advanced cleaning solutions

WHITEPAPER

# Derouging of discoloured sterilisation chambers

## Supporting device value conservation

# Contents

# Derouging of discoloured sterilisation chambers

## Supporting device value conservation

Stainless steel surgical instruments tend to discolour if they are frequently sterilised with steam when being reprocessed. Even brand-new instruments being reprocessed for the first time can exhibit such discolouration.

The cause is often assumed to be silicate deposits from the ultra-pure water used in the sterilisation process, however the transfer of flash rust from the steriliser to its contents is an obvious culprit, especially in the case of sterilisation chambers that already have reddish discolouration.

Incredibly, even the high-quality stainless steel surfaces of sterilisation chambers develop reddish discolouration caused by corrosion, a process known as «rouging», since they are exposed more frequently to the harsh sterilisation conditions than the instruments they are used to reprocess. After considering this phenomenon, we present the patented «derouging process» below for removing rust under gentle conditions and for passivation and renewing sterilisation chambers.

## 02.01

# Rust on stainless steel

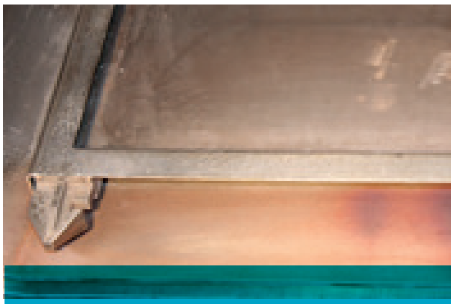
## The role of the passive layer

Surgical instruments can exhibit various types of surface change due to incorrect handling after use or during reprocessing, as well as due to inadequate water quality. The «Red brochure» from the AKI [1] provides a summary of these. However even with correct handling and reprocessing, mechanically stressed areas such as joints found on scissors can be exposed to the risk of corrosion when the protective «passive layer» on the stainless steel surface is damaged.

> « If the protective passive layer is damaged, the stressed areas are exposed to the risk of corrosion. »

This problem can present in individual areas in the form of pitting, through fretting corrosion or as a result of laser marking.

If, on the other hand, corrosion phenomena occur over a large area, e.g. as reddish discolouration in ultra-pure water systems, distillation columns and pure steam systems or in chambers of steam sterilisers, they are referred to as «rouging». The reddish-brown coatings («rouge») are iron oxides and hydroxides of varying degrees of oxidation [2]. Depending on temperature, pressure and availability of oxygen, FeO, $Fe_2O_3$, $Fe_3O_4$ or FeO(OH) are formed [3].On the one hand, the rouge itself acts as a kind of passive layer. On the other, in sterilisers with a heavy rouge coating, there is a risk that during the harsh conditions generated during sterilisation (vacuum, overpressure, water vapour-saturated atmosphere) the rouge will also transfer to the medical devices being sterilised.



> «Extensive, reddish discoloured corrosion phenomena are referred to as rouging. »

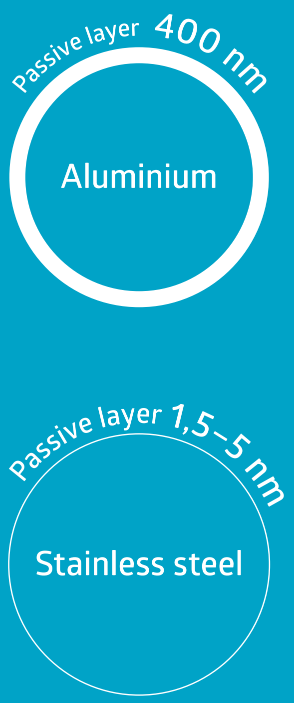
# Rust on stainless steel

## The role of the passive layer

Normally, steriliser chambers are made of high-quality stainless steel. These are typically austenitic chromium-nickel-molybdenum steel alloys with titanium stabilisation (material No. 1.4571 or AISI 316 Ti) and a high chromium content of approx. 17.5% by weight [4]. With a minimum chromium content of ≥10.5% by weight and a carbon content of ≤1.2% by weight, the passive layer provides sufficient protection against corrosion to be able to be described as «stainless» according to DIN EN 10088-1: 2005-09 [5].

