Improvements in passivation using citric acid formulations

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Although citric acid formulations have been used for a number of years very successfully for the passivation of stainless steel, there has been considerable doubt expressed in the industry about the viability of this chemistry to replace nitric acid formulations.

In recent years more and more companies have run tests to determine whether the proprietary formulations developed to improve the performance of citric acid really can be used to replace nitric acid. In nearly every case the test data has shown that citric acid products are not only equal to nitric acid, but indeed are superior in performance, cost and ease of use.

Until recently, most of the data derived was either proprietary in nature or developed by companies like Stellar Solutions, which has been promoting the sale of its own products. Although some public data was available, it was not enough to satisfy the desires of many companies. This article provides some of the latest data that has been made public, and data which has been developed by completely independent testing agencies.

Introduction

For those who are unfamiliar with the citric acid passivation history, we will present a bit of the background. Although citric acid formulations have been used for quite a few years in particular industries, they were relatively unknown until around 10 years ago. They have since been promoted and sold as a substitute for the hazardous nitric acid systems that have been state of the art for many years.

The reasons for the advent of citric acid passivation as *the* state of the art in recent years is because of new information and data that has been presented, allowing the cancellation of QQ-P-35c, which had been the standard specification used by government and industry. This specification was replaced by the new ASTM A-967 specification for passivation. This new specification allowed the use of either the old nitric formulations or the new citric acid systems.

The move to citric acid systems was driven by a number of factors. First, there have been a number of new EPA and OSHA regulations in the US, which required onerous expenditures and safety procedures in order to continue using nitric acid in the workplace. We will not attempt to go into these issues here, but just mention that the difficulties in using nitric acid systems has forced manufacturers to look at other options.

As I said, citric acid has been used around the world for a number of years. However, one of the problems in its use had been the higher cost of citric acid compared to nitric acid. In recent years this has changed. Citric acid prices have dropped, and the cost of purchasing, storing, using and disposing of nitric acid has risen dramatically. Also, there have been new citric acid formulations developed, which further lower the cost and improve the performance.

With the advent of new incentives to find alternative passivation methods to replace nitric acid, many companies have run tests on citric acid and especially citric acid formulations designed to not only take advantages of the good properties of citric acid, but improve upon them. Although most of the data developed is still of a proprietary nature, it is the purpose of this paper to present a sampling of some of the publicly available data that now shows the distinct advantages of citric acid, when formulated correctly.

Because of the new and continuing good test data being obtained by private companies and the public sector, there is continued acceptance in changing specifications and procedures to allow the use of citric acid formulations. Recent studies have also shown that the total process of cleaning and passivation with these new formulations has given results before unattainable in the industry.

Test data

There has been data available in recent years showing that citric acid formulations developed by Stellar Solutions Inc. have given excellent performance in meeting the requirements of ASTM A-967, including salt spray data on most grades of stainless steel. It has been generally accepted that these products meet all of the test requirements of this standard.

ESCA and AES tests: Many industries use much more stringent testing requirements than those specified in ASTM A-967. The surgical, medical, orthopaedic and semiconductor industries have all required more sophisticated testing. An example of this is the requirement of many of these companies to use ESCA (Electron Spectroscopy for Chemical Analysis) and AES (Auger Electron Spectroscopy) tests for determining the surface properties and corrosion resistance. This data shows conclusively that the citric products give improved results. So, let us quickly review some of the data.

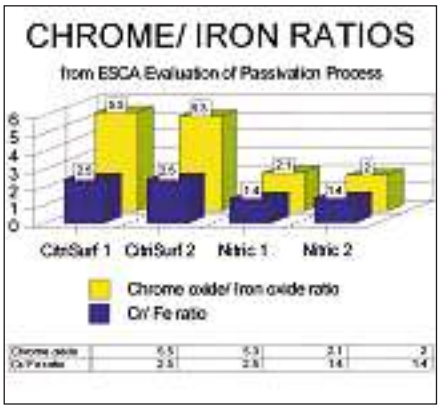

Figure 1. *This figure shows the relative degree of chromium enrichment of the surface of 316L VIM/VAR stainless steel. The data shows the two tests run with a commercial citric acid formulation (Citric Type 4) vs nitric acid (Nitric Type 2).*

