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IMPORTANCE OF FINISHING FOR THE INTEGRITY OF STAINLESS STEEL SURFACES DURING SANITATION TREATMENTS

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Abstract. In food industries, production lines are cleaned and disinfected. The samples of differently finished AISI 304 were exposed to various disinfectant solutions and then examined by scanning electron microscopy – SEM. The chemical processes that take place on stainless steel surfaces during disinfection, were put into evidence by measuring the pH of the working biocide solutions after their contact to stainless steel samples. Stainless steel AISI 304 (SS) was chosen due to the fact that most containers, pipe works and food contact equipments are made of it. As new 2G No 4 304 AISI was compared to new finishing BA 304 AISI and obsolete 304 AISI. It was studied the action of 5 commercial disinfectants: Actisept (sodium dichloroisocyanurate: 0.25% sln.), Neoseptal (2% sln. of H_2O_2 30%), Anasept (mixture of hexamethylenediamine, polyhexamethylene biguanide and quaternary ammonium compounds, 0.5% sln.), Propano (ethanol and propan-1-ol) and Rouasan (ethanol, propan-2-ol, quaternary ammonium compounds and dodecylpropane-1, 3-diamine). SEM analysis demonstrated that disinfectants induced structure modifications of stainless steel AISI 304 surfaces, the damages depending on the alkaline or acidic nature of the disinfectant. It was concluded that the smoother the surfaces are the better they resist to disinfectants.

Keywords: stainless steel, disinfectants, pH, SEM.

AIMS AND BACKGROUND

The aim of this work was to investigate the manner in which different finishing surfaces of the stainless steel AISI 304 are affected during sanitisation process. Using SEM could be evaluating the influence of disinfectants on metallic surfaces, and to identify the one that better resists during disinfectant treatments.

In many food industries, production lines are daily cleaned and disinfected[1]. These processes are essential steps in preventing food contamination with pathogenic and spoilage microorganisms[2]. Disinfection is the process of applying a disinfectant against unwanted microbial contaminants[3]. A disinfection protocol

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usually ends with the elimination of the disinfectant traces by rinse but there are authors that consider the disinfectant application being the last step of a disinfection protocol and rinsing with water is not necessary[4]. Also, some biocide producers support the idea that as long as the remaining disinfectant in the processing food lines does not exceed the legal limits[5], it does not represent a chemical risk for the consumers health and it may reduce the general food contamination. In other words, the remaining disinfectant serves as a sentinel against microorganisms. But the residual disinfectant can potentially lead to a significant degradation of equipments materials via corrosion that, in turn, can increase the adhering of soil[6–8]. Some authors[8] have emphasised the importance of the chemical nature and finishing of materials in relation to the surface cleaning ability. Material texture and topography are also influencing the surface clean ability. Dirts attachment in pits and crevices would not receive the same cleaning shear forces as dirt attached to a smooth surface, the rough surfaces being much difficult to clean comparing to smooth surfaces. Surface finishing of materials, exposure time, concentration, temperature and pH, are the most important factors affecting the activity and efficiency of the sanitising agents[9]. In general low pH values cause high corrosion; acidic environments can cause a breach in protective layer of metallic surfaces, whereas high pH can decrease metal solubility. Stainless steels (SS) are widely used in food and beverage manufacturing and processing industries for manufacture, bulk storage and transportation, preparation and presentation applications. Alloys of SS 304 AISI are the most familiar materials used in food applications because are easy to clean, durable, inert and sanitary.

EXPERIMENTAL

Samples characterisation and pretreatment procedures. Tests were performed on using stainless steel samples with different surface finishing. Three types of SS 304 AISI were used: BA 304 AISI (obtained by rolling in skin-pass line), obsolete 304 AISI (BA finish from plant, obtained in this study through manual unidirectional polished 1200 µm grit abrasive) and 2G No 4 304 AISI (obtained through cold rolled, heat treated, pickled and skin passed and unidirectional polished 150 µm grit abrasive). The chemical analysis of the samples was performed using the optical emission spectral analysis technique on Spectromax equipment (SPECTRO Analytical Instruments Gmb H & Co. KG, Germany). All SS AISI samples were chemically cleaned and washed in deionised water before testing[10]. The samples roughness (Ra) was assayed by BioScope II (OLYMPUS 1X71, Japan). The characteristics of the tested samples are presented in Table 1.

