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Analyzing the Impact of Zineband Ziram As Booster Biocides in Antifouling Paints

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Abstract
Maritime structures such as waterfronts, offshore platforms and hulks all face different maritime sediments. There are different methods to prevent the growth of organic and non-organic material on humid surfaces, but the utilization of antifouling paints has had the most efficiency. The growth of these maritime pollutions has been stopped on hulks by the antifouling paints. Ever since the nineteenth century, antifouling paints have been utilized with different mechanisms and the most important one was the TBT self-polishing paints that were banned in 2003 by the International Marine Organization (IMO) because of the high pollution it creates in the environment. There have been many efforts ever since then to add to manufacturing antifouling paints with high efficiency that create the least amount of pollution for the environment. Therefore, in this study, it has been tried to manufacture antifouling paints with the two organic combinations of Zineb and Ziram as boosting toxins. The rosin acrylic copolymer paint is utilized as the paint matrix. The paint's main toxin is zinc (Zn) and the organic combinations of Zineband Ziram have been used as biocide boosters. Scaling the release rate of zinc in sea water, the impact of biocide boosters in comparison with paints with only zinc-oxide as the antifouling element is analyzed and compared.

*Keywords :*biocide boosters, Zineb, Ziram, Antifouling Paints

1. Introduction
Plumbic biocides TBT (Tributyltin) as the added factor in antifouling paints that prevent the growth of marine sediments have been used since the early 70s. But because of its negative impacts on the marine environment, its utilization has been stopped since 2003 [1]. Therefore, trying to devise and manufacture antifouling paints that have the least damage for the environment, has led to the production of different antifouling paints. In several of the utilized paints in recent decades, elements Cu and Zn were utilized as the main biocides in antifouling paints and they were mostly in the form of oxides inside the paint matrix [2]. While the use of copper, because of its high toxicity and pollution for the marine environment is decreasing. Therefore, using boosting biocides that mostly consist of organic combinations and have high antifouling capabilities, the utilization of oxides of metal minerals, especially copper is decreasing. Among the boosting antifouling combinations, hydrophilic organic combinations such as Zineb and Ziram, as intensifiers and boosters of the antifouling and biocide impacts are used in antifouling paints. In this paper, the impact of two different boosting toxins of Ziram and Zineb that include 3 and 6 percent of the weight of the paint with zinc-oxide as its main biocide is analyzed. In the paint composed of copolymer acrylicrosin, which is rosin with the capacity to absorb water, it is utilized as the paint matrix with the controlled solubilisation capacity and causes the release of the biocide by dissolving into the natural water of the sea.

2. Utilized materials and methodology

2.1. Antifouling paints

Among the different types of antifouling paints, based on their mechanism and function, self-polishing TBT paints had the most function and effect until 2003. After the use of these paints was banned because of their high toxicity and the pollution of marine environment, Electro depositionPaints (CDPs) were utilized. The biocide used in these paints determines their effectiveness on fouling and marine organisms. Among these boosting biocides, Zineb and Ziram, in spite of their high effect on reducing the growth of these organisms, pose the least amount of damage to the environment. These two organic combinations, as the boosters for the main toxin (ZnO) are utilized in the paint combination and are placed in the paint matrix. By absorbing the ions in the water by the utilized rosin, the zinc element in the paint forms a complex and egresses from the paint matrix. On the other hand, the zinc in the boosting biocide egresses in the form of Zn^{2+} and enters the marine environment [3].

2.2.Zineb and Ziram

Zineb ($C_4H_6N_2S_4Zn$), with a molecular weight of 275.8 g/mol (monomer) is a yellow powder whose antifungal capacity is the reason for its utilization in different industries. Ziram ($C_6H_{12}N_2S_4Zn$), with a molecular weight of 305.8 g.mol is a white powder that, similar to Zineb, has function in different types of pesticides and industries as an antifungal material [4].

