

The effect of inhibitors on the corrosion of mild steel in acidic and sea-water environments

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THE CORROSION of mild steel in dilute sulphuric acid, acetic acid and sea-water environments, inhibited in turn with triethylamine, diethylamine, sodium benzoate and zinc oxide inhibitors, was studied in this work using the weight-loss and potential-measurement techniques. In particular, the inhibitors were very effective in dilute sulphuric acid, where their efficiency was very significant. Diethylamine inhibitor was found to be very effective in acetic acid, while triethylamine's effectiveness was slightly above average and that of sodium benzoate and zinc oxide were less than average. Only diethylamine and sodium benzoate inhibitors, with triethylamine and zinc oxide, were not inhibitive at all in the concentrations used in the sea-water medium. The synergistic effect of some of the inhibitors was also confirmed by potential measurement.

Introduction

Corrosion, which is a universal problem, is the deterioration and loss of material due to chemical attack involving chemical and electronic changes. Apparently, corrosion cannot be avoided, but its severity can be prevented. Techniques and methods to combat corrosion efficiently are continually being sought, as a result of the exorbitant amount spent on corrosion annually. This has run into billions of dollars in the USA, for example.

One of the means of combating corrosion in aqueous and process industry environments is the application of corrosion inhibitors. An inhibitor is a substance which retards or slows down a chemical reaction. Thus, a corrosion inhibitor is a substance which, when added to an environment, decreases the rate of attack by environment on a metal[1]. Numerous papers have been published world-wide on the action of corrosion inhibitors[2-8].

The costs of corrosion and the savings gained through the use of appropriate corrosion inhibitors are considerable in process industries (such as refineries and petrochemicals), and in aqueous environments. Inhibitors can be broadly classified according to the rate at which the process is controlled[9]. Anodic inhibitors suppress anodic reactions, and the rate of metal ions being transferred into the aqueous environment is reduced. Cathodic inhibitors impede the cathodic reaction — for example, oxygen reduction. Mixed inhibitors hinder both reactions. On the basis of their mechanism of operation, four major categories of corrosion inhibitors have been identified[10]. These are: neutralizers, filming

inhibitors (or barrier-layer formers), scavengers, and miscellaneous types.

In this work, filming inhibitors have been used. Instead of reacting with or removing an active corrosive species, filming inhibitors function by strong adsorption, or chemisorption, and decrease attack by creating a barrier between the metal and the environment[10]. A filming inhibitor must possess a hydrocarbon portion attached to a strongly polar group. The molecules are oriented on the metal surface with the polar group adsorbed on to the metal surface, and the hydrocarbon component extending away from the surface. The hydrocarbon end will attract the molecules of the process stream to provide an additional barrier to a potentially-corrosive aqueous solution[10]. The performance of an inhibitor can be assessed by its effectiveness in reducing the corrosion rate.

For a corrosion inhibitor's protection to be effective, it must protect all exposed metal from corrosive attack, must be effective at low concentration, must not cause deposits on the metal surface, must remain effective under a broad range of pH, temperature, water-quality, and heat-flux conditions, must prevent scale formation and disperse deposits, and must have a minimum toxicological effect when discharged[9].

An attempt at making a further contribution to research into the use of inhibitors as a corrosion protective means by further identifying a group of chemicals suited to some specific environments is therefore the object of this work. The ultimate aim is one of economic and technological benefits to industrial concerns.

Experimental procedure

Material

The mild steel used for this work was Swedish (SIS) made cold-rolled mild steel of average % composition: 0.092C, 0.48Si, 1.47Mn, 0.009P, 0.0025S, 0.0114N, 0.050Al, 0.004Nb, 0.01V and 0.01Ti, the rest being Fe.

Test media

The test media used for the investigation were:

- (i) sea water obtained from the Atlantic ocean at the Lagos Bar beach;
- (ii) dilute sulphuric acid — 0.1M;
- (iii) acetic acid — 0.5M

Inhibitors used were:

- (i) triethylamine — pH 7.5 (as received)
- (ii) diethylamine — pH 9 (as received)
- (iii) sodium benzoate — 167g/dm³ concentration
- (iv) zinc oxide — 200g/dm³ concentration

Each of these materials was separately added in turn to each of the above test media (corrodants), in the ratio one part inhibitor to 10 parts corrodant.

