Research and development of acid corrosion inhibitor for single stage process of isoprene synthesis

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Abstract. New acid corrosion inhibitor OPC-2000 has been developed for a single stage process of isoprene synthesis. Gravimetric method has found high effectiveness of the inhibitor in conditions of dilute ortho-phosphoric and sulfuric acids towards alloys Incoloy 825 and 12X18H10T being applied within the range of 10-16 g/dm³. According to electrochemical investigation, OPC-2000 is an anodic class inhibitor. It has high dispersing properties (no sediment formation in reactors), the fact being confirmed in the course of PJSC Nizhnekamskneftekhim's industrial trials while a single stage of isoprene synthesis.

Acid corrosion of chemical and petrochemical facilities is one of the major challenges of industries and one of the most important factors, determining the run life of process facility.

One of the most effective ways of protection from the acid corrosion is using inhibitors, generally improving mechanical properties of steels and alloys [1].

Ortho-phosphoric acid is used as a catalyst in the single stage process of isoprene synthesis which, due to entry of the process materials (i.e. hydrocarbons) becomes very corrosive, making the run life of Incoloy 825 reactors very short and raising the risk of emergency shut-down of production facilities. In spite of high corrosion resistance of this alloy, the run life of the reactors is not more than two years, as a result. Incoloy 825 is an alloy of nickel (38-46%), chromium (19-23%), iron (28-31%), and molybdenum, titanium and copper. Considering this fact, metal salts soluble in these conditions should be used as inhibitors of the acid corrosion due to employment of these salts (salts of chromium, copper, nickel, molybdenum) as alloying components for the major reactor materials [1-3].

A great number of gravimetric corrosion tests in different acid conditions were carried out to determine the optimal composition of inhibitor and its dosing. As a result of the research, the inhibiting composition of OPC-2000 grade [4] with the most effective and optimal composition and its formulation was developed at R&D of PJSC Nizhnekamskneftekhim.

The work depicts an influence of the new acid corrosion inhibitor of OPC-2000 grade in conditions of pure 6% sulfuric and 6% ortho-phosphoric acids containing added quantities of 2% TMC (trimethyl carbinol) and 0.2% formaldehyde. The research was carried out with specimens made of alloy Incoloy 825 and stainless steel 12X18H10T, as this steel is one of the most commonly used, strong and less expensive constructive materials.
Metal specimens of 20x10x3 mm size were kept in solutions of corrosion media containing the inhibitors under study as well as without using the latter. Protecting effectiveness of the inhibitor was determined as loss of mass of the metal specimen being kept in corrosion medium for 6 hours, at temperature 150°C. High temperature corrosion tests were carried out in a reaction vessel namely, in bomb calorimeter of a self-sealing type. Electrochemical studies were carried out using potentiostat PI-50-1.1 in the standard three-electrode electrochemical cell (V = 0.08 dm3) having cathode and anode compartments separated and naturally aerated at 50 °C [5-6]. The metal specimens were analyzed by scanning electron microscopy with the help of microscope (SEM, HITACHITM-3030) and accelerating electric potential 15 kW in the StandardMode, using special current-conducting adhesive tape as a support for the tested specimen (ConductingDouble-sidedTape). In parallel, we detected elements composing the surface of the specimens using the method of energy-dispersive microanalysis and spectrometer Quantax 70 (Bruker).

To evaluate the influence of admixtures on corrosive activity of phosphoric acid, some preliminary tests were performed employing pure ortho-phosphoric acid.

Table 1 – Inhibitor Effectiveness towards Stainless Steel 12X18H10T and Alloy Incoloy 825 @ 150°C. Exposure Period – 6 Hours.

| Tested Medium | Concentration of Inhibitor, g/dm³ | Corrosion Rate, mm/year | Inhibitor Effectiveness, Z, % |
|---------------|------------------------------------|-------------------------|-------------------------------|
| **12X18H10T** |                                    |                         |                               |
| 6% solution of H₃PO₄ (control) | -                                  | 0.0915                  | -                             |
| + OPC-2000    | 5                                  | 0.0365                  | 60                            |
|               | 10                                 | 0.0000                  | 100                           |
|               | 16                                 | 0.0000                  | 100                           |
| **Incoloy 825** |                                    |                         |                               |
| 6% solution of H₃PO₄ (control) | -                                  | 0.0398                  | -                             |
| + OPC-2000    | 5                                  | 0.0000                  | 100                           |
|               | 10                                 | 0.0000                  | 100                           |
|               | 16                                 | 0.0000                  | 100                           |

According to Table 1, OPC-2000 provides 100% protection both for stainless steel & for Incoloy 825 within the medium of diluted ortho-phosphoric acid.

As a result of the laboratory studies, OPC-2000 was found to have high dispersing properties, as no sediment formation was faced upon heating, all the solutions remaining clear (Figure 1).

