Technical Bulletin

Number: 2007/07

ROUGING - CLEANING AND REMOVAL

Pump casing before treatment

Introduction

Stainless steel is widely used in pharmaceutical applications. The surface treatment of this stainless steel is very important, as in the pharmaceutical industry, hygiene aspects are priority. From several studies it shows there is a relation between surface roughness and the ability to clean and the ability of micro organisms to attach to the surface. The lowest surface roughness can be achieved by (electro) polishing.

One of the phenomena that occurs on stainless steel, almost exclusively within the pharmaceutical industry, is rouging. Rouging is a reddish brown film of iron oxides and hydroxides and is found in ultra pure water systems. The rouging film mainly contains iron (ferric) oxides but also can contain chromium and nickel compounds which can give different colours to the rouge.
It seems AISI 304 (EN 1.4301) stainless steel is more sensitive to rouging than AISI 316 (EN 1.4401). It has been observed that an electropolished surface is less susceptible to this phenomenon than a mechanically polished one.

Mechanisms

One of the main properties of stainless steel is its passive chrome oxide film, which protects the underlying steel. Formation of this chrome oxide film is spontaneous with oxygen from the air and stainless steel has therefore the ability to repair itself and form this film after being damaged. In order to form this film, the stainless steel surface has to be uncontaminated as contaminants can disturb the formation of the chrome oxide film.
In an ultra pure water environment this protective chrome oxide film can be attacked (See figure 1 on the next page). As ultra pure water lacks any ions, the strength to pull ions into the solution is so strong it can dissolve the protective chrome oxide and leave an active and unprotected stainless steel surface. As chrome and nickel ions can dissolve in water at neutral pH, iron ions dissolve at pH three or higher, and is deposited as iron hydroxides on the active stainless steel surface as it repassivates. Iron hydroxides will oxidize to ferric oxide which is red (rouge). This passivation and repassivation process can cycle which results in various different colours. Formation of rouge can be dangerous for stainless steel. Under deposits, a micro environment can be formed with a total different chemistry than the bulk. When for instance, sulphides (compound of a stainless steel alloy) react with this micro environment, pitting corrosion can be initiated.

Besides the rouging by ultra pure water, rouging can be formed by external compounds in a water environment. One common source is ferrous bicarbonate. This is commonly used to soften hard water (lower calcium concentration). By means of several chemical reactions and with or without chlorine disinfection, iron hydroxides and ferric oxides are formed and deposit as rouge. Dissolved carbon dioxide gas also contributes the formation of rouge in ultra pure water systems.

Classification

Rouging has been categorized in three types:

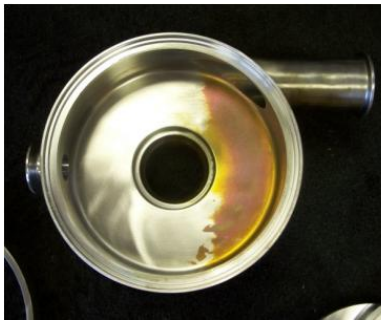
Class I
This type class rouge comes from an external source. Deposited rouge particles on the stainless steel surface are easily wiped off and the stainless steel surface itself is not corroded. The most common source is carbon steel materials in the system, where pumps etc are most suspicious.

Class II
Iron compounds originated in-situ by ultra pure water or improperly passivated stainless steel surfaces.

Class III
This type of rouge is coloured darker (purple / black) and forms in the presence of high temperature steam. The ratio iron/chrome in the protective passive film is altered as the amount of ferric oxide (typical black magnetite) is formed.

Cleaning and removal of rouging

Rouging will contribute to iron release into the ultra pure water. Even small amounts of other compounds as chrome and nickel might dissolve. Although there is no consensus of the fact how it interferes in a process, it seems the common practise is to prevent or minimize rouge and perform a chemical cleaning to de-rouge and passivate the stainless surface.



Pump casing after (partially treated)

Procedure for chemical cleaning

There are various ways in which rouging can be removed from an affected system. Conventional pickling will dissolve the passive layer and strip back the rouge, leaving a clean surface. The negative side is that this process will etch the surface of the steel, roughening and dulling the finish. Ra critical components will inevitably be ruined or at the very least, require further polishing to achieve the correct surface smoothness. Surfaces that have been pickled will subsequently become rougher and therefore more susceptible to further cases of rouging.
Where possible, (i.e., in vessels, etc) mechanical polishing can also remove this contamination. This is however an extremely expensive and time consuming process which is very dirty and will require extensive cleaning operations afterwards. It is also impossible to perform this process on the more commonly affected parts (pumps, pipework, valves, etc).

Vecom have developed a chemical formula that will remove the affected passive layer and remove the rouging with no detrimental effect.
Our sulphuric / phosphoric based solution can be easily pumped through a pharmaceutical system with minimum disruption to the plant, leaving no mess, totally removing all traces of rouging and most importantly, not affecting the Ra finish of the parts.

After this cleaning operation (or any other), the system should be fully repassivated. Vecom are able to offer this service using either a nitric acid based passivating solution, or a more environmentally / operator friendly citric acid based one.

Cover Plate before

Cover Plate after

Impeller Plate before

Impeller Plate after

Notes
http://corrosionlab.com/Failure-Analysis-Studies/rouging.htm
http://www.corrosion-doctors.org/MatSelect/rouging.htm
http://www.ispe.org/

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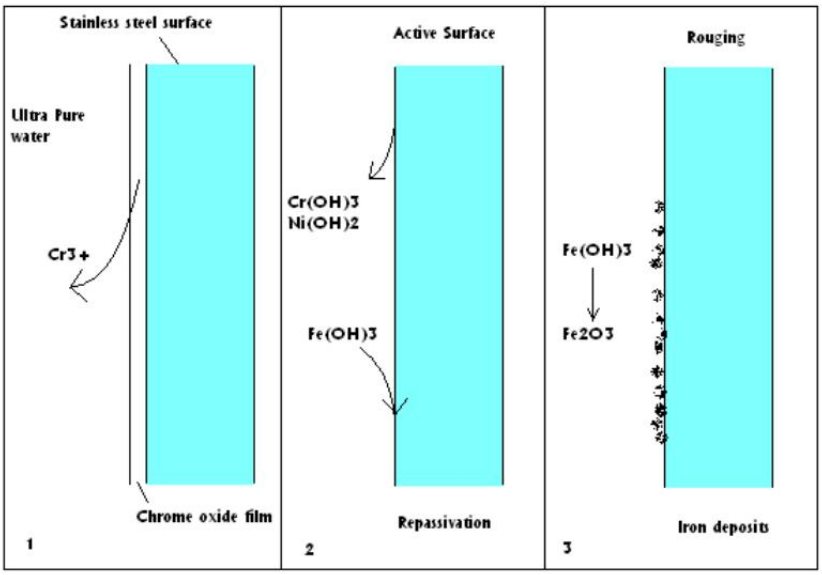

Figure 1: schematic view of the formation of rouge in ultra pure water.