

Passivation and the Passive Layer

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INTRODUCTION

Purity of fluids and gases are a critical issue in the food and beverage industry. Passivation techniques provide a way of achieving it. Contamination causes serious problems for a food and beverage company. Not only can it damage or fail the end product, but it can also require the replacement of valuable equipment resulting in unnecessary expense and costly system downtime. For these reasons, clean, corrosion resistant systems are essential.

Passivating chemistry using chelants is the most effective technology. Chelants (KEY-LANTS) are chemicals that form soluble, complex molecules with certain metal ions, thereby inactivating the ions in solution so they cannot normally react with another element or ions to produce precipitates or scale. Chelants enhance the solubility of scales and certain other contaminants do not precipitate when the cleaning solution's pH is adjusted for disposal, and can be used on some scales and contaminants that mineral acids will not attack. When properly used chelants minimize intergranular attack, pitting, and other harmful effects.

A TECHNICAL SUMMARY

PASSIVATION DEFINED:

Passivation is the chemical treatment process by which the electrochemical condition of passivity is obtained on the surface of metal alloys. Passivity as it relates to austenitic stainless steel is the state in which chemical reactivity is minimized under special environmental conditions, such that the metal exhibits a very low corrosion rate. 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.

PASSIVATION THEORY OF AUSTENITIC STAINLESS STEEL:

Stainless steel surfaces are rendered passive by the formation of a surface film that is a "barrier" to corrosion. This "barrier" establishes a very slow, controlled equilibrium of anion and cation diffusion across it. This passive layer consists primarily of chromium oxides, hydroxides and iron compounds, which form on the outermost surface of the metal phase. Initial passive layer establishment is achieved through chemical treatments, which remove foreign inclusions and more reactive metal ions. This treatment enhances the effective concentration of chromium, nickel and molybdenum (in the case of 316-grade stainless steel) at the surface of the metal phase. Through an unknown mechanism, these three metals together affect the creation of a more homogenous chromium oxide/ iron oxide passive layer. The uniformity and stability of the film will vary depending upon the method of treatment. Passive layer thickness and stability is critical to system longevity and product purity.

ELECTROPOLISHING:

While electropolishing does create a visually bright and shiny surface prior to installation, the micro-finish and passive layer that is developed by electropolishing is destroyed by heat during installation welding. The heat-affected zones (HAZ) of welds are noted for their straw color or "heat tint," which is indicative of the breakdown of the passive layer. Passivity must be chemically restored to all weld areas prior to placing a system into operation, or rouging and contamination will result.

Furthermore, cleanliness resulting from electropolishing cannot be maintained over time in corrosive environments due to the dissimilar metallurgical make-up of milled alloys. In addition to primary constituents, milled alloys contain various inclusions such as sulfides, aluminum, manganese, and others, which act as contaminants by diffusing or leeching through the base metal, the metal phase, and even the passive layer, and ultimately into the media stream. These unwanted inclusions must be removed by chelation during passivation, or product contamination and corrosion will result.

CHELATION:

The concept of sequestering or “chelating” specific contaminants found on metal surfaces is not as complicated as it may seem. Chelants, according to ASTM-A-380, are “chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale.” This process is called Specific Ion Coupling, and results when the new molecules bind and hold unwanted metal ions, preventing them from re-depositing on the treated surface until they are removed through the effluent stream. The chemicals that we refer to as chelating agents work in aqueous solutions (such as Citric acid mixtures) to “enhance solubility of scales and certain other contaminants that even mineral acids do not dissolve.” When properly applied, inter-granular attack, pitting, and other forms of corrosion are eliminated.

NEW SYSTEM PASSIVATION:

Passivation of new systems is an important part of the “start-up” phase of construction. As previously discussed, newly fabricated and welded piping and vessels may have a very shiny appearance, but inclusions in the metal can present major problems in the future.

New stainless steel contains a host of impurities, largely because much of it is recycled from lower grade alloys by adding substances such as chromium, nickel and molybdenum, among others to improve the heat/corrosion resistance of the steel. During the reconstitution process, aluminum is also added to deoxidize the “melt” to decrease porosity. These inclusions must be removed from high purity systems or corrosion will result.

