Proceedings of the 2006 IASME/WSEAS International Conference on Energy & Environmental Systems, Chalkida, Greece, May 8-10, 2006 (pp254-256)

STUDY OF AN ENVIRONMENTALLY FRIENDLY ANTIFOULING COATING FOR FISH CAGE NETS

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Abstract: - In the present work we have studied the synthesis of a suitable water dispersion organic coating that provides antifouling protection to fish cage nets. In the optimized formula we used a water based wax emulsion with lower VOC than other binders like acrylic or alkyd resins. Cu_2O was the main antifouling pigment in all our synthesis but it was used in lower concentrations than in other commercial products. Furthermore other oxides, as well as some additives, were mixed in order to achieve the desired technological properties of our coating.

Key-Words: - Antifouling, coatings, biofouling, fish cages, wax emulsion, Cu_2O

1 Introduction

It is known that nets made from materials like nylon are used widely in the manufacture of fish cages. In marine water environment thousands of form types of life such as plankton, shells, clams, algae etc exist. These organisms are attached onto the surface of the fish cages or other marine constructions, causing biological pollution known as biofouling, which creates the following problems:

- The complete cover of the fish cage holes, which results to the death of fish due to the insufficient quantity of oxygen.
- The loss of operational capacity of nets and the time-consuming procedure for cleaning and resetting in the marine environment.

2 Problem Formulation

Organic coatings, known as antifouling, are used for confronting the problems that arise from the accumulation of biological organisms on the fish cages. Cu_2O, ZnO, organotin compounds and particularly the TBTs (compounds that are limited due to their toxicity) are usually used as active pigments in antifouling coatings. The use of organometallic compounds of tin is prohibited from 2003 in the European Union. Currently, a lot of antifouling products are not allowed in the European Union market.

Copper is considered as one of the most suitable biocides and has been used through time in coatings for the prevention of fouling of ship's hull [1]. Today is the most widely used biocide for the confrontation of biofouling. When we use copper as biocide, we have to pay particular attention at its release rate, as Cu^{+2} is a heavy metal which in big concentrations can cause health problems to the marine organisms and human beings.

Apart from copper, a lot of chemical compounds are utilised for the formulation of antifouling coatings. The binder (acrylic and alkyd resins) is the most important component and is used in a percentage 20-30%. Acrylic and alkyd resins contains volatile organic compounds (VOC) which are not environmentally friendly. Furthermore we have to use some other chemical compounds like white spirit, NH_3, hexaphosphate, a wetting agent, a degassing additive etc, in order to achieve the desirable technological characteristics and properties.

3 Problem Solution

Our effort was focused on the production of an environmentally friendlier antifouling coating. We thus made an effort to replace the resins which are used as a binder, with a material of a lower VOC concentration. Moreover we attempted to decrease the initial percentage of Cu_2O in our synthesis, maintaining a satisfactory release rate of Cu^{+2}.

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3.1 Experimental

After having tested a lot of different laboratory products, we worked out an optimized formula with a total amount of water of 75%. This final product is constituted of 60% water, 25% water based wax emulsion as binder (content 60% in water), 11% of Cu_2O as the main antifouling pigment, 4% of other oxides and additives. After each synthesis the product viscosity was calculated by the DIN Cup 4 method, according to ELOT 389-1982 [2]. Pieces of net were covered with the antifouling coatings in order to study the technological characteristics such as coverage, drying time etc. In order to determine the release rate of Cu, pieces of net were covered with our synthesis and with a known commercial product as reference, and finally were immersed into tanks containing 10L of marine water for an interval of 49 days. Every seven days we received sample of marine water and measured its concentration in Cu with Atomic Absorption Spectrophotometry [3].

3.2 Results and discussion

The conclusions regarding the study of the technological characteristics are presented hereunder:

Our product is compatible with nylon, has very good adhesion and complete impregnation of net was achieved.

The rheological behaviour of our product is very good and its viscosity is 12 sec.

The elasticity of the net covered with our product resembles that of the commercial product.

The drying time (1h and 15min) of our product is satisfactory and better than that of the commercial product (1h and 30min).

The covering consumption of our product reaches to 43% of the net weight.

