

Synergistic inhibition of mild steel corrosion by sodium phosphate with sodium tungstate

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IT IS NOT feasible to use tungstate alone as a corrosion inhibitor in industrial cooling water systems due to its low oxidizing ability and high cost. The objective of this paper is to develop efficient synergistic inhibitor combinations that include very low concentrations of tungstate, keeping in a view their application in industrial cooling water system. The other inhibitor selected for this work is sodium phosphate, one of the cost-effective conventional inhibitors. Even though all the synergistic combinations studied in the present work showed high inhibition efficiency, a 4:1 ratio of sodium phosphate and sodium tungstate of total 1000ppm (800ppm SP + 200ppm ST) was found to be the optimum. The effect of temperature and depletion of the inhibitor solution were also studied. The metal oxide layer incorporated with tungstate and phosphate was found to cause effective passivation.

Introduction

The toxicity of chromate has restricted its use in recent years and directed the search towards new anodic inhibitors. Based on the similarity in chemical structure and periodicity between chromates and other Group 6 ions, attention has been focused on molybdate and tungstate. Among these two inhibitors, tungstate is more effective than molybdate in terms of its inhibition efficiency and applicability under a wider range of experimental conditions, such as broader pH. The first published information on corrosion inhibition by tungstate appeared as a patent describing its use in organic antifreeze solution [1], and in 1951, Robertson reported that tungstate lacks the oxidizing properties of chromate and nitrite [2]. Since then, it has been extensively studied for its use to protect iron, zinc, and aluminum substrates in neutral, acid, and alkaline solutions.

The presence of dissolved oxygen or an appropriate oxidizing agent in the solution is essential for Na_2WO_4 to act as an anodic

inhibitor [3, 4, 5]. Abd el Kadher *et al.* have shown that inhibition by tungstate requires its simultaneous presence with oxygen in solution, and the formation of an orderly arrangement of these two species on the metal surface [5]. It is not feasible to use tungstate alone as a corrosion inhibitor in industrial cooling-water system due to its low oxidizing ability and high cost. The successful formulations described in the literature combine tungstate with one or more coinhibitors [6, 7, 8].

In practice, many non-chromate treatment programmes have poly-, meta-, or ortho-phosphate as a corrosion inhibitor along with zinc and a dispersant. However, it is difficult to avoid reversion of meta-/poly-phosphates into orthophosphate in the case of physical mixtures, which necessitates close control of pH and other parameters. Now, direct orthophosphate along with zinc is also used as a corrosion inhibitor. Generally, organophosphonates are added to stabilize the solution containing orthophosphate-zinc. This combination requires good iron dispersant along with copolymers to avoid excess

Table 1. Test results of individual evaluation of sodium phosphate and sodium tungstate at 30°C, under stagnant conditions.

Inhibitor composition		OCP (V) vs SCE	E _{corr} (V)	I _{corr} (mA.cm ²)	Corrosion rate		
Sodium phosphate (ppm)	Sodium tungstate (ppm)				Weight loss (mpy)	Colorimetry (mpy)	Polarization (ipy)
10	0	-0.490	-0.430	0.1980	1.732	1.832	0.1829
100	0	-0.430	-0.415	0.0850	1.314	1.432	0.0785
1000	0	-0.360	-0.395	0.0305	-	0.0780	0.0282
10000	0	-0.200	-0.340	0.0082	-	0.0042	0.0075
0	10	-0.400	-0.320	0.1810	1.806	1.890	0.1672
0	100	-0.355	-0.305	0.0730	1.500	1.625	0.0674
0	1000	-0.265	-0.289	0.0264	-	0.1012	0.0244
0	10000	-0.195	-0.250	0.0150	-	0.0092	0.0046
Blank		-	-	-	2.7824	2.998	-

phosphate precipitation and sludge formation. Na₃PO₄ is eco-friendly in nature and is also very attractive in terms of cost and availability. It has also been reported to be a good synergistic coinhibitor with molybdate in cooling water [9, 10, 11].

