

**SURFACE CHEMISTRY
IMPROVEMENT ON 316L STAINLESS
STEEL WELD ZONES WITH
GELLED CITRIC ACID-BASED
ULTRA PASS® SYSTEM**

Authored by:
Daryl L. Roll, P.E. and Brent Ekstrand, PhD

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 pharmaceutical 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 Ultra Pass® Gel for two (2) and four (4) hours as well as the passivated weld surface chemistry after treatment with a standard immersion solution-based nitric acid treatment.

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 proprietary Ultra Pass® Gel chemistry and technique 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 proprietary Ultra Pass® Gel chemistry and technique for 240 minutes.

The Ultra Pass® Gel chemistry is the same to Astro Pak Corporation's standard Ultra Pass® chemistry, 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, but has been the subject of significant published passivation research. 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 Ultra Pass® solution 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 gel-based proprietary passivation mixture. 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 (CO_2) gas

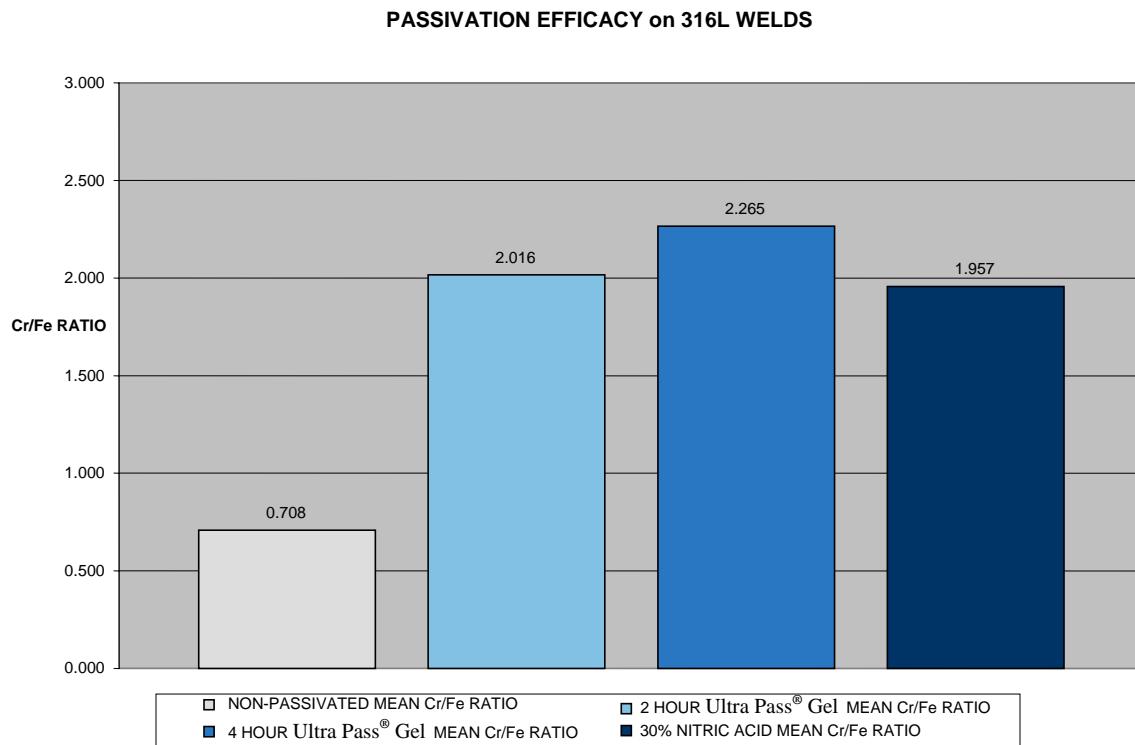
from the surface of the samples, the samples were rinsed thoroughly using deionized water at ambient temperature. The samples were subsequently dried using a stream of nitrogen gas at ambient temperature, and then individually packaged in clean room grade polyethylene bags.

The samples were then sent to an independent testing laboratory for surface analysis by the ESCA technique. The laboratory personnel were blinded to which treatment (or lack of treatment) had been applied to each sample. The ESCA 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 ESCA measurement process. After the ESCA measurements were complete, the laboratory reported the data to Astro Pak using the assigned alphanumeric identifiers.

DATA

The complete ESCA raw data is available upon request; however, the following is a summary of the data from all testing samples. The graphical results precede the tabulated data to show the chromium to iron ratios calculated from the surface analyses by ESCA technique. 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 citric acid gel-based passivation process.

The most relevant data is summarized here:



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 Ultra Pass® Gel						
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 Ultra Pass® Gel						
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 (ambient)						
Sample	W28	W29	W30	W31	W32	MEAN
Cr/Fe ratio:	1.949	2.450	1.944	1.320	2.123	1.959

Statistical significance of the data was determined using unpaired two-tailed Student's 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 Ultra Pass® Gel	0.00000319527	Very Highly Significant
Non-passivated versus 4 hour Ultra Pass® Gel	0.00260815448	Highly Significant
2 hour Ultra Pass® Gel versus 4 hour Ultra Pass® Gel	0.526827069	Not Significant
Nitric Acid versus 2 hour Ultra Pass® Gel	0.791191203	Not Significant
Nitric Acid versus 4 hour Ultra Pass® Gel	0.468366968	Not Significant

CONCLUSIONS

Astro Pak Corporation's proprietary Ultra Pass® Gel mixture and process is effective at ambient temperatures for passivating weld areas on 316L stainless steel tubing. These techniques are also 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 Ultra Pass® Gel passivation process 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 ASTM A-380 and 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 Ultra Pass® Gel,

and 4 hour Ultra Pass® 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 gel-based citric acid agents at ambient temperature, and that the citric acid gel-based agents were equivalent to the traditional solution-based nitric acid passivation technique. 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.

About the Authors:

Daryl L. Roll, P.E., Chief Technology Officer

As CTO, Daryl leads the development and management of corporate technology objectives, safety and training programs, and monitoring of government compliance requirements.



Daryl also serves as the primary senior technical advisor to clients and employees. He has more than 30 years of experience in chemical processing, including the design of process cleaning equipment, chemical process technology, and precision cleaning of ultra-high purity systems. His expertise also extends to project engineering, chemicals and metals testing, corrosion research and project management. Daryl holds a B.A. in Chemistry and Earth Science from Cal State University, Fullerton and a Professional Engineer's license from the State of California.

Dr. Brent Ekstrand, Director of Quality

Dr. Brent Ekstrand is tasked with oversight of all quality-related programs, serving as Astro Pak Corporation's Director of Quality. Brent also serves as a technical advisor for complex clean room, 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, clean room operations, biofilm remediation and control, and passivation, as well as quality assurance and quality control. Brent received his doctorate from the University of the Pacific.

