Surface Chemistry Improvements on 316L Stainless Steel Weld Zones with Gelled Citric Acid-Based Passivation Agent

Daryl L. Roll, P.E. and Brent Ekstrand, Ph.D

INTRODUCTION

The Astro Pak Corporation Technology Group performed a study to determine the efficacy of a gel-based citric acid chelant passivation agent on welds and heat affected zones. Questions regarding this type of passivation arise from data developed in experiments using commercially available citric acid solutions, which demonstrate that elevated temperatures are necessary for adequate passivation of weld areas to occur when citric acid is the primary passivation agent. Citric acid gel passivation processes use ambient temperatures for practical reasons (such as the tendency for the gel to liquefy at elevated temperatures). As elevated temperatures are not seen in the citric acid gel-based processes, some in the food and beverage industry question the efficacy of these citric acid gel-based passivation procedures, as the process temperatures seen conflict with the data developed from citric acid solution experiments which indicate that elevated temperatures are necessary. In this study, we compared the original weld surface chemistry to the passivated weld surface chemistry after treatment with a gelled citric acid-based passivation agent for two (2) and four (4) hours as well as to the passivated weld surface chemistry obtained after treatment with a standard solution-based nitric acid treatment.

PASSIVATION TECHNOLOGY

Passivation of austenitic stainless steel surfaces has been practiced on high purity water systems for many years, and is generally defined as the removal of iron and iron compounds from the surface to improve the passive film and increase corrosion resistance. The surface chemistry, structure and related corrosion resistance of austenitic stainless steel is affected by mechanical polishing, welding, and most fabrication techniques. Passivation reduces or eliminates this damage while forming a more corrosion resistant passive film higher in chromium oxide. There have been many technical papers that have presented evidence on effectiveness of passivation and especially for the benefits of citric chelant processes 1, 2, 3.

Weld areas produce relatively high corrosion rates unless treated and repaired by chemical passivation. Most high purity water systems are passivated with the technique of circulating heated alkaline cleaning and acid passivation chemistries as described in other referenced documents. The technique of gel passivation of welds has been performed for over 50 years. Citric acid has been utilized for this treated type in recent years. Published data to confirm citric acid-based gel's effectiveness of passivation on the weld area at ambient conditions as compared to nitric acid gel systems is not readily available.

METHODOLOGY

ASTM 316L stainless steel electropolished sanitary tubing was used as the substrate. A series of orbital welds were made on a single lot of one (1) inch tubing by a single operator using a single welder at constant settings. The reason for the use of a single lot of tubing, as well as welds made in one session by the same operator using the same welder at identical settings, was to control for unmeasured variables that could possibly tend to confound data analysis. After welding, the tubing was then sectioned using a cold-cut technique. Cold-cutting was again used to control for unmeasured changes in surface chemistry that could be caused by heating of the welds during the cutting operation. Samples of the weld, approximately 1/2" by 3/8", were created and identified by engraving an alphanumeric identifier on the outer diameter of the samples.

Five of the samples, labeled W70 through W74, were cleaned with a heated alkaline cleaning process. These non-passivated samples were then individually packaged in clean room grade polyethylene bags. The second set of five samples, labeled W60 through W64, was cleaned with a heated alkaline cleaning process. The set was then passivated at ambient temperature using the gelled citric acid-based passivation agent for 120 minutes. The third set of five samples, labeled W65 through W69, was cleaned with a heated alkaline cleaning process. This final set was then passivated at ambient temperature using the gelled citric acid-based passivation agent for 240 minutes.

The gelled citric acid-based passivation agent formula is based on the same formula seen in solutions which meet the requirements of ASTM A967 citric acid type IV passivation chemistries, with one exception: a gelling agent is used to thicken the mixture so that better adherence to metal surfaces is achieved. The actual chemistry of the formulation used is proprietary in nature. The researchers formulated the gel-based passivation mixture used in this experiment by blending an organic gel solution, heated to decrease viscosity and improve mixing, with the ASTM A967 citric acid type IV ingredients. When thoroughly mixed, the resultant mixture was poured into a precision cleaned glass jar and allowed to cool.

Weld samples W60 through W69 were passivated using the gelled citric acid-based passivation agent. Two exposure times were tested - samples W60 through W64 were passivated for a period of 2 hours, and samples W65 through W69 were passivated for 4 hours. The passivation technique entailed wetting the samples with the passivation gel by rubbing it on using an applicator. Every 15 minutes, fresh gel was re-applied, and the mixture was agitated on the surface using the applicator. This continued for a total of 2 and 4 hours for the two groups of samples, respectively.

A final group of samples, labeled W28 through W32, was treated with a standard liquid nitric acid process (30% nitric acid at ambient temperature for 30 minutes). This group was treated with nitric acid solution in order to gain a “gold standard” point of comparison for the gel-based passivation results.

