehensive review of passivation processes, test methods and acceptance criteria. However, these standards provide little help to medical device designers and manufactures for determining the best process for a particular part or stainless alloy material, and certainly not for laser marked devices. In addition, the limited guidance that is provided is not based on recent advanced passivation formulations. Developing the optimal passivation process to balance the need to create a passive layer while not degrading the mark beyond its designed purpose is extremely important and requires controlling every aspect of the process, such as precleaning, fixturing and handling, mark quality, solution concentration, pH, temperature, dwell time, rinsing and the acceptance testing. Inconsistency in any of these process steps may impact the passivation result. This article provides guidance for process selection and control for laser marked medical devices.

Passivation Basics

Stainless material consists of three distinct zones:

- The deepest zone is the alloy bulk phase.
- The shallowest zone is the passive layer.
- The zone in between is the transition area.

A graphical representation of these zones can be seen in Figure 1. The passive layer and the transition zone are only about 3 to 4 molecular levels thick; therefore, both layers are very susceptible to damage.

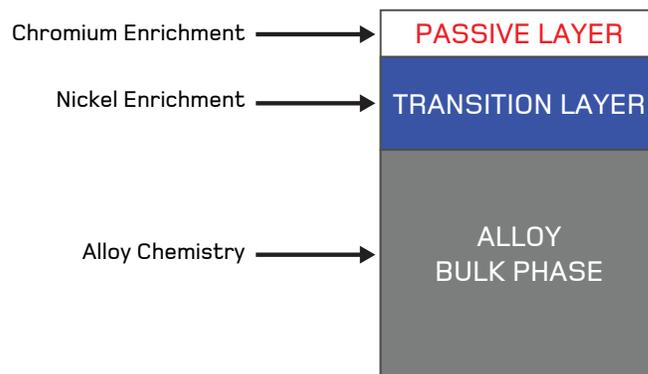


Figure 1: Zones of Stainless Steel

During machining, fabrication and laser marking, the chromium-enriched passive layer is damaged and iron contained in the alloy bulk phase, or deposited on the surface from fabrication tooling, is exposed making the surface susceptible to corrosion. To restore this passive layer, the surface iron (free iron or iron oxide) must be removed without removing the corrosion resistant chromium and nickel elements. Exposing the surface to nitric or citric acid removes the iron, raises the chrome-to-iron ratio and establishes the passive layer in the upper part of the surface. For medical devices, this process is commonly performed according to ASTM A967-05, one of several specifications for chemical passivation treatments for stainless steel. ASTM A967-05 recognizes many formulations of both nitric and citric acid. While nitric acid is traditionally the most common formulation, citric acid has gained favor in recent years due to an increasing appeal for “green” technologies and because it provides better passivation results in most cases. Advanced citric acid formulations contain “chelation” additives that prevent dissolved iron and other metallic ions plating, or reattaching, back on the surface after initial removal. This chelation process significantly contributes to the improved results of citric versus nitric.

In addition, ASTM A967-05 lists several acceptance tests for determining if the passivation process created an adequate passive layer. Table 1 lists these tests with characteristics of each. Common among the tests is the qualitative interpretation of results through visual inspection. Also noteworthy is the varying severity and sensitivity of the tests. The lack of clarity for proper test selection and unlikely correlation of results and interpretations among the tests due to different severity and sensitivity levels allow manufactures to choose a test based upon convenience or likelihood of a passing result irrespective of whether an adequate passive layer is restored.

ASTM A967 Acceptance Tests						
Test Name	Summary	Application	Acceptance Criteria	Approx. Time	Test Severity	Comments
Water Immersion	Immerse in water and dry 1 hour each, cycle for 12 hours.	Stainless Steel	No visual rust or staining from free iron.	12 hours	Low	
High Humidity	Clean and subject part to 97% humidity at 100F in chamber.	Stainless Steel	No visual rust or staining from free iron.	24 hours	Moderate	
Salt Spray	Subject part to 5% salt solution for 2 hours.	Stainless Steel	No visual rust or staining from free iron.	2 hours	High	
Copper Sulfate	Subject part to 10g/500 ml DI of potassium ferricyanide & 30 ml of 70% nitric, all diluted w/ 1000 ml DI.	200, 300, precipitation hardened, and 400 with \geq 16% chrome	No visual copper accumulation.	10 min.	Moderate	Not to be used for parts used in food processing or 400 series with < 16% chrome.
Potassium Ferricyanide	Subject part to 4g/250mL DI of copper sulfate and 1ML sulfuric for 6 min., rinse & dry.	When small amounts of iron detection needed for 200, 300, precipitation hardened, & 400 with \geq 16% chrome.	No visible blue color after 30 seconds.	1 min.	High	Not to be used for parts used in food processing or 400 series with < 16% chrome.
Free Iron	With part temp \geq 50F for 60 min., cover 20 sq. in. with distilled or demineralized water - time unspecified - remove and air dry.	Large parts not conducive to humidity or salt spray chamber.	No visual rust or staining from free iron.	60 min. minimum	Moderate	Soak time not specified.