Another impurity frequently found in mechanically polished stock is residual abrasive material left in the surface from the mechanical finishing procedures that precede electropolishing.

This abrasive material can consist of up to 15% iron oxide, and might be more appropriately termed “rouge pending” or “rouge initiator”. Another favorite mechanical finishing abrasive is corundum or aluminum oxide. Because it is so hard, these materials get embedded in the stock surface and provide sites for severe pitting to begin.

To further complicate matters, welding operations create a crystalline structure of corrosion cells and carbon inclusions that are present in the heat affected zone. Anytime heat tint is present, the passive layer has been compromised. Dust and other forms of debris which may exist in proximity to the system being fabricated can contaminate. Grinding, cutting and deburring of dissimilar metals, such as structural (carbon) steel which then accidentally contacts the micro-finished surface, can begin corrosion before construction is even completed.

The benefits of pre-operational passivation include removal of residues, light heat tint, scales, inclusions, residual abrasives, free iron and other metallic dusts, galvanic corrosion and moisture cells, and migrational oxidation. A collateral benefit is lower carbon content of the stainless surface following chelation.

EXISTING SYSTEM PASSIVATION:

Existing systems also benefit from passivation through the elimination of process application residues. Corrosion occurs due to metal salts in product, galvanic corrosion due to dissimilar metallurgy and oxygen depletion cells. Migrational corrosion from rouge (pre-rust) resulting from extreme temperatures and improper pumping system practices may appear;

in addition, corrosion due to compromised systems is often observed. Cleaning and passivation of these systems will remove the residues and control corrosion of the system.

THE VALUE OF PASSIVATION:

1. Product quality – enhanced by the minimization of corrosion material introduction into the product. This could be a liquid, gas or light stream (in the case of LASERS).
2. System integrity – enhanced through proper applications. Stress corrosion, rouge formation, inter-granular attack, pitting and other degenerative conditions when permitted to spread can compromise a portion or all of the affected systems.
3. Cost (direct or indirect) – The expense of one wasted batch of product or one production day lost far exceeds the cost of a properly applied passivation procedure. Maintenance expenditure for new and existing systems can be held to a minimum and by including regular re-passivation into a planned maintenance program, these costs can be avoided.

PREPARATION OF PRODUCT CONTACT SURFACES:

General Pre-cleaning and degreasing is performed in order to remove grease, oil, soil, grit and other gross contamination prior to final cleaning and passivation per ASTM A-967. Pre-cleaning is accomplished in accordance with Astro Pak's proprietary Passivation Procedures Section 6.0. ASTM A-967 is the most current passivation document in print and in paragraph 7 addresses the Citric acid method on which our procedure is based.

Phase 1: Chemistry is designed to render the system free of organic contaminants such as light oils and residual grease while chelating out some of the potential corrosives. Chemicals such as detergent phosphates, non-ionic surfactants, and EDTA chelant may be utilized in this phase depending on the system's history and condition. Chemicals are mixed and heated, to the correct concentration, then re-circulated per the applicable Astro Pak procedure.

Phase 2: Chemicals are added to the solution. Typically, these would include materials such as tripoly phosphate and gluconate as a second detergent and chelating agent, respectively. Again, chelation of potential corrosives is initiated utilizing precise mixtures and by carefully controlling temperature. Chemicals are mixed and heated, to the correct concentration, then re-circulated per the applicable Astro Pak procedure.

Following phases 1 & 2 the system is drained and rinsed with high purity water, the system cleanliness analyzed, and then sent to drain. The system is now pre-cleaned and ready for passivation.

Phase 3: involves the actual passivation step and is accomplished per the Astro Pak procedure. Passivation chemicals consist primarily of high purity water, surfactant, Citric acid, reducing acids, chelants, intensifiers and ammonium hydroxide. Chemicals are mixed and heated to the required temperature, and re-circulated.

