

Developments In Citric Acid Passivation Of Stainless Steel

*R. Kremer, Stellar Solutions, Inc.
McHenry, IL USA*

Stainless steel passivation is a mysterious process to many, but one that is important in the metal finishing industry to get the full benefit from corrosion resistant steel alloys. The principles of passivation are explained. Traditional nitric acid based passivation methods are compared to more recent citric acid based methods, including differences in safety, disposal issues, ease of use, and resulting corrosion protection. Grades of stainless steel that require special methods are pointed out, such as the need for alkaline precleaning of high sulfur grades and the benefits of higher pH citric acid solutions for the martensitic and precipitation hardening grades. The difficulties of passivating stainless steel castings and laser marks on stainless steel are discussed. Passivation testing methods and industry specifications for stainless steel passivation are discussed.

For more information, contact:

Ray Kremer
Stellar Solutions
4511 Prime Parkway
McHenry IL 60050
Phone - 847-854-2800
E-mail - ray@citrisurf.com

Introduction

Stainless steel is a very important material to modern society. It is used in many places that high strength and corrosion resistance are required. Many people not familiar with the industry or metallurgy are often surprised to hear that even stainless steel can rust. Since the main constituent of stainless steel is iron, passivation is required to gain the full potential of its corrosion resistance. This process was traditionally done with nitric acid, but recently introduced citric acid processes show many benefits and have rapidly gained popularity. This paper will discuss the history of citric acid passivation in industry, the advantages of using it instead of nitric acid, special variations and procedures that are used when needed, and methods for testing the effectiveness of a passivation treatment.

Basics Of Passivation

Passivation by a chemist's definition is to make a material resistant to a chemical reaction, such as corrosion. Most metals self-passivate upon exposure to air, forming a thin layer of metal oxide on the surface. ASTM's stainless steel passivation specification, A967, defines passivation as the removal of iron and other exogenous materials from the surface. If there is no free iron exposed on the surface, rust will normally not form. The chromium present in the alloy, and also the nickel in the austenitic 300 grades, are then able to form an oxide layer that protects the underlying steel from normal environmental conditions. The same holds true for non ferrous metals that have acquired contamination surface iron during tooling and other processes.

History Of Citric Acid Passivation

The use of citric acid for passivation of stainless steel was first discovered over twenty years ago by the Adolf Coors brewing company in Germany. They had begun using stainless steel kegs for their beer but discovered that the first time each keg was used the beer gained a metallic taste. Insufficient passivation of the kegs left iron on the metal surface, which then was taken into the beer. This effectively passivated the kegs for future use, but at the expense of much wasted beer. A study was run testing many chemicals for their stainless steel passivation potential. Citric acid emerged as the clear winner, as shown in Table 1.

Table 1 Coors Passivation Test Of Effects On Beer Flavor¹

Passivating Agents (All at 70°C (= 158°F))	S. S. Alloys	Flavor Results
4% Citric Acid	304 & 304L	Acceptable
2% Citric Acid	304 & 304L	Unacceptable
4% Sulfamic Acid	304 & 304L	Unacceptable
2% Sulfamic Acid	304 & 304L	Unacceptable
4% Tannic Acid	304 & 304L	Unacceptable
2% Tannic Acid	304 & 304L	Unacceptable
4% Phosphoric Acid	304 & 304L	Unacceptable
2% Phosphoric Acid	304 & 304L	Unacceptable
Calcium Oxalate	304 & 304L	Unacceptable
Ozonated Water	304 & 304L	Unacceptable

Years later we discovered this study while searching for a solution for a company that was using nitric acid to passivate their stainless steel springs but was under pressure from OSHA to eliminate it from their plant. Further experimentation led to improved formulations and they went into production with citric acid passivation baths. Many more companies followed suit, happy to rid themselves of nitric acid.

The standard reference for stainless steel passivation at the time was the military specification QQ-P-35c, which of course described only nitric acid processes. Many companies eager to switch to citric acid were unable to because they were beholden to this spec. Fortunately this came at a time when the Department of Defense was working with industry groups to phase out military specs in favor of industry versions. ASTM developed the new specification A967, adding the newly introduced citric acid methods alongside the established nitric methods, and QQ-P-35c was canceled by the DoD in 1998.

The aerospace industry maintained use of the old spec under the designation AMS-QQ-P-35 until 2005 when it too was canceled and superseded by AMS 2700, a newly developed specification that offered a choice between citric acid and nitric acid stainless steel passivation.