Preparation of test specimens

The mild-steel plate was cut into a number test specimens measuring 20mm x 20mm x 1.5mm. Some of these were then ground with silicon carbide abrasive papers of 240, 320, 400 and 600 grits. These abraded mild-steel specimens were then thoroughly rinsed with distilled water, cleaned in acetone, and stored in a desiccator for further weight-loss tests.

Selected specimens were individually mounted in araldite resin after spot welding to flexible wire connections at one end. They were then similarly ground, and polished with 1.0µm diamond, washed with distilled water, rinsed with methyl alcohol, dried, and similarly stored in a desiccator.

Weight-loss experiments

Weighed test pieces were totally immersed in each of the various test media contained in a 100-ml beaker for 18 days with and without inhibitor addition. They were taken out every three days, washed with distilled water, rinsed with acetone, dried, and re-weighed. The tests without inhibitors were deliberately done to enable a comparison of the inhibited environment's rate of corrosion to be made. Plots of weight loss versus time of exposure were made (Figs 1 to 3). Curves of corrosion rate (calculated) versus time of immersion were also plotted (Figs 4 to 6).

The % inhibitor efficiency, P, was calculated from the relationship:

$$P = 100 [1 - (W_2/W_1)]$$

where W_1 and W_2 are the corrosion rates in the absence and the presence, respectively, of a predetermined concentration of inhibitor. The % inhibitor efficiency was calculated for all the

Time of Immersion	Test Specimen	Test Environment	Inhibitor	Inhibitor Efficiency %
18 days	Mild Steel	0.1M H ₂ SO ₄	Triethylamine	100
			Diethylamine	92.9
			Sodium Benzoate	85.8
			Zinc Oxide	85.8
18 days	Mild Steel	Acetic Acid	Triethylamine	54.2
			Diethylamine	92.4
			Sodium Benzoate	47.3
			Zinc Oxide	37.4
18 days	Mild Steel	Sea Water	Triethylamine	0
			Diethylamine	60
			Sodium Benzoate	60
			Zinc Oxide	-20

Table 1. Inhibitor efficiency (%) calculated on the 18th day of the experiment.

inhibitors as at the 18th day of the experiment; the calculated results are presented in Table 1.

Potential measurements

Different combinations of inhibitors were used for the potential measurements. A predetermined concentration of sodium benzoate (167g/dm³) was added to triethylamine to make a combination. Similarly, zinc oxide (200g/dm³) was added to diethylamine to make another different combination of inhibitors. These mixtures were prepared arbitrarily.

Each of the mounted specimens was immersed in the prepared test medium with and without inhibitors in the different corrosion cells. The potentials were recorded at three-day intervals using a digital voltmeter and saturated calomel reference electrode. The potentials were plotted against exposure time (Figs 7-9). All the potential measurements were carried out at ambient temperatures.

Results and discussion

Weight-loss method

Results obtained for the weight-loss method showed that the behaviour of the inhibitors differs in different solutions. This further confirms that inhibitors are specific in their mode of action. Further analysis of the inhibitors' action and performance is discussed below.

1. Dilute sulphuric acid environment: The curves of the weight loss vs. exposure time curves for the mild-steel specimens immersed in 0.1M dilute sulphuric acid, with and without inhibition, are presented in Fig.1. The greatest amount of corrosion throughout the experimental period was recorded for mild steel immersed in the acid without any inhibitor addition. This was expected, as mild steels are known to be susceptible to corrosion in this acid, as well as in many others. Though there was no further increase throughout the experimental period, in the amount of corrosion relative to the exposure time as indicated by the weight loss per unit area of the metal specimen, the corrosion remained high due to the

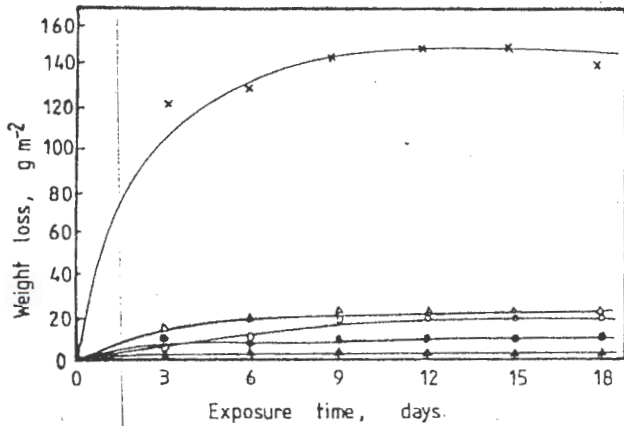


Fig.1. Variation of weight loss with exposure time for mild-steel test specimens immersed in 0.1M sulphuric acid with different inhibitors:

- x = no inhibitor;
- ▲ = triethylamine;
- = diethylamine;
- △ = sodium benzoate;
- = zinc oxide.

strong nature of the acid (pH 3.5). However, contamination of the acid environment by corrosion deposits weakened the acid, and this tends to stifle further increases in the amount of corrosion relative to time.