The functioning of a passive layer can be easily understood using the example of the passive layer on aluminium. Since aluminium itself is a relatively «base» metal, i.e. it easily oxidises spontaneously, it forms a protective aluminium oxide layer on the surface which protects the base metal from further oxidation (corrosion). In the case of steel however, it is the alloying elements chromium (Cr), nickel (Ni) and molybdenum (Mo) that oxidise easily and form a protective layer of metal oxides on the steel surface. While the passive layer is relatively thick in the case of aluminium (up to 400 nm), its thickness in the case of stainless steel is only a few nanometres (approx. 1.5-5 nm). The thickness, quality and corrosion resistance of the passive layer of steel is determined by the weight proportions of the various alloying elements chromium (Cr), nickel (Ni) and molybdenum (Mo) [6].

**Comparison of passive layer**



The passive layer of stainless steel, which can be compared to tooth enamel, consists of the alloying elements chromium, nickel and molybdenum. The metallic alloy underneath corresponds to the dentine.

The passive layer is formed by the reaction of the metallic chromium on the surface of the stainless steel with oxygen from the environment and is only 1.5 to 5 nm thick.

## 02.03

# Rust on stainless steel

## The role of the passive layer

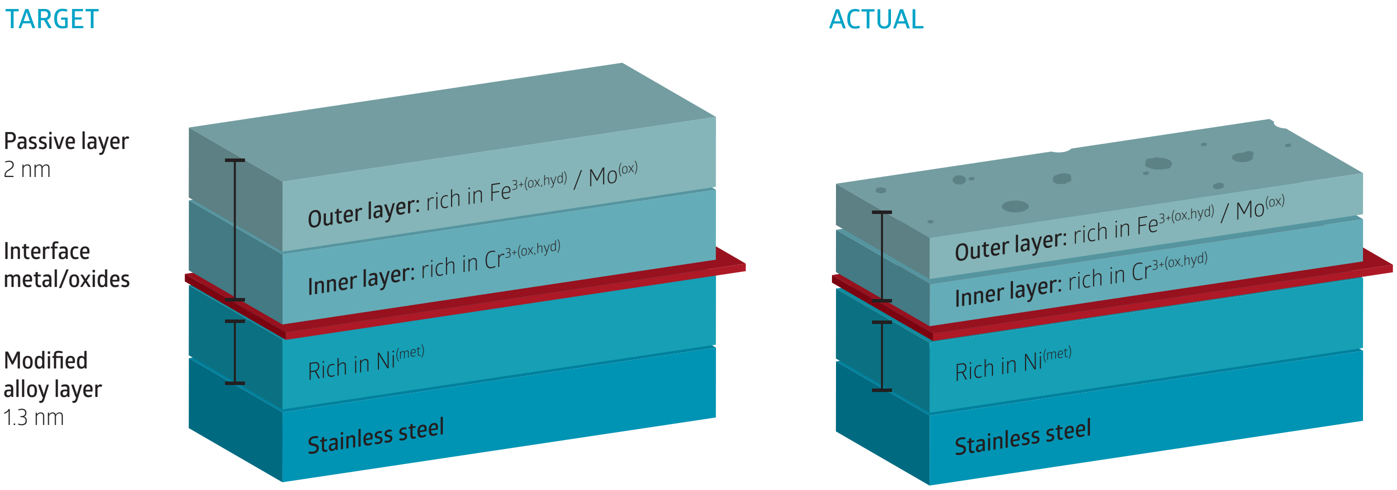


**Figure 1**
Model of the passive layer on stainless steel (modified after Wang et al. [7])

So far, the exact mechanisms of corrosion inhibition by the passive layer of stainless steel have not been fully explained. However, experimental data has produced various scientific theories [6]: there is evidence that the iron oxides and iron hydroxides contained in the passive layer, as well as chromium, nickel and molybdenum oxides, act as a bi-directional, bipolar barrier (Fig. 1, Fig. 2). On the one hand, a cation-selective layer of molybdate anions exposed to the medium prevents aggressive halide anions (such as chloride from saline solution) from migrating in, while the underlying anion-selective layer of chromium oxide prevents iron cations from migrating out to the surface [9].
Recent studies confirm the structure of the passive layer with an upper layer rich in iron and manganese oxide and an inner layer rich in chromium oxide [7]. The exact mechanism of depassivation by chloride ions is still the subject of debate.

