Citric Acid Passivation Executive Summary

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1 Introduction

1.1 Purpose

This document presents a short summary of the work undertaken for the Citric Acid as a Green Replacement for Steels Passivation project. This work has been performed by ESR Technology on behalf of the European Space Agency (ESA) under contract 4000114892/15/NL/KML. For further information to this summary please see the final report [ESA-ESTL-0469].

1.2 Summary of Project Objectives

Stainless steels are major manufacturing materials used in spacecraft and ground support structures. Stainless steels are typically used in applications requiring a high corrosion resistance. Passivation of stainless steel helps improve the surface's resistance to corrosion. Passivation removes free iron contamination, left on the surface from machining and fabrication, and forms a stable oxide film to protect the surface from corrosion.

Nitric acid is currently the most widely used passivating solution. However, nitric acid has multiple environmental, safety, and process disadvantages. Nitrogen oxides (NOx) are considered greenhouse gases and are volatile organic compounds (VOCs). NOx increase the nitrogen concentration in bodies of water, leading to oxygen depletion. Nitric acid passivation also poses worker health and safety issues, and incurs notable handling and disposal costs due to nitric acid (and other chemical(s)used in the process) being hazardous. Nitric acid can also remove beneficial heavy metals (including nickel and chromium) from the surface of the substrate.

Citric acid passivation has been recently proposed as a green replacement for stainless steel passivation processes. Citric acid passivation offers many advantages over nitric acid passivation. It has a lower environmental impact as it is biodegradable, is not considered a hazardous waste, and does not create toxic fumes during the passivation process. Citric acid passivation provides greater worker safety, versatility, and ease of use, whilst offering less maintenance and lower costs. Also, citric acid does not remove beneficial heavy metals from the steel surface.

The study described here refers to an activity of common interest to the whole space industry and this work compliments current projects being conducted at ESA and NASA. The overall aim of these projects is to develop environmentally friendlier materials, processes and coating systems able to provide the same or better performances when compared to the existing technologies.

2 Programme of work

The overall programme of work that was followed is summarised in Figure 2-1.