There was considerable reduction in weight loss, and hence reduced corrosion, with the introduction of the inhibitors into the acidic medium. All the inhibitors used at their predetermined concentrations were very effective in the order:

triethylamine > diethylamine > zinc oxide > sodium benzoate.

The zinc-oxide and sodium-benzoate inhibitors maintained equal effectiveness after the first nine days to the end of the experiment. The zinc oxide was, however, more effective during the first nine days of the experiment; the reason for this behaviour is difficult to explain.

2. Acetic-acid environment: Fig.2 shows the curves of the weight loss vs exposure time for the mild-steel specimens immersed in acetic acid (pH 1.5) with and without added inhibitor. Weight loss and hence corrosion of mild steel in acetic acid was

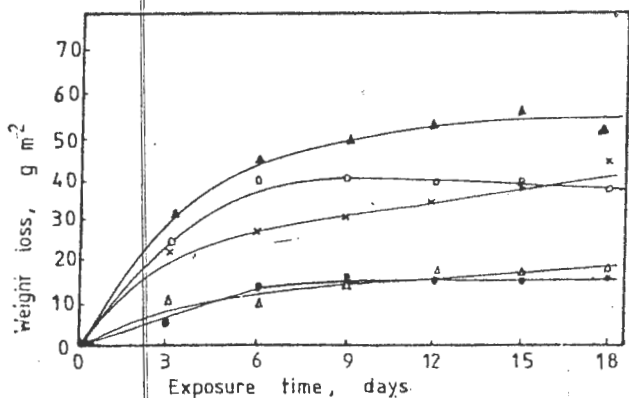


Fig.3. Variation of weight loss with exposure time for mild-steel test specimens immersed in sea water with different inhibitors according to the key in Fig.1.

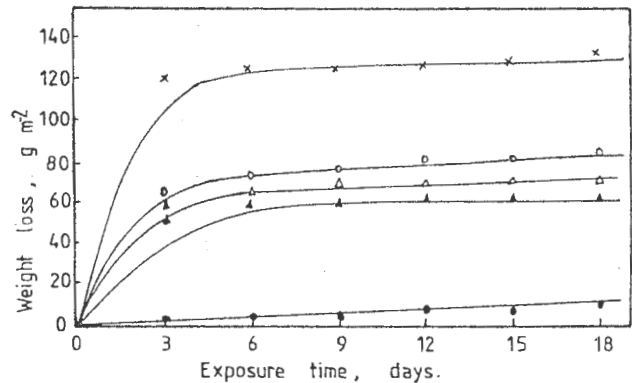


Fig.2. Variation of weight loss with exposure time for mild-steel test specimens immersed in 0.5M acetic acid with different inhibitors according to the key in Fig.1.

high, though comparatively less so than in dilute sulphuric acid. Acetic acid is also known to be very corrosive to mild steels, particularly at high concentrations. The various inhibitors used were all effective at reducing the corrosion of mild steel, but to different extents. In this environment, diethylamine was by far the most effective, with zinc oxide the least effective. The order of effectiveness obtained was:

diethylamine > triethylamine > sodium benzoate > zinc oxide.

This trend differs from that of the dilute sulphuric acid environment, and therefore further confirms the distinctness of the characteristics of different inhibitors for different environments. Further explanation about the inhibiting mechanisms will be presented later in this discussion.

The corrosion rate for the specimens immersed in acetic acid follows the same trend as for those immersed in dilute sulphuric acid, decreasing with increasing exposure time. Diethylamine was extremely effective, closely followed by triethylamine.