During this phase, pH and effluent analysis tests are conducted throughout the process at prescribed intervals. Astro Pak measures the removal of iron and other substances, as necessary, with the aid of a portable spectrophotometer. When testing indicates the passivation process is liberating no new contaminant ions, the procedure is typically stopped. The system components, i.e., tees, valves, and user points are regularly cycled to assure proper contact with the heated solution.

In new systems, and where possible in old systems being re-passivated, many companies require the testing of stainless steel "coupons" by a ferroxyl test for surface iron contamination. Astro Pak can provide this service as an additional test.

Finally, the system is thoroughly rinsed with high quality, heated DI or RO water. The pH and conductivity are monitored until the quality of effluent is equal to quality of influent rinse water. The surface residue can be tested with a wipe test or

a solution rinse analysis for confirmation of treatment removal of cleaning solution.

A DISCUSSION OF THE PASSIVE LAYER

Fundamental to the understanding of the passivation of stainless steels is a comprehension of the film that lies in the surface of the metal in the passive state. Here we will outline the composition and various physical aspects of the passive film as it relates to Stainless Steels, primarily austenitic stainless. If the reader desires a more in-depth and technical analysis of this material they may refer to the section in the reference volume on passive films.

The surface of the metal has been variously described as being composed of either two or three layers. The three-layer model includes the base metal, a metal phase or transition zone, and the passive layer. The two-layer description counts the base metal and the metal phase layer as one. The reason for the distinction between the two and three layer model is that the boundary of the metal between the base and the passive layer (the metal phase) contains differing concentrations of alloys than is present in the base metal.

The passive state exists when the metal is covered by a thin oxide layer and is protected from the contact of contaminants. This is in contrast to the active state, where the base metal is exposed.

The passive layer is the thin outer film (measured in Angstroms) that exists on the surface of the metal. This film protects the base metal from contact with corrosive media. The composition of the film is dependent on the composition of the underlying base metal. The selective dissolution of iron and the subsequent enrichment of chromium and other elements in the metal phase form the film. As the iron content decreases, the percentage of chromium present in the film increases (in relative terms), thus becoming enriched. The chromium content in the passive film is dependent on both the concentration of the element in the base metal alloy and the exposure time to the passivating solution or media. This chromium enrichment increases with exposure time up to a maximum point, after which it stabilizes.

The passive oxide film will develop under almost any condition, for example upon exposure to only air or water. However the protective ability of the film varies depending upon the conditions under which it was developed. "Natural" films created upon exposure to air or water often lack the uniformity and chromium richness that makes a film a good protectant.

Natural passive films tend to break down more quickly than the more viable films that can be created using other acid media (i.e. Citric or Nitric). The exposure time is also a critical variable in the development of the film. What will facilitate the formation of the passive film on limited exposure times can become corrosive under conditions of prolonged exposure, causing the film to degenerate and causing damage to the underlying base metal.

Thus it is critical to pay attention to the specified exposure time when passivating because overexposure can be damaging. with mineral acid passivation. The thickness of the passive film remains constant throughout the period of chromium enrichment up to the maximum chromium concentration. The reversal of the chromium build-up coincides with the beginning of film thickening. This reversal is also attributed to the beginning of the breakdown on the passive state. This breakdown is suggested to occur non-uniformly, beginning at a number of activated sites from which it spreads. Iron oxide will form at the surface and grow.

Other alloys present in the base metal affect the passive layer, although they may not be present in the passive layer. In nickel (Ni) bearing austenitic Stainless Steel, Ni is enriched in the metal phase but is only detected in trace amounts in the passive film or not at all. The presence of Ni serves to reduce active dissolution in the active-passive transition and to inhibit localized anodic dissolution during film breakdown. This translates to an improvement in pitting resistance.

