Effective Green Chemstry for Cleaning And Passivation of Stainless Steel

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1. INTRODUCTION

Stainless steel has found widespread applications in industries such as process plant and equipment, Food Processing, Beverage, Dairy, Pharmaceutical, Biotechnology, Nuclear, Marine, and Architectural.

It is now possible to use effective, “green“ chemical treatment technologies for stainless steel to maximise product quality in all stages of the fabrication life cycle, from initial cleaning, to spatter protection, pickling, passivation, waste treatment and final cleaning of the finished product.

Stainless steel is often perceived as being resistant to corrosion, relatively inert and requiring minimal treatment in fabrication, and little maintenance. However, this is not always the case, and is dependent on correct alloy choice, surface finish and degree of passivation.

The term passivation refers to the natural corrosion resistant property of many metals and alloys including chromium, titanium and stainless steels. Passivation is conferred on stainless steel by an invisible nanometre layer of chrome oxide. The stability of this film depends largely on the corrosive environment in which the stainless steel is found.

In a clean environment the passive film forms spontaneously following its removal over a period of at least 8 to 24 hours. This means that stainless steels are self passivating “under favourable conditions”.

Disruption of the passive film by chemicals, mechanical action, embedded iron particles, or oxygen starvation can readily occur in the workshop or during fabrication. Surface free iron particles, dust, grit and iron oxide contaminants arise from handling, fabrication/forming, welding, grinding, machining, paint and crayon marks, polishing, tumbling and workshop cross contamination.

These contaminants penetrate the passive film, absorb and generate chlorides, ferric chloride or produce inorganic chlorides by the decomposition of organic compounds such as PVC and marking materials.

Traditional use of toxic and corrosive mineral acids such as nitric and phosphoric acids can now be replaced with highly effective, proprietary blends of non toxic chemicals, typically citric acid combined with surfactants in water based solutions or gels, as well as advanced portable electro-polishing manchines which use safe electrolyte cleaners.

Citric acid provides superior passivation by chelating free iron and eliminating it and other chloride contaminants from the surface of the stainless steel.

2. STAINLESS STEEL CHMICAL TREATMENT PROCESSES

All stages of the fabrication life cycle of stainless steel require specific chemical cleaning treatment, and green chemistries find a niche in each area. These include :

- surface preparation, cleaning and / or degreasing
- weld spatter protection
- descaling / pickling
- passivation
- treatment of acidic waste for trade waste compliance
- appearance cleaning of finished product
- maintenance cleaning for rust removal & passivation

Degreasing

Traditionally, readily available and low cost petroleum based products such as white spirits, kerosene, thinners or chlorinated solvents have been routinely used for surface cleaning and degreasing.

In many countries today, occupational health and safety and environmental regulations have focused attention on safer non toxic and biodegradable alternatives to these flammable and/or toxic chemicals.

Solvents were generally preferred over water based detergents in order to minimise the presence of water which may aid corrosion in some cases, especially when held in crevices and corners. Typical applications can include removal of adhesive protective laminates, finger prints, permanent marker pen or crayon marks and machine oil.

However, today non corrosive water based degreasers which include corrosion preventitive additives are available, including some interesting biobased solvents which are water dilutable.

It is important for all stainless steel fabricators to understand that, the cleaner the stainless steel is before welding, the better the quality of the welds, and the less chance there will be for contamination to affect the fabrication later in the construction process.

Anti Spatter Chemicals

Electrode or MIG welding of metals often results in molten spatter falling on the surface of the steel being welded which can only be removed by abrasion or polishing. Every spatter point on stainless steel is a potential corrosion site since the chrome oxide protective layer has been damaged.

Mechanical removal of the spatter deposits is time consuming and costly, and this re-work can be avoided by the use of special anti spatter sprays. The anti spatter spray leaves a protective oily film on the surface of the steel to prevent spatter from sticking once solidified.

Solvent based products have been preferred for stainless steel, while water based products are now emerging as low cost products for treatment of mild steel.