Table 1. Characteristics of the stainless steel coupons

Material		Surface finishes and samples dimensions	Chemical composition (wt.%)	Roughness, Ra (nm)	Remarks
AISI 304	new	BA bright reflective 20× 20 × 0.3 mm	Fe: 70, Cr: 18.8, Ni: 8.5, Mn: 1.9, Si:0.70, P: 0.38, C:0.07, S:0.012	13–37	exceeds in alloys: Si, P, C and S, comparing to obsolete stainless steel
	obsolete	manually lustrous 20 × 20 × 1.5 mm	Fe: 70.8, Cr: 18.3, Ni: 8.36, Mn: 1.61, Si:0.49, Cu: 0.19, Co: 0.15, Mo: 0.08, V: 0.05, C:0.04, As: 0.02, Nb: 0.02, P: 0.02, W:0.01	39–85	a low carbon content than new stainless steel. The traces of alloys: Cu, Co, Mo, V, As, Nb, W
	new	2G No 4 uniform polished with a certain grade of roughness 20 × 20 × 1.0 mm	Fe: 70, Cr: 18.8, Ni: 8.5, Mn: 1.9, Si:0.70, P: 0.38, C:0.07, S:0.012	54–473	exceeds in alloys: Si, P, C and S, comparing to obsolete stainless steel

Disinfectant solutions. Fresh disinfectants were applied at the maximum concentration established by the suppliers (Table 2). All these disinfectants are approved by the Romanian National Register of Biocide Products[11] to be used in processing areas, except Propano, which is designated for the laboratory surfaces.

Experimental set-up. To investigate the disinfectants influence on the finishing surfaces, there were placed 5 samples of each SS AISI type, in glass cylinders with fresh disinfectant solutions at room temperature, carefully so that the whole surface would be exposed to the disinfectant solution. Each glass cylinder was covered by acrylic plate with hole. The pH measurements of the disinfectants action were tested at 1, 3, 24 and finally to 72 h in time using the WTW INOLAB 720 pH-meter, to evaluate disinfectants stability for longer period of time. The results are presented in Figs 1–5. The experimental data were revealed using OriginPro 7 program and graphing software. After disinfectants action the modifications of AISI SS surfaces were performed by scanning electron microscope (SEM) (Ref. 12) using a Quanta 200 (Philips) with high magnification, in about 20 fields with area 100 μm^2 for each sample. SEM images are presented in Figs 6–11.

Table 2. Disinfectant used in investigations

Commercial name	International common name	Working concentration	pH	Action time (min)	Remarks
1. Neoseptal ®D liquid (Dr.Weigert, Germany)	hydrogen peroxide, 30%	2%	2.67	30	must be rinsed
2. Actisept tablet (Medicarom, Romania)	sodium dichloroisocyanurate	0.25%	5.85	10	less toxic and less corrosive than other chlorine compounds; long-term stability; resistance to organic load; environmentally friendly; good biocidal effect; release chlorine only when dissolved in water; low cost
3. Anasept liquid (Rou – Asept, Romania) additives against corrosion	mixture: hexamethylenediamine polyhexamethylene biguanide, quaternary ammonium compounds, propylenglicol	0.5(%)	6.80	60	highly concentrated; non-corrosive; low toxicity; low cost; produces foam
4. Propano spray (Esteer Pharma Germany)	mixture: ethanol 40.5 g *n*-propanol 9.12 g	20 ml/m²	8.55	5	rapid effect; ready-to-use; not be rinsed
5. Rouasan spray (Rou – Asept, Romania)	mixture: ethanol 60–65% quaternary ammonium compounds dodecylpropiltriamine	50 ml/m²	9.25	5	

RESULTS AND DISCUSSION

The surfaces with great roughness are easily damaged, while smooth surfaces present better corrosion protection. It is important to clean and to rinse with clean water all surfaces that may come into contact with, e.g. chloride ions. Every production process in the food industry requires different disinfectants, which vary from one type of equipment and food product type.

Modifications of pH. In general variation of ± 0.5 units of pH indicates a constant behaviour of the system studied[13]. As a rule, for Neoseptal pH of the biocide working solution was practically constant, varying less than 0.5 for all type of SS. After 72 h it observed an increasing with 0.67 pH units for obsolete SS AISI and 0.72 pH units for 2G No 4 304 AISI (Fig. 1).

