Passivation of Aerospace Stainless Steel Parts with Citric Acid Solutions

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AMS-QQ-P-35 (which replaced federal specification QQ-P-35) is an SAE standard used in the aerospace industry to passivate stainless steel parts. AMS-QQ-P-35 recommends the use of different concentrations of nitric acid (with and without chromates), and these solutions are used either at ambient temperatures or heated. The type of stainless steel that is being passivated dictates the nitric acid solution that should be used. In addition, the aerospace industry also has their specific list of preferred nitric acid passivation solutions that are variations of the AMS-QQ-P-35 solutions. Basically, this requires aerospace metal finishing job shops to maintain several passivation tanks (as many as four or more) in order to meet all of their aerospace customers' requirements. ASTM (American Society for Testing and Materials) has issued a specification for stainless steel passivation that allows the use of citric acid solutions as an alternative to nitric acid solutions (ASTM A967-99). This paper describes the results of an evaluation of citric acid solutions used to passivate stainless steel alloys for aerospace applications. The evaluation includes sample preparation of stainless steel for conducting passivation tests, design of experiment studies to determine optimum operating range for nitric and citric acid solutions, and comparison of AMS-QQ-P-35 nitric acid passivation solutions with citric acid solutions. Conclusions state the effectiveness of citric acid to passivate stainless steel, and the potential to have citric acid replace nitric acid passivation solutions that are currently being used in the aerospace industry.

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Introduction

A material is considered passivated when it shows a high resistance to corrosion in an environment that one would normally expect corrosion to occur.[1] Stainless steel is considered a material that naturally passivates because it contains chromium as an alloying element that forms a very thin chromium oxide layer on the surface of the stainless steel.[2] This thin chromium oxide layer is responsible for passivating stainless steel. A properly passivated stainless steel can resist corrosion in humid air and salt water. Common examples of passivated stainless steel are forks and knives, and pots and pans used in the kitchen. None of these kitchen utensils typically show red rust corrosion because they are passivated.

However, if the passive oxide is damaged or destroyed then passivation is the process used to restore or reform the passive oxide layer on stainless steel alloys, and this passive oxide layer is critical to make stainless steel corrosion resistant. One method that damages the passive oxide layer is by machining or forming stainless steel with steel tools.[3] These steel tools leave small particles of iron embedded in the stainless steel part. These iron particles disturb the passive chromium oxide layer that is normally present. A stainless steel part with embedded iron particles would quickly form rust spots if subjected to high humidity or salt spray conditions.

Aerospace parts that have been machined or formed with steel tools need to undergo a passivation process to remove this iron contamination. AMS-QQ-P-35 is the passivation process that is typically performed on aerospace parts. This specification requires the use of nitric acid solutions for passivating stainless steel alloys. The nitric acid dissolves the iron particles and restores the passive chromium oxide layer. The nitric acid passivation solutions in AMS-QQ-P-35 have been formulated to dissolve iron particles and restore the chromium oxide passive layer, but not etch or attack the stainless steel alloy.

Recently, an ASTM specification has been issued that allows the use of citric acid solutions to passivate stainless steel alloys.[4] ASTM A 967 allows solutions containing 4 to 10 weight % citric acid at solution temperatures ranging from 70 to 160 ^{o}F. This paper describes the tests performed at Boeing to evaluate citric acid as an alternative to nitric acid passivation of stainless steel for aerospace parts.

Experimental Procedures

Selection of Test Method to Evaluate Passivation – AMS-QQ-P-35 specifies several tests that can be used to determine if a part is passivated. This study selected the salt spray test to verify passivation because it is simple to use, quick, and a relatively severe test. The test requires the passivated stainless steel test specimens to be placed in an ASTM B 117 salt spray cabinet for two hours. After the two hours, remove the test specimens and look for signs of red rust. The presence of red rust is considered a failure and the specimen has not been properly passivated.

Test Specimen Preparation –
Before the evaluation of passivation solutions could begin, a method had to be developed that would consistently "unpassivate" the stainless steel test specimens and cause them to fail the salt spray test. This was necessary because it was known by the author that samples of stainless steel received from the warehouse, and not subjected to a passivation treatment, will typically pass the 2-hour salt spray test and not show any red rust. This is not surprising because stainless steel is naturally passivated and typically will not rust. Figure 1 shows a set of stainless steel alloys that were received from the warehouse, cut into test specimens, degreased with a solvent, and then subjected to the 2-hour salt spray test. All specimens passed except for the 420 and 440C test specimens.