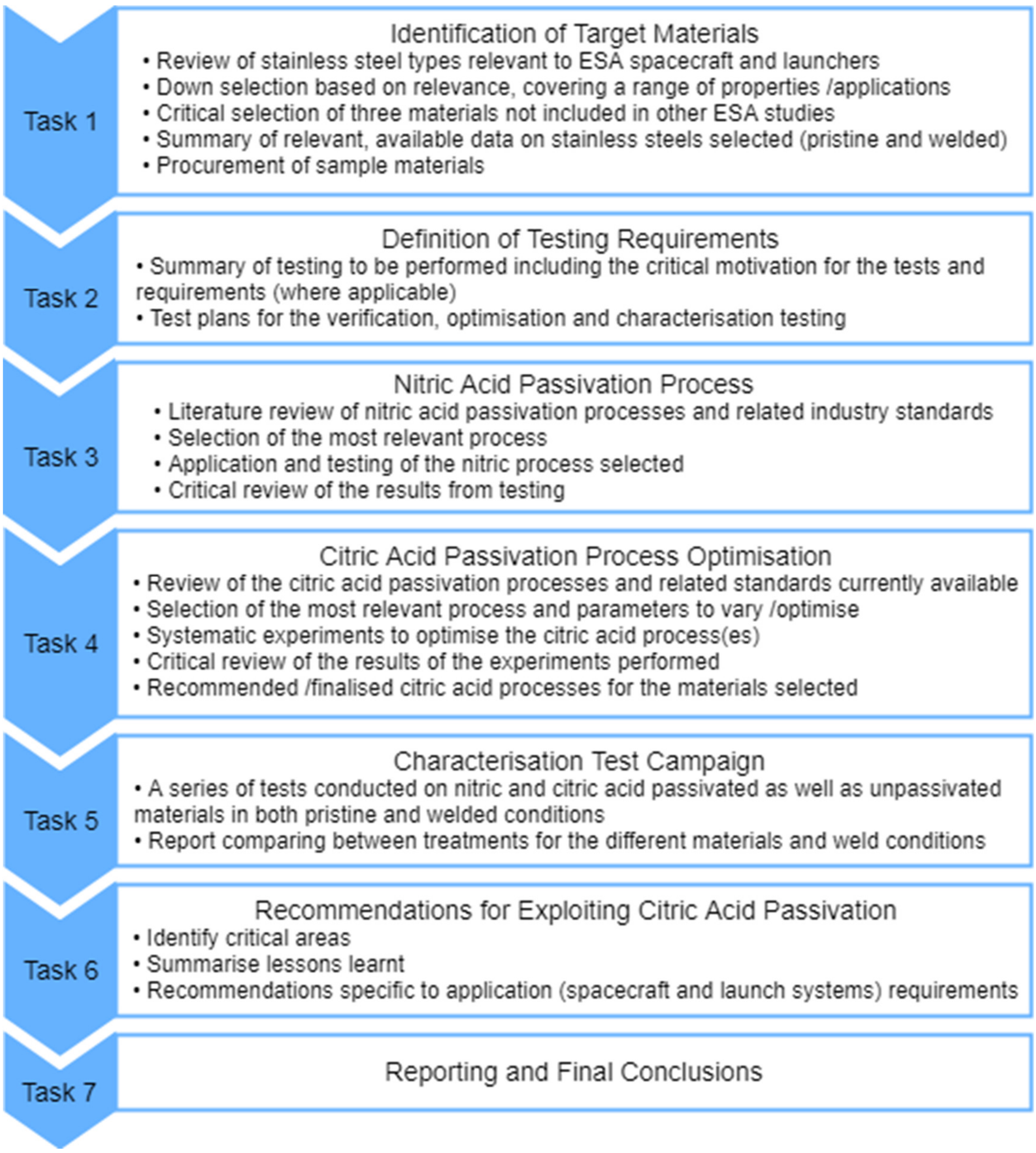

Figure 2-1 Programme of work

A Life Cycle Analysis (LCA), carried out in parallel to the main project flow, was used to compare the environmental impact of the nitric and citric acid processes.

During the first two tasks of this activity AISI 410, AISI 302 and 17-7PH, were selected as the test materials as they represented a wide range of stainless-steel properties and were not being studied in other, parallel ESA studies. Suitable sample geometries and preparation processes were then identified to meet the testing required, defined in consultation with the agency.

3 Nitric Acid Passivation Process

There is not one definitive nitric acid passivation process for any one steel type. A literature survey was performed to establish the most commonly applied nitric acid process relevant to the three steels selected for this study. Based on the available literature, the most suitable overall process for the alloys used in this study is defined in Figure 3-1. The contamination step was introduced for testing purposes and is not part of a standard passivation treatment.

The nitric acid passivation properties selected were: 50%vol. nitric acid, held at 55°C for 30 minutes. These passivation parameters are ones that are repeatedly found in the literature for the treatment of 17-7 PH and ASIS 410 steels. The passivation parameters are higher temperature and /or higher acid concentration than usually needed to passivate 302 steel, however the variation was thought to be most likely to improve the passivation performance and allowed the use of only 1 process for all 3 steel types.

