EFFECT OF MIXTURES OF SULFUR-BEARING SUBSTANCES WITH TIN CHLORIDE ON HYDROGEN CHARGING OF IRON AND CARBON STEEL IN NITRIC ACID SOLUTIONS

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This article describes the results of experiments on the determination of the rate of diffusion of hydrogen through armco iron or steel St. 45 diaphragms in 1N and 2N HNO₃ solutions containing separate additions of thiourea or potassium rhodamine, or mixtures of thiourea with KSCN or SnCl₄. The effect of thiourea and thiourea–SnCl₄ mixtures on hydrogen embrittlement of steel was determined, and so was the magnitude of the inhibiting effects of the above additions to 1N HNO₃ solutions on the dissolution of armco iron and steel St. 45. A mechanism of the inhibiting action of the additives studied and of their influence on hydrogen charging of iron and steel was postulated.

Hydrogen charging of metals and alloys in various aggressive media has been the subject of several studies [1–7]. However, only a few investigations [6–7] were concerned with this phenomenon in nitric acid solutions although they are widely used in industry as pickling solutions.

Due to a fast dissolution rate, the pickling of iron and carbon steel parts in nitric acid is possible only in the presence of corrosion inhibiting additives. The aim of this investigation was therefore to study the effect of certain sulfur-bearing inhibitors and their mixtures with tin chloride (IV) on hydrogen charging in dilute nitric acid solutions.

The experiments were carried out on discs (1 mm thick, 40 mm diameter) made from a single batch of armco iron corresponding to UMTU–2900.

The hydrogen charging was done in a simple diffusion apparatus designed by Edwards [8]. A mercury-filled funnel with a capillary (Fig. 1) was covered with an iron disc on which a cylinder was placed. Washers coated with a vacuum grease were used to seal the joints, and the ground cylinder flange was secured with three screws.

The cylinder contained the corrosive medium (1N or 2N HNO₃ solutions containing additions of CS₂H₂NO₃, KSCN, their mixtures or thiourea–tin chloride mixtures). Hydrogen evolved during corrosion partially diffused through the iron diaphragm and displaced mercury. The quantity of mercury displaced from the capillary was measured every 30 minutes, the results being used (with appropriate corrections) to calculate the volume of hydrogen at the normal conditions.

The embrittling effect of hydrogen charging was studied on 10 mm long steel St. 70 wires. The specimens were pickled for 1 hr in a 1N HNO₃ solution containing the additive studied and stressed in tension under a specified load in a special machine, after which the number of bending reversals through 180° C to rupture was determined.

When iron is dissolved in HNO₃ (<20%), the reduction of nitric acid is accompanied by the discharge of ions H₂O⁺ these two processes competing with each other [9, 10]. The reduction of HNO₃ is promoted by the formation of nitrous acid which acts as a catalyst.

The reduction of HNO₃ on an inert electrode can take place only in the presence of nitrites. The process takes place in the following way [11]:

\[
2\text{NO}^+ + 2e^- \rightarrow 2\text{NO} \quad \text{(electrode reaction)}; \\
\text{HNO}_3 + 2\text{H}^+ \rightarrow 2\text{NO}^+ + \text{H}_2\text{O}; \\
\text{H}^+ + \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O} \rightarrow 3\text{HNO}_2.
\]

The reaction (3) proceeds at a slow rate which is practically independent of the concentration of nitrogen oxide formed in excess as a result of the relatively fast reaction (2). The formation of HNO₂ in accordance with the above scheme may take place when iron is dissolved in dilute HNO₃ due to the absence of HNO₂ in the starting solution, however, the role of the cathodic depolarizer in the initial stages will be played by ions H₂O⁺. Atomic hydrogen evolved under these conditions can reduce HNO₃ according to the following reaction:
Moreover, the formation of HNO₂ is possible also as a result of the oxidation of cation Fe^{2+} whose appearance marks the progress of the dissolution of iron. At the same time, cations Fe^{3+} may form complex ions as a result of the following reaction:

\[ 2\text{Fe}^{3+} + 3\text{HNO}_3 \rightarrow 2[\text{Fe(NO)}]^2^+ + \text{H}^+ + \text{NO}_2^- + \text{H}_2\text{O}. \]  
(5)

A rapid accumulation of cation [Fe(NO)]^{2+} in the layer adjacent to the electrode may inhibit further reduction of HNO₃, as a result of which oxygen depolarization is replaced by hydrogen depolarization. Later, as the destruction of the [Fe(NO)]^{2+} ions and formation of HNO₂ take place, the reduction of HNO₃ begins anew. The lower the acid concentration, the larger is the contribution of the hydrogen depolarization to the total balance of the cathodic process.

