

## Inhibitor composition for corrosion protection of steels in water systems based on polymers and inorganic salts

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Received February 11, 2008, Revised March 19, 2008

The inhibiting properties of various compositions of polyethylene glycol and some inorganic salts ( $\text{Na}_2\text{MO}_4$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) in respect to the corrosion of carbon steel in water environment have been studied using electrochemical polarization techniques, gravimetric measurements, electron microscopy (SEM) and metallography observations. As a model medium of non-treated water 0.1 N  $\text{Na}_2\text{SO}_4$  solution (pH = 6.7) is used. It is established that the composition of polyethylene glycol (molecular mass 1000) and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  is the most efficient – the inhibition effect is up to 90%. It is shown that the inhibitor composition affects most significantly the anodic behaviour and susceptibility of the steel to passivation. The addition of the composition results in considerable decrease in the rate of anodic dissolution of the steel and increase of the width of the passive region as well as in lowering of the passivation current density. Formation of protective film of mixed oxide-adsorption nature on the steel surface in the presence of the inhibitor composition is suggested.

**Key words:** corrosion, carbon steel, inhibitors, water system, electrochemical measurements.

### INTRODUCTION

The water circulation systems, widely used in metallurgy, power and chemical plants, heat-supply installations, etc., are among the equipments most affected by corrosion. The corrosive agent in this case is the water, which contains mineral salts (most often chlorides and sulphates) as well as various microorganisms causing additional damages of installations because of the biocorrosion processes. The construction materials for water systems are usually ordinary carbon steels and cast iron.

The most effective and broadly applied method for corrosion protection of those systems is the addition of inhibitors in conjunction with biocides [1–3]. The literature survey shows that at first as inhibitors have been used various inorganic oxidizing salts. The increased environment restrictions, however, have limited the application of most of those inhibitors because of the toxicity of the heavy metals (e.g. chromium). The attempts for replacement with simple N-, S- or P-containing organic compounds have not been very successful. Thus, in recent years the interest in inhibitor compositions based on high-weight molecular compounds is increasing because of their non-toxicity and stability in water environment in a wide range of pH and temperature [4–7].

The aim of the present work is to study the

inhibiting action of composition of polymers (polyethylene glycol) and some inorganic salts ( $\text{Na}_2\text{MO}_4$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) in respect to corrosion of carbon steel in a model water medium.

### EXPERIMENTAL

The corrosion rate of low-carbon steel (0.10% C) and the effect of the inhibitor compositions on the corrosion behaviour of the steel have been studied using gravimetric and polarization resistance measurements and potentiodynamic polarization method. As a model medium of non-treated water 0.1 N  $\text{Na}_2\text{SO}_4$  solution (pH = 6.7) was used. The polarization resistance was measured after a contact of the steel sample with the medium for 1 and 24 h. An apparatus for direct resistance measurement with alternating polarization voltage of a rectangular pulse and amplitude of 10 mV in respect to the corrosion potential was used. The polarization curves of the steel were recorded using a potential sweep technique (PAR Corrosion measurement system with potentiostat 263A and Soft Corr III package) at a scanning rate of 1 mV/s. The electrode potentials were measured against saturated calomel electrode (SCE). All measurements were performed at room temperature.

The surface morphology of the samples after exposure in the corrosion medium was studied by scanning electron microscopy (SEM). The average thickness of the protective films formed on the steel surface after exposure in the solution with inhibitor

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composition was determined by metallographic observations of the sample cross-sections.

### RESULTS AND DISCUSSION

The gravimetric measurements of the corrosion rate of the steel in 0.1 N Na<sub>2</sub>SO<sub>4</sub> solution, without and in the presence of composition of polyethylene glycol (PEG) with various molecular mass (up to 100000) and the oxidizing salts Na<sub>2</sub>MO<sub>4</sub> or Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, showed that the most effective is polyethylene glycol with an average molecular mass 1000 (PEG-1000) at a concentration in the medium of about 1 g/l. The inhibition effect for such compositions reaches 85–90%.

The main results from polarization resistance measurements are illustrated in Table 1. It is seen that the composition of PEG-1000 and Na<sub>2</sub>WO<sub>4</sub> is more effective as inhibitor of the steel corrosion in comparison with this of PEG-1000 and Na<sub>2</sub>MO<sub>4</sub>. The increase of *R<sub>p</sub>* with time is obviously related with the formation of protective films. The film formed in the presence of the inhibitor composition is uniform, without any cracks and with an average thickness of about 5 μm (Fig. 1).

**Table 1.** Polarization resistance (*R<sub>p</sub>*) of steel in solution of 0.1 N Na<sub>2</sub>SO<sub>4</sub> without and with inhibitors.