Phosphates also require the presence of oxygen for their inhibitive action. The dissolved oxygen in the system oxidizes Fe to form γ-Fe₂O₃ and the discontinuities in the oxide film are filled with ferric phosphate [12].

The present paper aims to develop efficient synergistic inhibitor combinations including sodium phosphate and very-low concentration of tungstate, keeping in mind their application in industrial cooling-water systems.

Experimental

Commercial-grade mild steel coupons with composition Fe, C 0.189%, Mn 0.535%, Si 0.284%, P 0.043%, S 0.031%, Cr 2.75%, Ni 0.148%, Cu 0.043%, Al 0.358%, Ti 0.006%, and Sn 0.178%, and measuring 30 x 20 x 1 mm, were used for weight-loss and OCP measurements. The specimens were polished in standard sequence using different grades of emery paper down to

metallographic grade, degreased with trichloroethylene, and washed with distilled water before introduction into the test solution. All solutions were prepared with distilled water and analytical-grade reagents. Different batches of samples were immersed in 300-ml stagnant inhibitor solution contained in a 500-ml corrosion cell kept at room temperature (30°C). The containers were normally closed, although opened frequently for the OCP measurements. The thiocyanate method was used for determination of the ferric ion content of the test solution by colorimetry [13, 14], using a UV-visible spectrophotometer. Electrochemical polarization experiments were done with a potentiostat, while the corrosion rate was determined using the corrosion current value noted from the Tafel plot. A saturated calomel electrode was used as the reference electrode, and platinum was the counter electrode. Prior to commencement of each polarization experiment, the OCP of the working electrodes was allowed to reach a steady equilibrium value. High-temperature experiments were done with a thermostatic water bath with magnetic stirrers, and a spectrophotometer was used to record the FTIR spectra of the samples of the passive films scratched from the substrate.

Results and discussion

Comparison of individual inhibitor performance

In spite of extensive reports available on the evaluation of sodium phosphate and sodium tungstate, this study also proposed to evaluate these inhibitors individually under the present experimental conditions. The corrosion rates of sodium phosphate and sodium tungstate, determined from weight loss, colorimetry, and polarization experiments, are compared in Table 1. The weight-loss data correspond to a period of 1000hrs of immersion. Weight-loss tests could not be completed in a few cases, as no appreciable corrosion was noticed, and hence the iron present in the solution was estimated colorimetrically in such cases. The corrosion potential of sodium phosphate marginally decreased cathodically with increasing concentration. A similar trend was obtained for sodium tungstate, even though these values were little anodically higher than that of sodium phosphate at the respective concentrations. The corrosion rates, calculated by both colorimetric and polarization techniques were found to be significantly reduced when the individual inhibitor concentration was 1000ppm or above. However, severe localized attacks were visually observed on the specimens immersed in the individual inhibitor solution of 1000ppm. Still-higher concentration, of the order of 10,000ppm, might also yield high inhibition efficiency, but the cost factor should be considered. Since no appreciable inhibition efficiency was observed with still lower concentrations of sodium phosphate or sodium tungstate individually, the present study proposed to arrive at an optimum synergistic inhibitor combination. At this stage, both the inhibitors, at a combined total concentration of 1000ppm, were fixed to formulate different synergistic combinations and to evaluate their performance for longer periods.

The OCP values presented in the table were noted prior to commencement of each polarization experiment. The OCP decay of each specimen was also monitored continuously in a separate set of experiments, some of which are included in Fig.1; variation of the OCP as a function of duration of immersion corresponding to each 1000-ppm of sodium phosphate and sodium tungstate is also shown in the figure. A significant cathodic shift of the OCP of the specimen immersed in 1000ppm

