

Why Passivate Stainless Steel and What Happens If You Don't

By: Patrick H. Banes, Astro Pak Corporation

To insure having the maximum corrosion resistance that austenitic stainless steel has to offer, the stainless steel surface must be in a passive state. The passive condition on the surface of the stainless steel is obtained by formation of a chromium oxide film on the metal's surface. This is accomplished by passivating the metal. Chemical passivation procedures using alkalines, wetting agents, chelants, and organic or inorganic acids are used to clean the metal surface thoroughly and in conjunction with an oxygen rich atmosphere, a uniform chromium oxide film forms. The key is to have a uniform chromium oxide film with an acceptable chrome to iron ratio (typically >1) and thickness (20-50) angstroms. Passivation is required to restore or enhance the chromium oxide film on the stainless steel surface when it has been manipulated by surface finishing, welding, grinding, external contamination, etc.

Mechanical finishing of stainless steel surfaces allows for a very smooth surface and is a prerequisite for subsequent electro-polishing. The mechanical action disrupts the existing passive surface and results in a surface with a low chrome to iron ratio. The possibility of surface contamination getting pushed or smeared into the metal surface or sub-surface also exists.

Welding stainless steel is one of the primary reasons for passivating. The metal surface is altered and free iron is released from the alloy. The chrome to iron ratio is also lowered in the heat affected zone of the weld. The free iron on the metal surface can initiate corrosion and/or rouging. It should be made clear that a successful passivation operation depends on having a proper weld. Passivation cannot make problems associated with lack of a suitable welding purge go away, i.e. severe weld discoloration or sugared welds.

Cutting, grinding and mechanical polishing also alters the stainless steel surface and can affect the passive surface. It is very important to use tools dedicated for use with stainless steel when performing these operations. Use of non-dedicated tools can result in leaving contaminants such as iron on the metal surface or even worse embedding contaminants into the stainless steel. Stainless steel surfaces with embedded iron can be passivated and pass criteria such as a ferroxyl test, only to exhibit a bloom of rust after being cleaned-in-place, steam sterilized or put into service. Performing multiple passivation procedures or refinishing the affected area may be required to alleviate the problem of the embedded iron.

Anytime a system is being fabricated there is the possibility and a likelihood that residues from the fabrication process end up in the system. Small particles, shavings of stainless steel, are not in a passive state and tend to have a high free iron content. Extreme care must be taken to prevent the stainless steel particles from getting into the system during construction. Evidence of particles in a system can be found embedded in valve diaphragms, inside spray balls and at valved low points. Corrective action to remove particulates needs to be taken during subsequent flushing and or passivation procedures by using filtration.

When a high purity water system is modified, the issues previously discussed: welding, cutting, grinding and polishing come into play and are reason to passivate. There is another situation that arises when an existing system is being modified. New tubing is being joined to existing tubing. What is the condition of the existing tubing? Is it rouged? New tubing requiring preoperational passivation may in fact be welded to tubing that is rouged. Typical preoperational passivation procedures will not remove rouging, thus the passivating chemicals never touch the stainless steel surface. Thought has to be put into the possibility of this situation and the

options that are available. Do I derouge the existing system prior to welding new tube to the existing tubing? Do I install ferruled connections, passivating the new tube, swab passivate the new ferrules on the existing tube and clamp the new and old tube together? Do I weld the new tube to the existing and derouge and passivate the combined new and existing system? When a system is being modified, it is an excellent opportunity to deal with existing conditions such as system rouging. The system is down, the passivating contractor is on site, chemicals are going to be put into part if not all of the system, so why not derouge and passivate the entire system while the opportunity presents itself.

System contamination from an external source introducing iron, chlorides and other unwanted contaminants, would be another reason to chemically clean and passivate a system. The issues associated with free iron contamination have already been discussed. Chlorine contamination can be a serious problem. The presence of chlorides on stainless steel surfaces is profound. Chlorides can penetrate the chromium oxide film and pit the base metal. This type of corrosion leads to system rouging and ultimately metal failure. In my many years of being involved with passivating systems for the pharmaceutical industry, I have seen multiple cases where metal failure is directly related to chloride contamination. Few if any failures could be linked solely to iron contamination. Austenitic stainless steels used in the pharmaceutical industry have a very low tolerance to chloride attack and should be avoided at all costs. In the proposed multiple step reaction the presence of chlorine causes the dissolution of the chromium oxide film, formation of ferric iron oxide and hypochlorous acid.⁵ The significance of the formation of the hypochlorous acid is that it oxidizes free iron and releases more chlorides, thus self-perpetuating the reaction.

Systems can also be passivated on a regular basis as a form of preventative maintenance. Regular passivation can nip future problems in the bud while maintaining the system in a pristine passivated condition. The reality of being able to passivate a system on a regular basis is not that simple. Lost production time, scheduling issues and the costs associated with system passivation often prevent scheduled maintenance passivation of systems from being performed. The alternative is to clean and passivate a system when it is deemed necessary. System inspection can be a useful tool in helping to make that decision.

One of the best ways to determine what is going on inside a water system is to take a look. Is rouging occurring in the system? Is the rouge very light or well established? Where is rouge found in the system? Is it evenly distributed throughout the system? Regular inspection of a system can identify a trend determining how fast rouge is developing and spreading through a system. The key places to look for rouge in a system are: pump head, pump suction and discharge, tank (above and below normal liquid level), and tank spray ball.