Table 1: Acceptance Tests

The health and product risks corrosion presents for medical devices along with an increase in process scrutiny from the FDA, drives the desire for device manufacturers to improve the passivation process to achieve the best possible result, i.e., the highest chrome-to-iron ratio. Even so, ASTM A967-05 provides little guidance to device manufactures for selecting the formulation that will yield the best result. Passivation process development prior to device validation is now commonplace. Developing the best process is particularly challenging for laser-marked devices since maintaining mark integrity must be balanced with creating an improved passive layer.

Characteristics and Challenges of a Laser Marked Surface

The laser marking process applies heat to etch the mark into the surface, similar to welding. The two modes of laser marking are the ablative mode, which uses high power with short contact time, and oxidation mode, which uses lower power with longer contact time. The surface characteristics within the marked area will vary based on the laser mode used.

The ablative mode evaporates and oxidizes material from the surface but otherwise does not significantly change the base material, although the layer is thinner, higher in iron oxide and susceptible to localized corrosion such as pitting. The oxidative mode, on the other hand, melts the surface material completely, forming a thick iron oxide layer and loss of passive characteristics¹.

The loss of the passive layer from the oxidation mode of laser marking is the same result observed in welding of stainless pipe in high purity applications such as pharmaceutical process systems². Experience can be drawn from advanced passivation processes proven effective in these applications for restoring the passive layer. However, there are very different objectives in the two applications. Alloy components oxidize and turn black during either welding or laser marking, similar to a charred forest after a fire. The black color is an oxide layer and results from exposing the elements to oxygen when they melt from the heat, forming iron oxide, chromium oxide, carbon and other oxidized compounds. A laser mark visually contrasts with the natural color of the alloy to make the mark visible – the purpose of the mark. For welding, the discoloration is not desired and the passivation (pickling) process is designed to remove it by chemically etching the surface.

The opposite is true for laser marks. It is important not to significantly remove or dull the oxide layer during passivation so the mark remains visible. Thus, restoring the passive layer without degrading the mark beyond the intended purpose is the challenge for developing a passivation process for laser marked devices. This requires precise process controls and quantitative, not qualitative, analysis to chemically profile the surface, otherwise the passive layer may not be restored or the laser mark will be dulled beyond the intended purpose. Since degradation of the laser mark is immediately noticeable, the tendency is to under passivate so the mark is not dulled, but this does not adequately restore the passive layer. Without a quantitative test, this quality flaw only comes to light after corrosion develops well after the part has been released to the market and, even more concerning, perhaps in use.

For the medical device manufacturer interested in achieving the best possible result to minimize corrosion risk, a more quantitative test is preferred to determine the extent to which the passive layer has been established. This test is completed to initially prove effectiveness when the process is being developed. Once the process is in control, the quantitative test can be correlated to one of the qualitative tests listed in ASTM A967-05 for production process and quality control purposes.

Since the objective of the passivation process is to create a passive layer by raising the chrome content relative to the iron content, an indication of the quality of the passive layer, a quantifiable determination of the chrome-to-iron ratio seems most applicable. This is accomplished using Auger Electron Spectroscopy (AES). Refer to Figures 2 and 3. The vertical axis plots the percent composition of the elements present and the horizontal axis plots the depth in angstroms for laser markings on 17-4 and 304 stainless, respectively. The marks were made using the oxidation mode as evident by the thick iron oxide layer shown by the high concentration of oxygen (the top green line) and iron (the blue line). This layer makes up