Figure 1 – Appearance of Stainless Steel 12X18H10T and Incoloy 825 Specimens after 6-hours Test in 6% Ortho-Phosphoric Acid

Besides, the inhibitor was studied in more aggressive conditions of sulfuric acid to evaluate its protective properties. The results are summarized in Table 2 and in the Figure 2.
Table 2 – Inhibitor Effectiveness towards Stainless Steel 12X18H10T and Incoloy 825 @ 150°C. Exposure Period – 6 hours.

| Tested Medium | Concentration of Inhibitor, g/dm³ | Corrosion Rate, mm/year | Effectiveness of Inhibitor, Z, % | Inhibition Factor, γ |
|---------------|----------------------------------|-------------------------|---------------------------------|---------------------|
| 6% solution of H2SO4 (control) | - | 57.3289 | - | - |
| +OPC-2000 | 5 | 47.4247 | 17 | 1.2 |
| 10 | 27.0550 | 53 | 2.1 |
| 16 | 0.1727 | 99 | 332.0 |
| Incoloy 825 | 6% solution of H2SO4 (control) | - | 0.4252 | - | - |
| +OPC-2000 | 5 | 0.0000 | 100 | -* |
| 10 | 0.0000 | 100 | -* |
| 16 | 0.0000 | 100 | -* |

Note * - It is not possible to calculate γ (inhibition factor) at 100% protection (Formula 3).

The most effective dosage of OPC-2000 inhibitor for Incoloy 825 in 6 % sulfuric acid is 5-16 g/dm³ (Table 2). The optimal dosage of OPC-2000 for the stainless steel in 6% sulfuric acid is 16 g/dm³, and the rate of corrosion shows 332 time decrease.

High effectiveness of the studied inhibitor for the Incoloy 825 protection makes possible to mitigate negative environmental impact being used in smaller dosages (10 g/dm³).

Figure 2 - Stainless Steel 12X18H10T and Incoloy 825 Samples after 6-hours Test in 6% Sulfuric Acid

The gravimetrical and electrochemical polarization measurements of inhibitor OPC-2000 show good consistency, i.e. high effectiveness of inhibitor in acid conditions is confirmed by polarization curves. Anode polarization curve, plotted without inhibitor (control), has a classic appearance with all standard regions of this curve, namely: intensive anodic dissolution (I), active-passive state (II), passive region (III) and transpassive region (IV – the region where well-soluble metal complex with higher oxidation number is formed).

The anode polarization curve (Figure 3), plotted against the values for the stainless steel 12X18H10T in 6% solution of ortho-phosphoric acid without the inhibitor shows very low current density in potentials area from 650 to 750 mW, meaning passive state of the steel surface due to protective film formed to- gether with oxygen (i.e. oxide formation). The anodic passivation region of the stainless steel when the latter is in passive state is expanded from 250 to 620 mW at optimal dosage of inhibitor. Such expansion of the region in the presence of OPC-2000 is associated with protecting film formed against higher amount of the passivating substance on the surface and probably, improvement of protecting properties of the passivation layer formed by chemical
absorption of the salts of alloying metal components. Shifting of 2,2\textsuperscript{*} curves towards positive values witnesses the deceleration of anode metal dissolution, meaning that corrosion rate is slowdown by anode pattern.

As for the new inhibitor OPC-2000 for Incoloy 825 protection, it shows similar behavior. Most likely, that OPC-2000 inhibits hydrogen charging by several ways, namely: barrier film formation and changing in rate-controlling step of the hydrogen release or by film formation with simultaneous hydrogenation of some inhibitor’s molecule part.

![Cathode and Anode Curves of Stainless Steel 12X18H10T in 6% Ortho-Phosphoric Acid at 50 °C](image)

**Figure 3** – Cathode and Anode Curves of Stainless Steel 12X18H10T in 6% Ortho-Phosphoric Acid at 50 °C

Comparative examination of samples photomicrograph, received by the scan electron microscope (SEM, HITACHI TM-3030), shows the most vivid picture taken for alloy 12X18H10T in conditions of 6% sulfuric acid, as the latter promotes the most intensive corrosion processes. According to our observations, the surface of alloy 12X18H10T sample, tested in conditions without the inhibitor, was covered with crumbly crystal deposits, consisting of 70% iron oxide, with corrosion pits being detected underneath. The surface of the specimen, tested in the presence of inhibitor OPC-2000, had also spongy structure, but free from any visual signs of corrosion (Figure 4).

As for Incoloy 825 specimens, tested in 6% sulfuric acid with the inhibitor and without it, no deposits were found. The difference was in number of surface pittings formed with and without the inhibitor. Lines and grooves that can be observed on the surface are caused by abrasion treatment of metal specimens before the corrosion studies. Similar situation is observed for the investigations of Incoloy 825 and 12X18H10T in 6% ortho-phosphoric acid.

Thus, this recently developed corrosion inhibitor OPC-2000, representing a multicomponent mixture of inorganic salts (chromium, copper, nickel, molybdenum), showed high effectiveness in Incoloy 825 and 12X18H10T alloys protection tested in 6% ortho-phosphoric acid and in more corrosion active medium of 6% sulfuric acid. According to the results electrochemical studies, OPC-2000 inhibitor belongs to anodic type. Tests with added process materials (i.e. trimethyl carbinol and formaldehyde) have confirmed high effectiveness of inhibitor OPC-2000 being used at optimal levels of 10-16 g/dm\textsuperscript{3}. OPC-2000 possesses high dispersing properties, proved by the absence of the sediments formation upon heating as the solutions remained clear.

The industrial trials of a single stage isoprene synthesis at PJSC Nizhnekamsneftekhim have confirmed the inhibitor effectiveness.
Figure 4 – Specimens’ Picture after Testing (Scanning Microscopy)

Reference
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