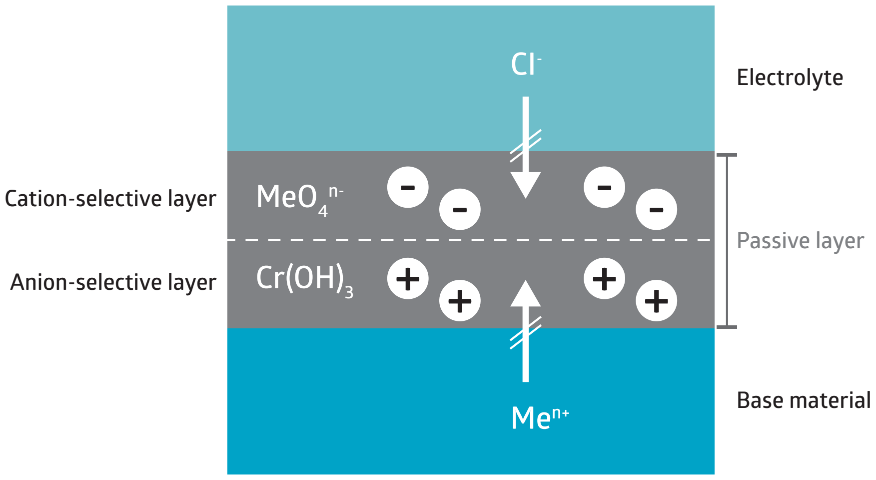


**Figure 2**
Schematic representation of the bipolar passive layer model (after Chung et al. [8])

# Accelerating the formation of a passive layer
## with chemical processes

> «The passive layer should not be considered as a static layer; it is continuously influenced by the environmental conditions and is in a dynamic equilibrium between degradation of the layer («de-passivation») and its reconstruction («re-passivation»).
> [10]»

Under atmospheric conditions, the passive layer on steel forms spontaneously, but very slowly, through oxidation of the alloying elements Cr and Mn [11]. However, the passivation process can be accelerated considerably by using chemicals. The oxidation of the chromium and molybdenum atoms can be supported by oxidising agents such as nitric acid or hydrogen peroxide. Free iron ions can be removed by using iron-binding chemicals such as phosphoric or citric acid, which can also increase the chromium content in the surface. The concentration of the oxidising agent significantly influences the success of the passivation [11].

If only an iron-binding chemical, such as citric acid, is used for passivation, free iron is effectively brought into solution and retained, but the formation of the chromium oxide layer is slow due to oxidation by oxygen in the air. Oxidising agents such as nitric acid, but also hydrogen peroxide, accelerate this oxidation process and the build-up of the passive layer. Ultimately, a combination of both chelating and oxidising properties is required for the rapid build-up of a high-performance passive layer.

> «The concentration of the oxidising agent influences the success of the passivation. [11]»

## 04.01

# Impairment of the passive layer

## and influence of steam sterilisation

The passive layer can be damaged by the application of mechanical force, such as instruments colliding with each other, which exposes the base metal of the instrument to unprotected corrosive environmental conditions at the damaged points [12]. Similarly, mechanical surface treatments such as sandblasting, brushing or welding attack the passive layer and promote corrosion, depending on how much the steel surface has been treated.

> « Passivation after surface treatment significantly increases the resistance to corrosion. »

Therefore passivation after surface treatment significantly increases the resistance to corrosion. However, it is not just the surface finish that influences corrosion resistance, but also the quality and processing of the stainless steel itself. It has been shown that non-metallic impurities in the steel alloy promote corrosion, which may be related to incomplete formation of the passive layer [8].

Another mechanism that can destroy the passive layer of a stainless steel surface is influenced by the stainless steel structure: under mechanical stress, displacements can occur within the material in areas known as persistent sliding bands which can in turn cause a crack in the passive layer, which ultimately becomes visible as fatigue corrosion [13].