Several tests were conducted to contaminate the stainless steel specimens so that they would consistently fail the salt spray test, and the preferred method selected was steel grit blasting. The method used steel grit that was full hard with a mesh size of 120. The steel grit was blasted onto the surface of

the stainless steel at a pressure of 70 psig. Two passes with the grit blast media were applied on the surface, and the direction of the second pass was 90 degrees to the first. This produced a contaminated test specimen that consistently failed the 2-hour salt spray passivation test. Figure 2 shows a set of stainless steel alloys that were received from the warehouse, cut into test specimens, degreased with a solvent, contaminated by steel grit blasting, and then subjected to the 2 hour salt spray test. All specimens failed.

Optimization of Citric Acid Passivation Solution – ASTM A 967 allows solutions containing 4 to 10 weight % citric acid at solution temperatures ranging from 70 to 160 ^{o}F. The combination of citric acid solutions available to test was too large to handle so a 3 factor - 2 level Design of Experiment[5] (DoE) was conducted to determine the optimum citric acid concentration, solution temperature and immersion time. The citric acid was controlled at 3 and 15 weight %, solution temperature was controlled at 75 and 150 ^{o}F, and immersion time was controlled at 5 and 30 minutes. The DoE results showed that concentration was not significant, but temperature was important. 150 ^{o}F at short or long immersion times produced good passivation results, but long immersion time at room temperature was also good. In order to conserve energy, it was determined that the optimum citric acid passivation solution was 15 weight %, at ambient temperature, and an immersion time of 2 hours. The higher citric acid concentration level was selected because the passivation tank used for this evaluation was small in relation to the amount of test specimens that were passivated, and it was thought that the higher citric acid concentration would provide a more consistent passivation treatment for all of the test specimens processed.

Optimization of Nitric Acid Passivation Solution – ASTM A 967 allows solutions containing 20 to 55 volume % nitric acid at solution temperatures ranging from 70 to 140 ^{o}F. The combination of nitric acid solutions available to test was too large to handle so a 3 factor - 2 level DoE was conducted to determine the optimum nitric acid concentration, solution temperature and immersion time. The nitric acid was controlled at 20 and 55 volume %, solution temperature was controlled at 75 and 150 ^{o}F, and immersion time was controlled at 20 and 120 minutes. The DoE results showed that concentration was significant. The 20 volume % solutions performed better than the 55 volume %. Temperature was also important. 150 ^{o}F at short or long immersion times produced good passivation results, but long immersion time at room temperature was also good. In order to conserve energy, it was determined that the optimum nitric acid passivation solution was 20 volume %, at ambient temperature, and an immersion time of 30 minutes.

Comparison of Nitric and Citric Acid Passivation Solutions –

Table I lists the wrought stainless steel alloys that were used for this evaluation of passivation solutions.

Table II lists five passivation solutions used in this evaluation and the operating conditions for each solution. In addition to the optimized nitric acid and optimized citric acid determined by DoE, three additional passivation solutions were added to this study. One is a commercially available citric acid passivation solution that contains citric acid and cleaning compounds and meets ASTM A 967 (*Citric 4*), and the other two passivation solutions are Type II and Type VII from AMS-QQ-P-35. These AMS-QQ-P-35 solutions are used by the aerospace industry to passivate stainless steel parts. Type II is nitric acid with sodium dicrhromate and Type VII is moderately concentrated nitric acid that is heated.

The evaluation of the passivation solutions was conducted as follows: the test specimens were contaminated with steel grit, passivated in nitric or citric acid solutions (per Table II), subjected to ASTM B 117 salt spray testing for 2 to 3 hours, and then evaluated for signs of red rust. Red rust is considered a failure for passivation.

In addition, the stainless steel test specimens were also examined for signs of IGA (intergranular attack) and pitting after being treated in the optimized nitric, optimized citric acid, and

commercially available citric acid passivation solutions. The etch rates for each passivation solution with most of the stainless steel alloys were also determined.

Results and Discussions

Figure 3 shows the stainless steel test specimens that were passivated in the AMS-QQ-P-35, TypeVII Solution and then exposed for 3 hours in an ASTM B 117 salt spray cabinet. This passivation solution performed very well at removing the heavy iron particle contamination caused by the steel grit blast on all but two of the test specimens. The 420 and 440C were the only test specimens that failed the salt spray test.