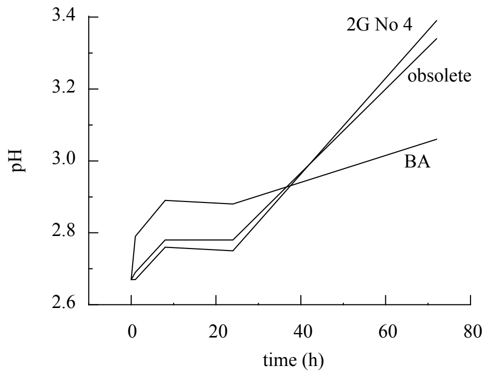

Fig. 1. pH versus time for Neoseptal with different finishes SS 304 AISI

For Actisept biocide working solution, a continuous pH increase was observed from 5.85 to 6.78 units until up 8 h, and after that pH was practically constant, varying less than 0.5 units in case of BA SS. In case of obsolete 304 AISI pH was increased after 24 h with 0.71 units. In case of 2G No 4 304 AISI, pH was increased with 0.80 units after 8 h (Fig. 2).

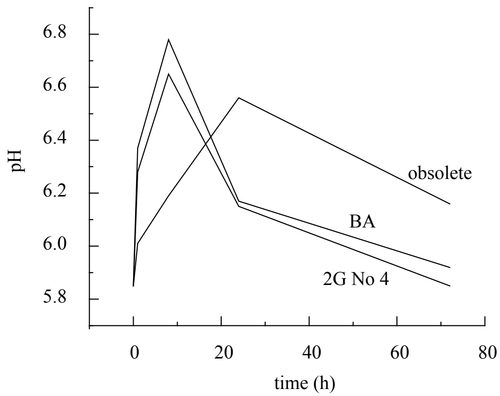

Fig. 2. pH versus time for Actisept with different finishes SS 304AISI

For the Anasept disinfectant the pH value after 1 h was increased with 0.52 units and after 24 h it was increased with 0.75 units for BA 304 AISI. In case of obsolete 304 AISI, the pH remained constant but a decrease after 8 h in pH value with 0.84 units was observed (Fig. 3).

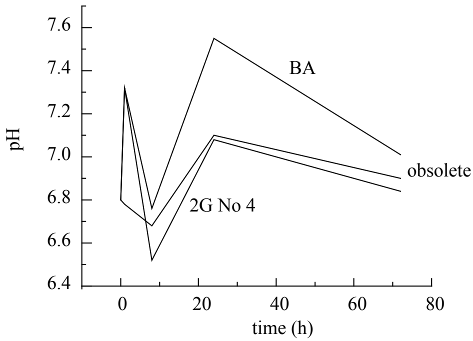

Fig. 3. pH versus time for Anasept with different finishes SS 304 AISI

In the case of Propano disinfectant pH of solutions was practically constant for surfaces, except for the obsolete SS, when after 72 h it was observed an increasing with 0.70 units (Fig. 4).

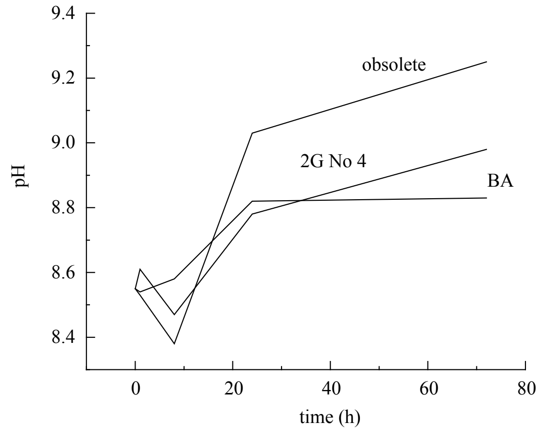

Fig. 4. pH versus time for Propano with different finishes SS 304 AISI

For Rouasan biocide, pH was increased for BA 304 AISI after 8 h with 0.69 units, while pH value was remained constant in case of obsolete 304 AISI. For 2G No 4 AISI, pH was decreased with 0.75 units after 1 h (Fig. 5).

