Bulgarian Society for NDT
International Journal "NDT Days"
Volume VI, Issue 4, Year 2023
ISSN: 2603-4018
eISSN: 2603-4646

The Equilibrium between Rouging and Derouging: A New Method for "Green" Derouging and Rust Removal for Industrial Applications

Nikolay T. TZVETKOV[1], Tsvetomir R. BORISOV[2]

[1] Department of Biochemical Pharmacology and Drug Design, Institute of Molecular Biology "Roumen Tsanev" at the Bulgarian Academy of Sciences, Sofia, Bulgaria,
e-mail: ntzvetkov@bio21.bas.bg

[2] Institute of Mechanics at the Bulgarian Academy of Sciences, Sofia, Bulgaria,
e-mail: ts.borisov07@gmail.com

Abstract
The present work is focused on a huge economic and environmental problem worldwide – rusting and rouging. The process of deposits formation of different types, structure and layer thickness, in the form of fine iron oxides/hydroxides on the surface of special chromium-nickel stainless steels (Cr/Ni, AISI class 304, 304L, 305–308) and/or chromium-nickel-molybdenum (Cr/Ni/Mo, AISI class 316, 316L, 904, 904L) austenitic alloys, is known in the practice as rouging. This is a specific form of corrosion of special steel alloys. Herein, we present a novel procedure for a pH neutral "GREEN" derouging and rust-removal of austenitic alloys (all-in-one CIP), useful for different industrial branches, such as biopharmacy, chemistry, and energy. The novel CIP-procedure is easy to perform, convenient, and environmentally friendly.

Keywords: Corrosion, derouging, rust removal, cleaning-in-place (CIP), austenitic alloys, pH neutral

1. Introduction

The aim the of the present study is to offer an innovative, effective, cost-efficient, and importantly, environmentally friendly procedure for non-destructive derouging and rust removal. As well-known, rusting and rouging represent a huge economic and environmental problem worldwide. The process of deposits formation of different types, structure and layer thickness, in the form of fine iron oxides/hydroxides on the surface of special chromium-nickel stainless steels (Cr/Ni, AISI class 304, 304L, 305–308) and/or chromium-nickel-molybdenum (Cr/Ni/Mo, AISI class 316, 316L, 904, 904L) austenitic alloys, is known in the practice as *rouging*. This is a specific form of *corrosion* of special steel alloys.
These partial or massive deposits have a typical red-orange or orange-black color of varying intensity and are characteristic of equipment, apparatus, and installations, as well as supply piping systems (operating with ultra-pure water WFI/UPW with a temperature above 70°C and/or water vapor), used mostly in the high-tech production of pharmaceutical and biotechnological products, and other relevant industrial branches like chemistry and energy suppliers. In other words, the blushing phenomenon is typically found in the so-called "clean/sterile productions", where it is mandatory to work under the modern requirements of good manufacturing practice (GMP/cGMP/GAMP). In most cases, such colored deposits, dirt and other visual changes can only be removed mechanically by wiping from the surface of the steel, which is practically impossible. Prolonged deposition of various forms of oxidized iron and other heavy metals on the surface of different types of stainless steel can lead to varying degrees of corrosion, leading to the formation of permanent rust, and subsequently, to contamination of the final products. In addition, such pollution also leads to technological problems related to the security and safety of the production itself. The process of removing traces of oxidized iron (Fe^{3+}) and other heavy metals is known in the practice as *derouging*. The necessary instructions and requirements are given by the International Health Organization

(WHO), the International Society for Pharmaceutical Engineering (ISPE), the International Council on Technical Requirements for Medicinal Products for Human Medicine (ICH), as well as the most important regional pharmaceutical and biotechnology control organizations such as FDA (USA) and EMA (Europe) [1,2,3].
The implementation of rehabilitation activities (derouging, removal of incipient corrosion and re-passivation) takes place in accordance with the requirements of good manufacturing practice (GMP) and the internal production Quality Management System (QMS) through the application of the relevant Standard Operating Procedure (SOP). The frequency of carrying out this type of activities depends on the intensity, type (working parameters), and volume of the respective production, which are specific for each production company [4].
The aim of this study is to present a novel procedure for a pH neutral "GREEN" derouging and rust-removal of austenitic alloys (all-in-one CIP). The industrial application of this procedure is feasible due to the newly developed aqueous formulations allowing an efficiently and residual-free cleaning of austenitic steels, which are used in different industrial branches, such as biopharmacy, chemistry, and energy. The novel CIP-procedure and the pH neutral derouging/rust removing formulations are easy to perform, convenient, and environmentally friendly.