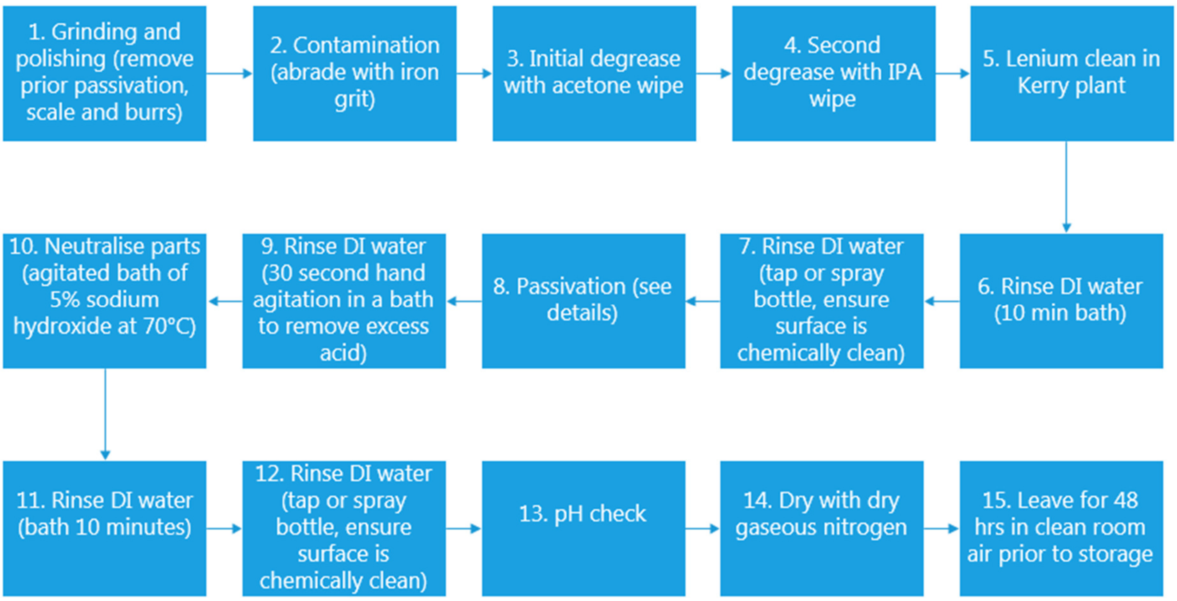

Figure 3-1 Nitric Acid Process Definition.

Electrochemistry and salt fog testing were performed on unpassivated and nitric acid passivated steel samples. Overall it was shown that the nitric acid process provided a corrosion resistance benefit to the steels in this testing. This improvement was quantified in both electrochemical and salt fog testing to compare to samples subjected to the citric acid process.

Salt fog testing was selected as a benchmark measure as it is a commonly used test for assessing corrosion resistance. It consists of surrounding the test samples in a controlled, dense and corrosive salt water fog atmosphere. Test samples were evaluated according to a standardised visual score criteria to measure the onset and progression of any corrosion.

Electrochemical testing allowed for a more precise quantification of the passivation performance. The test involved immersing the test sample in an electrolyte and passing a small current through the test sample. The electrochemical data was characteristic of corrosion resistance of the steel not true passivation: this was thought to be due to the required contamination the samples and not the passivation process. However, a series of figures of merit could be taken from the data, characteristic of the resistance to corrosion.

4 Citric Acid Passivation Process Optimisation

The overall citric process, in terms of preparation and rinsing, is the same as for nitric acid (as shown in Figure 3-1) and it was only the passivation bath details that were varied. The extensive literature review identified two potential processes. Due to the green aims of this project, the lower energy process was selected as the control process: 4%wt citric acid, 70℃ for 60 minutes

Optimisation tests were performed to refine the passivation process to achieve the best possible performance on the three steels. The electrochemical figures of merit were used to assess performance improvement, prior to final salt fog testing. The test logic for the Optimisation Tests is shown in Figure 4-1.