AES Depth Profile Results

Sample	Oxide thickness	Max. Depth of Enrichment	Depth of Enrichment
CitriSurf 1	27.0 Å	18.0 Å	17.0 Å
CitriSurf 2	28.0 Å	19.0 Å	17.0 Å
Average	**27.5 Å**	**18.5 Å**	**17.0 Å**
Nitric 1	21.0Å	13.0 Å	12.0 Å
Nitric 2	17.0 Å	11.0 Å	11.0 Å
Average	**19.0 Å**	**12.0 Å**	**11.5 Å**

Table 1. *This shows the relative chrome oxide layer thickness between the citric acid and nitric acid formulations used in the above test. Again, it shows that the citric acid formulation gave a significantly deeper penetration of the layer into the steel, indicating better corrosion resistance.*

This dramatic increase in the percentage of chromium and chromium oxide on the surface compared to iron and iron oxide is very important in determining the relative corrosion resistance of the steel (*Figure 1 and Table 1*). But the long term corrosion resistance to chemical attack is also enhanced by the depth of the chromium enrichment. Many studies have been undertaken by many companies, and most test data has shown the improvement of citric formulations over nitric acid in this important feature.

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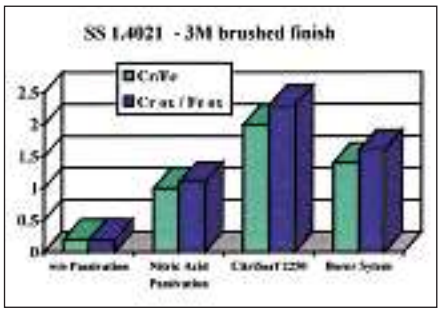

Figure 2. *This shows the relative chromium enrichment on the surface of 1.4021 grade stainless steel (a 410 type surgical instrument grade). In this case it illustrates the difference between unpassivated, nitric acid passivation, formulated citric acid passivation, and a Swiss formulation. The highest degree of chromium and chromium oxide on the surface is again attained by using the proprietary citric acid formulation.*

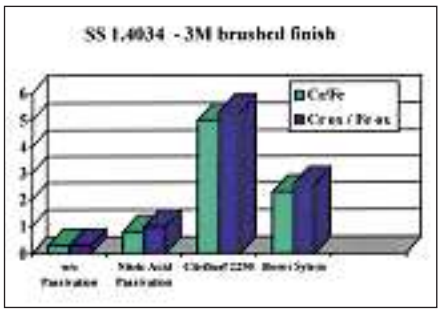

Figure 3. *This shows another study on SS 1.4034 grade stainless steel, another German grade of surgical steel. In this case the difference is even more demonstrative, with very high chrome oxide ratios being attained using the citric acid formulation.*

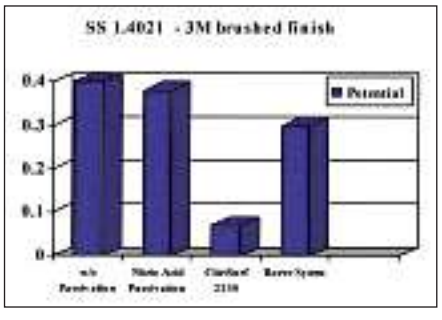

Figure 4. *Electrical conductivity of the surface in NMI tests showed again that the Citric acid formulation was less susceptible to corrosion than the other systems tested.*

NMI Research Data: Finalisation of a very large study by NMI Research Institute in Germany in 2002 gave much more validity to the surface analysis run by the semiconductor industry here in the United States. This study was funded by the surgical industry in Europe*.

NMI Research Institute also ran tests on surface conductivity, another method to look at the relative corrosion resistance of various passivation treatments. This data has to be analysed in much more depth than we have time to do today, but the data again shows in *Figure 4* that the proprietary citric formulation treated parts showed the best electrical resistance on the surface (lowest conductivity).

Aerospace data

The aerospace industry has been especially reluctant to accept test data from other industries. However, recent data and presentation of a paper to AESF by the Boeing company has again shown that the citric formulations are superior to nitric acid. This data was presented in August 2002 at the AESF aerospace meeting, and was presented again at the *SurFin* meeting in 2003, with the updated data.

This data was verified in salt spray tests, in which the citric formulation yielded more hours before onset of any rusting of the various grades of stainless steel. More data is available on this upon request.

Recent studies by aerospace companies have verified Boeing's data. In fact, some grades of stainless steel that were reported to be impossible to passivate are showing excellent results with the citric acid formulae.

