Investigation of the resistance of protective coatings to fouling by the mollusk *Dreissena polymorpha*

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**Abstract.** Fouling of hydraulic structures with a wide variety of organisms is a worldwide problem. Fouling organisms not only increase the load on technological equipment, but also contribute to the occurrence of bacterial corrosion, including symbiotic. One of the methods of prevention is the use of anti-fouling coatings. Universal anti-fouling coatings do not exist, since the mechanisms of fouling are different. The main ways to create coatings are a decrease in adhesion or the use of biocidal additives. The authors investigated the mechanisms of fouling of the mollusk *Dreissena polymorpha* in fresh water. For the prevention of mollusk fouling and symbiotic biocorrosion, we analyzed the results of experiments using epoxy coatings containing a biocidal additive (bottoms from aniline production). Based on the experiments, it was concluded that epoxy compositions with biocides for the prevention of fusion of zebra mussel are ineffective. More effective are coatings with low adhesive characteristics, for example, fluoroplastic, but difficult to apply and quite expensive.

1. **Introduction**

The fouling of hydraulic structures by the mollusk *Dreissena polymorpha* has been known since the 19th century. The manifold increase in the scale of hydraulic engineering in the 20th century led to an aggravation of this problem, which even now remains unresolved.

The most critical is the mollusk damage to the structures during the operation of the hydroelectric station. At the stations of the Volga-Kama cascade, the first difficulties in the operation of the equipment caused by the overgrowth of zebra mussel were noted as far back as 1958.

Fouling of the zebra mussel surface of hydraulic structures leads to a decrease in performance or a complete failure of the equipment for technical water supply systems. In addition, the presence of fusion of zebra mussel creates favorable conditions for the life of microflora, causing biocorrosion, which accelerates the corrosion processes of structural materials several times [1].

At hydroelectric power stations, external non-draining surfaces of hydraulic structures, water conduits, filters, covers and tube sheets of heat exchangers are most prone to fouling of zebra mussel (figure 1) [2, 3].
The main method for preventing surface fouling at present is the use of anti-fouling coatings, the effect of which is based on the gradual release of certain types of toxins from the coating into the water, which should lead to the death of fouling organisms. But, as practice shows, universal anti-fouling coatings do not currently exist. On the other hand, many antifouling coatings are so toxic that they harm not only fouling organisms, but also all inhabitants of the water area, which is unacceptable [4].

One of the methods that can significantly reduce the ability of the mollusk to attach to the surface of the equipment is the method of reducing the adhesive properties of surfaces subject to fouling. But for the implementation of this method, it is necessary to have a clear understanding of the mechanism of fixation and fouling of the mussel Dreissen on various surfaces [5, 6].

2. Experimental part

To assess the effectiveness of antifouling coatings, field studies of epoxy compositions based on ED-20 epoxy resin were carried out with addition of bottoms of aniline production (BAP), as a biocide and WG-Weleforce LS control coatings manufactured by Velesgard LLC, which also represents a two-component thick-layer epoxy coating [7, 8].

Individual compounds within the composition of BAP, capable of reacting with the functional groups of the epoxy resin to form polymers, and can also exhibit biocidal properties.

The biocide content in the coating was 20-70% by weight of the ED20 epoxy resin (table 1). KPA content varied in increments of 10%. (BodytextIndented style).

| Coating component                  | Content, % mass. by weight of polymer | Functional purpose       |
|------------------------------------|--------------------------------------|--------------------------|
| Epoxy resin ED20                   | 100                                  | Basis of composition     |
| Dioctyl phthalate                  | 20                                   | Plasticizer              |
| Polyethylene polyamide             | 10                                   | Hardener                 |
| Bottoms of production of aniline   | 20-70                                | Biocide (Toxin)          |

The tests were carried out in the area of the Volga hydroelectric power station in the waters of the Volgograd reservoir. For testing, a stand for the installation of samples was designed and manufactured. Coating samples were made of structural steel. Testing of the samples was carried out in the zone of complete immersion at a depth of 2-2.5 m.
3. Results
Regardless of the content of BPA in the composition of the protective coatings on their surface corrosion was observed. Moreover, in the places of formation of colonies of Dreissena there was always a microbial film.

Analysis of corrosion changes in samples (microscopy and visual examination of corrosion products) indicate the presence of thionic and nitrifying bacteria, iron bacteria, and nitrogen fixers in the bacterial film (figure 2) [9, 10].

![Figure 2](image)

**Figure 2.** Appearance of samples of epoxy coatings with BPA after field tests: a) 30% BPA; b) 50% BPA; c) 60% BPA; d) 40% BPA; e) 20% BPA; f) 70% BPA

On samples containing BPA, zebra mussel colonies were more numerous than on epoxy coatings without additives (pure ED20 and WG-Weleforce LS).