Inhibitor addition	<i>R<sub>p</sub></i> , ohm·cm <sup>2</sup>	
	after 1 h	after 24 h
None	2140	2200
1 g/l PEG-1000 + 1 g/l Na <sub>2</sub> MO <sub>4</sub>	2360	3300
1 g/l PEG-1000 + 1 g/l Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	4750	6570

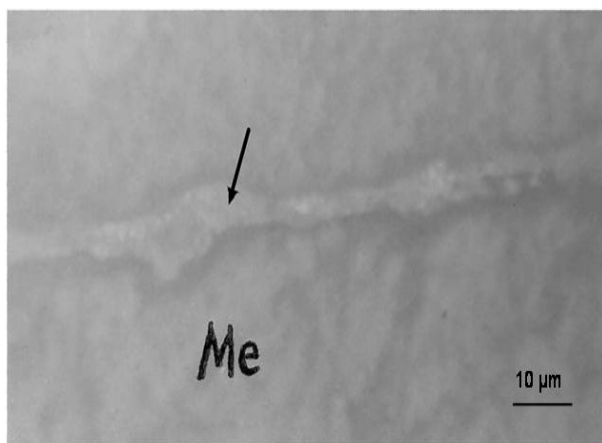


Fig. 1. Cross-section micrograph of a steel sample with protective film formed in 0.1 N Na<sub>2</sub>SO<sub>4</sub> in the presence of the inhibitor composition (1 g/l Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O + 1 g/l PEG-1000).

The potentiodynamic polarization curves of the steel in the model medium without and with addition of inhibitors are shown in Figs. 2 and 3.

In the presence of PEG-1000 and Na<sub>2</sub>MO<sub>4</sub>, and especially Na<sub>2</sub>WO<sub>4</sub>, the rate of anodic dissolution of

the metal decreases. The inhibitor compositions lead also to a considerable increase in the susceptibility of the steel to passivation in water solutions, the effect is more strongly expressed for the composition of PEG-1000 and Na<sub>2</sub>WO<sub>4</sub>.

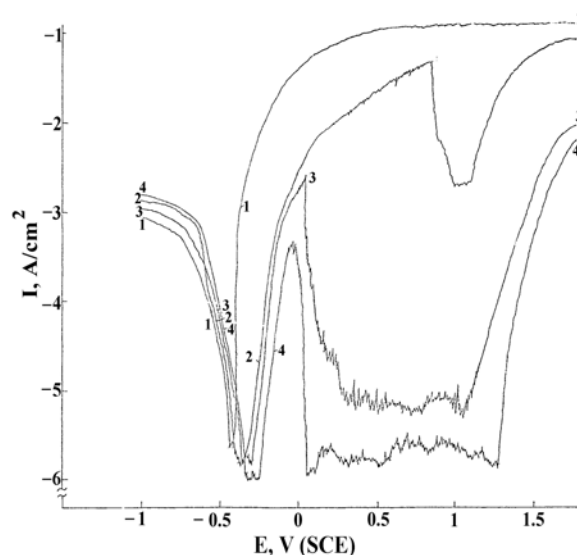


Fig. 2. Potentiodynamic polarization curves of steel in solutions: 1 - 0.1 N Na<sub>2</sub>SO<sub>4</sub>; 2 - 0.1 N Na<sub>2</sub>SO<sub>4</sub> + 1 g/l PEG - 1000; 3 - 0.1 N Na<sub>2</sub>SO<sub>4</sub> + 1 g/l Na<sub>2</sub>MO<sub>4</sub>; 4 - 0.1 N Na<sub>2</sub>SO<sub>4</sub> + 1 g/l PEG-1000 + 1 g/l Na<sub>2</sub>MO<sub>4</sub>.

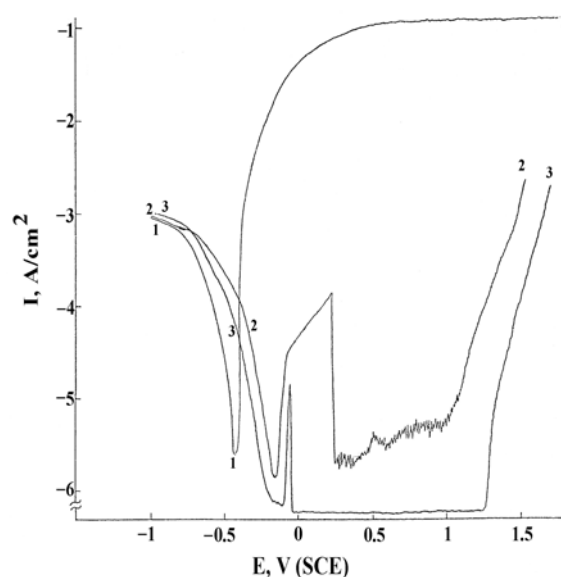


Fig. 3. Potentiodynamic polarization curves of steel in solutions: 1 - 0.1 N Na<sub>2</sub>SO<sub>4</sub>; 2 - 0.1 N Na<sub>2</sub>SO<sub>4</sub> + 1 g/l Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O; 3 - 0.1 N Na<sub>2</sub>SO<sub>4</sub> + 1 g/l PEG - 1000 + 1 g/l Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O.

