Pitting corrosion of AISI 420 stainless steel in detergent–disinfectant solutions based on Catamine AB. Inhibiting effect of sulfate ions

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Abstract

The possibility of pitting corrosion of AISI 420 stainless steel in solutions based on Catamine AB is considered. It has been shown that at the concentrations of Catamine AB used in practice, there is a possibility of pitting corrosion. This probability increases with an increase in Catamine AB concentration. Catamine AB is a commercial product used for processing various materials, including steels, for the purpose of washing and disinfection. The product contains chlorides in the form of quaternary ammonium salts. Chlorides can be the cause of pitting corrosion. In this paper, the resistance to pitting of AISI 420 stainless steel used in medical devices has been investigated. The influence of Catamine AB concentration range recommended by the manufacturer has been studied. The studies were carried out with the polarization curves of the forward and reverse sweep. The dependence of the pitting formation potential on the concentration of Catamine AB, which is described by a straight line in logarithmic coordinates, has been obtained. Based on this dependence, three areas of Catamine AB concentrations can be distinguished for which it is possible to predict the different behavior of steel in relation to pitting. The first area of low concentrations of the product provides complete resistance to pitting formation. In the region of average concentrations of Catamine AB, pitting is possible when the potential is shifted to the anodic region due to a decrease in cathodic depolarization. And finally, in the third area of high product concentrations, steel is unstable to pitting. Thus, the concentration range recommended for use by the manufacturer includes the area of occurrence of pitting even on stainless steel. The possibility of increasing the threshold concentration of Catamine AB by adding sulfates to the solution has been studied. The results showed that although a certain positive effect can be achieved, it is not as great as we would like, since too much sulfate is required to suppress pitting corrosion. This is hardly acceptable due to the possible deterioration of the consumer properties of the product.

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Introduction

Catamine AB (hereinafter simply "Catamine") is a cationic surfactant: quaternary ammonium salt – a mixture of alkyldimethylbenzylammonium chlorides [1]. Alkyl(C_{10-18})-dimethylbenzylammonium chloride in the form of an aqueous solution (5–52%) is the main component of the commercial product. Catamine, having surface-active properties, is a highly effective antimicrobial disinfectant against *Escherichia coli*, *Staphylococci*, *Salmonella*, molds and yeasts. It is recommended both as an independent agent and as a basis for disinfectant detergents in food industry [2], for the disinfection of lumber [3], as an impregnation solution for imparting antimicrobial properties to tissues [4–7], disinfection of surfaces in rooms, dishes, linen, patient care items, sanitary equipment, cleaning equipment during current, final and preventive disinfection in foci and medical institutions for infections of bacterial and fungal etiology [8]. Recently, it has been actively studied with the aim of using it as an extractant in the liquid extraction of metals [9–11]. Since the product belongs to the class of compounds that are effective inhibitors of hydrogen sulfide corrosion and hydrogenation of steel, there are studies concerning the inhibitory properties of Catamine [12–16]. At the same time, in practice, an unpleasant feature of this product was discovered. When using Catamine to disinfect stainless steel products, pitting corrosion with the formation of through holes has been revealed. In this regard, it is necessary to investigate in more detail the effect of Catamine on the process of pitting formation on stainless steels, in particular, AISI 420 steel. The choice of this steel grade for research is determined by its wide use in various fields of industry, for example, in medicine and in the manufacture of surgical instruments. For a number of reasons, pitting corrosion of steel products, especially those used in medicine, is completely unacceptable. On the one hand, such lesions cause a decrease in the strength of the tool, and, with concomitant hydrogenation, lead to its fragility, which is dangerous for thin products with a small cross-sectional area. On the other hand, sometimes even pitting cavities that are invisible to the naked eye with a diameter of up to several microns can serve as a place for the various deposits accumulation, containing microbes and viruses that are difficult to remove by disinfection and subsequent washing.