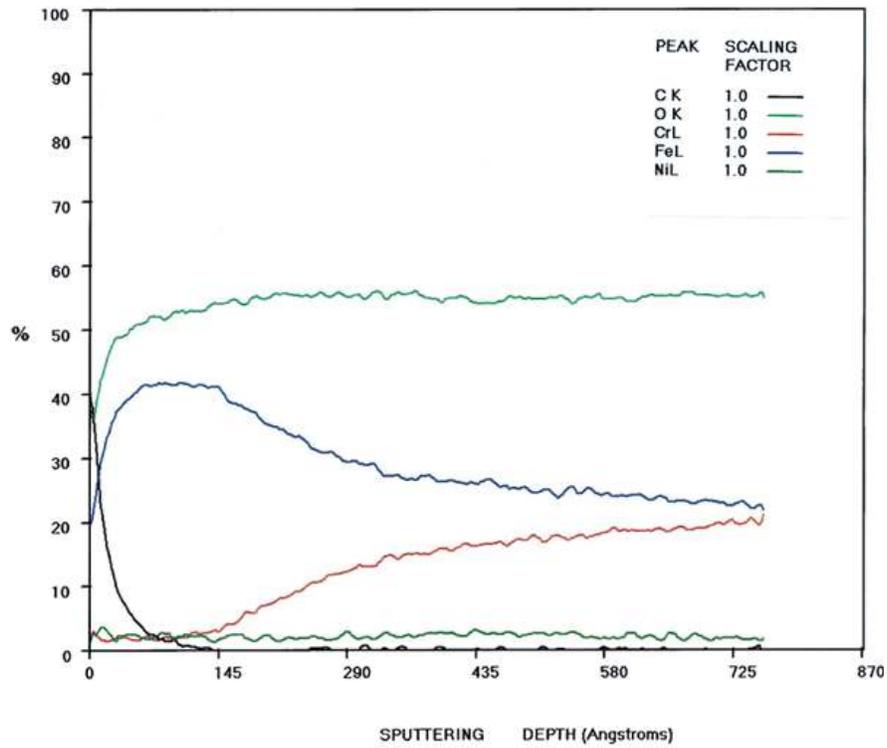


Figure 2: Unpassivated 17-4 Mark

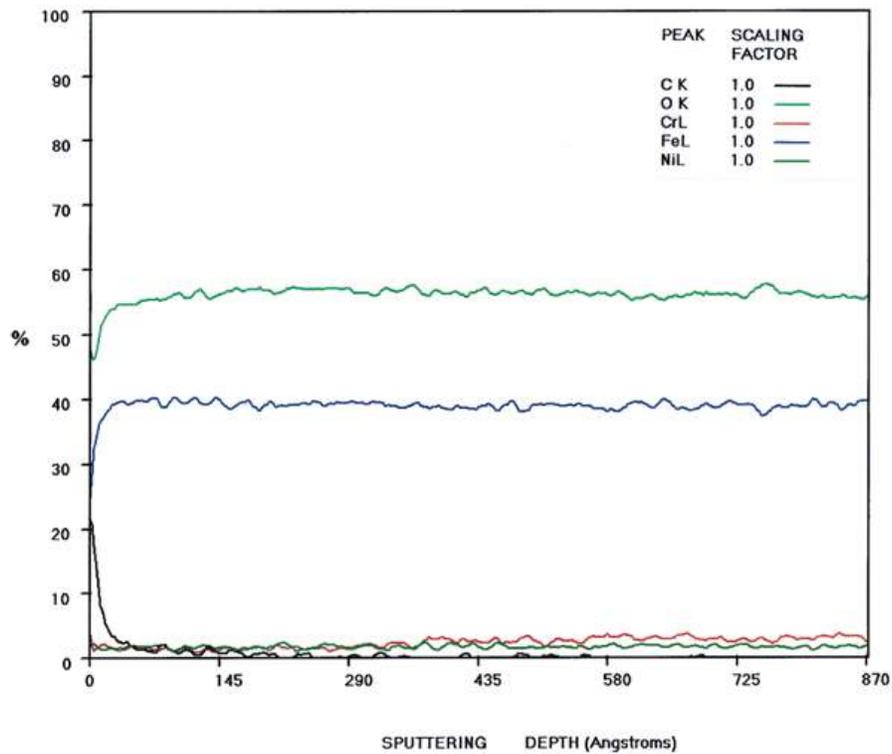


Figure 3: Unpassivated 304 Mark

approximately 90% of the surface composition. Chromium is indicated by the red line and is significantly lower in content than iron (blue line) throughout the depth of the surface. Chromium rises to 20% at 725 angstroms in the 17-4 sample, equal to the iron content but at a very deep depth, and remains constantly low relative to iron in the 304 sample. The high iron with low chromium and nickel content indicates corrosion susceptibility at the surface, as the iron is in the ferrous oxide state and, with moisture and oxygen, will oxidize to ferric (red) oxide. Formation of ferric (red) iron oxide will result in growth and release of the iron from the surface as particulate. There