BAT for electrochemical processing of stainless steels installation

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Introduction

When looking at worldwide production of stainless steel, its increase from 19 mln of tons to 31 mln of tons was observed in a period of ten years, since the year 2001 [1]. That result is undoubtedly influenced by China, which increased its production from the level of 730 thousand on 11 000 thousand of tons. However the economic crisis considerably affected the interim decrease in the worldwide consumption and production of stainless steel, and in 2009 the production on a level of 24 900 thousand of tons was noted, the result from the year 2010 should be considered as optimistic one. The prices of stainless steels depend to a high degree on fluctuating prices of alloy additives, i.e. chromium, nickel, molybdenum. In Poland, also EUR exchange rate has a significant influence, since the import constitutes 98-99% of these steels consumption in the country, and only 1-2% is a domestic production [2]. The distinct trend in Poland is continuous increase in their popularisation. The sample may be railings, stairs, balustrades or lifts made of stainless steels in shopping centres and office buildings. The huge advantage of such elements is their long exploitation time, very well resistance on corrosion, and due to smooth surface, easiness in writings and graffiti removing.

Stainless steels pickling and electropolishing

With an increase in an application of stainless austenitic steels, the demand on final processing services, i.e. pickling and electropolishing processes, increases gradually. In chemical industry branch, utility values of pipelines, chemical tanks, batches for fertilizers production and heat exchangers positively influence the abundance of that kind of processing application. Moreover, due to hygiene [3] and esthetic requirements, i.e. easy cleaning of smooth surfaces and their high gloss, electropolished austenitic stainless steels find a wide application in food and pharmaceutical industry as pharmaceutical containers, tanks for cheese production, containers for milk and baskets for cutlery sterilisation [4]. AISI 304, 304L, 316 and 316L steels are the most commonly subjected to electrochemical processing. The chemical composition of these steels is presented in Table 1.

Table 1

The most often electropolished stainless steels (chemical composition according to PN-EN 10088 standard)

Classification		Chemical composition % wt.								
AISI	PN-EN 10088-1	Cr	Ni	C	Mn	Si	S	P	Mo	N
				max.						
304	1.4301	17-19	8-10.5	0.07	2	1	0.015	0.45	-	0.11
304L	1.4306	18-20	10-12	0.03	2	1	0.015	0.45	-	0.11
316	1.4401	16.5-18.5	10-13	0.07	2	1	0.015	0.45	2-2.5	0.11
316L	1.4404	16.5-18.5	10-13	0.03	2	1	0.015	0.45	2-2.5	0.11

Chemical pickling enables removal of surface layer of the material together with residues after previous processing, e.g. removing of abrasive material after mechanical processing, heat tint after welding or fatty dirt. The pickling process may be proceeded with degreasing, which decreases the degree of material dirt and influences limitation of pickling solutions contamination. However pickling process may be performed in a form of covering the surface with pickling paste with a brush or using low-pressure devices, the immersing pickling is the most effective and economic method. The most often used solutions for stainless steel pickling are those containing hydrofluoric(I) acid and nitric(V) acid.

The pickling may be the final process ensuring homogeneous, grey-matt colour of material surface or be a preliminary preparation of the surface for electropolishing process. The smoothing of the surface in the process of electrochemical polishing is connected to higher rate of dissolution of surface unevenness peaks in relation to valleys [5]. In an industry, the solutions for polishing of austenitic stainless steels containing phosphoric(V) acid and sulphuric(VI) acid are dominating ones. In a technological process, except proper realisation of pickling and electropolishing processes, the rinsing plays a significant role. It ensures complete cleaning of the surface from acidic solutions residues, limits solutions carrying out and in and in a consequence decreases rate of mixing of solutions for pickling and electropolishing.

The IPPC installations

The performance of chemical and electrochemical processing decreases corrosive damages, but the installations significantly influence the natural environment. The Decree of the Minister of Environment of 26 July 2006 determines the kinds of installations which may cause considerable contamination of particular natural elements or an environment as the whole [6]. The appendix to that decree, among numerous listed installations, includes also installations for surface treatment of metals or plastics with an application of electrolytic and chemical processes, which total volume of processing vats exceeds 30 m^3. In Poland, the legal requirement to obtain an integrated permit for such installations results from the Environment Protection Act of 27 April 2001 (as amended) [7]. The Act and Decree are a consequence of European Union Directive 96/61/EC, referred as IPPC directive (*Integrated Pollution and Control*), which started the process of new approach to the protection of an environment as the whole [8]. The main assumptions of that directive were: contaminations formation preventing, control and limitation of emission and minimisation of unprofitable influences on natural environment. It was commonly accepted, that the installations included in the requirements of mentioned directive are called IPPC installations.

Best Available Techniques - BAT

It was demonstrated in article 204 item 1 of the Environment Protection Act that installations requiring an integrated permit should

fulfil environment protection requirements resulting from the Best Available Techniques (BAT) and cannot cause an outpass of emission boundary values [7]. BAT resolutions are enumerated in BREFs reference documents. In case of installation for electrochemical stainless steels processing, the reference document is "Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics" [9]. The use of a handbook elaborated by the Institute of Precise Mechanics in Warsaw entitled "The Best Available Techniques (BAT) Guidelines for surface processing of metals and plastics" [10] based, and in numerous points being a translation of an English version, may be useful in an interpretation of demises contained in it.