2.3.Manufacturing the paint

In manufacturing the antifouling paint, the acrylic copolymer rosin was utilized. This rosin has the capacity to absorb water and liquidation in predetermined times. The antifouling paint is used in the designed paint system as the final layer. In this experiment, the simple carbon steel is chosen as the base metal and the paint system is applied on it. The designed paint system in this research includes epoxy paints with aluminum fins as the primary layer, the corrected epoxy paint as the middle layer (sealer) and finally, the antifouling paint which is applied as the final layer (the over paint). The thickness of the primary dry film is 150 µm, the middle layer 120 µm and the final layer (antifouling paint) is 170 µm. The surface of the metal is blasted with a degree of $Sa2_{1/2}$and then, the first layer is applied on the surface and is placed in a temperature of $25^{\circ c}$ and becomes ready for the second layer. The second layer (middle layer) is also applied on the first layer and 48 hours after the application of the second layer, the final layer (antifouling paint) is applied. The drying time of the final layer (antifouling paint) is 24 hours in a temperature of 25˚C.

2.4. Testing the paint

To test the antifouling paint and its effectiveness, the painted samples are immersed and rotated in the antifouling paint testing machine for the sea water with a 60 r/min speed for 46 days. In this experiment, which is devised to determine the effectiveness of the antifouling paint, the conditions for fouling are quickened to determine the effectiveness of the manufactured antifouling paint. To analyze the release rate, using the atomic absorption experiment, the release rate of zinc in a period of 46 days is analyzed. Based on the experiments that were done, the critical amount of the release rate in paints in which the zinc-oxide toxin is used without boosting biocides is between 15 and 20 $\mu g/cm^2$ per day. Now, by analyzing the releasing rate of the manufactured paint and the daily observations of the antifouling paint that is being experimented upon, the mechanism and effectiveness of the boosting biocide are analyzed [5].

3.Argument and conclusion

Changes in the amount of release rates of the paints with boosting biocides of Zineb and Ziram in comparison with the immersion time are shown in figures 1 and 2. Based on the diagrams below, it is indicated that with the increase in the immersion time, the release rate of both types of paints have decreased.

The release rate of the Electro deposition self-polishing paints, at first, because of the high density of the elements in places close to the liquid phase (sea water) were high and reduce gradually [6].

In a similar study that was done regarding the antifouling paints in the sea environment in dynamic states (moving in the water), it is also observed that with the increase in the speed of the rotation of the samples inside the water, which is the simulation of the ship's movement, a higher release rate was recorded in the beginning of the experiment and then, there are states with lower speeds and in the end, all cases reduce the release rate. In figure 3, a combination of different speeds of the sample rotation in releasing the biocide is shown [7].