When the desired passivation time for each group had elapsed, the passivation agent was neutralized by rinsing and wiping the metal surface with a saturated solution of sodium bicarbonate in deionized water at ambient temperature. After neutralization was complete, as evidenced by the cessation of the liberation of carbon dioxide (CO2) gas from the surface of the samples, the samples were rinsed thoroughly using deionized water at ambient temperature. The samples were subsequently dried using a stream of nitrogen gas at ambient temperature, and then individually packaged in clean room grade polyethylene bags.

The samples were then sent to an independent testing laboratory for surface analysis by X-ray photoelectron spectroscopy (XPS). The laboratory personnel were blinded to which treatment (or lack of treatment) had been applied to each sample. The XPS instrument operators knew the samples only by their assigned alphanumeric identifier (W60 through W74 and W28 through W32). This blinding was employed to avoid the introduction of operator bias during the XPS measurement process. After the XPS measurements were complete, the laboratory reported the data to Astro Pak using the assigned alphanumeric identifiers.

DATA

The complete XPS raw data is available upon request. Figure 1 is a graphical summary of the mean chromium to iron ratios from all tested sample groups. Table 1 shows the calculated values for chromium to iron ratios for each of the individual test coupons. These ratios are calculated from the atomic percentage values as measured by XPS. The surface chromium to iron ratio is one means to evaluate the surface passivation and is the key evaluation technique utilized in this study. Additional studies are planned which will utilize functional corrosion testing such as Critical Pitting Temperature (CPT), or other direct corrosion testing methods, to further evaluate the gelled citric acid-based passivation process.

The means of the chromium to iron ratios for each of the test groups were calculated and are presented in the following graph:

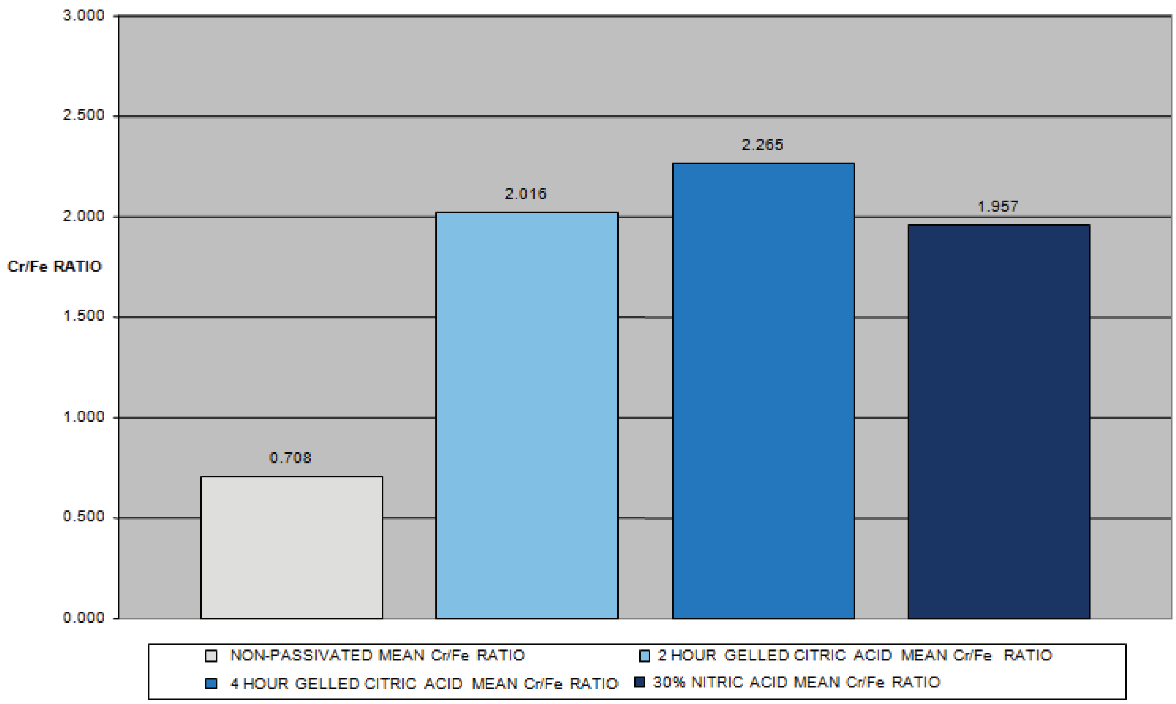


FIGURE 1 - PASSIVATION EFFICACY ON 316L WELDS

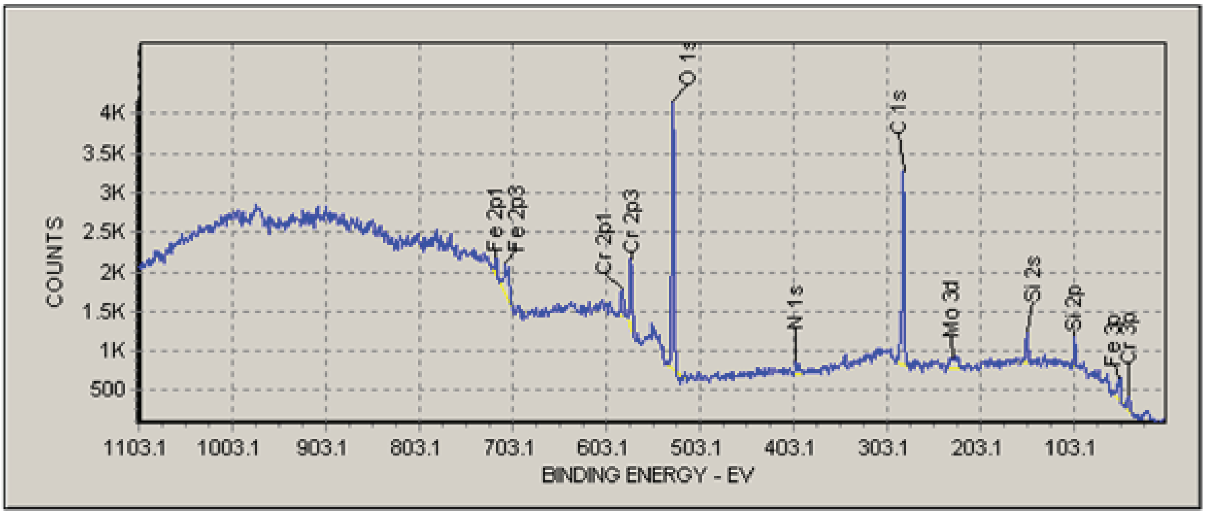
SEAL LABORATORIES

Project AstroPak_Oct0406 Acquired: 10/04/06 by DC

Experiment: W68

Description None Entered

Function:	Survey	Region:	Survey	eV/Step:	1.00	Cycle No.:	1
Scans/Time:	4	Res:	4	Spot:	3	Etch Time:	0



COMPOSITION TABLE

XPS Line	Adj'ed Be	CrossSec	Norm Area	Atom %
O 1s	531.437	2.93	582.369	31.361
N 1s	399.617	1.8	64.591	3.478
C 1s	284.603	1	968.871	52.175
Mo 3d	230.517	9.5	20.776	1.119
Si 2p	101.979	0.817	112.278	6.046
Fe 2p3	707.275	10.82	41.855	2.254
Cr 2p3	576.300	7.69	66.224	3.566

Figure 2 - Example Xps Analysis For Coupon Passivated With Gelled Citric Acid-Based Passivation Agent For 4 Hours

SEAL LABORATORIES

Project AstroPak_Oct0406 Acquired: 10/04/06 by DC

Experiment: W68
Description None Entered

Function:	Survey	Region:	Survey	eV/Step:	1.00	Cycle No.:	1
Scans/Time:	4	Res:	4	Spot:	3	Etch Time:	0

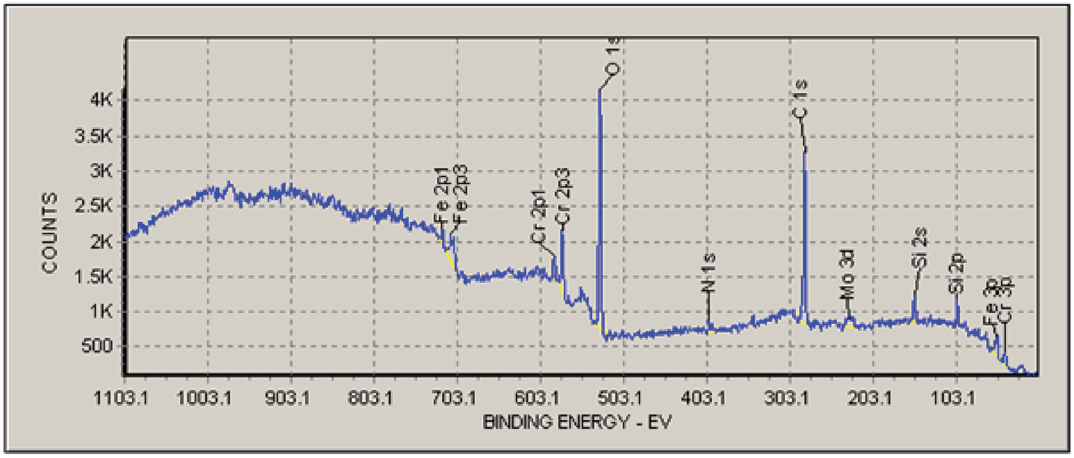


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Figure 3 - Example Xps Analysis For Coupon Which Received No Passivation