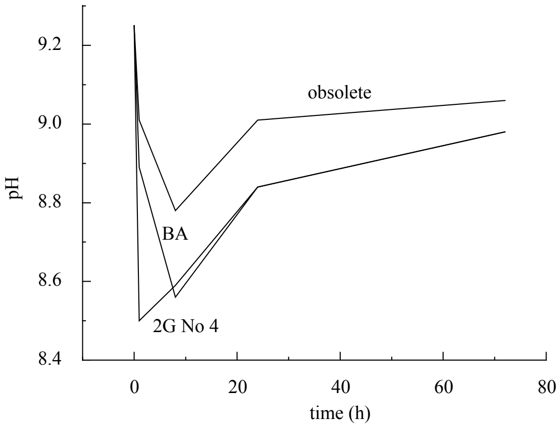

Fig. 5. pH versus time for Rouasan with different finishes SS 304 AISI

Modifications of pH could be explained by a balance of reactions which means a consumption of H^+ from the solution. A better pH stability on the BA 304 AISI interface at Neoseptal and Propano was observed, also for the Rouasan up to 8 h. Instability of pH in Actisept and Anasept was observed up to 24 h. The stability of pH was: Actisept > Anasept > Rouasan > Propano > Neoseptal (2 > 3 > 5 > 4 > 1). In case of the obsolete 304 AISI, it was observed the pH stability interface in the following order: Anasept > Rouasan > Neoseptal > Propano > Actisept (3 > 5 > 1 > 4 > 2) of the biocide solutions. The instability of pH solution with the 2G No 4 304 AISI was observed up to 24 h in Anasept. Finally, the stability of pH 2G No 4 304 AISI was in the order: Rouasan > Actisept > Anasept > Propano > Neoseptal (5 > 2 > 3 > 4 > 1). These results show that disinfectant solutions in generally are stable for their action time up to 8 h indicated by suppliers (Table 2). The biocide solutions studied presented different behaviours and pH, depending on the type, contact time and concentration disinfectant and finishing surface. These characteristics should be considered when choosing the disinfectants useful for metallic surfaces disinfection to keep the safety food.

Aspects of surfaces morphology. Materials that prevent surface changes due the chemical disinfection will remain more hygienic than materials which are more easily damaged on a microscopical scale and would, therefore, be less cleanable. Thus, the formulation of chemical compounds must consider finishing the stainless steel in addition to the kind of contaminant, and then an adequate type of sanitising. It is widely accepted in literature that disinfectant residuals increase the materials corrosion[14,15]. For the SS AISI surfaces the susceptibility to crevice corrosion is strongly depending on the surface finishing. When the roughness is near 500 nm there is a significant increase in corrosion. This fact occurs if the stainless steel had a larger surface area or because of an increase in roughness under cleaning conditions. The SS surfaces finishing could be evaluated from their roughness (Table 1) in the increasing order: BA>obsolete>2G No 4. In obsolete 304 AISI the different corrosive behaviour is mainly explained by its chemical composition, which includes traces of alloys: Cu, Co, Mo, V, As, Nb and W. The aspects of the surfaces morphology exposure to the various media are shown in Figs 6–11. Figure 6 presents the SS AISI surfaces finishing without any effect of disinfectant treatments.

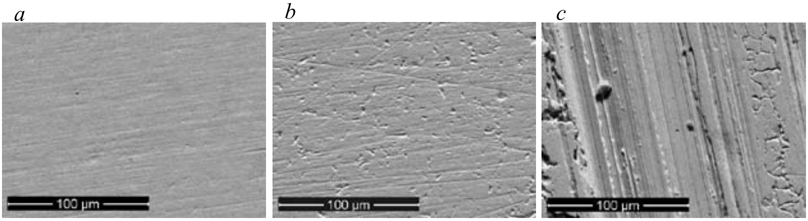

Fig. 6. SEM images on SS 304 AISI without disinfectants: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

Neoseptal effects. This disinfectant produces a modification of the surface through a levelling of the BA 304 AISI surfaces and deepness of imperfections for the obsolete surfaces. In case of the 2G No 4 304 AISI, it was observed a evenness of the surface, by reducing the structural aspect (Fig. 7). Low pH values cause higher corrosion; acidic environment can cause a breach in protective layer[16].

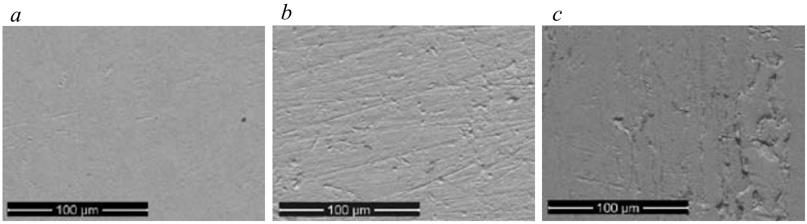

Fig. 7. SEM images on SS 304 AISI in Neoseptal: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

Actisept effects. For this disinfectant it was observed a visible destruction of BA 304 AISI surface, probably the layer does not resist to disinfectant attack. A pronounced destruction of the crystalline grains in case of the 2G No 4 304 AISI was observed while on the obsolete surface it was observed the lower destruction (Fig. 8).