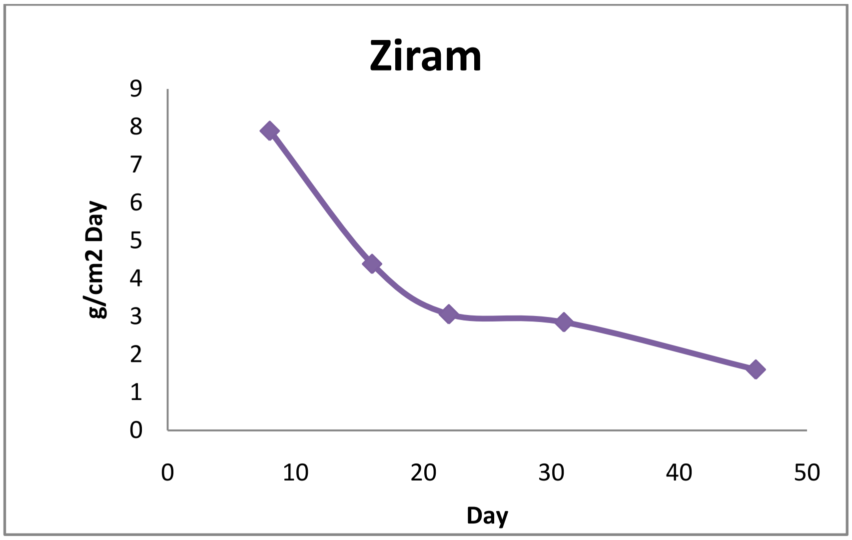

Figure 1: Release rate of the antifouling paint with the boosting toxin Ziram

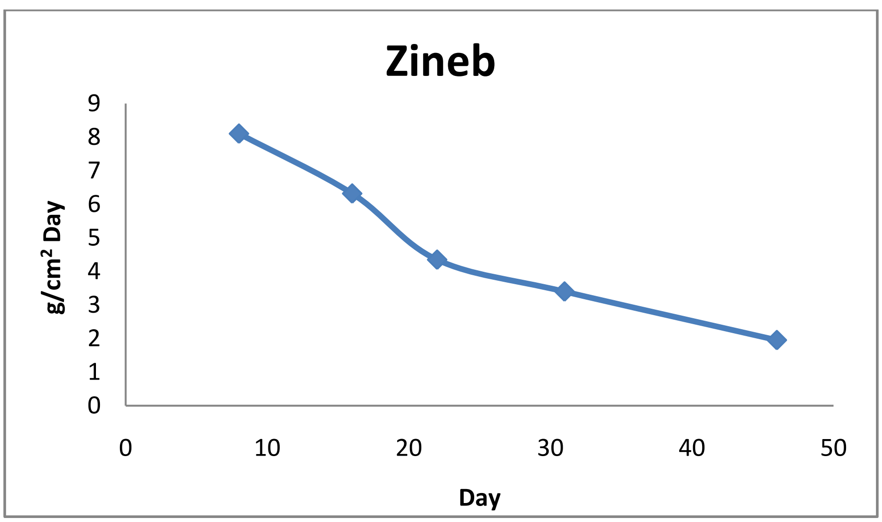

Figure 2: Release rate of the antifouling paint with the boosting toxin Zineb

3.1. Comparing the release rate in biocide boosters utilized in the antifouling paint

As it is seen in figure 4, the release rates of the antifouling paints in three types of biocide boosters are compared.As it is seen in the figure, the release rates in both paints with Zineb and Ziram are similar, because the rosins used in their experiments were the same. The release speed of the biocide in preventing the diffusion of water anions in the paint matrix is done and by doing a chemical reaction with the pigments, causes the release of biocides in the environment.

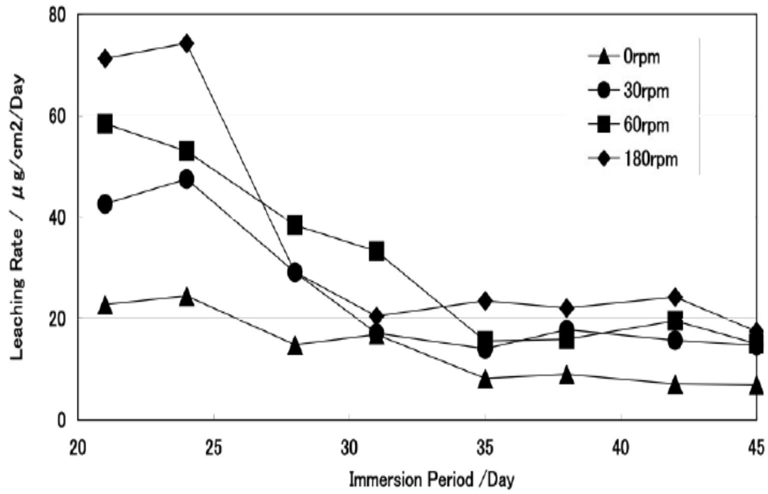

Figure 3: Changes of the release rate in comparison with the speed of the samples' rotation during the 45 days [7]

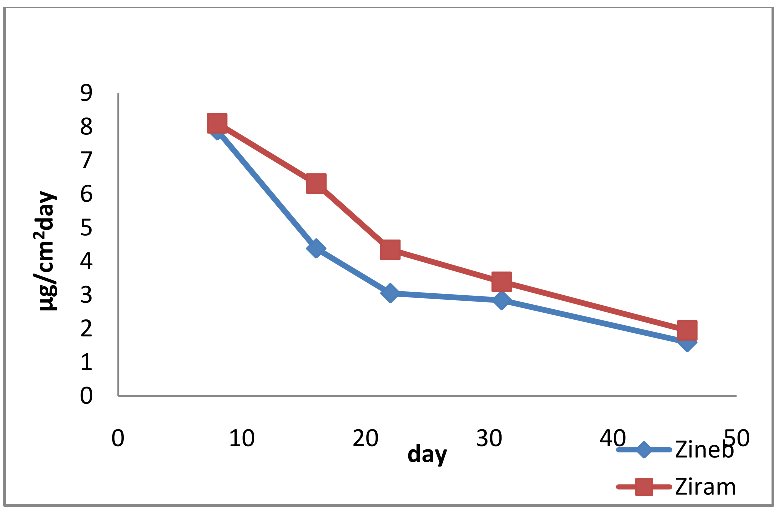

Figure 4: Comparing the release rate of zinc in two paints with Zineb and Ziram

3.2.Analyzing the increase of the thickness of the leach layer and the release rate