Figure 4 shows the stainless steel test specimens that were passivated in the optimized nitric acid solution and then exposed for 3 hours in an ASTM B 117 salt spray cabinet. This passivation solution performed very well at removing the heavy iron particle contamination caused by the steel grit blast on all but two of the test specimens. The 420 and 440C were the only test specimens that failed the salt spray test.

Figure 5 shows the stainless steel test specimens that were passivated in the AMS-QQ-P-35, Type II Solution and then exposed for 3 hours in an ASTM B 117 salt spray cabinet. This passivation solution had difficulty in removing the heavy iron particle contamination caused by the steel grit blast. Only two of the test specimens passed the salt spray test with no red rust (15-5PH and PH 13-8Mo), and all of the other specimens failed. This solution could not remove the heavy contamination of iron particles that were present on the surface of most of these test specimens. It appears that the sodium dichromate addition in this passivation solution inhibits the dissolution of the iron particles by the nitric acid. Longer immersion times would probably improve the passivation results, but this was not evaluated.

Figure 6 shows the stainless steel test specimens that were passivated in the optimized citric acid solution and then exposed for 3 hours in an ASTM B 117 salt spray cabinet. This passivation solution performed very well at removing the heavy iron particle contamination caused by the steel grit blast on all but two of the test specimens. The 420 and 440C were the only test specimens that failed the salt spray test.

Figure 7 shows the stainless steel test specimens that were passivated in the commercially available citric acid cleaning solution per the *Citric 4* treatment specified in ASTM A 967, and then exposed for 3 hours in an ASTM B 117 salt spray cabinet. This passivation solution performed very well at removing the heavy iron particle contamination caused by the steel grit blast on all but two of the test specimens. The 420 and 440C were the only test specimens that failed the salt spray test.

Table III shows a summary of the passivation corrosion test results observed in Figures 3 to 7. Stainless steel test specimens 420 and 440C could not pass the salt spray corrosion test with the passivation solutions used in this study. These alloys will need additional treatments to restore their passivation after being heavily contaminated by steel grit blast. However, it is recognized in the metal finishing industry that 400 series stainless steel alloys are difficult to passivate, and this evaluation showed that the citric acid solutions performed as good as the nitric acid solutions for passivating 400 series stainless steel alloys. In addition, AMS-QQ-P-35 also recognizes the difficulty for passivating some of the 400 series stainless steel alloys, and does not require 440C alloy to pass any of the passivation tests.

Table IV shows the etch rate that was determined for each of the passivation solutions and most of the stainless steel alloys used in this study. Some etch rates were not done because of insufficient metal sample size.

AMS-QQ-P-35 requires that parts shall show no etching after passivation treatment, and for this evaluation, etch rates were arbitrarily considered insignificant (not etching) if the etch rate was less than 0.001 mils/minute/surface. There were only three solution and alloy combinations that gave “significant” etch rates. The etch rate for 303 in optimized nitric acid was 0.0028 mils/min/surface,

and in the commercially available citric acid cleaner the etch rate was 0.001 mils/min/surface (this was almost classified as an insignificant etch rate). The etch rate for 440C in optimized nitric acid was 0.0017 mils/min/surf.

This study indicates that the optimized nitric acid solution should not be used to passivate 303 and 440C alloys, however citric acid solutions (including the commercially available citric acid cleaner) would be acceptable passivation treatments. However, the commercially available citric acid cleaner would probably fail the requirements of a non-etch cleaner for aerospace parts made from 303 alloy.

Metallographic cross-sections were made for all of the stainless steel samples that were passivated in the optimized nitric acid, optimized citric acid and the commercially available citric acid cleaning solution. Close examination of these cross-sections did not reveal any IGA on any of the test specimens. Pit depths and widths were measured on all of the cross-sectioned samples and the results are shown in Table V. Pit depths that are greater than 0.001 inch are considered a failure, and only one sample showed pits that exceeded this criteria. The 303 test specimen in the optimized nitric acid had a pit depth of 0.005 inch. Figure 8 shows typical pit depths for 303 alloy in optimized nitric acid and optimized citric acid. The pitting attack of 303 in nitric acid is expected because there are restrictions in AMS-QQ-P-35 (and other aerospace passivation specifications) to not use nitric acid solutions on free machining 303 stainless steel alloys. The preferred solution is AMS-QQ-P-35, Type II (nitric acid with sodium dicrhromate), but in this study it was found that a citric acid passivation solution would also be acceptable. The 303 sample processed for 2 hours in optimized citric acid had a pit depth of only 0.0003 inches.