Also referencing nitric acid for passivation of stainless steel is ASTM A380, which is not actually a specification but a standard practices document, a distinction not commonly recognized. A380 describes various methods for

cleaning stainless steel parts and gives procedures for nitric acid passivation. However, especially with A967 as a proper alternative, A380 should not be used as if it were a specification.

Comparison With Nitric Acid Passivation

Citric acid passivation offers many advantages over nitric acid passivation. Perhaps foremost among them is safety. Nitric acid is very hazardous while citric acid is quite the opposite, in fact skin contact is generally not a problem with citric acid, though of course good chemical handling practices dictate the use of protective gloves and goggles anyway. Nitric acid also gives off harmful fumes, from general fumes that cause corrosion in the surrounding structure and equipment (often requiring costly maintenance as a result) to large red clouds of very toxic fumes if the wrong reaction is accidentally set off. Citric acid, on the other hand, is a solid, so the only fumes that can be generated from a citric acid bath is water vapor.

Disposal of nitric acid is also difficult, as it and the associated rinse water is hazardous and when used to passivate stainless steel will contain heavy metals that are also considered hazardous. Citric acid is not hazardous, and as shown in Table 2, with stainless steel it usually only removes the iron, not the nickel, chromium, or other metals present. This not only keeps it from being considered environmentally hazardous, but is a benefit for the stainless steel being passivated as it means there is no worry of etching the surface if the parts are left in longer than the prescribed time.

Table 2 Metal Content Of Citric Acid Bath After 30 Days Passivation Of 316L SS

	Citric Acid Titration	Metals in Citric Acid Solution (mg/L)				
		Fe	Ni	Cr	Cd	Mn
Before Passivation	4.44%	<0.05	<0.05	<0.05	<0.02	<0.05
After Passivation	4.40%	0.72	<0.05	<0.05	<0.02	<0.05

Each company using citric acid passivation is responsible for making sure they meet local, state, and nation regulations for disposal, but in most situations neutralization all that is required, and then a citric acid passivation bath or the associated rinse water can be put to drain. One caveat is that plants using a precipitation system for waste treatment from their other processes cannot put citric acid into that system as it will chelate the metals present. While the chelation is beneficial for passivation, binding the iron ions so they cannot redeposit on the parts, it is undesirable for hazardous metal waste to come into

contact with a chelator.

For the aforementioned reasons citric acid is much easier to use for passivation. It can also be used with higher heat than is safe with nitric acid, allowing a faster process, and it can be used in an ultrasonic tank, which also speeds things up and adds cleaning benefits. With only the iron being removed, citric acid passivated parts have a thicker later of chromium on the surface, thus allowing a better chrome oxide layer to form, as shown in Tables 3 and 4 via Electron Spectroscopy for Chemical Analysis and Auger Electron Spectroscopy data.

Table 3 ESCA Evaluation of Passivation Process

	Citric Acid Sample 1	Citric Acid Sample 2	Nitric Acid Sample 1	Nitric Acid Sample 2
Crome oxide / Iron oxide ratio	5.5	5.3	2.1	2
Chrome / Iron ratio	2.5	2.5	1.4	1.4

AES Depth Profile Results

	Oxide Thickness	Max. Depth of Enrichment	Depth of Enrichment
Citric Acid Sample 1	27.0 Å	18.0 Å	17.0 Å
Citric Acid Sample 2	28.0 Å	19.0 Å	17.0 Å
Nitric Acid Sample 1	21.0 Å	13.0 Å	12.0 Å
Nitric Acid Sample 2	17.0 Å	11.0 Å	11.0 Å

Variations Of The Citric Acid Passivation Formula

Variations on the citric acid passivation bath are sometimes called for. The austenitic grades of stainless steel work well in a citric acid bath with a pH of around 2, but martensitic and precipitation hardening grades are better served by a pH of 3 or higher. Fortunately the higher pH is effective for the austenitic grades as well, so only one bath must be maintained even when a range of different grades are being passivated.

The high sulfur content of the free machining grades of stainless steel can cause both high sulfur levels in the passivation bath and sulfide blooms (that look very similar to rust) on the steel surface post-passivation. A hot alkaline bath used to preclean the parts prior to passivation will remove sulfur from the surface and avoid these issues.

Not all parts that need passivation are small enough to be dipped in a bath. Thickening agents have long been used with nitric acid and nitric/hydrofluoric acid mixes to form a paste that can be used to treat large and/or vertical surfaces. The same can be done with citric acid, and the same safety and disposal benefits apply.