2. Discussion and results

2.1 State of the art: standard methods for cleaning of stainless steels at pH < 2 or pH > 11

From a technological point of view, the removal of any type of contamination (also known as *decontamination*) on the contact surfaces of stainless Cr/Ni-, Cr/Ni/Mo- and Cr/Ni/Mo/Ti-alloyed steel used in the construction of equipment for pharmaceutical and biotechnological production includes four main and two preparation steps, as follows:

1) Preparation of aqueous cleaning solution (preparation step **1**)
2) Derusting/removal of traces of corrosion (main step **2**)
3) Intermediate cleaning with clean (RO/WFI/UPW) water (main step **3**)
4) Preparation of re-passivating aqueous solution (preparation step **4**)
5) Re-passivation of the cleaned metal surfaces (main step **5**)
6) Final cleaning with clean (RO/WFI/UPW) water (main step **6**) (*cf.* Figure 3).

For the removal of any type of contamination (rouge type deposits, early stage of corrosion and related to them visual changes) from the surface of stainless steels, the so-called *wet-chemical methods* for cleaning (decontamination) and recovering of the passive Cr_xO_y layer (re-passivation) of the contact surfaces of production installations and systems are widely used. These methods include mostly the use of concentrated and/or dilute aqueous solutions of strong inorganic mineral acids (e.g., 3–12% phosphoric acid, HNO_3 in different concentrations, and others) and for re-passivation also of the application of organic water-soluble acids (e.g., citric acid, and others). In some cases, concentrated aqueous solutions of inorganic strong bases (such as NaOH) in combination with ionic and/or non-ionic surfactants (detergents) are also used. However, in all cases, the decontamination and re-passivation processes are carried out under unfavorable pH conditions (pH < 2 or pH > 11), which is associated with several problems, including neutralization of wastewater mixtures, strict safety control when using strong acids and bases, possible secondary destruction of the passive chrome layer, faster wear of the material and destruction of metal components, increased costs, and last but not least – serious environmental (ecological) problems.

There are two main approaches for application of the wet-chemical methods for industrial cleaning: (i) cleaning-in-place (CIP) using an automatized fine injection and/or multiple circulation, and (ii) cleaning-out-of-place (COP), which is suitable for detachable elements or parts of production installations – both mechanical and automated methods of fine injection, circulation, and immersion water bath can be applied.

2.2 Innovative pH neutral formulations for cleaning of stainless steels at pH 5–7

In view of the number of shortcomings and the strict norms, introduced by the relevant regulatory authorities regarding the use of aggressive chemicals, the so-called "GREEN methods" have been rapidly introduced in recent years [2–4]. In these modern procedures, water-neutral chemical formulations (pH 4–8) are preferably used as for the main processes of derouging and rust removal as for (re-)passivation of production installations.
In this context, innovative aqueous pH neutral formulations *NTZ*$_{clean\ neutral}$ and *NTZ*$_{neutra\ pass}$ (NTZ Lab Ltd., www.ntzlab.com) have been recently developed in order to ensure an efficiently and residual-free cleaning of austenitic steels, which are used in different industrial branches, such as biopharmacy, chemistry, and energy. The series of universal and highly effective colourless aqueous formulations for water-neutral derouging in a pH range of 5–7 is useful for removing of all forms of rouge, corrosion (rust), coloured and other types of impurities (deposits) on the surface of stainless steels with Cr/Ni and Cr/Ni/Mo alloys (e.g., 304/304L and 316/316L). These aqueous formulations offer several benefits over the standard cleaning aqueous solutions used so far, as follows: (i) low costs, (ii) not necessary use of a protective nitrogen environment during their application, (iii) environmentally friendly and safe for people and nature, (iv) simple preparation, (v) quick and easy implementation, (vi) no special neutralization of wastewater is required, (vii) adaptive procedure for application depending on the client's requirements, (viii) conducting the cleaning and re-passivation process in the pH range 5–7, (ix) adaptive working parameters (pH, T, time), (x) optimal physicochemical characteristics, (xi) applicable for CIP and COP applications under GMP conditions, (xii) non aggressive against different polymers (e.g., PE, PP, PTFE, PVDF, EPDM, and others), (xiii) non special requirements for their long-time storage, and others. Some examples of the application of these new formulations under pH neutral conditions in laboratory and in the practice are presented in Figures 1 and 2, respectively.

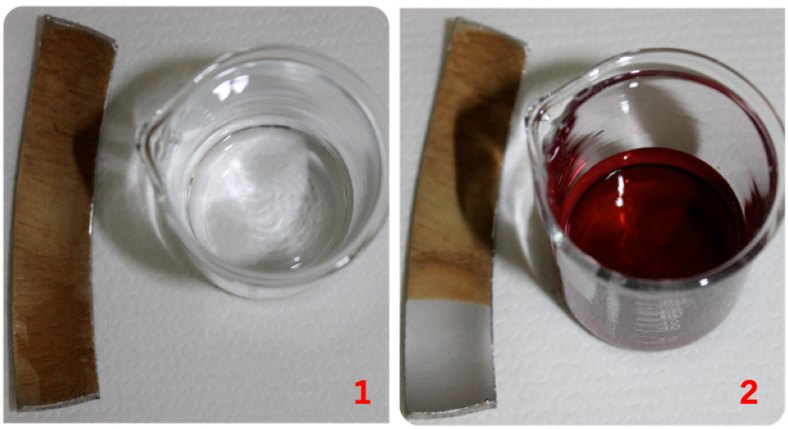

Fig. 1. An example of derouging with pH neutral NTZclean formulation (pH 6.93) of a sample plate made from stainless steel (AISI 316L) taken from a pharmaceutical WFI system (rust layer thickness >10 µM) before (1) and after (2) derouging for 5 min at 45°C. Solution discoloration into red provides the transformation of the insoluble Fe^{3+} oxides/hydroxides into their soluble form.