Conclusions

- Citric acid solutions used in this evaluation are as good as or better than Type II and VII nitric acid solutions specified in AMS-QQ-P-35 for removing iron particle contamination and passivating wrought stainless steel alloys.
- Citric acid passivation solutions produced no significant etching, pitting, or IGA on the 300 (including 303), 400, and PH series stainless steel alloys tested.
- None of the passivation solutions evaluated in this study were capable of passivating 420 and 440C stainless steel that were heavily contaminated with iron particles. The citric acid solutions performed as good as the nitric acid solutions on 400 series stainless steel.
- The nitric acid with sodium dichromate passivation solution per AMS-QQ-P-35, Type II was not capable of passivating a majority of the stainless steel test specimens that were heavily contaminated with iron particles, and the citric acid solutions performed better than the Type II solution.

Acknowledgements

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References

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2. H.H. Uhlig, Corrosion and Corrosion Control, 2nd Edition, 1971.

3. AMS-QQ-P-35, Passivation Treatments for Corrosion-Resistant Steel, Society of Automotive Engineers, Note 6.1.1, May 1998.

4. ASTM A 967, Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts, American Society for Testing and Materials, November 1999.

5. D.C. Montgomery, Design and Analysis of Experiments, 3rd Edition, 1991.

Figure 1 – As-Received Stainless Steel Test Specimens Subjected to 2 Hour Salt Spray. Test Specimens Did Not Receive a Passivation Treatment.

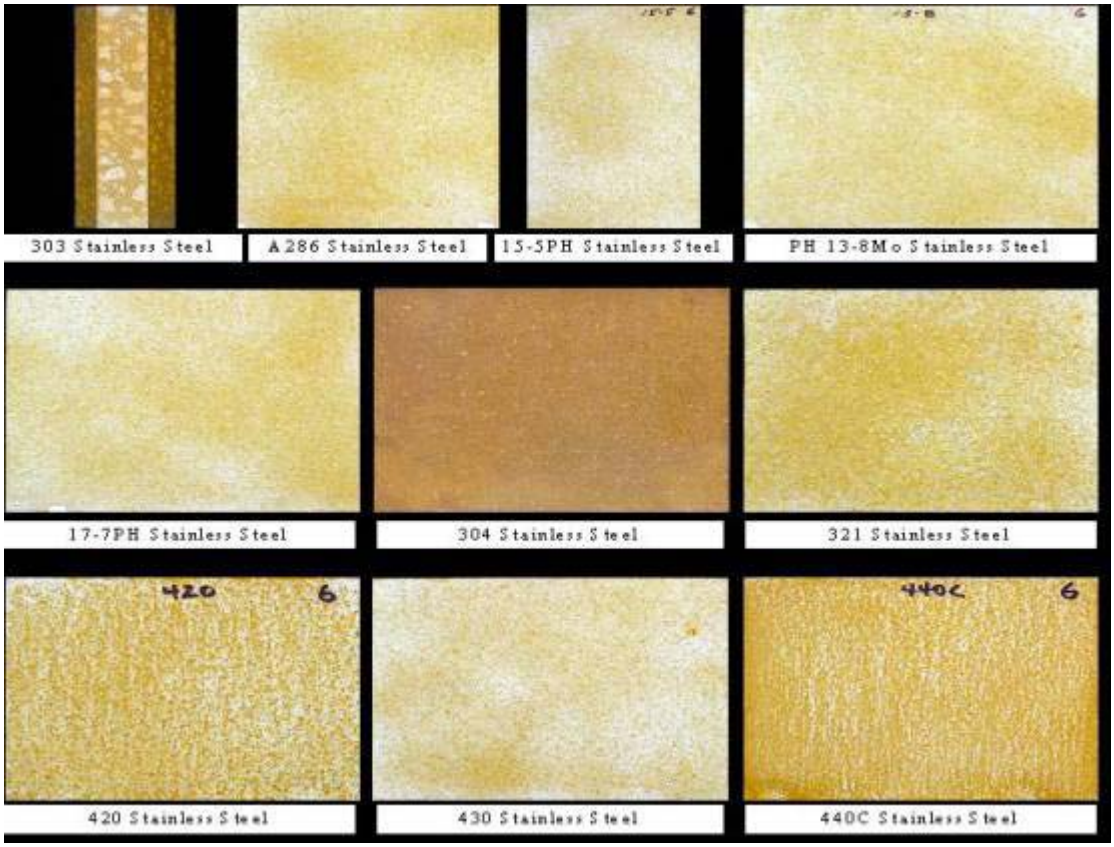

Figure 2 –Stainless Steel Test Specimens Grit Blasted with Steel Shot Then Subjected to 2 Hour Salt Spray. Test Specimens Did Not Receive a Passivation Treatment.