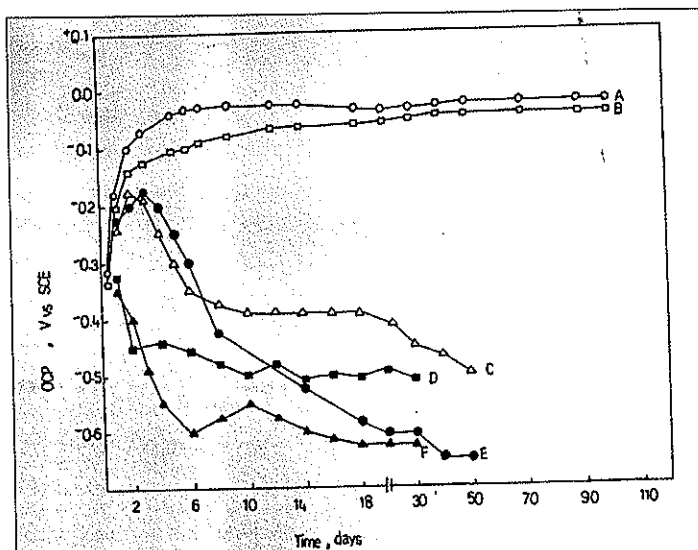


Fig.1. Variation of OCP as a function of duration of immersion, recorded for individual and synergistic combinations of sodium phosphate (SP) and sodium tungstate (ST):

- A. (800ppm SP + 200ppm ST)
- B. (200ppm SP + 800ppm ST)
- C. (1000ppm SP)
- D. (blank)
- E. (1000ppm ST)
- F. (400ppm SP + 100ppm ST)

sodium phosphate was observed after a period of five days, indicating corrosion attack, which was also supported by visual observation of localized attack. Similarly, the OCP corresponding to 1000ppm of sodium tungstate also shifted more cathodically within few days of immersion. These samples also indicated severe localized attacks on their surfaces. Such pits or localized attacks are normally observed on the metal surfaces when they were immersed in the inhibitor solutions at lesser concentrations than that of the threshold concentration that varies, depending on the system chosen [4, 5, 7]. Hence, still-higher concentrations of these individual inhibitors, or an optimum synergistic combination of these two inhibitors, was found required for effective protection of the steel surface.

Evaluation of synergistic combination

Based on the results of the preliminary experiments, different proportions of sodium phosphate and sodium tungstate at a total concentration of 1000ppm were chosen for detailed evaluations. Variations of the OCP decay recorded with such systems are compared in Fig.1. Curves A and B shows the variation of OCP values recorded with time for the two inhibitor

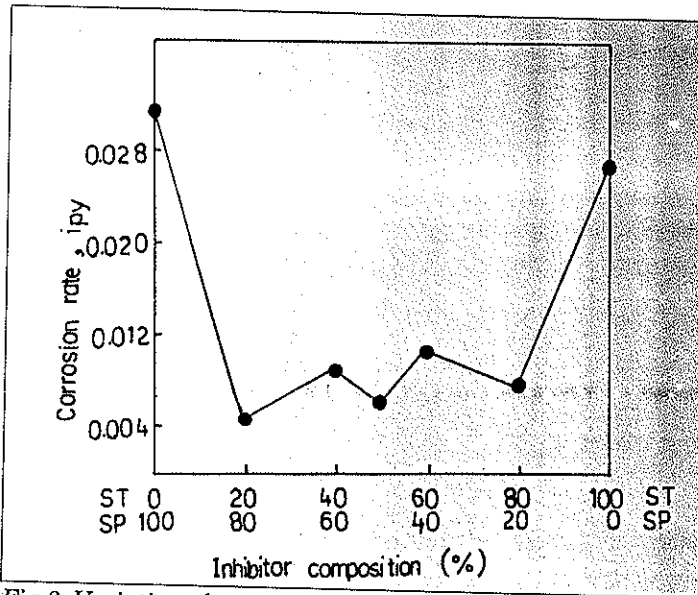
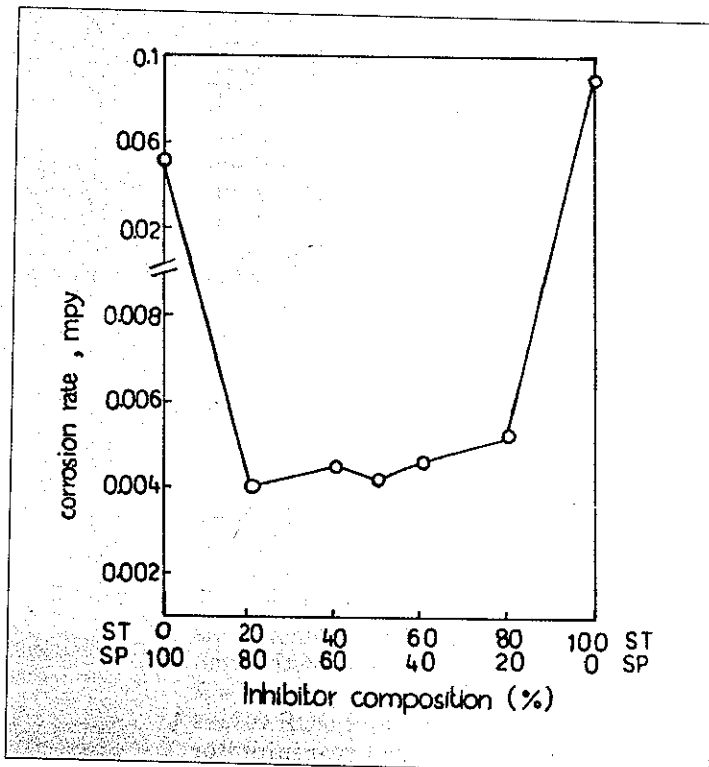