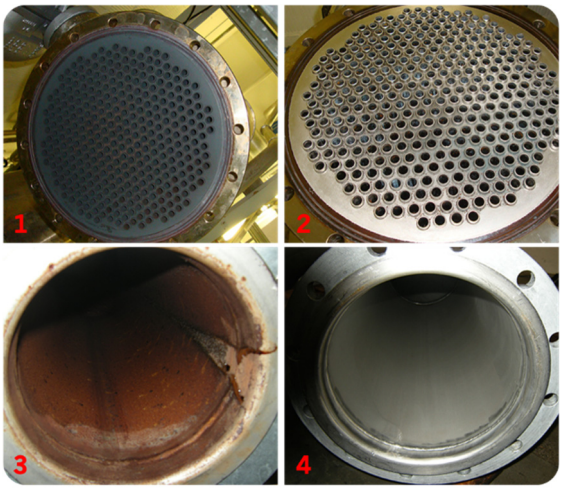

Fig. 2. Tube plate of a steam raising unit before (1) and after (2) derouging. Pipe system before (3) and after (4) rust removal with new pH neutral formulations with NTZ$_{\text{clean neutral}}$.

The technological scheme for application under pH neutral conditions is presented in Figure 3. The scheme offers the possibility of carrying out of either cleaning of the steel surface (e.g., derouging) or passivation (two-single step procedures), as well as successive re-passivation of the steel surface that is cleaned in the first step, completely carried out in a water-neutral environment.

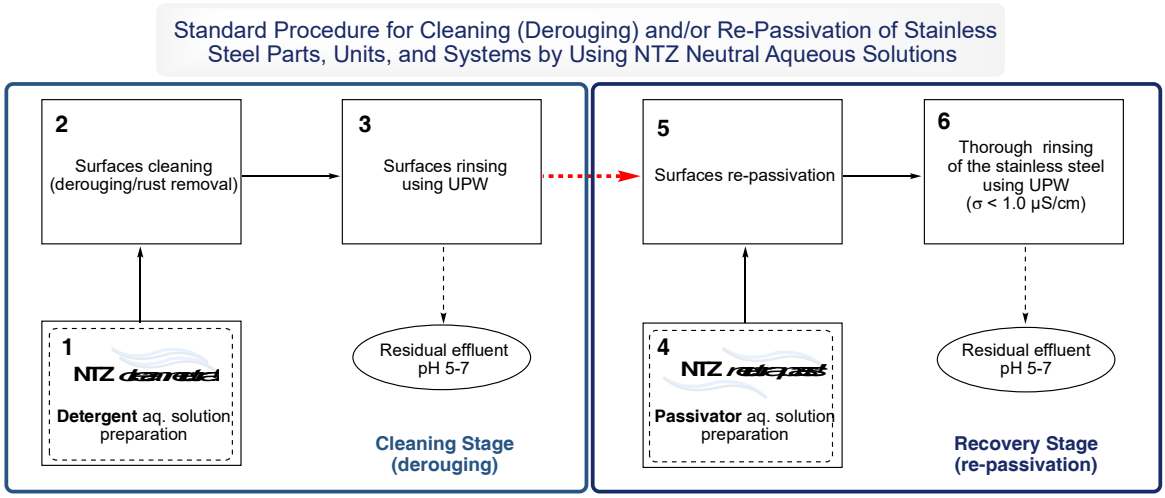

Fig. 3. Standard successive scheme procedure for derouging/rust removal and re-passivation with NTZclean neutral and NTZ neutral pass aqueous solutions.

References

1. Webpages of the cited International organizations: https://www.who.int/, https://ispe.org/, and https://www.ich.org/.
2. Henkel G., B. Henkel. Derouging von austenitischen Edelstahloberflächen mittels pH-neutraler Hochleistungschemikalien. TechnoPharm, Vol. 1, No. 1, 2011, pp 46-53.
3. Czech A. Rouging – Erfahrungen aus der Praxis am Beispiel einer WFI-Anlage. Pharmind Vol. 72, No. 1, 2011, 184-190.
4. Gohen N. How to determine rouge limits to initiate derouging and passivation. Pharmaceutical Engineering Vol. 34, No. 1, 2014, 1-4.