is virtually no passive layer as the chrome-to-iron ratio (Cr/Fe) is less than 0.10 in both samples near the surface.

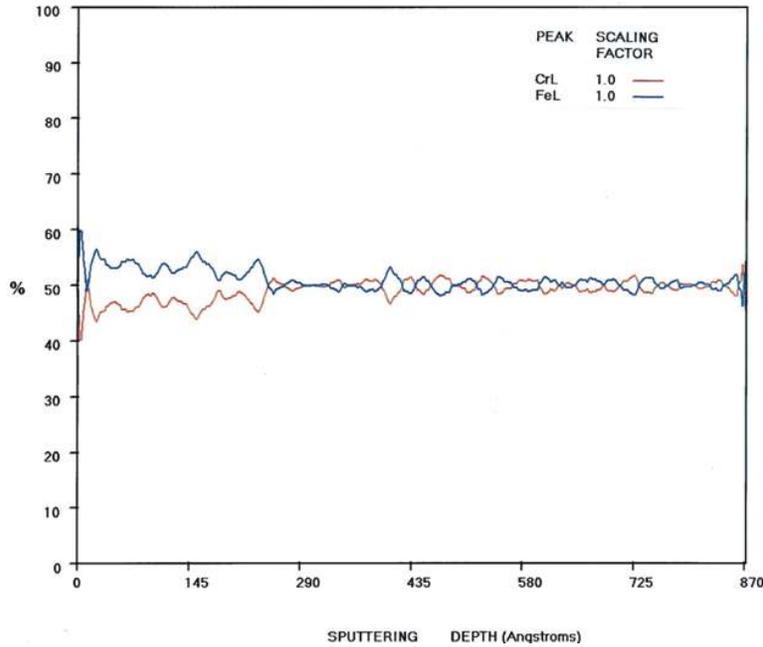


Figure 4: Passivated 17-4 Mark

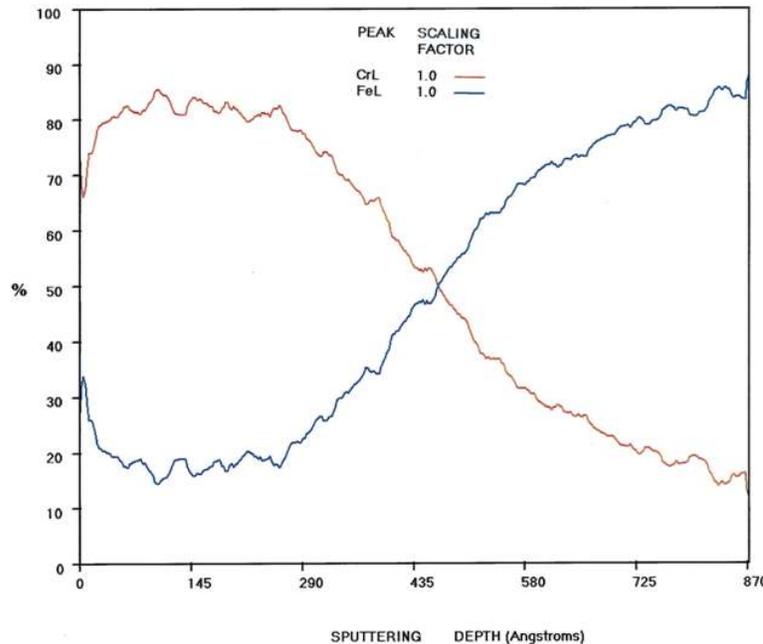


Figure 5: Passivated 304 Mark

Passivation of these surfaces results in significantly higher chromium-to-iron ratio and formation of a protective layer. Both samples (17-4 and 304) failed the medical device copper sulfate (CuSO_4) inspection test prior to passivation. After passivation, both passed the CuSO_4 test 100% of the time. The AES of the 17-4 and 304 surfaces after passivation are shown in Figures 4 and 5, respectively. The passivation has improved the surface layer of less than 0.1 Cr/Fe to a range from 0.8 to 1.0 Cr/Fe in the 17-4 sample and to over 3.0 in the 304 sample.