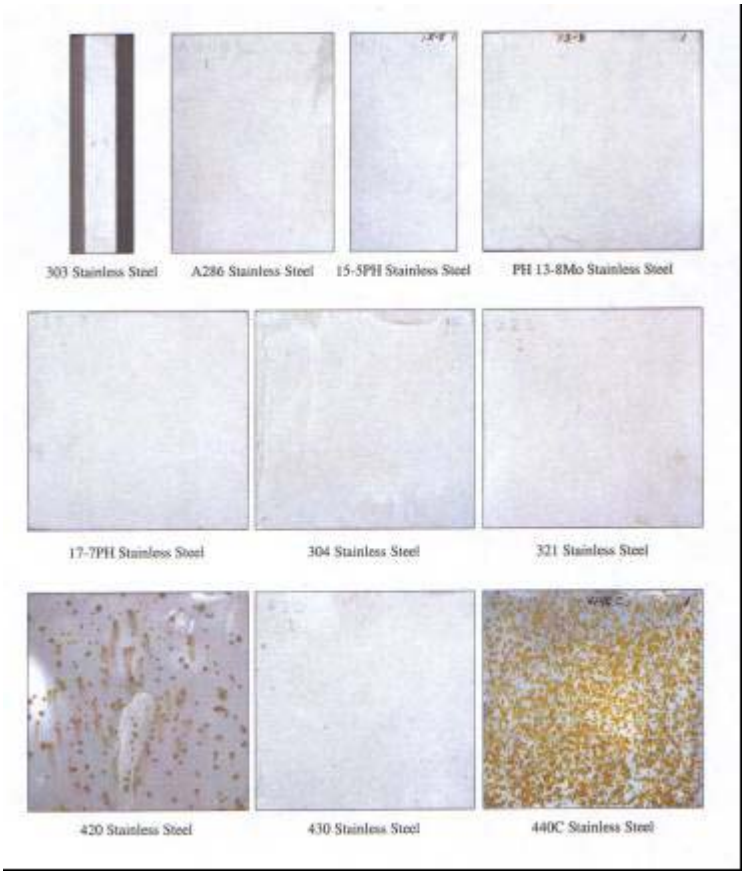

Figure 3 – Salt Spray Results for Contaminated Test Specimens Passivated in AMS-QQ-P-35, Ty VII.

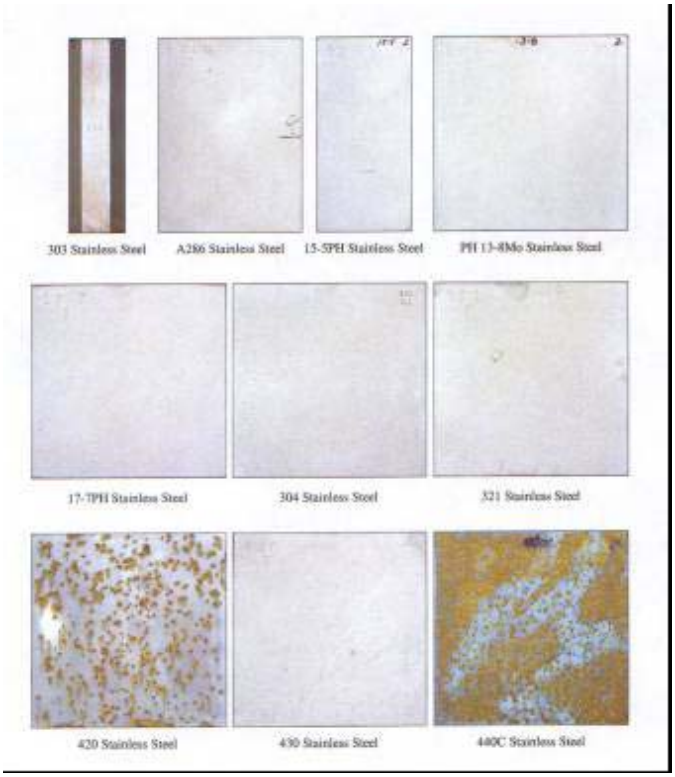

Figure 4 – Salt Spray Results for Contaminated Test Specimens Passivated in Optimized Nitric Acid.