Molybdenum is also present in an enriched form in the metal phase of those austenitic Stainless Steel grades that possess Molybdenum. It is also present in the passive layer but it is suggested that the beneficial effect of Molybdenum come not from its presence there but from the effect that it has on Chromium enrichment of the passive layer. Molybdenum

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is easily passivated immediately above its corrosion potential, therefore, the enrichment of Molybdenum in the metal surface should facilitate the passivation of the metal. It is surmised that Molybdenum affects the steps of adsorption and electron transfer, which precede the growth of the passive film. However, it should be noted that Molybdenum alone does not facilitate the passivation of iron, but only does so in combination with Chromium. Therefore, it can be assumed that there is a synergistic affect between Molybdenum and Chromium. This is supported by the fact that maximum Chromium enrichment is best found in grades of metal where Molybdenum is present. Molybdenum also serves to control defects in the passive film caused by Fe 2+ (Ferrous) ions.

It should be kept in mind that the main passivating species in austenitic Stainless Steel is Chromium. The effect of the other alloys present in the base metal serve primarily to better facilitate the Chromium enrichment of the passive film or to improve the protection and durability offered by the film. This enrichment is created by the removal of iron and other contaminants from the active surface.

KEY DEFINITIONS:

Metal Phase (Transition Area): The boundary between the base metal and the passive layer, which contains different concentrations of alloys than the base metal, with an increase in nickel concentration.

Base Metal: The main metal composition on which the film is formed (ie. AISI 316 stainless steel).

Passive Layer: The thin outer oxide film that exists on the surface of the metal, protecting it from corrosion.

Passive State: The condition existing when the surface of the metal is coated with a thin protective oxide film.

Enrichment: As related to Chromium and Nickel, this occurs when Iron present in the surface of the metal is removed and the relative percentage of Chromium present increases.

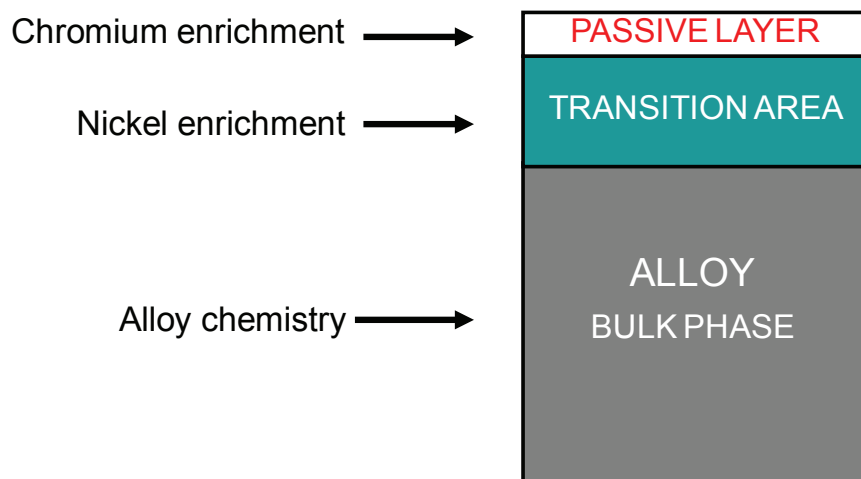
Ion: An atom or molecule that has a net positive or negative charge acquired either by gaining or losing electrons from its initially neutral state.

Cation: An ion with a net positive charge.

Anion: An ion with a net negative charge.

Electron Transfer: When electrons are passed from one atom to another resulting in a change in charge.

STAINLESS STEEL CROSS SECTION:



A DISCUSSION ON CORROSION

Corrosion is a major concern in the food and beverage industry. Not only does it cause damage to equipment, but also it can contaminate the product that it comes in contact with causing potential financial loss. There are a variety of corrosion problems that can afflict equipment in the food and beverage industry. This section will give a brief description of some of these problems and explain the circumstances under which they occur. It will also explore the topic of rouge or light rust. This form of corrosion and the damage it can cause to austenitic stainless steel has recently become of increasing concern in high purity systems.

TYPES OF CORROSION

There are two basic classes of corrosion under which more specific categories fall. The first is uniform or general corrosion. This class is the gradual erosion of the metal in very small amounts. This uniform oxidation is encountered in practical applications of stainless steel but can be significantly reduced by the protection offered by the passive film.

