

Synergistic effect of some antiscalants as corrosion inhibitor for industrial cooling water system

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Abstract In order to study synergistic effect, various combinations of antiscalants 1-hydroxyethane-1,1-diphosphonic acid (HEDP), sodium hexametaphosphate (SHMP), sodium tripolyphosphate (STPP), and trisodium phosphate (TSP), were investigated as corrosion inhibitors for carbon steel. Corrosion rate and percentage inhibition efficiency of various combinations of antiscalants as corrosion inhibitors (20/80, 40/60, 60/40, 50/50, 80/20, and 100 ppm of different combinations of HEDP, SHMP, STPP, and TSP) in synthetic cooling water VI (692 ppm of Cl^- ions) was determined by weight loss, electrochemical polarization technique, and metallurgical microscopy technique. It was observed that a 50/50 ppm combination of HEDP and SHMP gave 98% corrosion inhibition efficiency and maximum synergistic effect. The percentage inhibition efficiency of HEDP when mixed with other antiscalants as corrosion inhibitors at 50/50 ppm concentration was found in the following order $\text{HEDP/SHMP} > \text{HEDP/STPP} > \text{HEDP/TSP}$. The synergistic effect of HEDP/SHMP combination is due to intermolecular hydrogen bonding between the molecules of HEDP and SHMP, which results in the adsorption of uniform multilayered two-dimensional film of –HEDP–SHMP– molecules on carbon steel surface.

Keywords Corrosion inhibitors · Antiscalant · Cooling water system · Carbon steel · HEDP · SHMP · STPP · TSP

1 Introduction

There has been a substantial change in cooling water chemistry over the past decade. Use of high-performance antiscalants, corrosion inhibitors, polymers for better dispersion, total prevention of microbial deposits by using powerful biocides and biodispersants, pH boosters, and advanced hardness stabilizers is current practice for the treatment of cooling water. However, addition of so many different chemicals to the cooling water system (CWS) makes the cooling water chemistry very complex. Many problems such as high cost of operation, compatibility with other chemicals, difficulty in understanding the cooling water chemistry, mechanism of inhibition, dosage of inhibitor required, etc. arise in CWS. We have earlier reported that antiscalant can also work as a corrosion inhibitor in cooling water systems. Now we try to achieve complete protection from corrosion using a combination of antiscalants.

In the present work, several combinations of antiscalants have been investigated which may control scaling as well as corrosion problem in CWS. Weight loss, electrochemical polarization technique, and metallurgical research microscopy technique have been carried out using various concentrations and combinations of the inhibitor. If it is possible to find an antiscalant combination which can also provide protection from corrosion in cooling water systems, it will not only make cooling water chemistry simple but also reduce operational cost.

It has been reported [1] that a synergistic effect is observed when two or more corrosion inhibitors are mixed

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in a definite proportion. The corrosion inhibition efficiency of the mixed inhibitors is significantly increased compared with that of individual inhibitors in a corroding system. In order to study synergistic effect, various combinations of antiscalants [2] were investigated as corrosion inhibitors, and their percentage inhibition efficiency was determined by weight loss and electrochemical polarization techniques.

Influence of combinations of sodium dodecyl sulfate– Zn^{2+} –HEDP system [3] towards corrosion inhibition of carbon steel was studied by Rajendran et al., who found that this combination gave synergistic effect and provided complete protection in low chloride ion water. Venugopalan et al. [4] studied effects of HEDP, gluconate, and zinc on corrosion inhibition of carbon steel. They developed this ternary inhibitor formulation for carbon steel, which acts synergistically and gives maximum protection towards corrosion for carbon steel. Similar synergistic effects of HEDP with other combinations have also been reported [5–7].

All the antiscalants investigated as corrosion inhibitors were tried at different concentrations in order to find synergistic effect, if any, present in various possible combinations of the inhibitors. The combinations were studied at 20/80, 40/60, 50/50, 60/80, and 80/20 ppm concentrations along with pure inhibitor at 100 ppm concentration. All the experiments were carried out using a synthetic cooling water having 692 ppm Cl^- . Temperature of 40 °C was chosen for experiments as the temperature of cooling waters is usually in the 30–50 °C range.