Other Special Considerations

Passivation should always be the final step in the manufacturing process of a stainless steel part, as any alteration of the surface will expose new free iron. Some common operations require special consideration. Laser markings are commonly used, especially in medical fields. Laser marked areas on stainless steel are susceptible to rusting if they remain unpassivated. However, a mark made with the laser power set too low is removed relatively quickly upon exposure to acid. Correcting the laser setting often avoids the difficulty, otherwise it is useful to give the part a full passivation cycle prior to marking and a second, shorter cycle afterwards, enough to improve the corrosion resistance but stopping short of removing the mark.

Welds are often required on parts. The heat affected zone of the weld often shows up as a blue discoloration due to the formation of chrome carbide, which also shows the depletion of the chromium from the main metallic structure, thus reducing the corrosion resistance properties. Citric acid is effective in restoring corrosion resistance along a weld, however it is not strong enough to remove the discoloration. When the cosmetic appearance of the weld is a concern, the weld line requires something that can effectively remove all metals from the surface. Pickling chemistry such as nitric acid/hydrofluoric acid is effective. Abrading the surface via grinding or grit blasting is another option (though due to the danger of contamination, care must be used to not use carbon steel material or material that has been used on carbon steel parts). A third method is to apply electricity. A current applied through a wand-like apparatus to the discoloration, using the same principle as electropolishing, will quickly remove it. Which method is best to use depends on the equipment available and the amount of welds that need cleaning.

Problematic for Passivation

The introduction of citric acid passivation has allowed good corrosion resistance even for difficult grades of stainless steel that nitric acid could not do an effective job with. However, there are still some instances where stainless steel can resist the best of passivation efforts. Castings pose a challenge, particularly those with rough or porous surfaces that serve as an enormous source of free iron. There are citric acid based formulas that work better with many castings save those with extremely poor surfaces.

Also a rising problem in the industry is poor quality stainless steel, usually made in the far east, often due to increased amounts of scrap iron used in production. To meet the specification for any particular grade of stainless steel, an alloy must meet the prescribed percentages for chromium and other additives, and most people just presume that the remainder is iron. However this is not necessarily true, and inclusions of other materials greatly affect the corrosion resistance. This can be seen in stainless fixtures used in harsh environments such as swimming pools and coastlines. Traditionally 304 was sufficient, but with current steel 304 is often inadequate and the more expensive 316 must be used to achieve sufficient corrosion protection. Starting with high quality steel avoids a lot of problems.

Passivation Testing

Evaluating the corrosion protection imparted by passivation is a key item in finding and maintaining a good process. Several passivation tests are available. The most convenient test for speed and ease of use is the copper sulfate test. A few drops of copper sulfate solution is applied to the stainless steel surface. If free iron is present, copper will deposit on the surface and a color change will be visible after several minutes. The potassium ferricyanide test works in a similar manner. Both tests, however, can give false failures on 400 series stainless steels due to the lower chromium content in those alloys.

Slower but still fairly convenient in terms of not needing specialized equipment is the boiling distilled water test. The exact time periods used vary depending on what specification you are looking at, but in general it's sufficient to immerse the part in the boiling (or near-boiling) distilled water for an hour, then remove the heat and let it cool for an hour, then set the part out to air dry. Rust will often appear long before the end if the part is not well passivated. The test can be bumped up a notch by adding sodium chloride, common table salt, to the water, as chloride is damaging to stainless steel. (This is why coastal and swimming pool environments are bad for difficult for stainless, and why bleach should never be used to clean it.)

Moving up from there, the high humidity test and salt spray test also seek to accelerate corrosion, and typically require sending the parts out to a laboratory that has the necessary apparatus. Test results of a more quantitative manner can be acquired via electron spectroscopy for chemical analysis and auger electron spectroscopy, which can report the chemical composition of the surface layer, indicating the level of chromium enrichment (due to iron depletion from the passivation treatment) and the amount of chrome oxide formation.

Summary

The advantages of using citric acid for passivation of stainless steel combined with the knowledge of how to handle special application give the best possible corrosion resistance. With nitric acid no longer necessary for passivation, those in the industry who need to make use of it can benefit greatly in improved part quality and cost savings. This is borne out by tests run by thousands of companies worldwide.

References

[1] H. Olsson, J. Parra, and J. Ragno, Stainless Steel Flavor Contribution to Beer, *MBAA Technical Quarterly*, Vol. 20, No. 3, 1983, p 102-105