Product development is ongoing for the development of water based technology which has less potential to impact on weld porosity, with new technologies now available which are both metallurgically safe as well as environmentally compliant.

Parafin waxes have been used for protection of MIG Torches, but the level of purity of these agents differs widely around the world. New non wax technologies are now being developed to reduce the amount of imputities and organic load of nozzle dip gel agents.

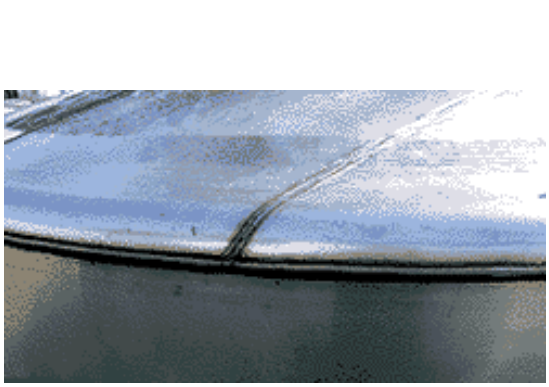
Pickling solutions and gels

Pickling of stainless steels is an industry recognised process and a critical one for post weld cleaning, but employs highly toxic nitric / hydrofluoric acid chemistry.

Pickling is the removal of the oxide film from the surface of the metal by chemical means. An exposure to high temperature (e.g. during welding or heat treatment) will scale the surface. In the case of stainless steel, such high temperature scale has inferior corrosion resistance and must be removed. ASTM 380-94 **"**Standard Practice for Cleaning, Descaling and Passivation of Stainless Steel Parts, Equipment and Systems" [1.] recommends pickling using formulations of hydrofluoric (HF) and nitric (HNO_3) acids, to remove the scale and helps to restore corrosion resistance through auto passivation providing the ambient conditions are appropriate.

For applications where stainless steel is to be installed in aggressive environments or used in corrosive industrial processes, it is necessary to develop full corrosion resistance by a passivation treatment subsequent to pickling.

Pickling agents can be sprayed over an entire surface, used in dip applications or as a gel applied to the weld and heat affected zone.



Pickling of stainless steel welds helps to remove both the oxide scale and free iron contamination. Once the pickling agent is completely rinsed away, the treated area will be chemically clean. As such, the surface has an enhanced ability to react with atmospheric oxygen to passivate, providing the area is free from dirt and outside sources of contamination. Newer generation gels are proving to be far more effective and easier to use than older paste based products.

Why is Pickling Recommended?

Several papers over the last 20 years highlight the importance of pickling as a superior post weld surface treatment method to mechanical treatment methods such as grinding and sandblasting. For improved corrosion resistance, Avery & Tuthill (Welding Journal, 1993) [2.] stated that "inadequate attention to post weld cleanup also leads to reduced corrosion resistance of stainless steel weldments …… and heat tint, oxides, embedded iron, surface defects and contaminants may initiate crevice or pitting corrosion well in advance of attack on clean surface areas."

Specialist stainless steel fabricators seem to know qualitatively that cleaning of stainless steel welds is critical to maximise the performance of that alloy, but few have provided quantitative evidence for why this is so.

Krupp VDM have shown that nitric/hydrofluoric acid pickling improves the corrosion resistance of surfaces that have been light ground or bead blasted.

Indeed, Tuthill & Avery have found that "light grinding with clean aluminium oxide abrasive discs or flapper wheels and glass bead blasting are effective methods of removing heat tint …. however, even properly mechanically cleaned surfaces are improved by Nitric-HF pickling."

They go on to say that "pickling also removes any metals transferred by wire brushing (low ally brushes – Types 410 or 304), and remove other foreign surface deposits such as abraded metals and oxides."

Other critical findings of Tuthill & Avery include:

- "Heavy grinding with grinding wheels degrades the corrosion resistance to a greater depth than can be restored by pickling"

- "Blasting with steel grit and steel shot also degrades the surface corrosion resistance beyond the ability of pickling to fully restore."