Experimental

The solutions were prepared from *puriss.* grade reagents. Cylindrical steel samples (S = 2.5 cm^2) were mounted on a conductive holder isolated from the solution in a glass tube with Teflon gasket. Before the experiment, the samples were polished on sandpaper with a grain size of 5 μm, washed, degreased in a mixture of acetone and alcohol in an ultrasonic bath, and washed again with distilled water. The tendency to pitting susceptibility was determined by the potentiodynamic method based on the pitting potential (E_P) estimation [17]. Polarization was carried out using IPC-PRO potentiostat (Russia) at a room temperature. A saturated silver chloride electrode was used as a reference electrode, and platinum was used as a counter electrode. All potentials in tables and graphs are given relative to a standard hydrogen electrode. The anodic sweep of the potential (0.1 mV/s) was started with an OCP established after ten minutes of exposure in the solution until the potential range was reached, at which a sharp increase in current was observed, determined by a pitting breakdown. Then the sweep direction was reversed to determine the repass potential (E_R).

Results and Discussion

The effect of Catamine concentration on the type of polarization curves is shown in Figure 1. The content of Catamine varied from 0.1% to 5%, which corresponded to a change in the chloride ion concentration from 50 mg/L to 2500 mg/L. This concentration range is determined by recommendations for the use of the product [1]. It is obvious from the curves that AISI 420 stainless steel is passive in these environments in the region of low anodic potentials, which corresponds to extremely low corrosion rates.

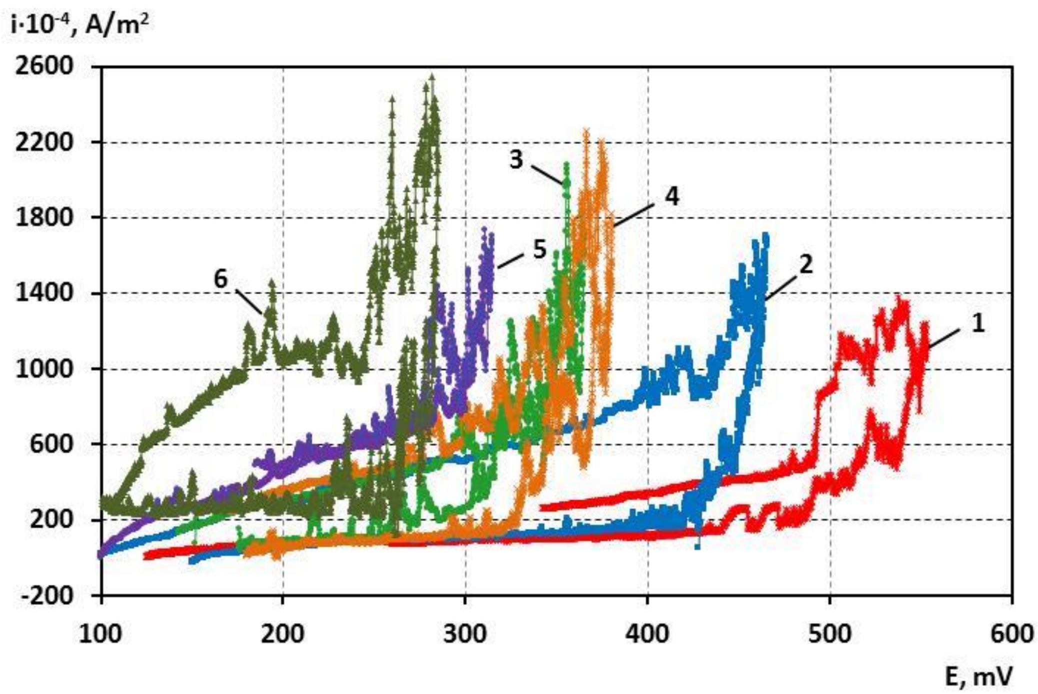

Figure 1. Polarization curves of AISI 420 stainless steel in the solutions with different Catamine concentrations: 1 – 0.1%; 2 – 0.2%; 3 – 0.5%; 4 – 1%; 5 – 2%; 6 – 5%.