3. Sea-water environment: Fig.3 shows the curves of the weight loss vs exposure time for the mild-steel specimens immersed in sea water with and without inhibitors. Only two of the inhibitors — sodium benzoate and diethylamine — showed some measure of inhibition effectiveness. Triethylamine and zinc oxide gave a negative effect by increasing the amount of corrosion. Sea water predominantly consists of sodium chloride (about 3.5%), and many other ions. Chloride ions are very strong, and could easily penetrate passive films. For any inhibitor to be effective in an environment containing chloride ions, it has to be very strong and well-formulated. It could be inferred here that the ineffective inhibitors could not provide a resistant protective film to withstand the penetrating effect of the chloride ions, as well as others present, such as the sulphate ion (SO₄²⁻). The

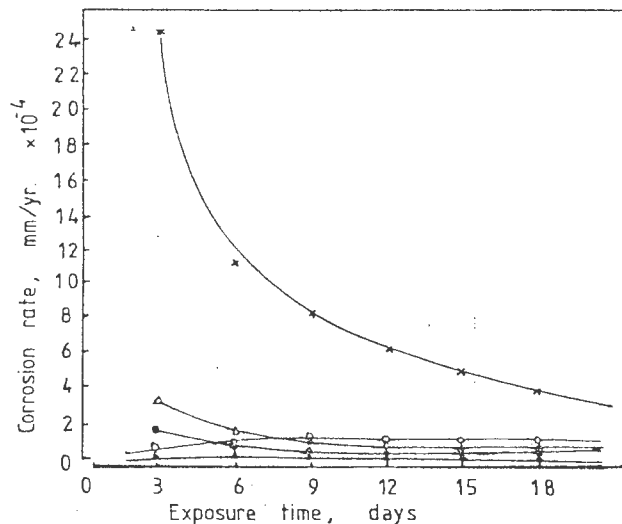


Fig. 4. Variation of corrosion rate with exposure time for mild steel test specimens immersed in 0.1M sulphuric acid with different inhibitors according to the key in Fig.1.

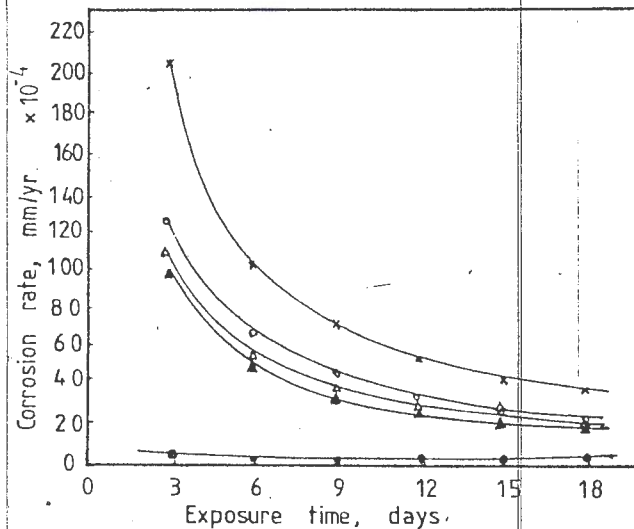


Fig. 5. Variation of corrosion rate with exposure time for mild steel test specimens immersed in 0.5M acetic acid with different inhibitors according to the key in Fig.1.

effects of sodium benzoate and diethylamine were very similar.

Corrosion rate of mild steel in different environments

Curves made for the corrosion rate vs the exposure time of the mild-steel test specimens in the different test media with and without added inhibitors are presented in Figs 4 to 6. In dilute sulphuric acid, Fig. 4, the corrosion rate of the mild steel decreased with time, particularly for the test without added inhibitors. For the triethylamine, no corrosion rate was recorded. The test without inhibitor addition had the highest corrosion rate. The corrosion rate for the test media containing diethylamine, sodium benzoate and zinc oxide inhibitors were also minimal; these reflected the effectiveness of all the inhibitors used. The decrease in recorded corrosion rate was due to the contamination of the dilute sulphuric acid by the corrosion deposits. This weakened the test environment, and reduced the chemical reactivities and hence the corrosion rate.

The decrease in corrosion rate with time for the mild steel was more pronounced in the acetic-acid environment than in dilute sulphuric acid, Fig. 5. The diethylamine inhibitor showed significant corrosion rate, and was the most effective inhibitor used in this medium; others were less effective.

Triethylamine's protective effectiveness in dilute sulphuric acid, and diethylamine effectiveness in acetic acid, are particularly significant. Both are amine-group organic compound inhibitors that provide good adherence and adsorption by chemisorption or electrostatic force to the metal's surface by means of their groups based on nitrogen and hence providing effective film protection for the mild steel.