Based on the studies done regarding the washable layer in antifouling paints, it is confirmed that by increasing the thickness of this layer, the release rate also decreases. By increasing the immersion time, the thickness of the leach layer increases (figure 5). The leach layer's mechanism is in a way that first, the diffusion of the determining factor and then, based on the synthesis, the liquidation and release are controlled. First, the ions of chlorine and other ions diffuse the polymer and form a complex with the zinc inside the paint matrix and then, based on their liquidation speed, egress from the matrix one by one. Consequently, the mechanism includes the three stages of the diffusionof the liquidated ions in sea water, formation of the complex with the biocide in the paint matrix and finally, their liquidation and then release. In fact, zinc-chlorine complexes diffuse to the outside. In water absorbing systems, the liquidation of pigment must be faster than the solid-liquid balance that takes place in the frontal pigment (close to the surface) [8, 9].

Based on the subjects above, the results of the experiment regarding the release rate in comparison with the immersion time can be analyzed in the way that first, the release rate of zinc inside the sea water increases, which can be held as a result of the diffusion of water ions inside the matrix and the liquidation of the pigment, after the liquidation of elements close to the surface, the density of these elements in layers close to the surface decreases and the diffusion is done again so that the elements in deeper layers are liquidated and can enter the water. If the diffusion speed of the ions in the sea water was more than the diffusion of the biocide to the outside and the liquidation of the paint matrix, the leach layer thickness increases and consequently, the release rate decreases.

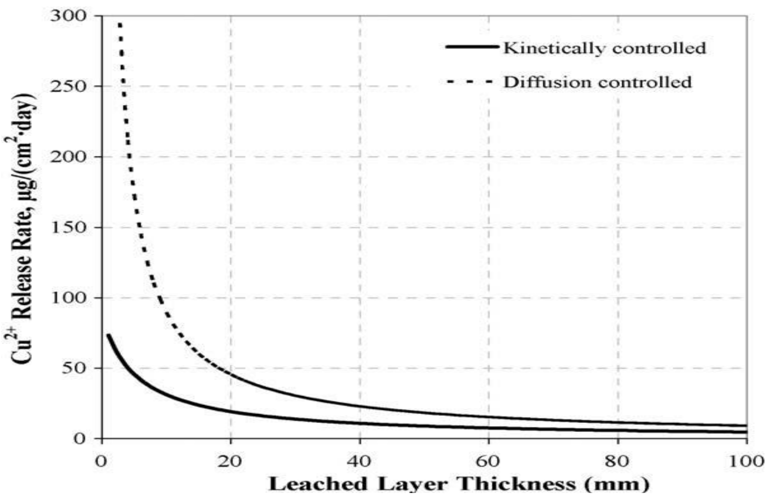

Figure 5: Release rate of the biocide based on leached layer thickness

3.3. Analyzing the mutual impact of the release rate and fouling and the growth of alga

A: Impact of antifouling paint on fouling

What is important regarding the release rate is its critical amount in relation with the growth of marine sediments on the structures and antifouling paints. On the other hand, the stoppage of any kind of marine pollution is done in a range of different amounts of biocide. The difference in the biocide and the boosting biocide and their deterrence power in the growth of marine sediments cause the difference in the compositions of antifouling paints and their function in different environments. Based on what is done in this paper and the manufactured antifouling paint, the boosting biocides Ziram, Zineb and also their combination were utilized. With regard to the curves resulted from the release rate in relation with the immersion time and also the daily reports of the experiment and the analyses of the samples' surfaces after the immersion time, it is observed that the release rate of Zineb is less than the release rate of the paint with Ziram in it. Furthermore, from the macroscopic observations of the sample surface, it is also inferred that the hypothesis in which as much as the release rate was higher, fouling is observed as interrupted and in the form of islands, whereas regarding Zineb, which has a lower release rate, fouling is seen both in the form of islands and in some places, uninterrupted. Figure 6 shows a part of the paint with 3 percent of Zineb on which the moss is formed uninterruptedly.