Data reproduced in Fig. 2 shows that the rate of diffusion of hydrogen through iron is fastest in a 1N HNO₃ solution containing thiourea (curve 1). The quantity of hydrogen permeating in the same time through iron in a 1N HNO₃ solution containing rhodanide ions (curve 2) is approximately three times less, the same applying to a solution containing a mixture of thiourea and rhodanide ions (curve 3). The rate of diffusion of hydrogen through iron in a 2N HNO₃ solution containing the same mixture of additives but with a higher content of rhodanide ions is faster than in a 1N solution (curve 5).

The diffusion of hydrogen through iron is almost completely inhibited in 1N and 2N HNO₃ solutions containing SnCl₄-thiourea mixtures (curve 4): the curve representing the diffusion of hydrogen through iron in a 2N HNO₃ solution containing \(10^{-2}\) mol/l SnCl₄ and \(5 \times 10^{-3}\) mol/l CS(NH₂)₂ is not shown in Fig. 2, since after 5 hr no evolution of hydrogen was observed.

The rate of diffusion of hydrogen through a steel St. 45 diaphragm (curve 3', 4') is faster than through iron diaphragms (curves 3, 4), and so, the quantity of hydrogen diffused in 4.5 hr through a steel diaphragm in a 1N HNO₃ solution containing a KSCN-thiourea mixture was almost twice that diffused through an iron diaphragm. The rate of diffusion of hydrogen through steel in a 1N HNO₃ solution containing an SnCl₄-thiourea mixture is also considerably faster.

The effect of cation Sn^{4+} on the hydrogen charging in a 1N HNO₃ solution containing thiourea is illustrated by the following data. The number of bending reversals to fracture recorded for a steel wire after pickling in a 1N HNO₃ solution containing \(10^{-2}\) M thiourea was reduced from 7 to 4.5. Pickling of steel in a 1N HNO₃ solution containing thiourea (\(5 \times 10^{-3}\) M) and cations Sn^{4+} (\(5 \times 10^{-5}\) M SnCl₄) had no effect on its strength (the number of bending reversals to fracture = 7), which is in agreement with data reproduced in Fig. 2 (curve 4).

The results of corrosion tests (see table) showed that the strongest inhibiting effect on the dissolution of both iron and steel is observed in HNO₃ solutions containing mixtures of thiourea and rhodanide ions and the weakest in a solution containing only rhodanide ions.

The chloride inhibits the hydrogen charging of iron and steel in HNO₃ solutions containing thiourea, but at the same time it reduces the stability of thiourea. And so, the protective action of a mixture of \(5 \times 10^{-3}\) M SnCl₄ with \(5 \times 10^{-3}\) M thiourea during the dissolution of iron in a 1N HNO₃ solution lasts only for 8 hr, while a mixture of the same quantity of thiourea and \(5 \times 10^{-3}\) M KSCN retains its protective properties for more than 20 hr.

It is known [6] that a relatively small quantity of hydrogen is absorbed by carbon steel during pickling in a 1N HNO₃ solution, since the predominant role in the cathodic process is played by the reduction of nitric acid (Eqs. 1–3). In the presence of sulfur-bearing substances (thiourea, rhodanide ions) the role of the cathodic depolarizer is played predominantly by ions H₂O⁺.

This view regarding the influence of thiourea has already been expounded [11] before. It should be added only that the protective action of thiourea during the dissolution of iron and steel in HNO₃ solutions is not due to the breakdown of nitric acid (this effect is produced by urea which, however, is not an inhibitor) but rather due to the chemisorption of ions HS⁻ formed as a result of its dissociation. Moreover, the undissociated thiourea molecules are also adsorbed on the metal surface, thereby intensifying the protective effect.