2 Experimental procedure

All the chemicals used were of analytical reagent (AR) grade and solutions were prepared using doubly distilled water. pH of all the cooling waters was maintained at 6.5 by adding sodium hydroxide or glacial acetic acid solution as per requirement. Duplicate or in some cases triplicate experiments were performed to verify the reproducibility and consistency of the experimental data.

The compositions of synthetic cooling water VI are shown in Table 1.

Table 1 Composition of synthetic cooling water VI (CW VI)

Composition conc. (ppm)	CW VI
Ca^{2+}	300
Mg^{2+}	24
HCO_3^-	305
CO_3^{2-}	30
Cl^-	692
SO_4^{2-}	120
Na^+	253

For weight loss measurements, carbon steel specimens of $3 \times 1.5 \text{ cm}^2$ size were cut from carbon steel sheet whereas for electrochemical polarization investigations specimens of size $5 \times 1.5 \text{ cm}^2$ were used. All the specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400, and 600 micron, and then thoroughly cleaned with doubly distilled water and then with acetone. The specimens were dried and stored in a desiccator over silica gel.

After recording the initial weight of carbon steel specimens, they were immersed in tilted position in 250 mL beakers each having 200 mL of synthetic cooling waters as corroding medium with or without the inhibitor. Experiments were carried out in an electronically controlled air thermostat at 40 °C with an accuracy of ± 1 °C. After exposing the specimens for 30 days, the specimens were taken out from the beaker and washed initially under running tap water. Loosely adhering corrosion products were removed with the help of rubber cork and the specimen was again washed thoroughly with distilled water and dried and then weighed again. Corrosion rate in mils per year (mpy) and percentage inhibition efficiency were calculated.

Electrochemical polarization studies were carried out in 500 mL glass cell with three-electrode system assembly. Potentiostatic polarization of the working electrode was carried out by using a potentiostat/galvanostat PGS 201 T (Tacussel, France).

The working electrode was carbon steel under study; platinum electrode was used as counterelectrode or an auxiliary electrode. All potentials were measured against a pencil-type saturated calomel electrode as reference electrode. A Luggin capillary filled with test solution was used to connect the reference electrode with the cell. The tip of the Luggin capillary was kept very close to the working area of the electrode but without touching in order to minimize the IR drop and this distance was kept constant during the whole study. Only 1 cm^2 area of specimen was used as working area and the rest of the area of the specimen was covered with a lacquer except the other tip of specimen which was used for making electrical connection. The specimen was left in the test solution until a constant open-circuit potential (OCP) was attained.

Linear polarization resistance (LPR) measurements were carried out potentiostatically by scanning through a potential range of 14 mV above and below the OCP value in steps of 2 mV. Experiments were carried out in absence and presence of inhibitors at their 20/80, 40/60, 60/40, 50/50, 80/20, and 100 ppm concentrations at 40 °C. The resulting current was plotted against the potential and slope of the line was measured.

The corrosion current, I_{corr} , is related to the slope of the line by Stern-Geary equation [8–10]. The corrosion current density, I_{corr} , is related to the corrosion rate by the equation,

$$\text{Corrosion rate (CR)}(\text{mpy}) = 0.1288 \times I_{\text{corr}} \times \text{Eq.Wt.}/D$$

where Eq. Wt. is the gram equivalent weight of metal/ alloy, D is the density of the metal (g/cm^3), and I_{corr} is the corrosion current density ($\mu\text{A}/\text{cm}^2$).

The anodic and cathodic Tafel slopes were measured after recording anodic and cathodic polarization curves of the specimen up to a maximum shift of ± 240 mV from OCP value in steps of 10 mV. Experiments were carried out in absence and presence of the inhibitor at their 20/80, 40/60, 60/40, 50/50, 80/20, and 100 ppm concentrations at 40 °C.

To study the morphology of corroded sample of carbon steel in CW VI, 200 ml synthetic cooling water VI with constant pH of 6.5 (maintained by dipping a pH electrode into the synthetic cooling water and adding dilute glacial acetic acid or NaOH solution), at 40 °C temperature was taken in 250 mL glass beaker placed in an electronically controlled air thermostat with ± 0.1 °C accuracy. Six samples of carbon steels having dimension 1.5 cm \times 3 cm were cut from carbon steel sheet and then specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400, and 600 and then thoroughly cleaned with doubly distilled water and finally with acetone. The specimens were dried and stored in a desiccator over silica gel until they were exposed to synthetic cooling water VI with and without various combinations of inhibitor. The samples were removed after 30 days of exposure to cooling water VI and morphology of corroded specimens was studied under a metallurgical microscope (Lobamed Make, New Delhi) attached to a computer, and the micrographs were recorded.