As it is seen in figure 7, fouling is seen in the form of islands on all samples.

During the studies that were done, the amount of fouling in paints in which boosting biocides were not utilized, regarding the paints with ZnO, the critical amount of the release of the zinc element to stop the fouling is approximately between 15 and 20 µg/cm^2 per day; and in paints were the combination CuO was utilized as the deterrent against fouling, the critical amount of the release rate was between 10 and 15 µg/cm^2 per day. Figure 8 shows this range for antifouling paints with cooper-oxide [6, 10].

The paint manufactured in this experiment has zinc-oxide together with boosting elements. As it was previously explained and based on the daily observations, it was seen fouling on the sample with 3 percent Zineb after 20 days of immersion was in some parts interrupted and in the process of the formation of small islands of moss. This happened after 24 days in the paint with 3 percent of Ziram. With regard to the diagrams of release rate in relation with time (figures 9 and 10), the critical amount of release rate in fouling is reached. The critical amounts of release rate for the manufactured antifouling paints are presented in table 11. Regarding the amounts that were reached, it is observed that the antifouling capacity of the paints with the two boosting toxins Zineb and Ziram in lower amounts of release rate is more than the other manufactured paints.

Figure 6: Fouling in an uninterrupted way on the antifouling paint sample with 3 percent Zineb

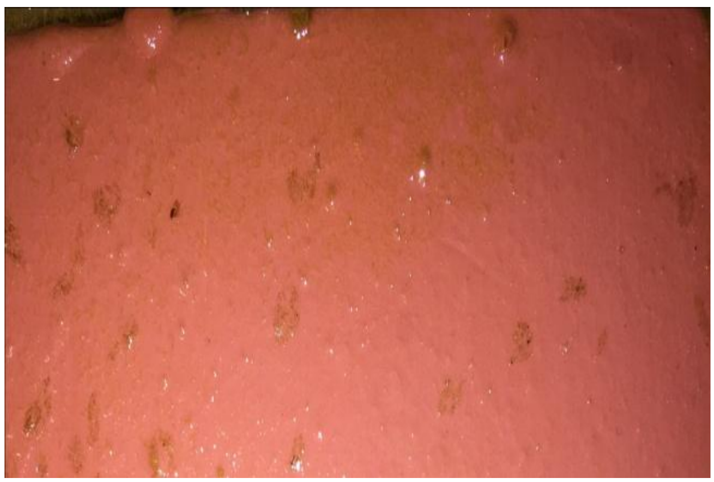

Figure 7: Fouling in the form of islands on antifouling paints with 6 percent Zineb and Ziram after 59 days of immersion in sea water

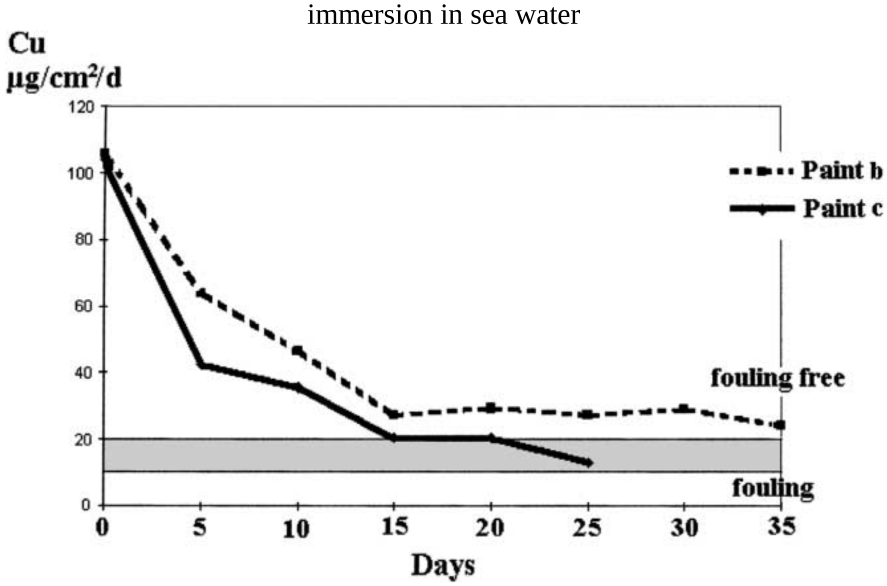

Figure 8: Release rate of antifouling paints with copper in a 35 days period [6]