To calculate this ratio, simply read the percent value of both chrome and iron at the depth point of interest (10 angstroms or point of maximum value) and divide the chrome value into the iron value. The result is the ratio of chrome to iron. The consensus in most industries to indicate the minimum acceptable passive layer is for the ratio to be at least 1 and most desirable to be 2 or more. In the 17-4 sample, the passivation improvement extends through the full depth of the surface, or 800 angstroms (0.8 microns) but has a lower chrome-to-iron ratio. This is typical of martensitic material with base alloy chromium content above 14%. The 304 result is more typical of austenitic material with a crossover at 450 angstroms (0.45 microns) but with a high chrome-to-iron ratio. Both are drastic improvements over the unpassivated samples.

The Importance of Pre-Cleaning

A common problem for achieving the desired passivation result is inadequate surface cleaning. A clean surface is required for the passivation solution to access the free iron or iron oxide and remove it. Surface contamination can mask the iron and it will remain on the surface, failing the inspection criteria (CuSO_4 test). ASTM A967-05 generally recognizes the need for pre-cleaning but does not specify it as a requirement. ASTM A380 discusses cleaning processes in more detail but does not specify quantification of surface cleanliness. It is highly recommended chemistry, particulate and non-volatile residue levels be measured to ensure a clean surface. If the surface is not clean, the AES profile will show a layer of organic (carbon) residue on the surface. See Figure 6. The black line is the carbon content and is 40% at the surface

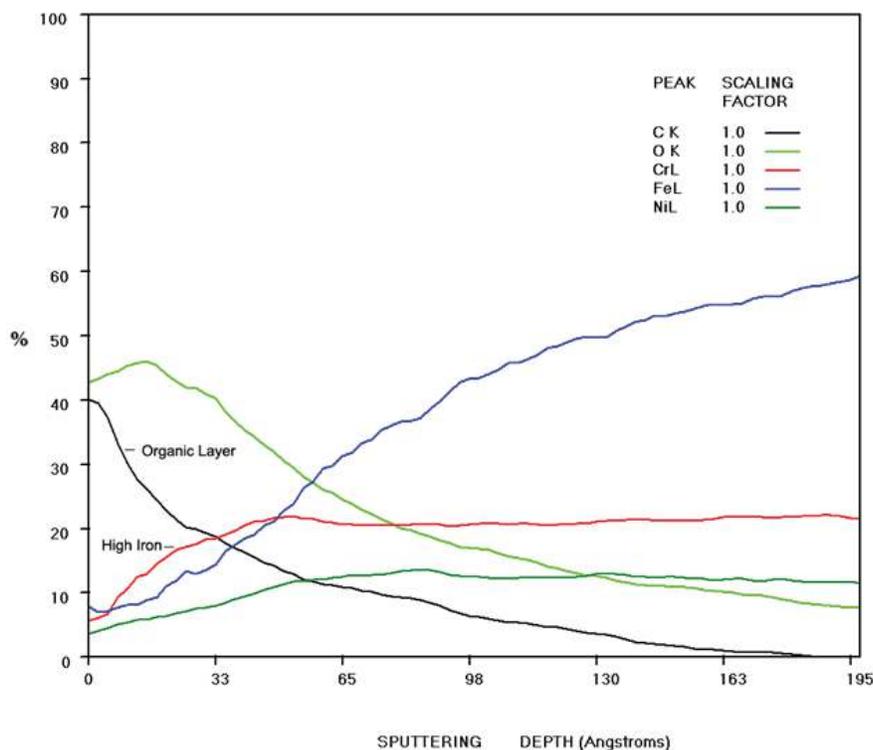


Figure 6: AES with Organic Layer

and above 20% at 30 angstroms depth. This carbon layer indicates the lack of cleanliness and the result is that the acid passivation did not remove enough of the iron to eliminate the high iron at the surface. The iron (blue line) is greater than the chromium (red line) concentration in the first 5 angstroms creating a detached iron oxide film on the surface. If such carbon layer is present, the passivation result will be detrimentally affected.