Group A: Not Passivated						
Sample:	W70	W71	W72	W73	W74	MEAN
Cr/Fe ratio:	0.627	0.776	0.790	0.695	0.953	0.708
Group B: 2 Hour Gelled Citric Acid-based Passivation Agent (ambient temperature)						
Sample:	W60	W61	W62	W63	W64	MEAN
Cr/Fe ratio:	2.129	1.909	1.642	2.274	2.126	2.016
Group C: 4 Hour Gelled Citric Acid-based Passivation Agent (ambient temperature)						
Sample:	W65	W66	W67	W68	W69	MEAN
Cr/Fe ratio:	1.984	1.869	3.642	1.582	2.250	2.265
Group D: 30 minute 30% Nitric Acid Solution Passivation Agent (ambient temperature)						
Sample	W28	W29	W30	W31	W32	MEAN
Cr/Fe ratio:	1.949	2.450	1.944	1.320	2.123	1.959

Table 1 – Xps Chromium To Iron Ratio Results

Statistical significance of the data was determined using unpaired two-tailed Students' T-tests. The calculated p-values and the statistical significance of the differences in the means of the data groups are presented in table format below:

Modalities Compared	p-Value	Statistical Significance
Non-passivated versus 2 hour Citric Acid-based Gel	0.00000319527	Very Highly Significant
Non-passivated versus 4 hour Citric Acid-based Gel	0.00260815448	Highly Significant
2 hour versus 4 hour Citric Acid-based Gel	0.526827069	Not Significant
Nitric Acid versus 2 hour Citric Acid-based Gel	0.791191203	Not Significant
Nitric Acid versus 4 hour Citric Acid-based Gel	0.468366968	Not Significant

Table 2 – Calculated Students' T-test p Values

CONCLUSIONS

The tested gelled citric acid-based passivation agent (based on ASTM A967 citric acid type IV requirements) is effective at ambient temperatures for passivating weld areas on 316L stainless steel tubing, as demonstrated by the measured improvements in the surface chromium to iron ratios. By the same criteria, this gelled citric acid-based passivation agent is equivalent to immersion in traditional nitric acid solution for passivation of the welded areas. The welds prior to passivation showed typical heat-induced depletion of chromium (mean Cr/Fe ratio 0.708). The post-passivation treated welds showed an improvement of the Cr/Fe ratio to 2.02 (2 hour exposure) and 2.27 (4 hour exposure) or 2.14 for combination of both 2 hour and 4 hour treatment times.

The Cr/Fe ratios achieved by the gelled citric acid-based passivation agent were consistent with a highly passive surface. The mean measured Cr/Fe ratios of passivated welds ranged between 285.3% (at 120 minutes exposure) to 320.6% (at 240 minutes exposure) of the non-passivated welds. This improvement in the Cr/Fe ratios is dramatic and compares favorably with traditional nitric acid passivation techniques. Five (5) samples were treated with nitric acid solution in accordance with specifications ASTM A-380 and ASTM A-967 resulting in a mean average of 1.957. The differences in the means of the Cr/Fe ratios for the 3 groups of passivated samples (nitric acid, 2 hour citric acid-based gel, and 4 hour citric acid-based gel) were not statistically significant.

The final conclusions which the data support are that adequate passivation of welds in 316L stainless steel (as defined by a minimum Cr/Fe ratio of 2.0) was achieved with both tested durations of exposure of the citric acid-based gel at ambient temperature, and that the citric acid gel-based agent is equivalent to the traditional solution-based nitric acid passivation technique as determined by the measured improvements in the surface chromium to iron ratios. Since the data from this study indicates that no statistical significance can be attached to the difference that existed in the mean Cr/Fe ratios at 2 and 4 hours of exposure time, no conclusion can be drawn about minimum times necessary or improvements expected in Cr/Fe ratios with increased durations of exposure.

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BIOGRAPHIES

Daryl L. Roll, P.E.

As Astro Pak's Science and Quality 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.

Brent Ekstrand, Ph.D

Dr. Brent Ekstrand is tasked with oversight of all quality-related programs, serving as Astro Pak Corporation's Director of Cleanroom Operations. Brent also serves as a technical advisor for complex cleanroom, aerospace, and pharmaceutical projects. He oversees the execution of all laboratory research funded by Astro Pak Corporation. He has over 10 years of experience in the precision cleaning and passivation industry. His areas of expertise include onsite project management, cleanroom operations, biofilm remediation and control, and passivation, as well as quality assurance and quality control. Brent received his doctorate in pharmacy from the University of the Pacific.