The elaborated integrated permit application based on BAT includes numerous issues like: water consumption, sewage collection, emission to the air, noise, waste materials formation including hazardous ones, limitation of industrial failures effects [11]. In order to ensure safe installation working conditions, the pickling and electropolishing vats equipped with air extractors should be situated in leakproof bowls without drainage. If air emissions are concerned, it should be stated that chemical and electrochemical treatment of stainless steel can only have an impact on the local environment. Reducing consumption of nitric acid(V) and hydrofluoric(I) can be obtained by adding inhibitors to pickling baths. Pickling and electropolishing processes don't generate dust or noise, which is one of the advantages of these processes in comparison to the mechanical processing of metals. An important recommendation of BAT is to apply available methods to minimize the elevating and depressing baths related to the type and shape of the covered products. In this case, the crucial role plays the contact with the client at the products design stage and also appropriate localization of technological holes, so that during processes being realized the size of the elevations and depressions of solutions in dips and even in closed profiles is minimized. The collaboration with the client according to BAT should also include minimizing the use of grease, oil and lubricant in the production process and increasing their removal by physical methods. It is also pointed to replace degreasing with solvents by other techniques. BAT require deceasing electrical losses and reduction heat losses from heating processes. In case of cooling BAT means to minimize water consumption, which can be obtained, e.g. through the use of closed circuits. It is also required to minimize the water consumption in the processes of rinsing, e.g. by using multistage cascade rinsing or rinsing with counter-current flow, without indication the only one or the most effective economically reasonable technique. BAT recommends to minimize consumption of raw materials and to maintain optimal physical and chemical parameters, which can be obtained e.g. by regeneration of the bath (filtration, sedimentation, crystallization, and electrochemical cleaning of the bath) or by a recovery of the bath from scrubber. In the case of pickling and electropolishing processes of stainless steel, the most significant for the environment and at the same time the most difficult to fulfil requirement is the correct technological sewage neutralization. Table 2 presents the allowable emission levels of Fe, Cr, Ni and Cu introduced into the sewage system and water and lands . These metals are pollutants being the products of stainless steels dissolution and dissolution of copper tickets enabling the proper current flow and electropolished elements fastening.

Non exceeding of thresholds of the emission of mentioned metals is possible while maintaining the recommended method of sewage neutralisation [10]. That process with minimisation of water consumption, should be started from Cr(VI) reduction using $Na_2S_2O_5$. Next, the sewage is adjusted to pH = 10, i.e. optimum for precipitation of metals like: ferrum, chromium, copper and nickel. The neutralisation is conducted using $Ca(OH)_2$. In order to precipitate metal ions remaining in solution in a form of hardly soluble sulphides, Na_2S is added. Addition of flocculent based on polyacrylic acid causes quick agglutination of precipitate formed. The precipitated formed is highly hydrated, and additionally high amounts of hardly soluble calcium compounds are contained in the precipitate, therefore filtration press may be used for precipitate dehydration. It enables to reach dehydration level up to approx. 60% of water. The precipitates are handled over to specialised company dealing with hazardous wastes utilisation, and purified sewage of parameters accordant to mandatory regulations is introduced to sewage system appliances.

Table 2

Permissible levels of copper, nickel, chromium and ferrum emission to sewage system appliances and water and land for the industry of surface metal treatment

Index kind	Permissible values connected to sewage collection to sewage system		
	To sewage system according to the decree of the Minister of Construction in mg/l [12]	To water and land according to the decree of the Minister of Environment in mg/l [13]	To sewage system according to BAT rules for selected installations in mg/l [9]
Cu	1	0,5	0,2-2
Ni	1	0,5	0,2-2
Cr(VI)	0.2	0,1	0,1-0,2
total $_{Cr}$	1	0,5	0,1-2
total $_{Fe}$	-*)	10	0,1-5**)

*) Contamination reduces the value of the easily falling suspension index,
**) Indicator does not apply to wastewater discharge to sewage system appliances

Environmental protection challenges

Multistage process of neutralisation ensures processing sewage purification, since neutralised sewage is diluted. For that reason, the exchange of technological solutions requires pumping to retention tanks and their gradual neutralisation. The advantage of solutions for electrochemical stainless steels polishing is their long exploitation period. Moreover, unlike the pickling solutions, the regeneration of solutions for electropolishing is profitable economically. The intense contamination of solutions negatively influences the effectiveness of the process, thus intensification of electropolishing process is a next important challenge. It is recommended that utility effects concerning processed material, would be obtained with concurrent limitation of electric energy consumption and lower amounts of material dissolution which gradually contaminates processing solution. BAT requirements included in reference document BREF [9] are not currently a law, but are only a recommendation. However, the Directive of the European Parliament and Council 2010/75/EU of 24 November 2010 on industrial emissions (IED) [14] which replaces inter alia IPPC directive 2008/1/EC of 15 January 2008 [15] completely changes that approach. IED directive increases and specifies BAT significance. After review of current BREF documents, the BAT conclusions will be formulated, which after approval by the Commission become a legal requirement. Especially difficult to fulfil will be obtaining of emission levels compliant with BAT conclusions, which will be legal standards and except special cases, would not be exceeded. The period for preparation is not long, since notations of IED directive must be introduced to the Polish law up to 7 January 2013. The notations concerning most of existing installations (except energetic sector) are to be implemented to 7 January 2014. BAT conclusions will be obligatory after the period of 4 years since the date of their official publication. With respect to etching and electropolishing processes, if the requirements are made more stringent and lower limits of emission level for Cr, Ni, Cu are accepted, i.e. about 0,1 – 0,2 mg/l, then reaching of these indices

become simply inaccessible for numerous existing installations. The solution will be sale of sewages to specialised companies dealing with wastes utilisation, what is consistent with BAT, but causes increase in costs and decrease in competitiveness on the market. There is only a hope that this scenario will not happen. Regular review of BREF documents and contained in them BAT requirements may help in preparation of the industry for fulfilling requirements which result from IED directive notations.

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