This technique was used to study the morphology of the corroded specimens of the carbon steel exposed to the synthetic cooling water maintained at pH 6.5 (by adding acetic acid solution) for 30 days at 40 °C with and without corrosion inhibitors. These experiments were carried out in synthetic cooling water VI only. The comparison of micrographs of the corroded specimens with and without corrosion inhibitors clearly gave an idea about the effectiveness of the various combinations of corrosion inhibitors.

Table 2 Various parameters of six different synthetic cooling waters

Parameters	CW VI
pH	8.08
Conductance	2.70
TDS	1,800
P alkalinity	0
M alkalinity	320
Ca hardness	480
Total hardness	750
LSI from activity coefficient	1.47
ΔG	1.63
SI	0.98

3 Results

pH, conductance, total dissolved solids (TDS), P and M alkalinity, total hardness, calcium hardness, Langelier saturation index (LSI) [11] ΔG [11], and saturation index (SI) [12] were measured for each synthetic cooling water and are shown in Table 2.

Weight loss experiments were carried out for different combination of inhibitors in CW VI at pH 6.5 and temperature of 40 °C for 30 days, in electronically controlled air thermostat; results are presented in Table 3. Percentage inhibition efficiency of various combinations of HEDP, SHMP, STPP, and TSP antiscalants as corrosion inhibitors against 20/80, 40/60, 60/40, 50/50, 80/20, and 100 ppm of different combinations of HEDP, SHMP, STPP, and TSP at 40 °C in synthetic cooling water VI are plotted in Figs. 1, 2, and 3 respectively.

Various corrosion parameters such as open-circuit potential (OCP), I_{corr} , β_a , β_c , R_p , corrosion rate, etc. were recorded from electrochemical experiments for carbon steel in CW VI in presence of different combinations of HEDP with SHMP, STPP, and TSP at 40 °C (Table 4).

Figure 4 shows anodic and cathodic polarization curve with and without HEDP/SHMP combination at different concentrations in synthetic cooling water VI at 40 °C and pH 6.5.

Table 3 Percentage inhibition efficiency of various combinations of antiscalants in cooling water VI by weight loss method at pH 6.5 and temperature 40 °C

Composition (mg/L)	Conc. I/II (ppm)	HEDP/SHMP	HEDP/STPP	HEDP/TSP	
Ca ²⁺	300	20/80	47.9	47.9	45.6
Mg ²⁺	24	40/60	39.2	43.5	51.9
CO ₃ ²⁻	30	60/40	30.5	69.7	32.7
HCO ₃ ⁻	305	80/20	43.5	74.0	36.9
Na ⁺	253	50/50	97.6	91.4	59.8
Cl ⁻	692	100 I	49.5	49.5	49.5
SO ₄ ²⁻	120	100 II	86.7	65.6	48.7

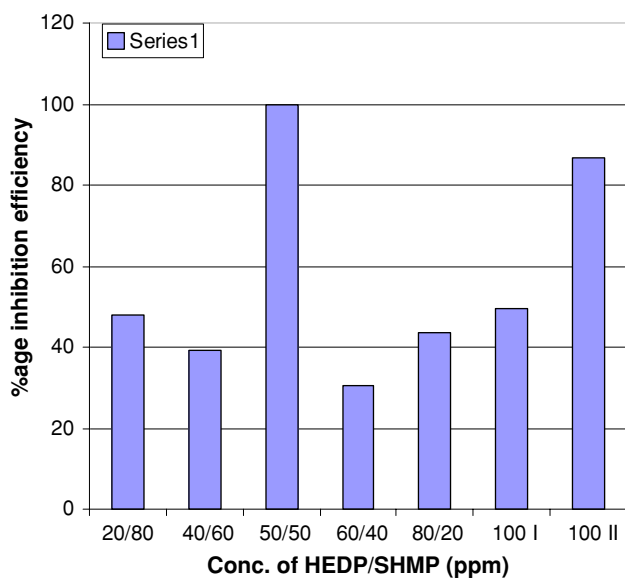


Fig. 1 Percentage inhibition efficiency of HEDP/SHMP at different combinations at 40 °C in synthetic cooling water VI