Systems prone to rouging, typically high temperature high purity water and steam systems are usually derouged and passivated on an annual or biannual basis.

Rouge is an iron oxide film that develops on the surface of stainless steel. A corrosion process at a localized or affected area on the stainless steel surface can initiate the formation of rouge. Intergranular, pitting, crevice, galvanic, stress, electrolytic, chemical and erosion are all types of localized corrosion that could damage or breach the chromium oxide film and lead to rouging. Once the chromium oxide film is damaged the exposed metal is oxidized. Dissolution of the oxidized metal allows movement through the system. At some point, the oxidized metal is deposited back onto the stainless steel surface as a metal oxide/hydroxide. The metal oxide/hydroxide or rouge is composed primarily of iron. Over a period of time, the rouge spreads through a system by a deposition process.

General or uniform corrosion can also be a source of iron that can be oxidized and form rouge. Does there have to be a measurable metal loss to see signs of rouging? In a recent study, rouge was reproduced under laboratory conditions. The study suggests that rouge was the result of a very slow metal dissolution while the stainless steel maintained its passive state. It was also documented that no corrosion was observed on rouged test panels. The study demonstrated that rouging develops faster in purging atmospheres of nitrogen and carbon dioxide containing air. Purging with atmospheric air resulted in less rouge, while purging with air with no carbon dioxide resulted in no visible rouge. I believe this information reinforces the fact that oxygen is needed to develop and maintain the chromium oxide film and that purging gases could have an impact on rouge development.

As there are different origins to system rouging, there are different rates of rouge development and there are different physical appearances of rouge. In some cases, the rouging appears quickly within a month or two after system start up. In other cases, it is several years before rouging is observed. In either case, rouging is an industry wide phenomenon. Due to the variety in the appearance and texture of rouging, it would appear to be a very site (facility) specific and more so, a system specific phenomenon. Rouge can be observed in a variety of colors including; orange, light red, red, reddish-brown, purple, blue, grey and black. It can vary from a very loose film, dust like in appearance, which can be readily wiped off, to a tightly adhered film that requires very aggressive acids such as hydrofluoric acid to etch the film off.

Studies performed by Mr. John Trevberg, categorize rouge into three classes. The classes help to identify the rouge by its origin and characteristics.

Class 1

Origin

- Mechanical action, evident in pump housings
- External iron contamination
- Deposition film from the upstream source in system

Characteristics

- Orange to red
- Ferrous iron oxide (FeO)
- Loosely adhered to the base metal by electrostatic attraction
- Metal surface under rouge not affected
- Typically found in water system pump head
- Rouge composition matches that of stainless steel not that of corroded stainless steel

Class 2

Origin

- Stainless steel surface with a low Cr/Fe ratio
- Chloride contamination
- Unpassivated stainless steel surfaces
- Surface corrosion: pitting, crevice corrosion

Characteristics

- Red to brownish red
- Ferric (Fe₂O₃) iron oxide
- Tightly adhered to the base metal
- Rouge on the surface of SS covers pitting, crevice and other types of corrosion

- ° Surface of the stainless steel is altered

Class 3

Origin

- ° In very high temperature systems, i.e. clean steam systems

Characteristics

- ° Blackish blue to black
- ° Iron oxide found in magnetite form (Fe₃O₄)
- ° Very tightly adhered to the base metal
- ° Stainless steel surface under the rouge has a low Cr/Fe ratio

Having a better understanding of the origins of rouge and how it spreads through a system is a helpful tool in the attempt to avoid or minimize system rouging. There still however, is the issue of rouge removal. Removing rouge is not as simple as we would always like it to be. The type of rouge described as Class 1 or Class 2 (red rouges) can generally be removed by using several different chemical processes using acids, acid/chelant combinations or reducing agents. As mentioned earlier, rouge within a system is rather specific to that system. Unusual circumstances can arise when red rouge, that one would think would be rather simple to remove, in fact is very difficult. The Class 3 rouge (black rouge) unlike the Class 1 and Class 2 rouge is typically very difficult to remove. Chemical procedures designed to remove red rouges are typically ineffective in removing the Class 3 rouge. The use of hydrofluoric acid may be needed to etch the black rouge off the stainless steel surface. Using hydrofluoric acid does not guarantee uniform removal of the black rouge. It also has the potential to etch or damage the base metal.

In conclusion, passivation of austenitic steel is essential to establish and maintain a uniform chromium oxide film on the stainless steel surface. This is especially true when the metal has been modified during fabrication and system construction. System contamination would also warrant passivation or re-passivation. The application of austenitic stainless steel in heated high purity water and steam systems sets the stage for the formation of rouge due to the corrosive environments associated with systems. Trace amounts of iron released by metal dissolution, a corrosion process or system contamination will initiate the rouging process. Regular system cleaning and/or derouging and passivation is the simplest method to control rouging and maintain a passivated system.

PatrickArticle is the Northeast Technical Sales Manager for Astro Pak Corporation. He holds a B.A. in Zoology and a minor in Chemistry from the University of New Hampshire and completed Inorganic Chemistry studies as Rutgers University. He is a member of the ASME BPE Surface Finishes Subcommittee and the ISPE New Jersey Chapter.

During his 26 years of experience, he has given presentations on the subject of passivation of stainless steel for ASME, BPE, ISPE, PDA, ASTM, AIChE, and Interphex. His papers on passivation and derouging have been published in Microcontamination, Pharmaceutical Engineering, and Ultrapure Water magazines. He has also been a featured PFI Conference speaker.

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