Fig.2. Variation of corrosion rate determined based on polarization experiments with different ratios of sodium phosphate and sodium tungstate (total concentration: 1000ppm).

combinations, having 4:1 and 1:4 ratio of sodium phosphate and sodium tungstate respectively (800ppm sodium phosphate + 200ppm sodium tungstate and 200ppm sodium phosphate + 800ppm sodium tungstate). A uniform trend of variation of

Fig.3. Variation of corrosion rate based on colorimetric estimation with different ratios of sodium phosphate and sodium tungstate (total concentration: 1000ppm).



OCP is observed for the two systems throughout the entire period of immersion. The OCP reached a steady value after five days of immersion, indicating effective passivation, which is maintained throughout the period beyond 100 days. But a combination of 400ppm sodium phosphate with 100ppm sodium tungstate (totalling 500ppm) was not able to maintain its OCP even for one day (curve F). The corrosion rates determined from the polarization experiments for individual and synergistic combinations of sodium phosphate and sodium tungstate (totalling 1000ppm) are shown in Fig.2. The corrosion rates corresponding to all the inhibitor combinations are found lower than that of the individual inhibitors, proving the synergistic inhibition effect.

Since the weight-loss experiments could not be completed for all the synergistic combinations even after a period of six months, the corresponding corrosion rates were determined by colorimetric estimation of the iron present in the solution (Fig.3). These colorimetric estimations were carried out intermittently after different periods of immersion of the specimens, and only the rates determined after 20 days of immersion are compared in the figure. Though the performance of all the inhibitor combinations was found far better than the individual inhibitors based on the OCP decay, polarization, and colorimetric experiments, a combination of 4:1 ratio of sodium phosphate and sodium tungstate (800ppm sodium phosphate + 200ppm sodium tungstate) was found to be the optimum and most efficient. The combination is highly impressive in terms of its cost factor, as well.

Several other experiments also indicated the significant performance of this ratio by actual weight-loss data, when the total concentration of the inhibitor mixtures was kept at 100ppm. However, localized attacks were visibly observed in such cases.

Effect of depletion of inhibitor solution

OCP of different batches of specimens were continuously monitored to evaluate the effect of depletion of the inhibitor solution. Two cases of such OCP shifts when the inhibitor solutions were depleted to 50% of its original concentration are represented in Fig.4. Since a minimum period of five days was found required for effective passivation to occur, depletion of the inhibitor solution was also done after five days of immersion of the specimen in

the original inhibitor solution. The OCP was retained for about three days after depletion of the optimum inhibitor combination viz. 800ppm sodium phosphate + 200ppm sodium tungstate (curve A). However, the OCP was retained even after 40 days, when the concentration of the original inhibitor solution was higher (1600ppm sodium phosphate + 400ppm sodium tungstate). These experiments were carried out in order to evaluate the probability of accidental corrosion of metals, if the inhibitor solution was unintentionally depleted in an industrial site. Hence, it should be inferred that even though the optimum inhibitor combination perform extremely well, still higher concentration is required for the passive layer to persist on the metal surface wherever depletion is predicted.