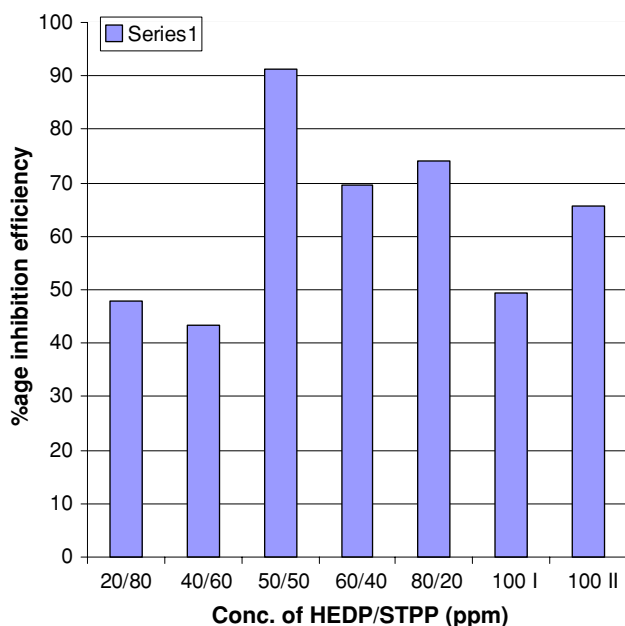


Fig. 2 Percentage inhibition efficiency of HEDP/STPP at different combinations at 40 °C in synthetic cooling water VI

Figure 5 shows micrographs of carbon steel samples when exposed to cooling water VI for 30 days at pH 6.5 and temperature of 40 °C with and without various combination of inhibitors.

Percentage antiscaling efficiency of all the investigated antiscalants [2] is shown in Table 5, only to show that these antiscalants show good antiscaling efficiency even in hard water such as synthetic cooling water VI.

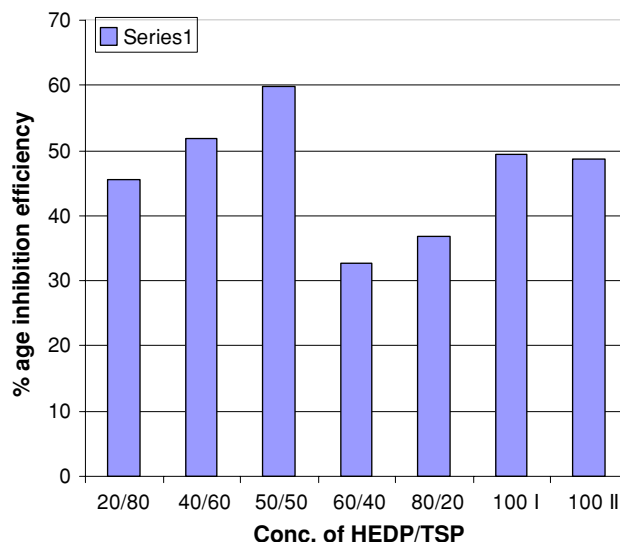


Fig. 3 Percentage inhibition efficiency of HEDP/TSP at different combinations at 40 °C in synthetic cooling water VI

4 Discussion

For HEDP/SHMP combinations, percentage inhibition efficiency decreases with increasing HEDP concentration up to 60 ppm. This combination gives complete protection against corrosion at 50/50 ppm combinations. When HEDP/STPP combination was tried, percentage inhibition efficiency decreased with increasing HEDP concentration up to 40 ppm and then increased to 80 ppm. This combination also gives maximum protection against corrosion at 50/50 combination. No significant increase in corrosion inhibition efficiency was observed in the HEDP/TSP combination. Only a small increase in corrosion inhibition efficiency was observed at 50/50 ppm combination of HEDP/TSP.