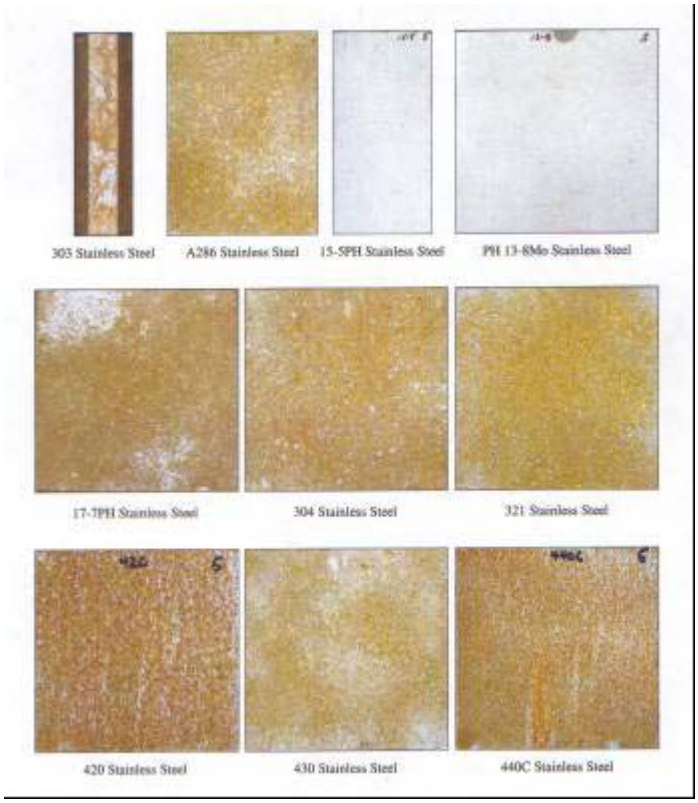

Figure 5 – Salt Spray Results for Contaminated Test Specimens Passivated in AMS-QQ-P-35, Type II.

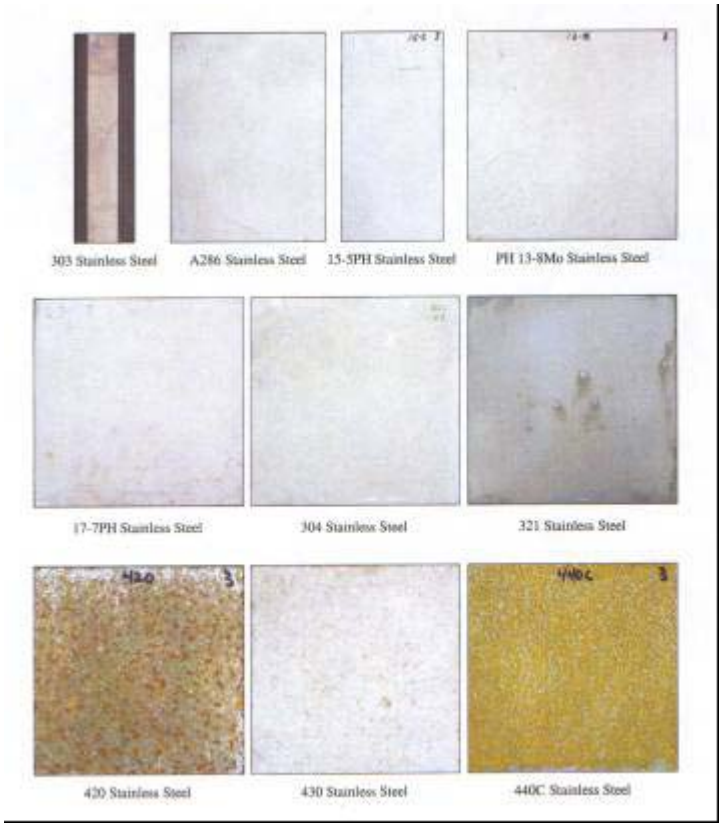

Figure 6– Salt Spray Results for Contaminated Test Specimens Passivated in Optimized Citric Acid.