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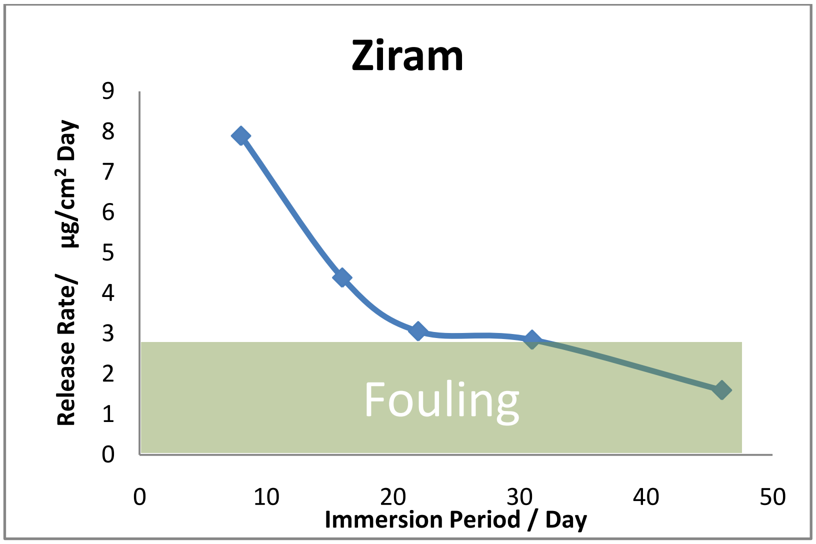

Figure 9: Release rate of antifouling paint with the boosting toxin Ziram

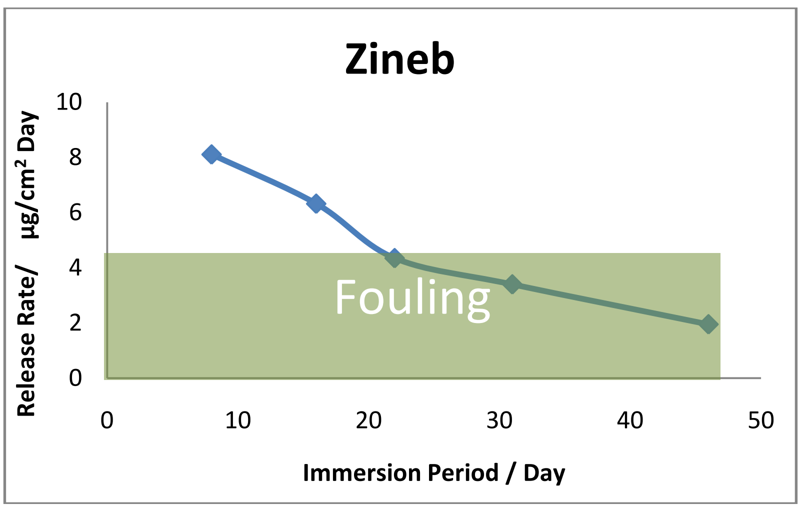

Figure 10: Release rate of antifouling paint with the boosting toxin Zineb

Table 1: Critical release rate for fouling

Antifouling paint	Critical release rate µg/cm^{2}day
Antifouling paint with Zineb	4
Antifouling paint with Ziram	3

Therefore, it is deducted that the amount of biocide release in the manufactured antifouling paints is an optimized amount and by minimizing the release rate, the most effect on fouling is observed.

B: Impact of fouling (bio-layer) on release rate of biocides

Based on the studies done in relation with the growth of the bio-layer on the release rate of the biocide, whenever the thickness of the formed bio-layer increases, the release rate decreases. As it is observed in figure 11, with the increase of the thickness of bio-layer, whose formation time depends on the type of toxin and rosin, the release rate also decreases [8].