In this case, the process of active anodic dissolution of the steel is almost completely suppressed while the passive region is very large (about 1.4 V) and the current density in this region is very small (less than 1 μA/cm<sup>2</sup>), which suggests a high stability of the passive state. The protective film is obviously of mixed oxide-adsorption nature – thin compact

oxide film on the metal surface and thick layer of adsorbed polymer molecules outside.

Figure 4 illustrates the surface morphology of the samples after exposure in the corrosive solution. It is seen that in the absence of inhibitor, the surface is heavily damaged and the corrosion attack is localized predominantly at the grain boundaries. In the presence of inhibitor composition, however, the corrosion damages are uniform and much less expressed.

The positive effect of the inhibitor composition is well expressed during anodic dissolution of the steel samples at a potential  $E_a = 0.5$  V (Fig. 5). In the solution without inhibitor, the steel at this

potential is an active state and dissolves with a very high rate ( $100 \text{ mA/cm}^2$ ). As a result, a large number of deep corrosion pits ( $1\text{--}3 \text{ }\mu\text{m}$ ) appears on the surface. The pits develop on the grain boundaries and other structural defects as non-metallic inclusions, etc. (Fig. 5A). In the presence of the inhibitor composition, however, the metal surface at this potential is in a stable passive state and localized corrosion damages cannot be detected even after 60 min anodic treatment of the sample (Fig. 5B). Thus, the inhibitor composition leads not only to decrease in the rate of general corrosion, but prevents also to a large extent the development of localized corrosion damages.

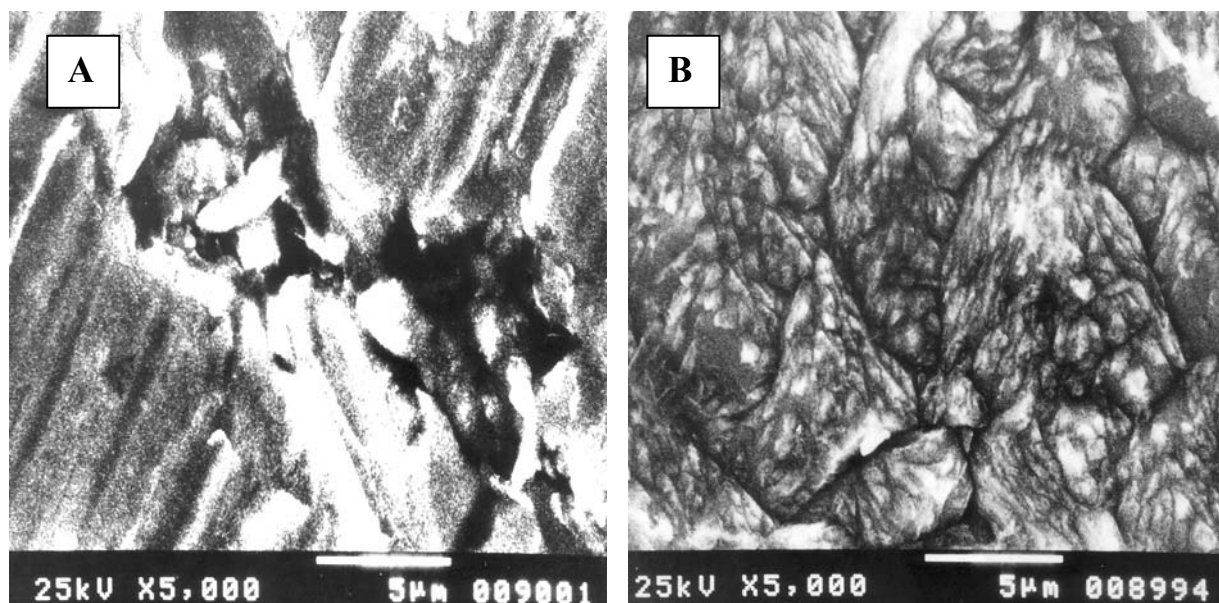


Fig. 4. SEM micrographs of steel samples after 24 h exposure in solutions:  
A -  $0.1 \text{ N Na}_2\text{SO}_4$ ; B -  $0.1 \text{ N Na}_2\text{SO}_4 + 1 \text{ g/l Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} + 1 \text{ g/l PEG-1000}$ .