Rouging occurs over a large area, as opposed to localised corrosion phenomena. Rouging promotes depassivation under the conditions found in the steam steriliser. A major cause of this is that hot water vapour, which, due to the high temperature has no or only a low oxygen content, comes into contact with the stainless steel in the overpressure environment and prevents passivation. Very pure water is also used for steam sterilisation (according to EN 285), which, due to its purity, favours the dissolution of ions from the stainless steel, such as chromium chloride ions from an already attacked passive layer. High temperatures also encourage the diffusion of iron atoms to the surface. The pH of the water influences the relative solubility in water of $Fe^{2+}$ and $Fe^{3+}$ ions and this in turn influences the ratio of the various resulting iron oxides and hydroxides, and therefore the colours of the deposits [14].

# Derouging of steam steriliser chambers

## and the influence of steam sterilisation

> In Borer Chemie AG's patented derouging process, iron oxides are removed from the rouge layer without the underlying stainless steel being etched by strong acids or parts of it being removed mechanically or electrochemically.

Depending on the origin and chemical composition, there are different categories of iron oxides on stainless steel surfaces that can be removed with varying degrees of ease [15]. On the one hand, there is the possibility that flash rust has been introduced upstream in the system. This can usually be easily removed by wiping. On the other hand, bluish-black, poorly soluble magnetite ($Fe_3O_4$) layers, which are primarily found in high-temperature steam systems, can usually only be removed with complex abrasive mechanical processes. In steam sterilisers, adherent corrosion products (likely to be primarily haematite, $Fe_2O_3$) are usually found which have developed *in situ* due to a damaged passive layer. These are removed using abrasive methods such as sanding, electropolishing and pickling or with a chemical, non-abrasive derouging method [4].

Mechanical removal of rouge, as well as the use of concentrated inorganic acids for pickling and electropolishing, requires enclosure of the steriliser due to the metal abrasion and aerosols produced, which significantly impairs the operation of the central sterilisation unit. The passive layer is also damaged by mechanical processes, which can promote the reappearance of rouge and make chemical passivation necessary. As an alternative solution, in Borer Chemie AG's patented derouging process, iron oxides are removed from the rouge layer without the underlying stainless steel being etched by strong acids or parts of it being removed mechanically or electrochemically.

05.02

# Derouging of steam steriliser chambers

## and the influence of steam sterilisation

Poorly soluble iron (III) oxides ($Fe_2O_3$) are reduced to sodium sulphate and bivalent iron (FeO) with the reducing agent sodium dithionite at approx. 70 °C. This can be dissolved as a water-soluble iron (II) oxalate dihydrate by binding as $Fe^{2+}$ to oxalic acid as the complexing agent and rinsed away from the surface (Fig. 3). Derouging is carried out in a closed steriliser using the circulation method, doing away with the need for enclosure. The impact on the operations of the central sterilisation unit is then merely the «outage» of the autoclave for one day. The removal of the iron oxide is followed by chemical re-passivation in order to accelerate the build-up of the protective layer of chromium oxide on the surface.