Evaluation at high temperatures

Figure 5 shows the variation of OCP of the specimens with time at two different temperatures. Curves A and D show the OCP variations for the specimens immersed in the solution of optimum inhibitor combination subjected to continuous heating to keep the temperature at 60°C and 75°C respectively. The specimen remained free from any corrosion even after an immersion period of one month in the first case, whereas the OCP shifted to a more negative value after six days when the temperature was 75°C. Experiments were also conducted with intermittent heating, with and without agitation of the inhibitor solution (curves B and C). In both the cases, the specimens remained free from any localized attack throughout the experiment, even after one month of immersion. Intermittent heating was carried out by keeping the solution at 75°C and 30°C alternatively, each for 12 hours. Magnetic stirrers having shafts that rotate at 720rpm were used for agitating the solution; these aggressive experimental conditions were selected to simulate industrial cooling-water systems. The lower performance of the inhibitors when subjected to continuous heating to a higher temperature (75°C) may be attributed to the lesser solubility of oxygen in water at high temperatures, as passivation at higher temperatures is generally poor. Thus, the optimum combination was found quite effective even at moderately high temperatures and under intermittent heating conditions, with and without agitation.

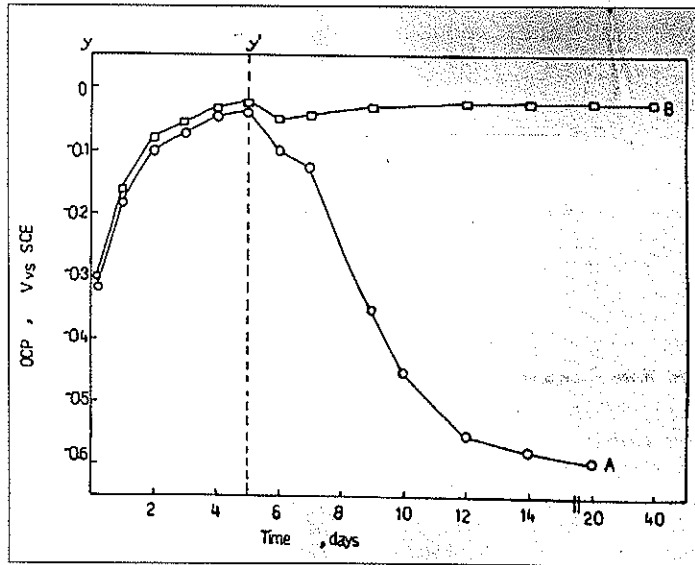


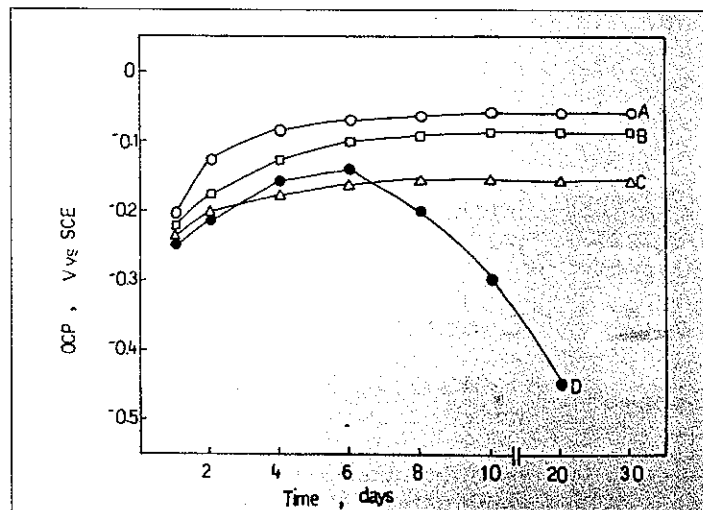
Fig.4. Variation of OCP due to the influence of depletion of the inhibitor solution (50% depletion):