- " Grinding is best limited to pencil grinding for removal of small defects or where required for other reasons for removal of weld reinforcement"

- "In conclusion, they found that "Pickling is very effective in restoring the corrosion resistance of stainless steel after the surface has been degraded by welding, light grinding, stainless steel wire brushing or glass bead blasting."

Laboratory work carried out by Halide Technology Pty Ltd [3.] using Koslow Passivation Tester 2026 on 304 and 316 emery ground, emery ground & pickled, and machine finished & pickled, indicated that passivation is a time dependent process and may take hours or days to achieve a degree of passivation necessary to resist corrosion [4.] .

Pickled surfaces passiaved faster because these surfaces are chemically cleaner, and have higher surface chromium and far less iron content.

Gumpel, Vollmer et. al. (Stainless Steel Europe, May 1995) [5.] reported that " the corrosion resistance of stainless steels depends not only on the alloy metal content but also to a consifderable degree on its surface quality, i.e. the formation of the passivc layer. The tests clearly show that the highest corrosion resistance is attained if pickling is the final surface treatment and that 'only ground' samples made of the same material had results that were clearly worse."

Pickling Alternative Using Electro-polishing for post weld cleaning

While pickling has been the dominant procedure for post weld cleaning of stainless steel, electro-polishing of stainless steel TIG welds has become much more popular in recent years in order to eliminate highly toxic pickling chemicals from the work place.

The electro-polishing process is achieved by electro-chemical cleaning using portable machines which have the tip of a cleaning wand covered with a heat and acid resistant material which is then dipped into an electrolyte and then used to remove heat tint from the weld and heat affected zone.

These portable technologies have historically been limited to TIG welding processes where a smooth weld profile will not tear and damage the wand cleaning pads on the tip of the wand.

New technologies utilising carbon fibre brushes instead of cleaning pads provide better cleaning performance, longer life cycle for the wand tip, and allow the electro-polishing process to include most MIG welds.

Electro-polishing provides a better surface profile finish compared to pickling and a greater potential to achieve surface passivation. The other major advantage over pickling is that there is no surface eteching, and subsequent rework of polishing out of the pickling etch mark is not required.

However, if the stainless steel is to be installed in high corrosion environmental, surface passivation with citric acid based passivation agent is still indicated.

Stainless Steel Passivation

Why passivate? The failure of stainless components due to corrosion can reach catastrophic proportions. The cost in time, materials, rectification and lost production can be tremendous.

If passivation is not carried out stainless steel can rust due to surface free iron, and since chlorides are also often absorbed from the atmosphere, ferric chloride will be produced.

Prolonged contact with ferric chloride will eventually initiate pitting and crevice corrosion on the stainless steel surface.

Therefore, proper passivation will remove the surface contamination and assist in the optimal restoration of the chrome oxide passive layer.

It should be understood that this passive surface condition is not a static situation. The chrome oxide layer is constantly affected by the environment and is slowly lost, but at the same time it reacts with oxygen to reform. The process is in dynamic equilibrium. Only when the balance is brought towards loss of the passive film does corrosion occur [3.] .

Passivating Chemicals

Many people still do not appreciate the difference between pickling and passivation. Pickling not only removes the scale around the heat affected area, but it also removes chrome oxide and surface iron and metal contamination, and therefore leaves the surface of the steel readily available to react with atmospheric oxygen to restore the passive film (i.e. auto passivation). *After pickling, the surface is still active*.

The passive film restoration is dependent on the availability of oxygen for its formation, and also subject to inhibition by atmospheric pollution, airborne chlorides (present as sodium chloride - NaCl - especially near coastal areas) and the presence of mild steel in the same workshop if not strictly controlled.

Where the chromium content is in excess of 12.0%, the formation of a chromium oxide passive film on the surface is possible either through auto-passivation or enhanced passivation with nitric acid.