It was observed that combination of HEDP with other inhibitors gives best protection against corrosion in comparison with other combinations. HEDP/SHMP combination gives almost 98% inhibition efficiency at 50/50 ppm combination of inhibitors. It is clear from Figs. 1, 2, and 3 that the 50/50 ppm combination provides much better protection than individual 100 ppm inhibitor, i.e., these combination show synergistic behavior at 50/50 ppm concentration.

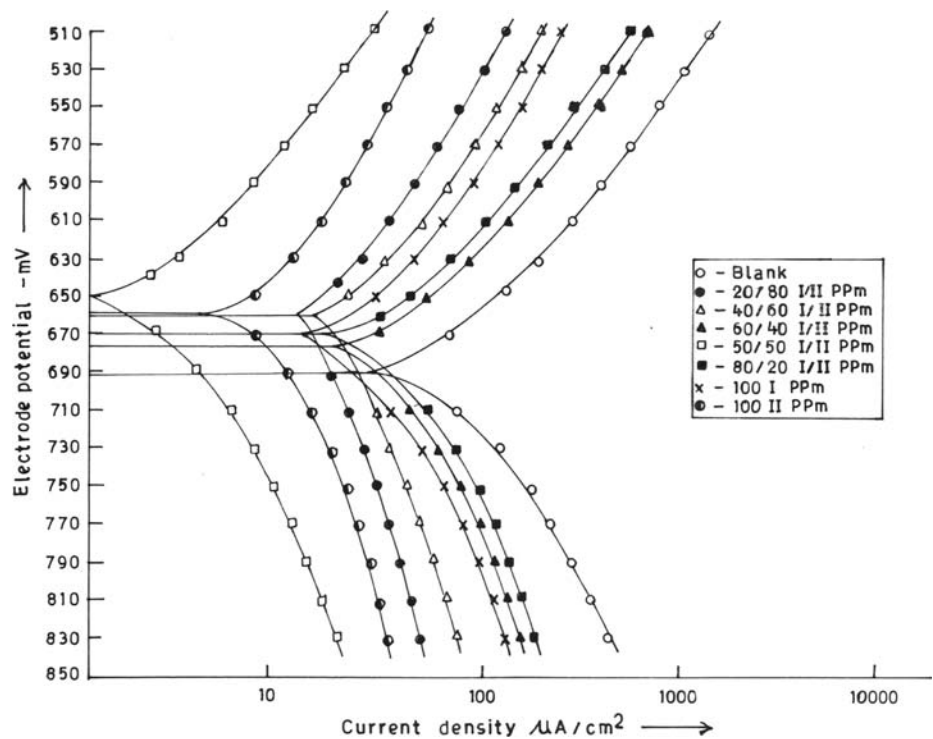
Other combinations of HEDP with other antiscalants were also tried, such as 45/55, 48/52, 52/48, and 55/45 ppm of HEDP/SHMP by weight loss method. It was observed that these combination do not provide significant increase or decrease in percentage corrosion inhibition efficiency. Hence, results of these combinations are not presented to save space.

From the electrochemical polarization studies, it was observed that both anodes and cathodes are polarized to

Table 4 Various corrosion parameters calculated from electrochemical experiments for carbon steel in CW VI in presence of different combinations of HEDP with SHMP, STPP, and TSP at 40 °C

Concentration of inhibitor (ppm)	Inhibitor combinations (I/II)	OCP (–mV)	β_a (mV/decade)	β_c (mV/decade)	R_p (Ohm/cm ² × 10 ³)	I_{corr} (μA/cm ²)	Corrosion rate (mpy)	Inhibition efficiency by polarization expt. (%)	Inhibition efficiency by weight loss (%)
Blank	–	690	92	206	1.01	27.4	12.5	–	–
20/80	HEDP/SHMP	665	110	240	2.3	14.2	6.5	48.0	47.9
40/60	do	670	115	230	2.0	16.4	7.6	39.2	39.2
60/80	do	676	107	225	1.7	18.6	8.6	31.2	30.5
80/20	do	670	110	230	2.1	15.1	7.0	44.0	43.5
50/50	do	650	150	280	18.5	01.8	0.9	93.8	97.6
100 I	HEDP	662	110	238	2.4	13.6	6.3	49.6	49.5
100 II	SHMP	655	130	250	10.0	3.7	1.7	86.2	86.7
20/80	HEDP/STPP	660	115	240	2.4	14.1	6.5	48.0	47.9
40/60	do	668	115	230	2.2	15.1	7.0	44.0	43.5
60/80	do	658	125	245	4.4	8.2	3.7	70.4	69.6
80/20	do	658	125	240	5.2	6.9	3.2	74.0	74.0
50/50	do	655	132	250	14.4	2.6	1.0	92.0	91.4
100 II	STPP	662	110	235	3.5	9.3	4.3	65.6	65.6
20/80	HEDP/TSP	665	105	240	2.1	14.7	6.8	45.6	45.6
40/60	do	663	107	240	2.4	13.0	6.0	52.0	51.8
60/80	do	678	102	225	1.7	18.2	8.4	32.8	32.7
80/20	do	670	103	230	1.8	16.9	7.8	37.6	36.8
50/50	do	660	110	240	3.0	10.8	5.0	60.0	59.8
100 II	TSP	665	105	242	2.3	13.8	6.4	48.8	48.7