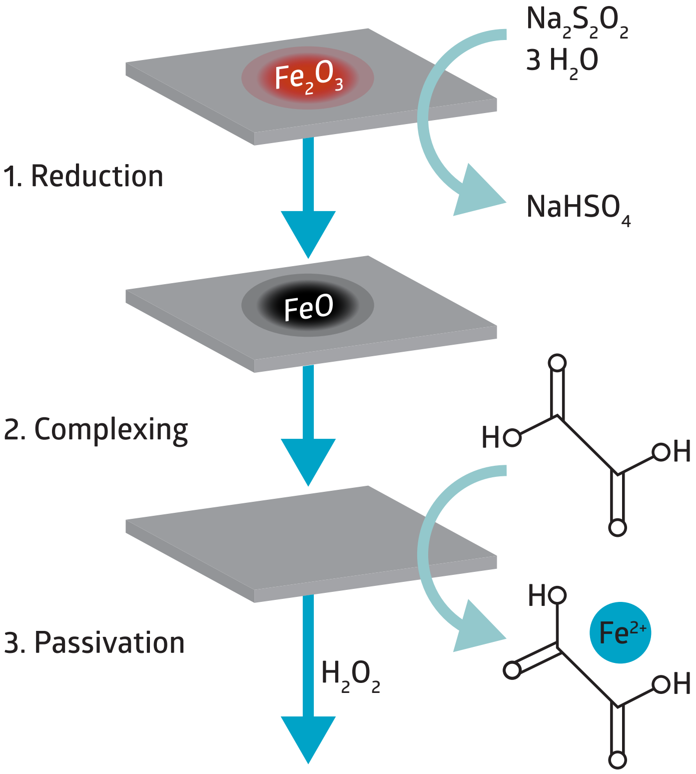


**Figure 3**
Derouging involves the following steps:
After preparatory work (manual pre-cleaning, e.g. removal of adhesives / glue, generation of an oxygen-free protective gas atmosphere, alkaline pre-cleaning and subsequent neutralisation), the three key steps of derouging are carried out: Using a reducing agent, poorly soluble iron (III) oxides are converted into iron (II) oxides, which can be dissolved and rinsed off thanks to their complexing with oxalic acid. After derouging, passivation takes place.

# Conclusion

> « Corrosion phenomena in steam sterilisers are a naturally occurring process that is difficult to prevent. This can be counteracted by periodic derouging. »

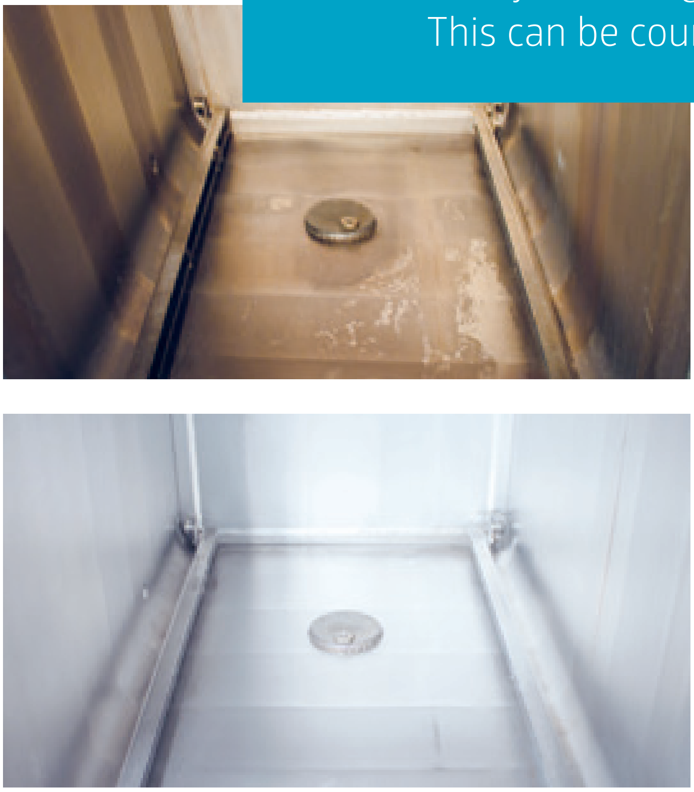


**Figure 4:**
Example of a steam steriliser before and after derouging.

Even at the procurement stage for medical instruments, the material and manufacturing qualities influence their corrosion resistance in the use and reprocessing cycle. Damage to the passive layer, as can happen in everyday clinical routines, are neutralised by periodic chemical passivation which can significantly extend the life of the instruments. Thus, repair costs can be reduced and/or the need for replacements is eliminated or delayed.

Corrosion phenomena in steam sterilisers and ultra-pure water systems, on the other hand, are a naturally occurring process that is difficult or impossible to prevent and can be counteracted by periodic derouging.

Discoloured steam steriliser chambers, look like new after a derouging process (Fig. 4), which also minimises the risk of transferring rouge and contaminants to the instruments.