The concentration of Cu^{+2} ions vs. time that were released in marine water for the interval of 49 days appears in Table 1.

Table 1: Cu^{+2} concentration (ppm) released in marine water at predefined time intervals (days)

Days	Cu^{+2} (ppm)	
	Our Product	Commercial Product
7th	1,11	1,01
14th	1,31	1,48
21th	1,39	1,48
28th	1,48	1,50
35th	1,51	1,55
42th	1,60	1,66
49th	1,65	1,78

In Fig. 1 depicts the % release rate of Cu_2O of our product and the commercial product vs. time. Observing the curves we note similar form, something which means that the binder (water based wax emulsion) that was used in our synthesis is suitable and has a better rate, releasing less copper in the marine environment.

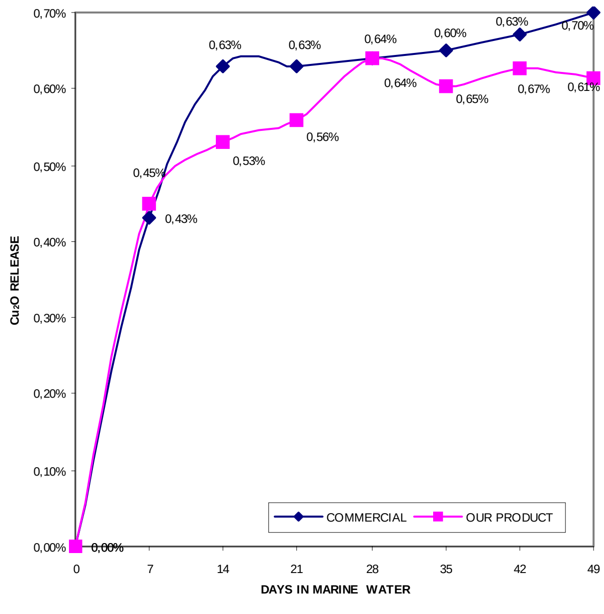

Fig. 1: Cu_2O release (%) vs. time (days)

The average release rate of Cu^{+2} in marine water was calculated as an evaluation criterion of the antifouling products. The average release rate expressed as copper weight per unit of antifouling product weight and per day. Similar results were found, **0,15mg Cu^{+2}/g.day** and **0,17mg Cu^{+2}/g.day** for our product and for the commercial product respectively. In a previous work of our group the average release rate of Cu^{+2}, of an antifouling product with acrylic resin as binder, was calculated at **0,25mg Cu^{+2}/g.day** [4]. According to bibliographic data the toxic limit of copper for the fishes is **0,01-1,7 ppm.** In marine water only 1% of the total Cu is biologically active (in ionic form), while the rest of it is in a complex form [5], [6]. Based on the above concession, it is calculated that the biologically active copper in our closed system will be 0,0211ppm. However, in real conditions of open marine environment, it is appreciated that the concentration of biologically active Cu from our product will be much lower than the toxicity limit for the fishes.

4 Conclusion

We synthesised an antifouling coating, decreasing the amount of Cu_2O at 11%. In most commercial products, as well as in our previous synthesis the percentage of Cu_2O was 16-24%. By using the wax emulsion as binder, it was not required to add chemical compounds like White Spirit, NH_3, hexaphosphate, wetting agent, degassing additive etc, in order to acquire the desirable technological properties of the final product, something that is necessary when acrylic resins are used. Finally our product was tested in real conditions of a fish farm in the open sea and gave satisfactory results regarding the time interval of operation (8 months).

Concluding we would like to mention that the antifouling coating that we have developed depicts the following advantages:

- The system is an aqueous emulsion, with lower VOC (~2%) than the acrylic resins (~10%), friendly to the environment
- The wax emulsion is friendlier to the environment, with a better release rate of Cu^{+2} from the active pigment when compared to the acrylic resin.
- It shows a satisfactory copper release rate in sea water, which does not exceed the toxicity limit for fish
- It is compatible with the material of the net (nylon)
- It satisfactorily covers the surface of the net, with good adhesion to the surface of the net and good elasticity

In the next stage, our aim is to prepare a repellent antifouling coating, which will not allow the marine organisms to attach onto the surface of the fish cages.

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