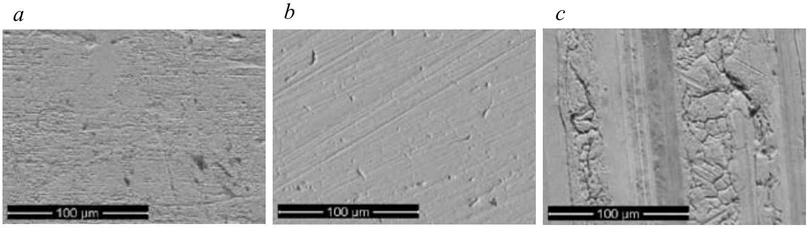

Fig. 8. SEM images on SS 304 AISI in Actisept: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

Anasept effects. The BA 304 AISI showed dark spots on the surface but the it was not observed any destruction of the finishing surface. In case of obsolete 304 AISI surfaces this disinfectant shown the lower destructions and for 2G No 4 304 AISI surface it is observed a reduction of the crystalline grains (Fig. 9).

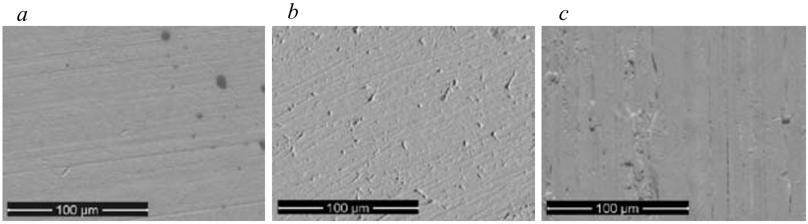

Fig. 9. SEM images on SS 304 AISI in Anasept: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

Propano effects. All surfaces of samples for BA 304 AISI tested presented dark spots. A pronounced destruction of finishing with a major emphasis for cracks caused through manual polished was observed in case of the obsolete surface. The 2G No 4 304 AISI presents significant chemical attack of the surface (Fig. 10).

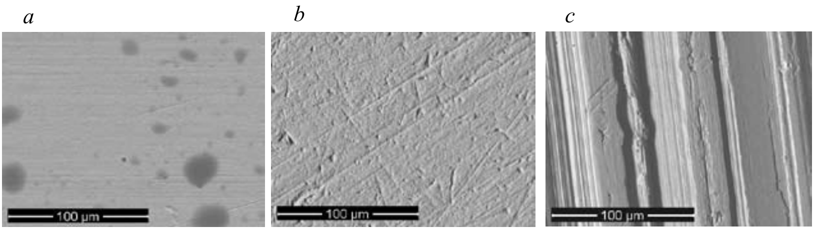

Fig. 10. SEM images on SS 304 AISI in Propano: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

Rouasan effects produced a chemical attack on BA 304 AISI surface but a pronounced destructions for the obsolete 304 AISI surface could be observed (Fig. 11*a*, *b*). A significant chemical attack at the crystalline grains in case of 2G No 4 304 AISI surface is also evident (Fig. 11*c*). As a conclusion this disinfectant produced the most remarkable surface modification compared with other disinfectants.

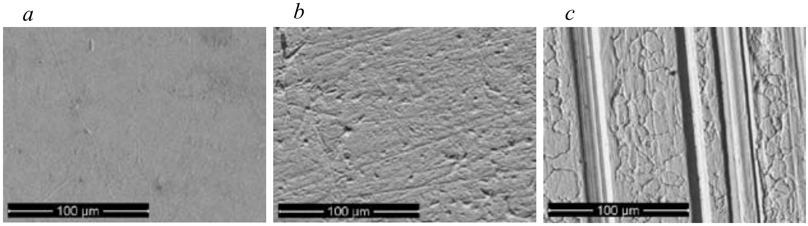

Fig. 11. SEM images on SS 304 AISI in Rouasan: BA (*a*); obsolete (*b*); 2G No 4 (*c*)

CONCLUSIONS

The samples of three different finished 304 AISI were exposed to various disinfectant solutions and their behaviour was examined by scanning electron microscopy and pH measurements. It was studied the action of 5 commercial disinfectants: Actisept, Neoseptal, Anasept, Propano and Rouasan. The disinfectants studied presented different behaviour and pH, depending on the type, contact time and concentration of disinfectant and finishing surface. These characteristics should be taken into account when choosing the disinfectants for metallic surfaces disinfection to keep the safety of food. SEM analysis demonstrated that disinfectants induced structure modifications of stainless steel 304 AISI surfaces. The surface damage morphology is mainly characterised by finishing modifications of 304 AISI, more destruction for the acidic and basic disinfectant action and less for the neutral disinfectant. It was concluded that the smoother the surfaces (BA) are the better they resist to disinfectants while 2G No 4 surface damage morphology is mainly characterised by intergranular destruction.

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