Therefore, bottoms of aniline production are not toxic to zebra mussel, or are toxic, but they do not sweat on the surface of the coating. Presumably, this can be explained by the following reasons: bottoms of aniline production are “eaten up” by a microbiocenosis that lives on the coating surfaces and appears in the first hours after immersion of coated plates in water (a bacterial film is observed less than 2 hours after immersion of the samples). Among the bacteria that make up the microbiocenosis of water and settle on the coatings, there are species that decompose organic substances, including BPA, using aniline as a source of carbon and nitrogen nutrition, thereby neutralizing it. As a result of the activity of such microorganisms, coatings become safe for zebra mussel and other fouling agents [3, 8, 10].

The monitoring also revealed that samples coated with epoxy coatings containing BPA, in addition to biofouling, were subject to biocorrosion. The sample based on the ED-20 epoxy composition without the addition of BPA (figure 3) and the control sample of the WG-Weleforce LS (figure 4) epoxy coating were practically not corroded, and the number of mollusks fixed on these samples was much smaller than on the samples with BPA.
Presumably, this can be explained by the fact that the “pure epoxy composition” is less attractive to microorganisms as a food source. Due to this, the surface of the epoxy coating is smoother, and zebra mussel has less chance of fixing it. Epoxy coatings containing BPA corrode more strongly, since microorganisms settling on it “eat out” BPA particles, forming various mechanical irregularities on the surface of the coating, in which Dreissen is easier to fix mechanically. Dreissena, in turn, creates favorable conditions for other microorganisms that feed on its secretions. These microorganisms are capable of causing further growth of microdamage to the surface of the polymer coating, up to ulcerative corrosion processes, affecting deeper layers until metal is reached. The last stage is water corrosion and biocorrosion of the metal surface of the sample [2, 3, 10].

Thus, zebra mussel contributes to the creation of a complex symbiotic biocenosis that contributes to the destruction of polymer coatings.

The process of surface fouling by the mollusk of zebra mussel can be divided into three stages: subsidence of shells or larvae of the mollusk on the surface, fixing and fouling. It is known that the fixing of the shell of the mollusk of zebra mussel on the surface occurs due to the muscle of the leg, and then the final attachment to the substrate (fouling) is carried out with byssus threads.

Byssus is a substance that is produced by the special (byssus) gland of zebra mussel. By structure, byssus is a natural polymer of protein origin, similar in composition to natural silk. The process of forming a byssus thread occurs in two stages: at first, the substance has the consistency of honey, adheres to stones, concrete, steel and other structural materials, while a special enzyme is secreted by the iron that binds the molecular chains of this protein into a single mass [5, 6, 11].

Due to the absence of corrosion and contrasting coloration, the byssus filaments are clearly visible during microscopic examination of a sample coated with WG-Weleforce LS (figures 5, 6).
Thus, zebra mussel contributes to the creation of a complex symbiotic biocenosis that contributes to the destruction of polymer coatings.

The analysis of the results of the process of fouling of various surfaces by the mollusk of zebra mussel, carried out by employees of the VPI (branch) of Volgograd State Technical University in laboratory and natural conditions, makes it possible to consider the fixation of byssus filaments on a substrate as a process of formation of an adhesive joint. In this case, it can be assumed that the most effective coatings against fouling of zebra mussel will be coatings of hardly bonded materials. Such materials include fluoroplastics having low adhesion properties [11].

4. Findings
Thus, as a result of the studies, it was found that all the tested samples of epoxy coatings are prone to fouling by the mollusk of zebra mussel. The fixation of mussel mussel mussel on a substrate with byssus filaments makes the use of traditional antifouling coatings containing toxic biocides ineffective, since a sufficient concentration of biocide to suppress the vital activity and death of moss moss is found only in a small parietal layer of water. The biocidal additive KPA does not affect the vital activity of bacteria, moreover, it serves as a source of carbon and nitrogen nutrition for bacteria.
The zebra mussel fixed on the byssus threads is quite distant from the substrate and uses water containing non-hazardous concentration of biocide for filtration. Moreover, even with the death of the zebra mussel, its shell remains attached to the substrate and, in turn, serves as the basis for fouling by other zebra mussel.

Overgrowing of zebra mussel due to the growth of some shells on others, both empty and with live zebra mussel, takes the form of a “fur coat”. Biocides contained in anti-fouling coatings have no effect on the strength of curing and physico-mechanical properties of byss.

In the case of biocorrosion and biofouling by the mollusk Dreisena on the technological equipment of the hydroelectric station, we can talk about the symbiosis of mollusks and several groups of bacteria.

Presumably, mutually beneficial cohabitation of organisms is as follows. Microorganisms, causing biocorrosion and changing the surface of the coating or material (it becomes rougher, with numerous injuries, recesses, etc.) prepare the medium for mechanical fixing in these irregularities of the mollusk using a byssus thread. The mollusk, in turn, secreting waste products, creates a food base and environment for the development of other groups of bacteria, and the process of biocorrosion goes further.

The use of fluoroplastic-based coatings gives a greater effect, in which the mollusk is difficult to fix on the surface, but fluoroplastic coatings are quite expensive and have poor adhesion, including to the main structural materials from which the technological equipment of hydraulic structures is made.

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