Fig. 4 Polarization curves of carbon steel in CW VI in absence and presence of different combination of HEDP/SHMP at 40 °C and pH 6.5



considerable extent in presence of various combinations of the inhibitors. The 50/50 ppm combination of HEDP/SHMP shows maximum anodic and cathodic polarization

and zero I_{corr} value. The OCP value shifts in the anodic direction with addition of various combination of HEDP. Anodic and cathodic Tafel slopes do not show a regular

Fig. 5 Carbon steel samples when exposed to CW VI for 30 days, pH 6.5, and temperature 40 °C under 400× resolution by metallurgical research microscope

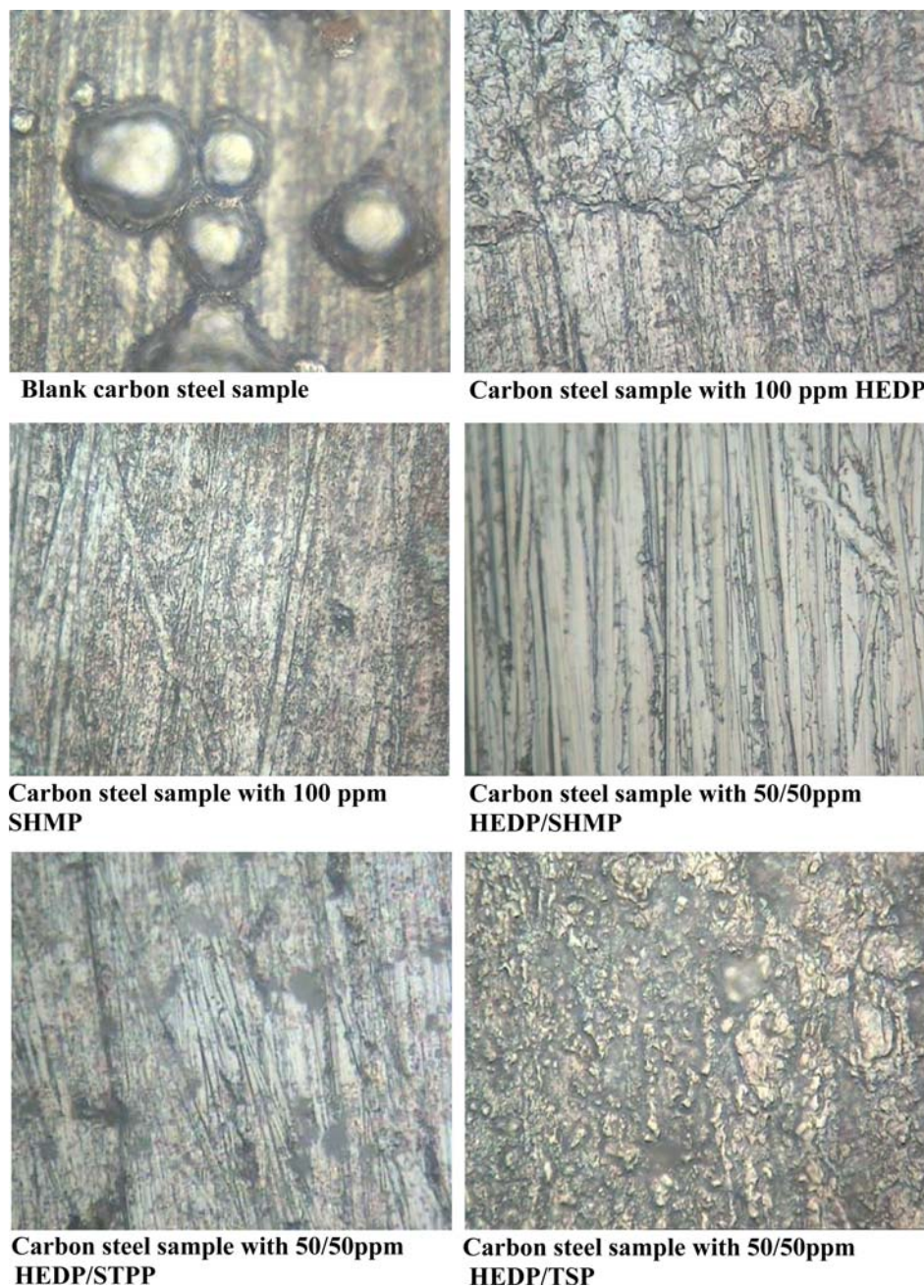


Table 5 Percentage antiscaling efficiency of various antiscalants at various concentrations in synthetic cooling water VI

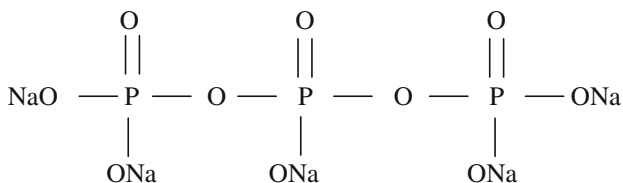
Water type	Composition of CW (mg/L)	Conc. of antiscalant (ppm)	Inhibi. effici. HEDP (%)	Inhibi. effici. STPP (%)	Inhibi. effici. SHMP (%)	Inhibi. effici. TSP (%)	
CW VI	Ca ²⁺	300	2	20.0	27.2	20.0	01.0
	Mg ²⁺	24	5	30.3	33.3	27.2	11.1
	CO ₃ ²⁻	30	10	33.3	38.4	33.3	18.0
	HCO ₃ ⁻	305	15	38.3	38.4	33.5	18.1
	Na ⁺	253	20	43.3	38.4	33.9	18.7
	Cl ⁻	692	–	–	–	–	–
	SO ₄ ²⁻	120	–	–	–	–	–