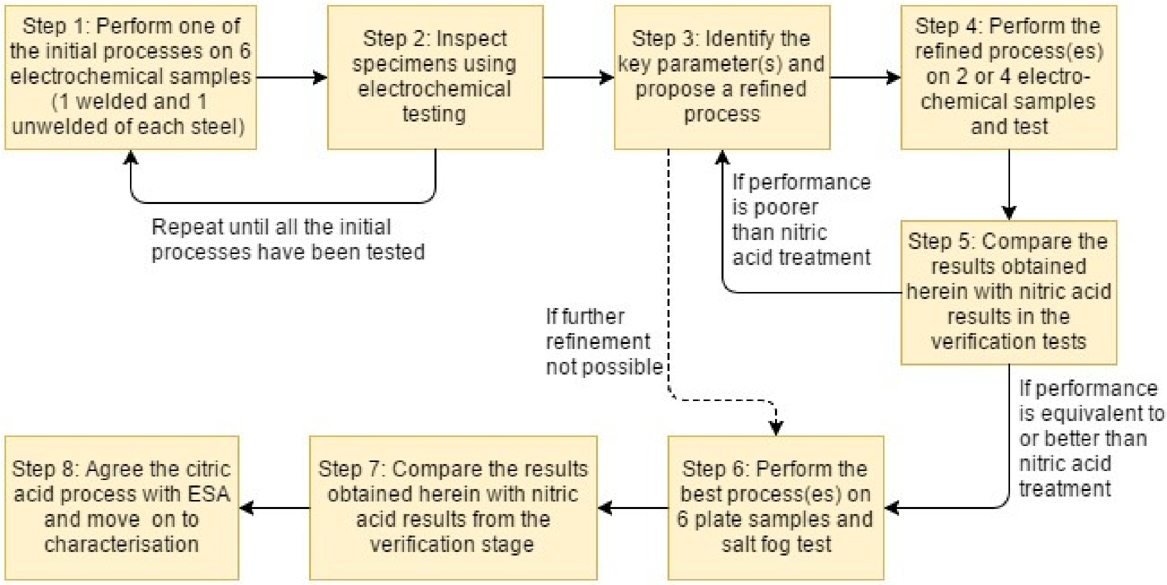

Figure 4-1 Optimisation test logic

A summary of the control process and the selected varied processes are summarised below:

Table 4-1 Optimisation Test Processes

Passivation Run	Acid concentration (%wt)	Bath Duration (minutes)	Bath Temperature (℃)	Agitation	Applicable Steel types
Control	4	60	70	Stirrer	All
Concentration	10	60	70	Stirrer	All
Duration	4	90	70	Stirrer	All
Temperature	4	60	60	Stirrer	All
Agitation	4	60	70	Ultrasonic	All
Refined 1	4	90	60	Stirrer	AISI 302 & PH 17-7
Refined 2	10	90	80	Stirrer	AISI 410
Refined 3	10	180	80	Stirrer	AISI 410

All citric acid processes offered worse performance for the AISI 410 than nitric acid. Hence prior to process refinement it became clear that a single process would not be suitable for all three alloys. Therefore, it was decided to develop two separate processes; one for the 410, and one for both 302 and PH17-7.

Electrochemical testing showed the Temperature process provided equivalent or better performance for alloys 302 and 17-7 than nitric acid. Refined 1 process, showed no significant benefits over the Temperature process and had a longer bath duration (requiring more energy). Hence the lower energy Temperature process was used to prepare salt fog test samples of AISI 302 and PH17-7.

The Refined 2 process for the AISI 410 still showed worse performance than the nitric acid process. The resulting Refined 3 process had the effect of improving the passivation of welded samples of AISI 410 but had worse performance than nitric acid on unwelded AISI 410. It was concluded that the Refined 3 process represented the best level of passivation possible and no further improvements were made: this process was used for salt fog testing.

After 168 hours salt fog exposure, the developed citric acid processes both showed better or equivalent salt fog results than the nitric acid samples, with the exception of the welded 17-7 (one score lower). Given the nature of the tests and the low number of samples being tested, a deviation of one ASTM grade point was not considered significant.

Overall, the developed citric acid passivation processes achieved better or equivalent performance to the nitric acid procees; a successful result.

5 Characterisation Test Campaign

The characterisation test campaign was a thorough assessment of the passivated samples and provided detailed information for future work. Characterisation testing measured the critical mechanical and chemical properties outlined in the following subsections.

5.1 EDX Characterisation

The aim of the EDX measurements was to determine if the amount of free iron was reduced and /or that the relative amount of sacrificial elements /compounds such as chromium has increased. It was unclear at the start of the test programme how accurate the process might be. Overall the margin for error and resolution of the EDX measurements were larger than the differences between the samples before and after passivation treatment.

5.2 Hardness Measurements

Hardness measurements were used to check if the process of passivation causes a change in the physical material properties of the surface. The hardness measured after citric acid treatment remained very close to the manufacturers' specifications and to goods-inwards values. Overall, it was concluded that the passivation process did not adversely affect the hardness of the surface.

5.3 Microstructural Characterisation

Metallurgical microstructure analysis was employed to ensure that passivation causes no significant differences to the microstructure of the steels. From inspection of the size and shape of grains in the steel, the citric acid processes did not significantly affect the material microstructure. Further, there were no signs of corrosion (intergranular or pitting) and there was no evidence of free iron either from optical microscope and SEM images.