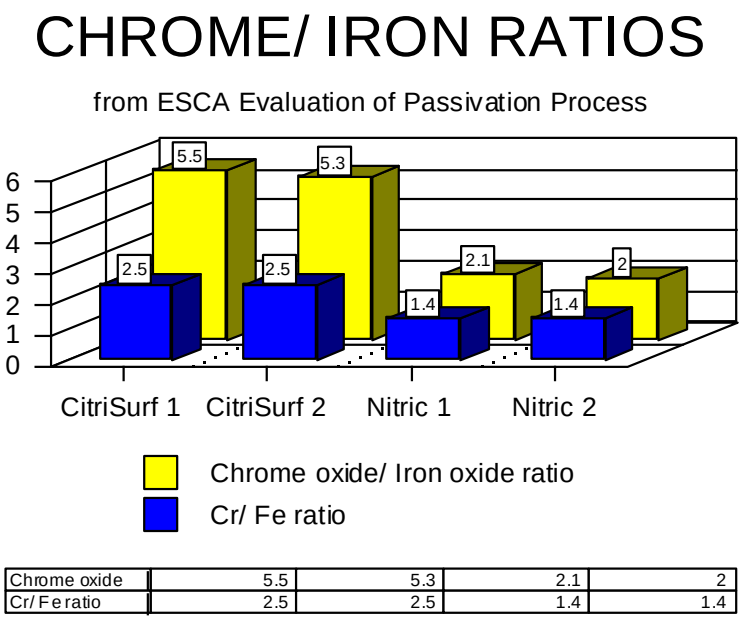
Enhanced passivation is recommended following grinding, pickling or polishing of stainless steel where the surface has been made more active by these processes. The passivating agent enhances the passivation process in a more uniform manner to restore the chrome oxide film and help to prevent future corrosion following installation of the fabricated product. When stainless steel is commissioned into high corrosion environments, such as at sea, near the sea, in polluted environments etc., then use of a passivating agent is highly recommended to ensure a resilient passive film is achieved.

If stainless steel is corroded in situ, it may be repaired by either polishing or chemical deoxidisation. In either case, the surface of the steel will be active and require a passivation treatment. Historically passivation treatment involved the use of nitric acid. However, environmental and occupational health and safety concerns have almost eliminated the widespread use of nitric acid for passivation. In the photos above, nitric acid would be inappropriate to use because of the presence of tiles and other fixtures which could be damaged by this acid, as well as the danger of working in confined areas.

The OHS&E issues have been a strong driver in the use of citric acid based formulations. Citirc acid alone will not achieve the desired result, however, special proprietary blends have been developed and independently tested to show greater passivation performance and better chromium enrichment than nitric acid.

Citric acid based formulations specifically been designed to eliminate the safety and environmental problems of nitric acid and other mineral acids used in the cleaning and passivation of stainless steel. When used as directed, these products yield excellent results without producing hazardous waste or NOx pollution in the air. Citric acid based products do not strip the nickel or chromium from the surface, the rinse water can normally be put directly to drain as long as the pH falls within local guidelines.

Use of citric acid based technology provides Chrome oxide:Iron Oxide ratios on the surface of 316 stainless steel that are higher than ever obtained with nitric acid (semiconductor industry). Ratios as high as 12.7 to 1 have been obtained.



Chrome oxide	5.5	5.3	2.1	2
Cr/ Fe ratio	2.5	2.5	1.4	1.4

Electron Spectroscopy for Chemical Analysis (ESCA) / Auger Electron Spectroscopy (AES) DATA

This combined with better life cycle costing and less damage to plant and equipment for citric acid based tecnology, have shown that nitric acid is essentially more expensive to use. Many Pharmaceutical and Food Processing companies are now implimenting inhouse passivation & cleaning using citric acid based technology rather than sub contracting expensive contractors to use more toxic nitric acid passivation methods.

Neutralising agents for trade waste compliance

Today many companies face the implementation of ISO 14000 Environmental Management Systems and ISO 18000 Occupational Health & Safety Systems.

Environmental and occupational health and safety issues are strongly impacting industrial firms which discharge liquid waste, especially pickling and passivating chemical waste which is high in acid and heavy metal content.