With the anodic direction of the sweep, the polarization curves before the pitting breakdown have a relatively smooth character. When reverse sweeping, strong current oscillations and hysteresis are observed, the greater the higher the concentration of Catamine. The appearance of significant current oscillations during reverse sweep and hysteresis indicate that when the concentration of Catamine exceeds 0.2%, pitting corrosion, having arisen, does not stop until the corrosion potential.

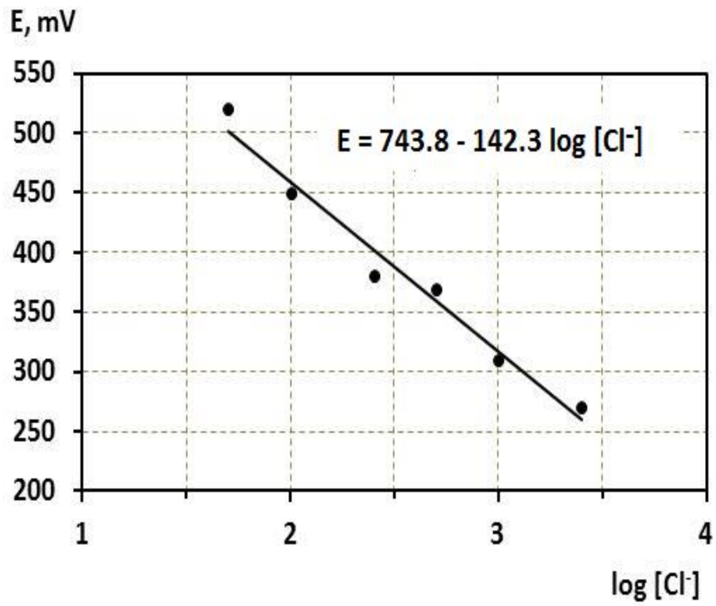

Figure 2. Influence of Cl^- ions concentration (mg/L) on pitting potential (mV).

The dependence of the pitting potential on the logarithm of the chloride ion concentration is linear (Figure 2) and described by the following Equation:

$$E = 744 - 142 \cdot \log C$$

where E is the potential (mV), C is the chloride ions concentration (mg/L).

Extrapolating this equation, we can distinguish three regions and find their boundary concentrations of chloride ions. The first region of complete "immunity" to pitting corrosion lies below a concentration of about 3 μg/L Cl^-. For this region, the potential for pitting exceeds the potential for anodic oxygen evolution and chromium repassivation (~1100 mV). The second region of "the absolute pitting" is below the concentration of about 33 g/L Cl^-, at which the pitting corrosion potential reaches the values of corrosion potential (~0.1 mV). And finally, the third region is located between these boundary concentrations. Here, pitting is possible when the potential is shifted to the anodic region due to a decrease in cathodic depolarization, an additional cathodic reaction in the presence of an oxidizing agent, or an increase in oxygen depolarization. Complete "immunity to pitting" is achieved by reducing the Catamine concentration below $6 \cdot 10^{-6}$% (which corresponds to 3 μg/L Cl^-). "The absolute pitting" is achieved at the concentration of Catamine above 63% (*i.e.*, 33 g/L Cl^-). Thus, almost any concentration of Catamine recommended by the manufacturer [1, 2] is dangerous and can cause pitting corrosion of stainless steel, while reducing the inhibition of the cathodic reaction, which often happens in practice. The main cathodic reaction under these conditions is the dissolved oxygen reduction. As a rule, this reaction is strictly limited by oxygen diffusion to the electrode surface. Therefore, any actions that contribute to an increase in the boundary concentration of O_2 will lead to an anodic shift in the corrosion potential and, as a result, increase the likelihood of pitting corrosion. Other stimulators of the cathodic reaction (and the occurrence of pitting) can be the presence of additional oxidants in the solution (dissolved chlorine, chlorates, permanganates, chromates and bichromates, hydrogen peroxide) and/or contact of the steel with other metals on which the cathodic reaction can be localized. In addition to the mentioned measures to decrease the cathodic depolarization to reduce the likelihood of pitting corrosion, it is possible to consider introducing anions into the solution that act as inhibitors of pitting corrosion proper due to competing adsorption with chloride anions. The simplest way is the addition of sulfate into the solution [18].