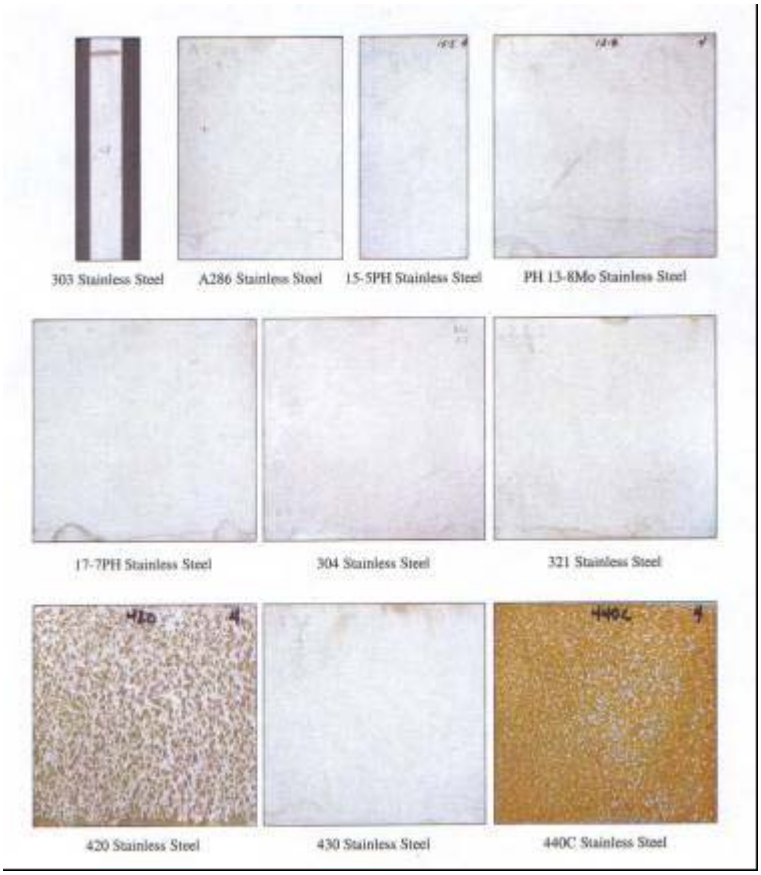

Figure 7– Salt Spray Results for Contaminated Test Specimens Passivated in Commercially Available Citric Acid Cleaning Solution (ASTM A 967, Citric 4).

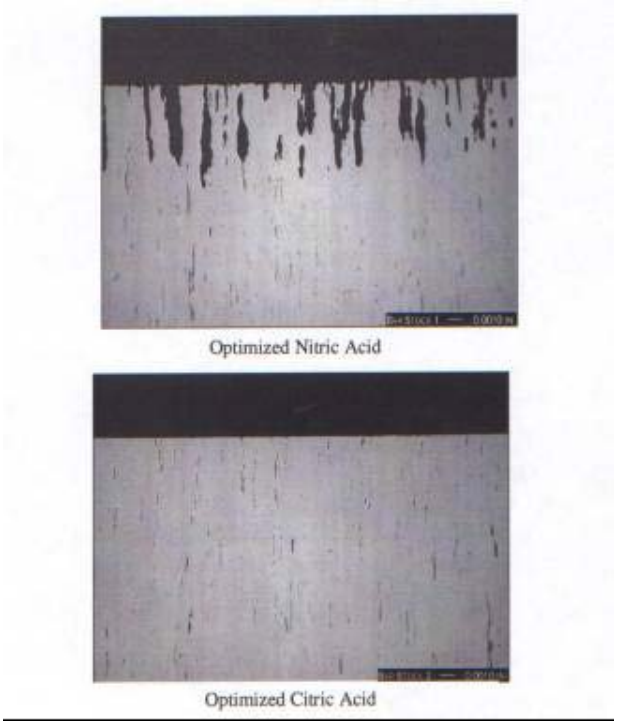

Figure 8 – Metallographic Cross-Sections of 303 Stainless Steel After Exposure to Different Passivation Solutions. (125X)