The old QQ-P-35c was cancelled and then replaced in the aerospace industry with AMS QQ-P-35. This has now also been cancelled in favour of AMS 2700, which allows the use of citric acid formulations.

Unmodified citric acid tests

There has been some recent information circulated that plain citric acid can be as good as the proprietary formulations of citric acid with other ingredients. Although there are a few applications where processors may be able to accomplish this, there are many problems associated with using plain citric acid solutions, and many advantages to using the various specialty formulations designed to improve performance, costs and bath stability.

In all cases known to us, the special proprietary citric acid formulations are lower in cost to use than the old nitric acid formulations or baths of plain citric acid. The overall costs of nitric or plain citric formulations are almost always higher than using the special formulations developed specifically for the passivation process. The problems associated with using unmodified citric acid with many grades of stainless steel can be severe, and need to be evaluated carefully to avoid damaging parts. The bath stability will also be a problem in normal situations.

New data to be published in 2006 by a University study will also show the damaging affects of nitric acid on austenite.

New discoveries in improved performance

While conventional processes with the citric acid formulations have produced excellent results, we have found ways to provide even superior results with all grades of stainless steel, especially some of the most difficult grades. Recent studies show that the pretreatment of many grades of steel is significant in producing optimum results. Removal of carbon and sulphur from the surface prior to passivation appears to be very critical in this effort. Special formulations have been developed to accomplish this, producing excellent passivation results with the difficult grades such as:

303
440C
416
420
430F
17-4 PH

Another breakthrough which is under study at this time is in the rinsing process. It has been proven that higher chrome oxide ratios and better corrosion resistance can be obtained simply by improving the method of rinsing after passivation with either nitric or citric systems. Details of this process will be reserved for a later paper, but the data to date is conclusive. We are anxious to complete our studies and share this with the entire industry.

Another study has shown that using hot blowing air for the drying of the surface after passivation can significantly improve the chrome oxide ratios attained. These studies are still under way, also.

In a recent study funded by the State of New York the data showed the advantages of proprietary Citric Acid formulations over nitric acid in cost, safety and environmental concerns. This study can be reviewed online or by contacting the author.

Studies on other alloys

Studies are also under way on many alloys used in the orthopaedic industry and other specialty products. There will be another paper presented on the data obtained on titanium, cobalt-chrome and nickel-titanium, as well as others. These studies look excellent in the beginning stages.

Conclusions

In conclusion, we can at this point in time conclusively state that the proprietary citric acid formulations are as good as or better than nitric acid formulations on all grades of stainless steel tested. This conclusion has been proven now by many independent studies.

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Conclusions

- New processes involving pretreatment of the parts produce excellent results with the most difficult grades, and on castings of PH grades.
- New processes of improved rinsing and drying also produce significant improvements in passivation and corrosion resistance.
- Independent studies show the advantages of proprietary citric formulations in performance, cost, safety and environmental impact.

* The complete 68-page test report in German is available from: Dr Reichl, NMI, Naturwissenschaftliches und Medizinisches Institut an der Universität Tübingen, Markwiesenstraße 55, D-72770 Reutlingen, Germany. Tel: +49 (0) 7121 51 53 00. Fax: +49 (0) 7121 51 53 0 16. *www.nmi.de*

'CitriSurf™' process now available in the UK

The Surface Treatment Division of Houghton plc, based at Trafford Park, Manchester, has recently forged a partnership and exclusivity deal in the UK with the US company, Stellar Solutions Inc, for the supply and marketing of the 'Citrisurf™' range of citric acid cleaning and passivation processes featured in this article. In essence, CitriSurf™ products provide:

- ***Improved removal of free iron from the surface***
- ***Faster removal of free iron from the surface***
- ***Low hazard chemistry***
- ***Environmentally safe chemistry***
- ***Lower cost***

Houghton plc is responsible for European and Middle Eastern markets and is an American owned company with a turnover of around $450 million. Over the last 10 years, Houghton has evolved from a supplier of oils and fluids with a service capability, to a global network of companies offering the highest level of service and technical expertise anywhere in the industrial world. The company is is one of the world's largest and longest established suppliers of specialist industrial metalworking fluids and fluid management systems.

More information about the CitriSurf range from: Peter Simms, Business Manager, Surface Treatment Division – Europe/Middle East, Houghton plc, Beacon Road, Trafford Park, Manchester, M17 1AF.
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