Process Development for Passivation of Laser Markings

The starting point for process development is to decide between a nitric or citric formulation. For the device manufacturer interested in determining which formulation and set of conditions provide the best passivation result defined by a quantitative requirement and test method, the selection should not be taken lightly. In general, citric formulations have advanced in recent years to outperform nitric for austenitic alloys and martensitic alloys with chrome content of at least 14%³. These formulations are not specifically recognized in ASTM A967-05 but are provided for in the catch-all provision in subsection 7.1.1.4 Citric 4.

Laser marked sample parts should be processed in the selected solution at the conditions providing the highest possible chrome-to-iron ratio without degrading the laser mark. Variable conditions to consider include solution concentration dwell time, temperature, and acidity. Undoubtedly, there will be some fading of the laser mark since any process will remove some of the oxide layer; however, the type and quality of the laser mark will impact how much oxide layer is removed at the desired passivation result. It will take several iterations of adjusting conditions to achieve the optimum desired result. The CuSO₄ test or other relatively real-time qualitative acceptance test may be used to quickly baseline results followed by AES to validate and maintain the final process and ensure consistent results. Once established, as long as the material and process remain in control, the results should be consistent.

Table 2 summarizes an example of a process development effort to balance the need to establish the passive layer while maintaining the mark integrity. In general, adjustment of the dwell time and temperature will have the largest affect followed by the acidity level and iron concentration of the solution with all other conditions controlled.

Conditions of Test	Cr/Fe Surface/Max	Oxide Film Thickness (angstroms Å)	Cu/SO ₄ test	Comments
Non-Passivated Laser Mark Surface	0.2 / 0.2	500+ Å	Fail	Typical unpassivated/weld surface
Passivation Process A – Series of Testing	--	--	Fail	Ambient Process
Passivation Process B – Series of Testing	--	--	Pass	Laser Mark Lost
Passivation Process C –30 minutes	--	--	Fail	Insufficient passivation
90 minutes	0.8 / 1.4	100 Å	Pass	Laser Mark – Light in color
60 minutes	0.4 / 0.8	250+ Å	Fail	Laser Mark - Good
75 minutes	0.75 / 1.2	200 Å	Pass	Laser Mark - Good
Validation Runs: Series 1	0.8 / 1.4	180 Å	Pass	Laser Mark - Good
Series 2	0.7 / 1.3	200 Å	Pass	Laser Mark - Good

Table 2: Development and Validation Tests

Conclusion

The laser marking process for stainless medical devices and components, particularly marks made using the oxidative mode, produces a black oxide layer on the base material. This effect is similar to welding in high purity applications and has long been proven to substantially and adversely affect the corrosion resistance of the stainless steel surface. Laser marking on stainless steel surfaces for medical devices also degrades the natural corrosion resistance of the material and must be reestablished by passivation. However, the same passivation process used to re-establish the passive layer for welds tends to remove the oxide film from the laser marking and reduce the appearance of the mark beyond its intended purpose. Proper design and validation, with associated process control of the passivation process, is required to achieve the optimum chrome-to-iron ratio indicating corrosion resistance.

Biographies



Daryl L. Roll, P.E.

As Astro Pak's Chief Technology Officer, Mr. Roll serves as the primary senior technical advisor for corrosion, surface chemistry and stainless steel passivation. With over 30 years of experience in chemical processing, Daryl has been published in MICRO, UltraPure Water Journal and Chemical Engineering for his papers on passivation and rouge control. He is a participant on the ASME BPE Subcommittees for Surface Finish and Materials of Construction requirements and a leading contributor for the Rouge and Passivation Task Groups. Mr. Roll holds a B.A. in Chemistry and Earth Science from the California State University of Fullerton and a Professional Engineer's license from the State of California.

Please contact Daryl with any further questions at droll@astropak.com.



Rod Webb, J.D.

Rod Webb is Corporate Development Manager for Astro Pak Corporation in Costa Mesa, CA. He has over 15 years experience in contamination control practices and testing technologies in aerospace, hydraulics, automotive, semiconductor and laser industries and has authored numerous articles on contamination control. He has a law degree from Oklahoma City University School of Law and an Economics degree from Southwestern Oklahoma State University.

Please contact Rod with any further questions at rwebb@astropak.com.

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