Alloy	Alloy Type	Heat Treat Condition	Hardness (Rockwell)	Sample Size
303	Free Machining	Cold Worked	C26	Hex Rod 0.875 O.D. x 3 inch long
A286	Precipitation Hardening	Condition A	B85	3 x 4 x 0.125 inch
15-5PH	Precipitation Hardening	H1100	C35	2 x 4x 0.090 inch
PH13-8Mo	Precipitation Hardening	H1100	C36	4 x 4 x 0.125 inch
17-7PH	Precipitation Hardening	Condition A	B88	4 x 4 x 0.125 inch
304	Austenitic	Annealed	B85	4 x 4 x 0.150 inch
321	Austenitic	Annealed	B80	4 x 4 x 0.140 inch
420	Martensitic	Annealed	B85	4 x 4 x 0.140 inch
430	Ferritic	Annealed	B81	4 x 4 x 0.125 inch
440C	Martensitic	Annealed	B98	4 x 4 x 0.140 inch

Table I – Stainless Steel Test Specimens

Method	Composition	Temperature ^{o}F	Immersion Time Minuntes
Optimized Nitric Acid (from Design of Experiment)	20% Nitric Acid (% by Volume)	Ambient	30
Optimized Citric Acid (from Design of Experiment)	15% Citric Acid (by Weight)	Ambient	120
AMS-QQ-P-35, Ty VII	22% Nitric Acid (% by Volume)	130	30
Citric Acid Cleaner ASTM A 967, *Citric 4* (Commercially Available)	12.5 % by Volume	155	15
AMS-QQ-P-35, Type II	22.5% Nitric Acid (% by Volume) + 2.5 oz/gal Sodium Dichromate	120	20

Table II – Passivation Solutions Evaluated

Passivation Solution	303	A286	15-5PH	PH13-8Mo	17-7PH	304	321	420	430	440C
AMS-QQ-P-35, Ty VII (22% HNO_3, 130°F)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
Optimized Nitric Acid (20% HNO_3, Ambient)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
AMS-QQ-P-35, Ty II (22.5% HNO_3+Dichromate, 120°F)	Fail	Fail	Pass	Pass	Fail	Fail	Fail	Fail	Fail	Fail
Optimized Citric Acid (15% Citric Acid, Ambient)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail
Commercially Available Citric Acid Cleaner (12.5%, 155°F)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Pass	Fail

Table III – Summary of Salt Spray Test Results for Nitric and Citric Acid Passivated Test Specimens.

Passivation Solution	303	A286	15-5PH	PH13-8Mo	17-7PH	304	321	420	430	440C
AMS-QQ-P-35, Ty VII (22% HNO_3, 130°F)	NS	NS	NS	NS	NS	NS	Not Run	Not Run	NS	NS
Optimized Nitric Acid (20% HNO_3, Ambient)	0.0028	NS	NS	NS	NS	NS	NS	NS	NS	0.0017
AMS-QQ-P-35, Ty II (22.5% HNO_3+Dichromate, 120°F)	NS	NS	NS	NS	NS	NS	Not Run	Not Run	NS	NS
Optimized Citric Acid (15% Citric Acid, Ambient)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Commercially Available Citric Acid Cleaner (12.5%, 155°F)	0.001	NS	NS	NS	NS	NS	NS	NS	NS	NS

Notes:

1/ Etch Rates are in mils/minute/surface.

2/ The designation NS (Not Significant) indicates that the measured etch rate was less than 1.0×10^{-3} mils/minute/surface.

3/ Not Run = Insufficient sample available for testing.

Table IV – Etch Rates for Stainless Steel in Passivation Solutions

Stainless Steel Alloy	Optimized Nitric Acid		Optimized Citric Acid		Commercially Available Citric Acid Cleaner	
	Pit Width	Pit Depth	Pit Width	Pit Depth	Pit Width	Pit Depth
303	0.001	0.005	0.0002	0.0003	0.0002	0.0009
A286	0.0004	0.0001	0.0004	0.0001	0.0003	0.0001
15-5PH	0.0008	0.0001	0.0006	0.0002	0.0006	0.0002
PH13-8Mo	0.0006	0.0001	0.0005	0.0001	0.0002	0.0001
17-7PH	0.0009	0.0002	0.0001	0.0003	0.0007	0.0004
304	0.0005	0.0002	0.0006	0.0002	0.0004	0.0002
321	0.0005	0.0002	0.001	0.0002	0.0004	0.0003
420	0.0007	0.0001	0.0009	0.0001	0.0004	0.0002
430	0.0007	0.0001	nil	nil	0.0005	0.0001
440C	0.0006	0.0002	0.0005	0.0001	0.0004	0.0002

Notes:
1/ Measurements are in inches.
2/ nil = not measureable

Table V – Pit Depth and Width Measurements for Stainless Steel in Different Passivation Solutions