**Directory of sources**
[1] Arbeitskreis Instrumentenaufbereitung (2017). Rote Broschüre «Instrumenten Aufbereitung–Instrumente werterhaltend aufbereiten», 11. Ausg. 2017 [2] Corbett, R. (2001). «Rouging – a discoloration of stainless steel surfaces.» Materials Performance (USA) 40(2): 64-66. [3]Wambach, J., A. Wokaun and A. Hiltpold (2002). «Oxidation of stainless steel under dry and aqueous conditions: oxidation behaviour and composition.» Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films 34(1): 164-170. [4] Rosenberg, U. B. (2017). «Die bräunlich verfärbte Sterikammer–ein altes Problem und seine Lösung.» Krankenhaus-Hygiene+ Infektionsverhütung 39(4): 122-129. [5] DIN, E. (2005). 10088-1. Stainless Steels–Part. 1: List of stainless steels [6] McCafferty, E. (2010). Passivity. Introduction to Corrosion Science. New York, NY, Springer. [7] Wang, L., A. Seyeux and P. Marcus (2020). «Thermal stability of the passive film formed on 316L stainless steel surface studied by ToF-SIMS.» Corrosion Science 165: 108395. [8] Chung, H. M., W. E. Ruther, J. E. Sanecki, A. Hins, N. J. Zaluzec and T. F. Kassner (1996). «Irradiation-assisted stress corrosion cracking of austenitic stainless steels: recent progress and new approaches» Journal of Nuclear Materials 239: 61-79. [9] C. D. Stockbridge, P. B. Sewell, and M. Cohen, J. Electrochem. Soc., 108, 928 (1961). [10] Yamamoto, T., K. Fushimi, M. Seo, S. Tsuri, T. Adachi and H. Habazaki (2009). «Depassivation–repassivation behavior of type-312L stainless steel in NaCl solution investigated by the micro-indentation.» Corrosion science 51(7): 1545-1553. [11] Wallinder, D., J. Pan, C. Leygraf and A. Delblanc-Bauer (1998). «EIS and XPS study of surface modification of 316LVM stainless steel after passivation.» Corrosion Science 41(2): 275-289. [12] Soltis, J. (2015). «Passivity breakdown, pit initiation and propagation of pits in metallic materials–review.» Corrosion Science 90: 5-22. [13] El May, M., N. Saintier, T. Palin-Luc, O. Devos and O. Brucelle (2018). «Modelling of corrosion fatigue crack initiation on martensitic stainless steel in high cycle fatigue regime.» Corrosion science 133: 397-405. [14] Sandle, T. (2015). «The Rouging Effect in Pharmaceutical Water Systems: Causes and Strategies for Prevention| IVT.» [15] Tverberg, J. C. and J. A. Ledden (2000). Rouging of Stainless Steel in WFI and High Purity Water Systems. Proceedings of Tube.

# Borer Chemie AG
## The specialists in cleaning and disinfection

**Competence and innovation – worldwide**

We have been researching, developing and manufacturing products in Switzerland for demanding applications in the field of cleaning and disinfection since 1965. Our deconex® and decosept® branded products are used in the industrial sector, in hospital hygiene, in laboratories, in the pharmaceutical sector and in hand and surface disinfection. We distribute our products worldwide through a network of subsidiaries and distribution partners.

**Highest demands on the reprocessing of medical devices**

For all healthcare facilities, the health and safety of patients and staff is paramount. Our deconex® product portfolio is synonymous with superlative cleaning performance and maximum protection of your investment. In-depth process expertise, closeness to customers and a comprehensive range of services from basic cleaning and passivation to the derouging of autoclaves and customer-specific product and application training round off our range of services.

**The Borer Competence Centre:**
**the only one of its kind in the world of reprocessing**

In our test and training centre at our headquarters in Zuchwil, we offer our customers and partners training programmes tailored to their needs in the field of application technology. This includes application tests on different types of washer-disinfectors with process chemistry of their choice, basic cleaning and passivation processes as well as customer-specific testing. The programmes are accompanied by our application specialists across all sectors.

borer
advanced cleaning solutions

Borer Chemie AG
Gewerbestrasse 13, 4528 Zuchwil / Switzerland
www.borer.swiss

Whitepaper_Derouging – MED BC-CH 1.2 2023-08-03 EN