increasing or decreasing trend with increasing HEDP concentration in different combinations. Linear polarization resistance value increases with increasing percentage inhibition value. Electrochemical polarization results confirm the results obtained from weight loss study. It can be clearly seen from the polarization results (Table 5) that the HEDP/SHMP combination gives maximum synergistic effect among all the investigated antiscalants combinations as corrosion inhibitors at 50/50 ppm concentration.

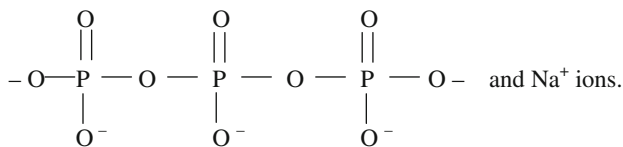
Similar results were obtained from microscopy technique, as shown in Fig. 5. Very clear smooth surface of carbon steel can be seen in presence of 50/50 ppm HEDP/SHMP combination. Carbon steel surface is not very smooth in presence of 100 ppm HEDP or SHMP alone. It is clear from the figure that 50/50 ppm HEDP/SHMP combination provides synergistic effect. It is also clear from the figure that, out of the HEDP/STPP and HEDP/TSP combinations, the HEDP/STPP combination provides much better protection from corrosion.

Mechanism of inhibition of all the investigated antiscalants is given below;

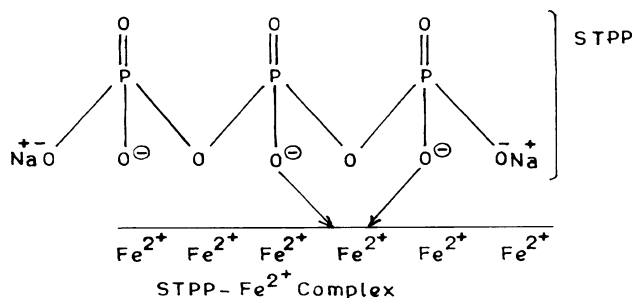
Sodium tripolyphosphate (STPP) having molecular formula, $\text{Na}_5\text{P}_3\text{O}_{10}$, has the following molecular structure.