5.4 Stress Corrosion Cracking

A critical test in assessing the passivation performance was measuring the susceptibility of the materials to corrosive cracking under mechanical stress. 3 unwelded, citric acid treated samples were subjected to an ECSS standard stress corrosion cracking test. All samples passed this test and were rated as Class 1 – showing a high resistance to stress corrosion cracking. A metallurgical examination of the samples showed there was no discernible change in the surface condition of the stressed samples compared to the unstressed control samples (at 50x magnification). This is a very promising result for the justification of using citric acid as a passivation medium for these alloys.

5.5 Atmospheric Testing

Samples were sent to ESA to include in their atmospheric exposure test facility; reporting of the results is outside the scope of this report.

5.6 Hydrogen Content Analysis

Hydrogen content analysis measured welded and unwelded samples from all three alloys which were unpassivated, nitric passivated or citric passivated. All samples tested showed a hydrogen content of less than 3 ppm. This is significantly below the threshold of 120 ppm that could indicate susceptibility to hydrogen embrittlement. Also, the amount of hydrogen in the citric acid passivated samples was equivalent to the amount in unpassivated or nitric acid passivated samples.

5.7 Fatigue Testing

An assessment of the fatigue performance of a unwelded citric acid passivated test sample was performed. No comparable data was found in the literature and so the characteristic data was taken for future reference. The nature of the fatigue tests, carried out under tension – tension testing, meant that some refinement of the process was required during testing. However, it was possible to gather characteristic data on the 3 unwelded materials and establish suitable test parameters for future reference.

5.8 Fatigue Crack Propagation Testing

The fatigue crack propagation testing successfully measured the crack propagation growth rate as a function of an applied stress intensity for a sample of each of the 3 unwelded steel types. Like the fatigue testing, crack propagation testing provided a reference measurement to guide any future more detailed test campaign, and not as a way to assess the citric acid process performance.

6 Life Cycle Assessment

The Life Cycle Assessment (LCA) was an analysis that sought to quantify the environmental impacts of the identified nitric acid process and the two, ESR developed, citric acid processes.

The life cycle impacts for each scenario were assessed and compared against each other to determine which is the environmentally optimal acid to use for passivation. This is shown in Figure 6-1.

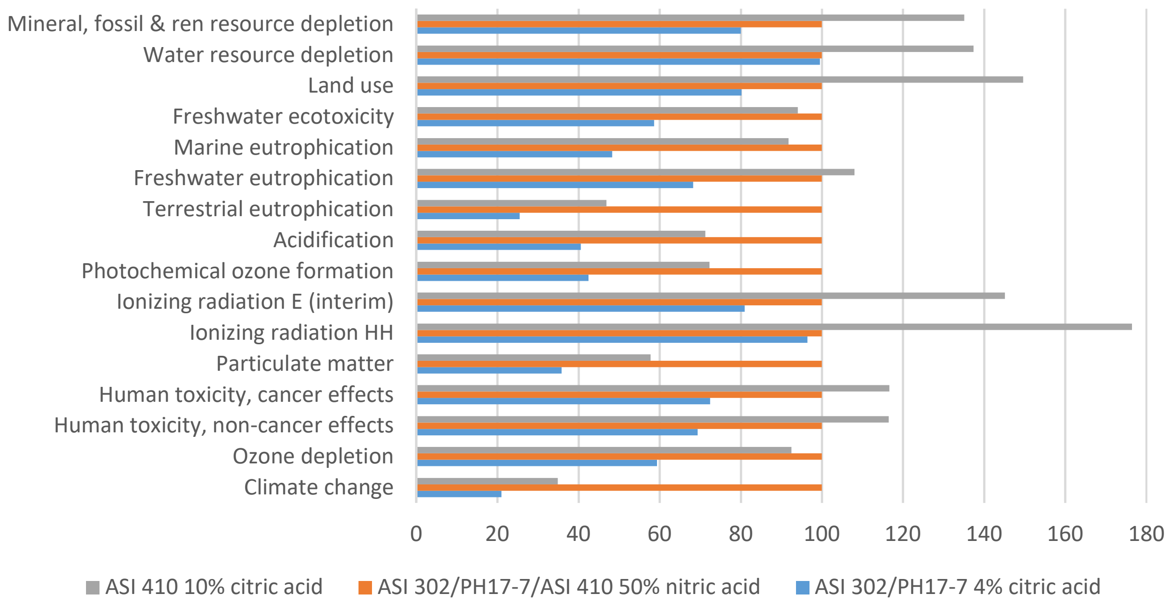

Figure 6-1 Comparison of Life Cycle Impacts for the Different Passivation Processes