The effect of sulfate addition has been studied in solutions with two constant Catamine concentrations: 0.1% (this is equivalent to 50 mg/L Cl^-) and 1% of Catamine (*i.e.*, 500 mg/L Cl^-). Na_2SO_4 served as a source of sulfate ions. In solutions without sulfate at a content of 0.1% of Catamine (50 mg/L chloride ion), pitting begins at potentials above 500 mV. With the addition of 100 mg/L Na_2SO_4, pitting is not observed up to the potentials of oxygen release/repassivation by chromium. That is, under these conditions, a twofold excess of the sulfate concentration over chloride completely suppresses the pitting corrosion of the steel under study. The results of the study in a solution containing 1% of Catamine (500 mg/L chloride ions) are shown in Figure 3.

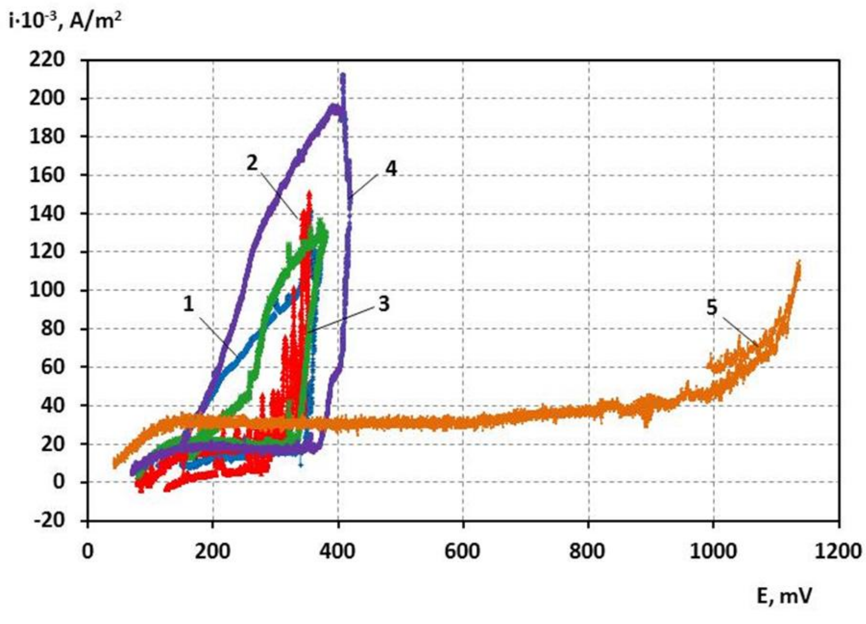

Figure 3. Potentiodynamic curves in a solution containing 1% of Catamine (500 mg/L Cl^-) with addition of sulfate anions: 1 without addition of SO_4^{2-}; 2 – 100 mg/L SO_4^{2-}; 3 – 500 mg/L SO_4^{2-}; 4 – 1500 mg/L SO_4^{2-}; 5 – 2500 mg/L SO_4^{2-}.

It follows from Figure 3 that at 1% of Catamine content (500 mg/L Cl^-), the addition of 100 mg/L and 500 mg/L of sulfate does not change the pitting potential level. A threefold excess of the concentration of sulfate compared to chloride (1500 mg/L SO_4^{2-} *versus* 500 mg/L Cl^-) increases the potential of pitting formation by only 50 mV. And only the introduction of 2500 mg/L SO_4^{2-} stops pitting completely. These results show that the addition of sulfate as an inhibitor of stainless steel pitting corrosion into solutions with Catamine is not as effective as we would like, since too much sulfate is required to suppress pitting corrosion. It is hardly acceptable due to the possible deterioration of consumer properties of the product.

Conclusion

Thus, a simple solution to prevent pitting corrosion using Catamine has not yet been found. There remains a high probability of pitting damage and failure of AISI 420 stainless steel metal products when they are treated with Catamine-based products.

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