The corrosion rate of mild steel in sea water with and without inhibitor, Fig. 6, follows a very similar trend to that reported above. Except in the initial case of the sea water containing diethylamine, all the corrosion rate curves decreased with time. This is a further indication of the corrosion products' contamination of the test environment, weakening the chemical reactivity. The thick deposit formed on the metal surface could increase the electrical resistance of circuit and thereby reduce the corrosion rate with time.

Diethylamine has the lowest corrosion rate in this environment, followed by sodium benzoate. The corrosion rates recorded with triethylamine and zinc oxide inhibitors, respectively, were high, indicating a lack of inhibiting protection.

Mechanistically, the effective inhibitors in the different test media used could cause an increased polarization of the anode (anodic inhibition), and

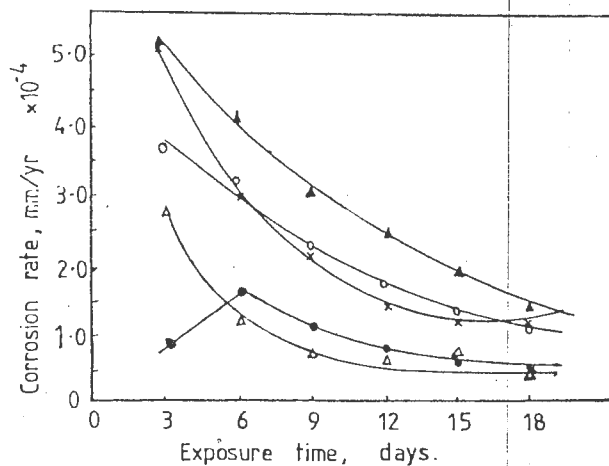


Fig. 6. Variation of corrosion rate with exposure time for mild steel test specimens immersed in sea water with different inhibitors according to the key in Fig.1.

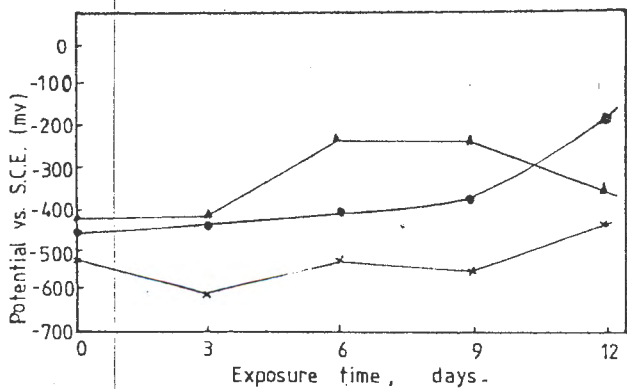


Fig. 7. Variation of potential with exposure time for mild-steel test specimens immersed in 0.1M sulphuric acid with different inhibitors according to the key in Fig. 1.

an increased polarization of the cathode (cathodic inhibition). The thick deposit formed on the metal surface in some instances, could increase the electrical resistance of the circuit, thereby inhibiting corrosion and reducing the corrosion rate with time.

Inhibitor efficiency

The efficiencies of the inhibitors used are presented in Table 1. The results obtained here (by calculation) are in agreement with those described above for the weight-loss method. Inhibitors selected for dilute sulphuric at the predetermined concentrations are most effective compared with the others. Further work on the concentration effect might improve the inhibitor efficiency of the others.

Potential measurement

The curves of potential (SCE) vs exposure time for the mild-steel specimen immersed in dilute sulphuric acid, acetic acid, and sea water with and without added inhibitors are presented in Figs 7-9 respectively. All the curves exhibit some form of fluctuating active and passivating corrosion phenomena.