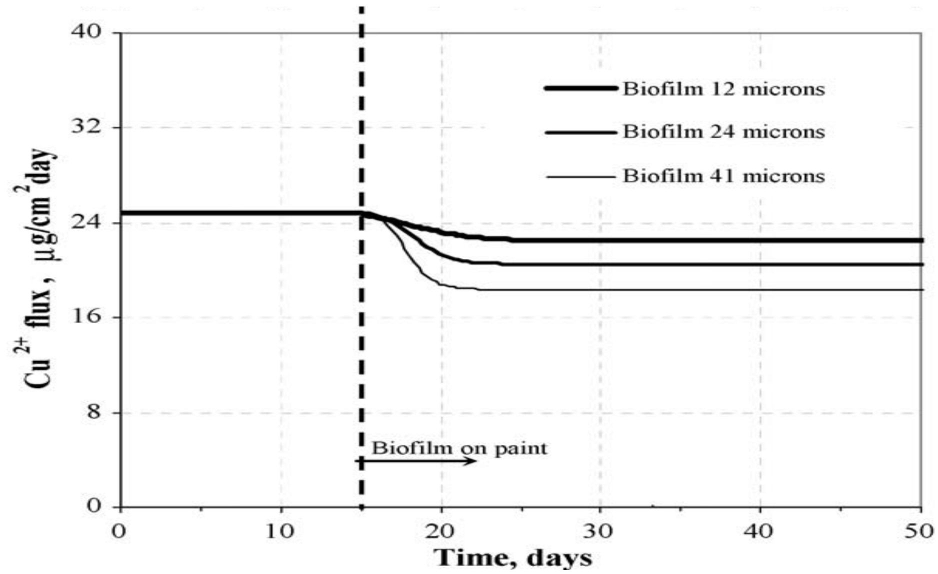

Figure 11: Changes in release rate with the increase in the thickness of the bio-layer [8]

As it is seen in the figure, the toxin used in this paint is copper. But, with regard to the amounts that are reached from the release rate, which is pointed out in table 1, it is only natural that the release rate is formed with the passing of time based on the antifouling paint mechanism. The increase of the thickness of the leach layer also decreases. Another factor that can be mentioned regarding the reduction of release rate is the formation of the bio-layer on the surface and the increase in its thickness, which leads to a drop in the release rate. With attention to the daily observations of antifouling paints, it is said that the reduction in the release rate of paints with Zineb and Ziram elements in the mentioned days is observed in terms of fouling. This does not mean that the reduction of release rate on its own is related with the formation of the bio-layer, but it increases the possibility that in longer periods of time in contact with antifouling paints, the formation of the bio-layer on the surface has a direct impact on the release rate.

Conclusion

By analyzing the release rate of the manufactured paints, it is observed that the release rate of both types of paint is a maximum amount at first, then, in time it drops. Some reasons can be cited for this drop:

- With regard to the mechanism of the manufactured paint which is based on layer by layer liquidation and to release biocides in the water at first the diffusion of water ions to the paint matrix and then, chemical reaction and eventually release are needed, it is evident that because of the layer by layer liquidation and the placement of the pigments in the paint matrix (different layers) the release of the biocide is done in a staged way and the synthetic of the liquidation of the primary layers is done quicker than the next layers because of the reduction of diffusion which is followed by the drop in the release rate.
- By analyzing the leach layer of the paint, the notion that with the increase in the thickness of this layer, release rate decreases and because of that, in choosing the paint rosin as the liquidating matrix, it must be noted that the amount of the diffusion of the sea water ions in the paint and the diffusion of pigments must be quicker than the balance of the liquid-solid phase in this layer is discussed.
- The mutual impact of fouling and release rate is notable in a way that by increasing the thickness of the bio-layer, the release rate drops and on the other hand, with the increase in the release rate, the bio-layer's thickness increases. Therefore, in a certain range of release rate, fouling and bio-layer are observed.

  With regard to the boosting biocides that were chosen in this test, the manufactured antifouling paints showed a high antifouling capacity in much lower release rates in comparison with the states in which these biocide is not utilized, which is a desirable result in terms of optimizing the release rate.

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