In this molecule P–O–P linkage is present and, when this is added to cooling water, it becomes dissociated as

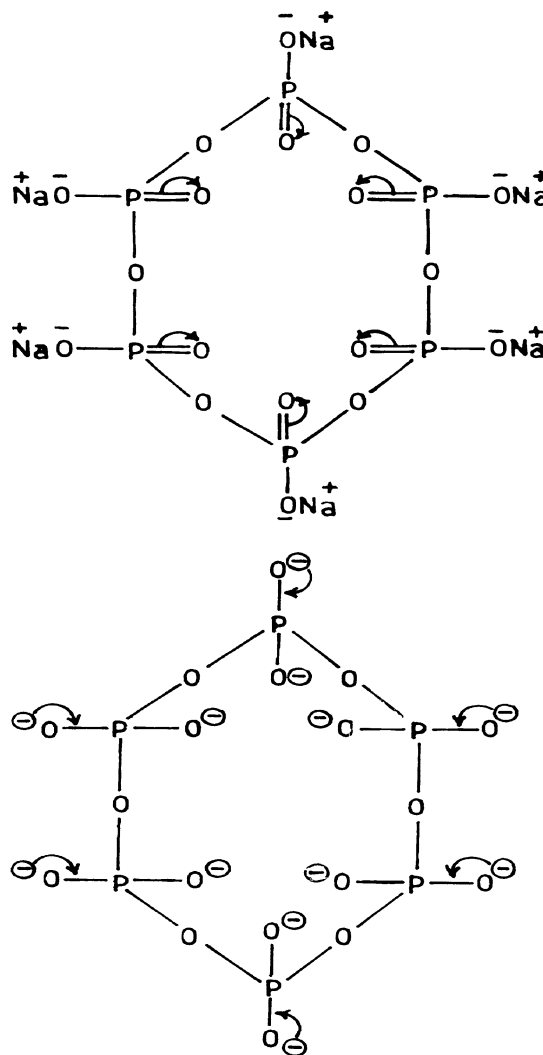


Here pentavalent phosphorous is tetrahedrally surrounded by four oxygen atoms. Any of the two adjacent phosphoryl oxygen anions can adsorb on the ferrous atom of carbon steel, thus making a continuous protective adsorbed layer of phosphate molecules across the whole carbon steel surface. Phosphate ions may incorporate into electrical double layer at the metal surface. It is also possible that PO_4^{3-} ions may be filled in the voids present in adsorbed film and accelerate protective film growth and, due to these plugs, any further diffusion of Fe^{2+} ions from the metal surface may be stopped.



The above figure shows film of sodium tripolyphosphate molecules adsorbed on the surface of carbon steel. The adsorbed film starts growing on the surface of carbon steel in the form of continuous film through terminal oxygen atom in the form of strong covalent –P–O–P– linkage, thereby reducing the chance of HEDP molecule being adsorbed on the carbon steel surface. Hence, the HEDP/STPP combination does not provide a synergistic effect.

The molecular formula of SHMP is $\text{Na}_6\text{P}_6\text{O}_{18}$. It is a cyclic polyphosphate and has the following molecular structure:



SHMP (Sodium hexametaphosphate)

steel in synthetic cooling water VI. This may be due to intermolecular hydrogen bonding possible between terminal hydrogen atom of two terminal hydroxyl groups present on HEDP and two oxygen atoms from two adjacent SHMP molecules giving rise to uniform two-dimensional multilayered film on the surface of carbon steel.

- (2) The percentage inhibition efficiency of HEDP when mixed with other antiscalants as corrosion inhibitors at 50/50 ppm concentration was found in the following order HEDP/SHMP > HEDP/STPP > HEDP/TSP.
- (3) All investigated 50/50 ppm combinations provide much better protection from corrosion than individual 100 ppm inhibitor.
- (4) Results obtained from weight loss study and electrochemical polarization experiments were also confirmed by microscopy technique carried out for the surface study of corroded specimens.

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