Overall, for all ILCD impact categories assessed, the 4% citric acid scenario performs the best with the lowest comparative environmental impact. Where 10% citric acid is used in the case of AISI 410 stainless steel this gave the highest comparative environmental impacts for: human toxicity (cancer effects and non-cancer); ionising radiation; freshwater eutrophication; mineral, fossil and renewable resource depletion; and water depletion.

For all other impact categories nitric acid gave the highest comparative environmental impact.

In all cases the reduction of energy in the passivation steps reduces impact, but most particularly in the higher concentration citric acid scenario due to the higher temperatures and longer retention time. The reduced carbon intensity of the grid has a similar patterned result, with impact reduction in all areas other than ionising radiation and water ecotoxicity.

Across all ILCD recommended impact categories 4% citric acid passivation is the most environmentally preferable scenario. The 50% nitric acid passivation scenario is the least environmentally preferable across the most impact categories overall.

7 Conclusions

The work here has shown that citric acid is a suitable replacement, in terms of passivation performance, and offers less environmental impact than nitric acid for the passivation of stainless steels AISI 302, AISI 410 and PH17-7. Two citric acid processes were developed for the three alloys that were demonstrated to be at least as good as a nitric acid process, and in most cases provided better performance, demonstrate through salt fog testing and electrochemical analysis.

The developed processes were applied to a range of test specimens, which were then subjected to a wide range of mechanical, metallurgical and corrosion testing. The results of these tests showed that the developed processes did not adversely affect the material properties and that the developed processes achieved good corrosion resistance.

In parallel with developing suitable citric acid processes, a Life Cycle Assessment was carried out that showed an overall environmental benefit to using the citric acid processes.

As expected, the citric acid using 4 % concentration showed the lowest environmental impact. It had the lowest impact in every metric of the LCA. This is encouraging for promoting the uptake of passivation, particularly on high alloy steels similar to AISI 302 and PH17-7, which responded very well to citric acid treatment.

Overall the nitric acid process had the least desirable environmental impact. The 10 % citric acid process had a similar waste disposal impact to the 4% process, but due to the long duration required and the high temperature performed worse in several specific areas than the nitric process.

8 Recommendations

All the relevant international standards for stainless steel passivation allow, and provide guidelines on, citric acid passivation. Therefore, any manufacturer/fabricator is already at liberty to use citric acid.

The space industry is inherently conservative and the barrier to the adoption of citric acid passivation is essentially that nitric acid offers a low risk, flight-tested, and cost-effective method of passivation.

It appears that the only way citric acid will be adopted as the mainstream process for passivation is for environmental reasons. Through the life cycle analysis, it has been shown quantitatively that citric acid has a lower impact on the environment than nitric acid passivation. In an increasingly environmentally aware world, standards such as ISO14001 are desirable accolades for organisations to sign up to. They promote the minimising of environmental impact and adoption of green practices and processes. The use of citric acid passivation over nitric, would be a tangible step in meeting the goals set out by ISO14001.

To further drive toward citric acid passivation, alongside other green initiatives, it may be desirable or even necessary to develop a space-specific standard(s) (either a new ECSS or incorporating new items into in existing specifications on materials and manufacturing) for cleaner space that strongly deters and perhaps prohibits the use of nitric acid when citric acid can provide equivalent or better performance.

PH17-7, in particular, responded very well to citric acid treatment in all tests, both on welded and unwelded material. It represents the most promising candidate for taking the citric acid passivation process further.

Only when a citric acid process was applied to the low-alloy content AISI 410 was there a significant environmental impact from a citric acid process. The development of the citric acid process showed it was difficult to achieve good corrosion resistance. However, even with nitric acid is known to be difficult to passivate. Ultimately the advancement of citric acid treatment for low alloy stainless steels requires more investigation.