In the dilute sulphuric acid environment, Fig. 7, the highest negative potentials, ranging between -520mV and -610mV were recorded throughout the experimental period for the solution without inhibitor addition. The figure shows continuous active corrosion throughout the period. The slight decrease in the negative potential around the seventh to the tenth day could be attributed to the weakness of the acid around this time. The corrosion deposits must have contaminated the test medium, rendering it chemically weak for a strong active corrosion reaction. The passivating or inhibiting effect of the mixed triethylamine and sodium benzoate on one hand and the combination of diethylamine and zinc oxide on the other hand is apparent. The inhibiting effects of these two combinations are very close. However,

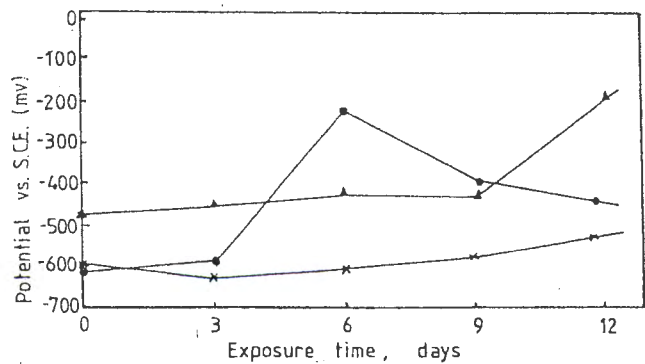


Fig. 8. Variation of potential with exposure time for mild-steel test specimens immersed in 0.5M acetic acid with different inhibitors according to the key in Fig. 1.

the potentials recorded with time throughout the experimental period indicate the combination of triethylamine and sodium benzoate to be more effective than the latter (diethylamine and zinc oxide).

The results obtained for the test specimens immersed in acetic acid with and without inhibitor addition, Fig. 8, are not very much different from those of Fig. 7. Here, also, the combination of triethylamine and sodium benzoate is slightly more effective than that of diethylamine and zinc oxide. The reason for this is not yet clear.

In the sea-water environment, Fig. 9, the combination of diethylamine and zinc oxide was slightly more effective than that of triethylamine and sodium benzoate. The two different combinations are however, effective, particularly with increase in exposure time.

Zinc ions are used to achieve a general reduction in corrosion by precipitating as zinc hydroxide at the cathode due to locally elevated pH. Zinc is synergistic when combined with other inhibitors, and it causes rapid development of a protective film over the metal surface. These characteristics account, in part, to the greater effectiveness of its combination with diethylamine when compared

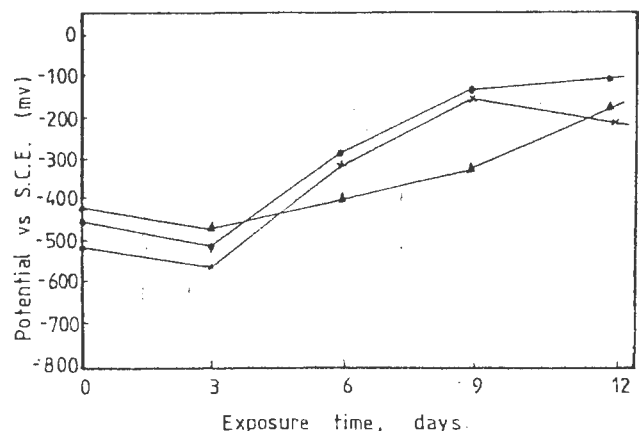


Fig. 9. Variation of potential with exposure time for mild-steel test specimens immersed in sea water with different inhibitors according to the key in Fig. 1.

with triethylamine and sodium benzoate (combined).

All the inhibitors used in this work are filming inhibitors. They consist of one polar group based on nitrogen and oxygen that is attached to the metal surface by chemisorption or electrostatic forces[11].

Conclusions

1. All the inhibitors used in this work are effective in inhibiting corrosion, to varying degrees according to the different test environments. This was indicated by the weight loss method, and the determination of the corrosion rates from the results obtained.
2. In dilute sulphuric acid, all the inhibitors used at their predetermined concentrations were very effective, in the order:
triethylamine > diethylamine > zinc oxide > sodium benzoate.
3. In the acetic-acid environment, the effectiveness of the inhibitors can be presented in the order:
diethylamine > triethylamine > sodium benzoate > zinc oxide.
4. Both sodium benzoate and diethylamine showed some measure of inhibiting effectiveness in sea water. Triethylamine and zinc oxide showed negative effects.
5. The synergistic effects of the inhibitors have been confirmed by potential measurements, particularly with respect to zinc oxide in sea water.
6. The overall effectiveness of these inhibitors in the test environments is yet to be fully documented.

as only predetermined concentrations of the inhibitors were used. However, their potential inhibiting effectiveness has been confirmed.

7. The results obtained confirm, in general, the distinctness of the inhibitors in their modes of action.

Acknowledgement

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