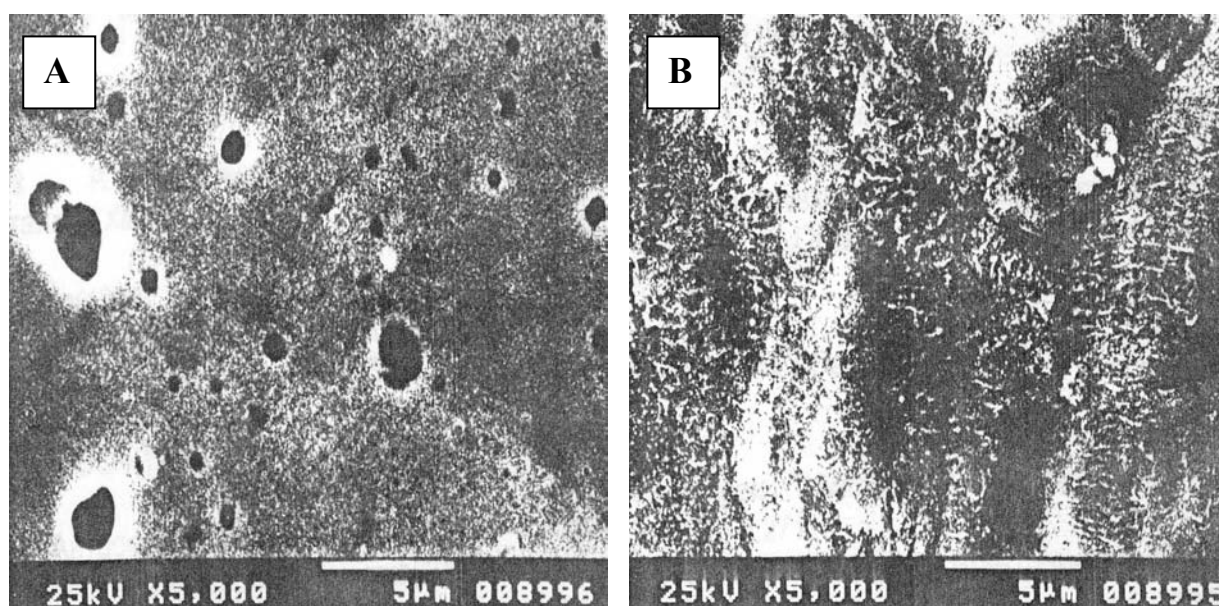


Fig. 5. SEM micrographs of steel samples after anodic dissolution at  $E_a = 0.5$  V in solutions:  
A -  $0.1 \text{ N Na}_2\text{SO}_4$  for 10 min; B -  $0.1 \text{ N Na}_2\text{SO}_4 + 1 \text{ g/l Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} + 1 \text{ g/l PEG-1000}$  for 60 min.

## CONCLUSION

On the basis of the results in the present study, the following conclusions could be made:

1. The composition of polyethylene glycol (PEG-1000) and  $\text{Na}_2\text{MO}_4$  and especially  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  is an effective inhibitor of corrosion of steel in neutral water environment.

2. The addition of the inhibitor composition results in a considerable decrease in the rate of anodic dissolution and increase in the susceptibility of steel to passivation and stability of the passivity.

3. The inhibitor composition leads to a decrease in the rate of general corrosion and may prevent the development of localized corrosion damages.

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## ИНХИБИТОРНА КОМПОЗИЦИЯ НА БАЗАТА НА ПОЛИМЕРИ И НЕОРГАНИЧНИ СОЛИ ЗА ЗАЩИТА НА СТОМАНА ОТ КОРОЗИЯ ВЪВ ВОДНИ СИСТЕМИ

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Постъпила на 11 февруари 2008 г., Преработена на 19 март 2008 г.

(Резюме)

Изследвани са инхибиторните свойства на различни композиции на базата на полиетиленгликол и неорганични соли ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{Na}_2\text{MO}_4$  и  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) по отношение на корозията на нисковъглеродна стомана (0.10% C) във водна среда, с помощта на електрохимична поляризационна техника, гравиметрични измервания, сканираща електронна микроскопия и металографски наблюдения. Като моделна среда на необработена вода е използван 0.1 M  $\text{Na}_2\text{SO}_4$  (pH = 6.7).

Установено е, че композицията от полиетиленгликол (молекулна маса 1000) и  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  е най-ефективна като инхибитор – защитният ефект е около 90%. Показано е тако също, че инхибиторната композиция оказва най-силно влияние върху анодните отнасяния и склонността на стоманата към пасивация. Добавката на инхибитор води до значително намаляване на скоростта на анодно разтваряне на метал и разширяване на пасивната зона на стоманата, както и до намаляване на анодния ток в тази зона. Инхибиторният ефект на изследваната композиция е обяснен с формиране на пасивен филм върху металната повърхност със смесена оксидно-адсорбционна природа.