Low cost alkaline solutions or pastes can be used to remove these chemicals after use from the surface of the steel, or caustics added to holding tanks containing the acidic waste prior to discharge into the sewer or water system. Pickling chemicals contain hydrofluoric acid and nitric acid and are hazardous. Removal of the pickling agent using a neutralising solution also helps to aid worker safely.

Pickling waste from fabrication plants have very low pH effluent, and high levels of heavy metal contaminants such as chromium and iron. Waste water treatment plants which sediment the heavy metals and neutralise acidic waste water are mandatory in many countries to protect the environment.

Where pH control is necessary for waste water treatment, a new synthetic technology has been developed called SynTech. Acids such as hydrochloric acid for lowering pH, and caustic soda for elevating pH, can now be replaced by SynTech chemistry which carry triple-zero Hazardous Materials Identification System (HMIS) parameters, are non-corrosive to metals, non-fuming, non-irritating to skin, non-mutagenic, and 100% biodegradable within 10 days.

Use of citric acid passivation technology will also reduce environmental pollution by permanently binding heavy metals in a form which make it easier for waste water treatment plants to handle this effluent.

Post Fabrication or Post Installation Cleaning

Following the fabrication or installation of stainless steel plant and equipment require cleaning to remove contaminants which can cause corrosion of welds, unsightly surface corrosion, and other blemishes and soils such as machine oil, grease, permanent marker pen, crayon etc.

Older cleaning agents for removal of organic contaminants such as grease, crayon and marker pen include are new generation, non toxic solvents (aliphatic hyrdocarbons and d-Limonene), and less worker safe products such as white spirits and thinners.

Phosphoric acid based surfactants have been used to remove light soils, and contaminants such as iron oxides and iron chlorides which may lead to corrosion. These acid based cleaners also have a mild passivating effect, and brighten the surface to improve appearance.

However, both environental and health concerns are eliminating these older technologies from the workplace. Also, in maintenace cleaning applications, especially in architectural situations, these aggressive chemicals are difficult or impossible to use due to confined space cleaning, worker reluctance, and also the potential damage these chemicals can impact on precious tiles, stone and fixtures in the building.

Today, citric acid based surfactants are also also available for light surface cleaning. The chelating effect of citric acid removes surface free iron, and thus assists the natural passivation process. Small quantities of less aggressive rust removal agents can be combined with citric acid based proprietary formulations to provide effective rust removal and passivation on hand rails, stainless steel exterior architectural features, marine fittings and hand rails etc.

3. SUMMARY

Quality finish during fabrication, after installation or for maintenance of stainless steel can be provided by green, non toxic chemical treatment prior to and after welding.

In particular, corrosion resistance can be maximised through the citric acid passivation of stainless steel following pickling, grinding or polishing during fabrication or maintenance.

Electro-polishing weld cleaning has proven to be more cost effective than traditional mechanical and labour intensive methods for stainless steel post weld treatment, and can replace pickling gels for treatment of TIG and/or MIG welds depending upon the technology employed.

REFERENCES

1. Full details of the pickling and passivation processes are available in ASTM A380-94a, Standard Practice for Cleaning, Descaling and Passivation of Stainless Steel Parts, Equipment and Systems

2. Welding Journal – A.H Tuthill & R.E. Avery, AWS Welding Research, February 1993

3. Guide to Stainless Steel Passivation - Halide Technology Pty Ltd

4. Proprietary Test Data – Halide technology, Sydney

5. Gumpel P., Vollmer T. et. al. – Stainless Steel Europe, May 1995

6. Chemical Treatment Enhances Stainless Steel Fabrication Quality – John W. Hill, Journal of the American Welding Society, May 2002

7. The Importance of Chemical Treatment Associated with the Welding of Stainless Steel and Aluminium – John W. Hill, Philippine Welding Society, October 1997

Further reading:

The Australian Stainless Steel Development Association - Australian Stainless Reference Manual 2012

Nickel Development Institute – Guidelines for the welded fabrication of nickel containing stainless steels for corrosion resistant services; Reference Book Series No. 11 007