The second class of corrosion is localized attack. These types of corrosion account for about 90% of failures in process applications. Localized forms of attack include such corrosion types as pitting, crevice, erosion, selective (plug), stress corrosion cracking (SCC), fatigue, and intergranular. Stainless steels are subject to pitting, intergranular and stress corrosion cracking forms of corrosion so we shall focus our discussion on these types. Localized attacks occur when there is a breakdown of the passive film in a specific area. It is susceptible to localized penetration by small aggressive ions of high diffusivity. In food and beverage process applications this is often chlorides. As was noted in the section on passive films, molybdenum and nickel enhances the resistance of stainless steels to attack from chlorides.

PITTING (CREVICE) CORROSION

In chloride-rich environments, stainless steels are susceptible to pitting. This occurs when the chloride ions penetrate the passive film and attack the exposed base metal. Pitting often occurs in the presence of various inclusions on the surface of the metal. These inclusions act as preferential sites for pit nucleation and subsequent pit growth. Passivation techniques using a standard nitric acid solution will not remove all inclusions present, for example it fails to remove aluminum inclusions, which can lead to pitting. Precautions should be taken to avoid pitting of metal surfaces because once pits have formed the component becomes very difficult to clean and often must be replaced entirely.

INTERGRANULAR CORROSION

Intergranular corrosion is a preferential attack at the metal grain boundaries. This problem usually arises in the weld area and results from chromium depletion caused by carbon present in the metal. As the weld area cools the carbon can deplete the alloy of 17 times its own weight of chromium. This occurs by forming complex chromium carbides along the grain boundaries. These chromium carbides do not possess the same corrosion resistance and can lead to intergranular attack by a corrosive fluid. This problem has been minimized by the use of lower carbon content stainless steels such as 316L with a maximum carbon content of 0.03 percent.

STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) in stainless steels is most frequently aggravated by the presence of chlorides, low pH, and high temperatures. Chloride SCC is rare at temperatures below 40-50°C, however, a combination of sulfides and chlorides greatly aggravates the propensity for SCC. SCC can occur even at ambient temperatures in the presence of this

combination. Hot caustic can also cause SCC.

ROUGE

Rouge is a problem that is often encountered in WFI (Water for Injection) systems. It is a complex layer that can taint any products handled in the system and can accelerate the initiation of serious corrosion of the system. Rouge in stainless steel is typically composed of ferric oxide (Fe_2O_3) with aluminum, calcium, traces of manganese, and possibly a number of other impurities depending upon the components in the system.

Rouge will appear in a number of different forms. These include a layering of yellowish-green powder over a dense brown deposit, which is lying on an ingrained black layer. It has also appeared as a gelatinous and hydrated bottom layer covered by a dry upper crust. Most frequently, it appears as a dense reddish-brown over a black substrate.

There are a number of factors, which can cause rouge. One of these factors is known as heat tint. Heat tint occurs as a result of improper welding gas purge technique. It appears as a slight straw color on the boundary layer of the heat affected zone. If this is not removed at the onset, rouge will begin to develop at the area of the affected weld. Other possible causes of rouge include the introduction of different types of steel parts (such as martensitic or carbon steel) into the system, mechanical or electropolishing surface preparation techniques, and/or improper passivation techniques.

DISSIMILAR METALS

One of the common causes of corrosion in food and beverage systems is dissimilar metals. Often components such as water and steam regulators, safety valves, feedwater pumps, impeller setscrews, valves and steam traps are made of other alloys or another grade of stainless that is unsuitable for the application. This creates a situation where the adage, "a chain is only as strong as its weakest link" applies. Once corrosion can gain a foothold in this component, it will spread throughout the entire system. Additionally, dissimilar metals can often actually cause corrosion by introducing free iron into the media stream where they can be deposited on other surfaces and cause galvanic corrosion cells. Consequently, when inspecting a system it is important to be sure that all components are constructed of the same material. Failure to adhere to this basic construction and maintenance protocol and any work done cleaning and passivating the system may be rendered useless.

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.

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