Y = time of immersion
 $Y1$ = time of depletion
 A = 800ppm SP + 200ppm ST
 B = 1600ppm SP + 400ppm ST

Spectral analysis

The samples of the passive layer formed by different individual and synergistic inhibitor combinations were analyzed by FTIR spectroscopy to correlate the composition of the passive layer with the role of the inhibitors. The samples were collected after scraping the passive layer from the substrate. The spectrum obtained for 1000-ppm individual sodium phosphate predominantly showed four peaks at 3401,

Fig.5: Variation of OCP of the mild steel specimen in the solution of optimum inhibitor combination (800ppm SP + 200ppm ST) at different temperatures.



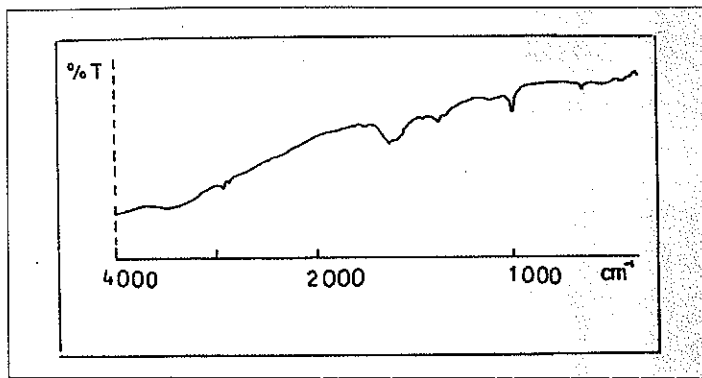


Fig.6. FTIR spectrum of the sample of the passive layer formed in the solution of optimum inhibitor combination.

1618, 1384, and 1018cm^{-1} (not shown here). The peak at 3401cm^{-1} revealed the strong broad absorption due to -OH stretching of water, while the peak at 1618cm^{-1} revealed the -OH bending. The peak at 1384cm^{-1} revealed the metal oxide of the passive layer, while the peak at 1018cm^{-1} confirmed incorporation of orthophosphate in the passive layer. The spectrum recorded for the passive layer corresponding to 1000ppm of individual sodium tungstate showed two significant peaks, one at 1383cm^{-1} and the other at 1018cm^{-1} . While the peak at 1383cm^{-1} revealed the metal oxide of the passive layer, the peak at 1018cm^{-1} confirmed incorporation of the metal tungstate in the passive layer. The spectrum (not shown here) also showed two other peaks corresponding to -OH stretching and -OH bending of water at 3402cm^{-1} and 1636cm^{-1} , respectively [15]. The spectrum of the passive layer corresponding to the optimized inhibitor combination did not reveal any significant peak other than those obtained with individual sodium phosphate and sodium tungstate (Fig.6). Hence it was inferred that the metal oxide layer incorporated with tungstate and phosphate causes effective passivation. Incorporation of tungstate and phosphate in the metal oxide passive layer was seemed to be the significant role of the synergistic inhibitor mixture, causing very effective passivation on the metal surface. The process never allows any pit formation, as the sites susceptible to pit formation immediately became adsorbed with the inhibitor and passivated.

Conclusions

The inhibition efficiencies of sodium phosphate, sodium tungstate, and their synergistic combinations, were evaluated by different techniques. All the synergistic combinations studied in the present work

showed higher inhibition efficiencies than that of the individual inhibitors. An inhibitor combination with a 4:1 ratio of sodium phosphate to sodium tungstate at a total concentration of 1000ppm was found to be the optimum synergistic combination. This optimum combination was found effective at high temperatures under agitated conditions. Depletion of the test solution caused breaking of the passive layer after a tolerance period that depended on the initial concentration of the original inhibitor solution. The FTIR spectra revealed that incorporation of tungstate and phosphate in the metal oxide passive layer was the significant role of the synergistic inhibitor mixture, causing very-effective passivation on the metal surface.

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