Biodegradation of filled styrene-acrylic coatings in a laboratory kinetic plant

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Abstract. Styrene-acrylic polymer coatings rank among the most popular materials of the construction industry that protect structures from corrosion. Biocorrosion is considered to be one of quite dangerous and less studied types of destruction. There is a State standard method of testing materials for biostability in which a qualitative assessment of the resistance of coatings to biodegradation is carried out, but still it doesn’t provide the full picture of the destruction degree of the material caused by the biodegradation. Besides, the test duration is 28 days. The most informative and convenient is the kinetic method of research. It includes the applying of the facility involving exposure of coating samples in a solution of carboxylic acids (model medium) which significantly reduces the test period and also eliminates the work with microorganisms. The studies were carried out on styrene-acrylic filled free films. The changes in material was evaluated by quantitative and qualitative indicators: the change in the mass of the initial and exposed samples of free films, their geometric parameters, as well as a visual assessment (using a microscope) of the surface state of the coatings before and after exposure, including the use of the CIELab method. It was found that the level of the determined characteristics of styrene-acrylic free films when exposed in a model medium is reduced by 10-15%.

Key words: styrene-acrylic copolymer, biodamage, biodeterioration modeling, laboratory kinetic methods, simulated medium, paint and lacquer materials, carbonic acid.

1 Introduction
Corrosion of structures is one of the important problems of the construction industry. One of the most technologically advanced and easy methods of protection is the application of paints and varnishes (coatings). Due to the increasing requirements in the field of environmental protection and ecology water-based coatings (water-dispersion, waterborne) get more attention [1-3]. Paints and varnishes based on acrylic and styrene-acrylic copolymers are widely used in the construction industry [4-7].

Paints are known for being exposed to external factors in particular biological corrosion while protecting structures. This problem is widely studied by scientists from different countries [8-11]. For example, the studies on the determination of the biostability of optical glasses [12] and free films [13, 14] based on acrylic polymers and copolymers are widely used. Paint and varnish coatings are a composite material and each its component determines and affects its durability [14, 15]. The adopted regulatory documents for the determination of biological resistance offer only a qualitative assessment which is the determination of biodeterioration by the degree of fouling of the material by colonies of microorganisms [16, 17]. But more emphasis is put on the information on the quantitative changes in the characteristics of the material.
Therefore, one of the urgent tasks for the construction industry is the research of the effect of biodegradation on the qualitative and quantitative indicators of water-dispersed styrene-acrylic paint coatings. The purpose of the article is to study the effect of aqueous solutions of carboxylic acids (metabolites of the vital activity of microorganisms) on styrene-acrylic protective films.

2 Methods

2.1 Obtaining a paint composition

The object of study was the aqueous styrene-acrylic dispersion of brand "Lacroten®": E-21 (production-commercial company OOO "Orgkhimprom") most often used as a binder in polymer protective compositions for construction purposes [17-19]. The fillers in the formula of the paint composition were kaolin, microtalc, chalk, wollastonite and titanium dioxide as well as functional additives such as dispersant, antifoam, coalescent, thickener.

The preparation of the paint and varnish composition was carried out on a dissolver according to the method [20, 21] which consists of the following steps:
- dry components were mixed in predetermined proportions at the beginning, then distilled water and functional additives were added;
- the mass was placed in a dissolver and mixed at a speed of n = 2000 rpm for 30 minutes to obtain a pigment paste;
- the obtained paste was mixed with styrene-acrylic film agent in a ratio of 1: 0.5 (pigment paste: film agent).

The mixing (~30 min.) didn’t stop until a homogeneous composition that did not contain aggregates and air bubbles was obtained.

2.2 Characterization of free paint films

The identification of changes in the quality indicators of coatings was carried out using compositions deposited on stainless steel plates and free films.

The study of water absorption of control samples of coatings was carried out according to GOST 21513-76. The pre-weighed non-rusting steel plates were coated with the obtained paint composition. After the polymer coating induration the weighing was carried out again and then the plates were placed at a distance of 10 mm from each other (in a suspended state) on stainless steel hooks in a container filled with distilled water at a temperature of (20 ± 2) °C. Air bubbles formed on the surface of the sample during the immersion were removed with a brush (within 0.5-1 hours). After 24 hours of exposure the plates were removed from the container, dried with filter paper, immersed in a pre-weighed bottle and then the bottle was covered with a lid and weighed. The value of water absorption was calculated by the equation (1):

\[ W = \frac{m_2 - m_1}{m_1 - m_0} \cdot 100\% \tag{1} \]

\( m_0 \) – plate weight, g;

\( m_1 \) – coated plate weight before test, g;

\( m_2 \) – coated mass after the test, according to the difference between the masses of the plate with wax and the mass of wax, g.

The arithmetic mean of three parallel determinations of \( W \) was taken as the test result, the permissible differences between them did not exceed 10% in terms of the calculated average water absorption result.

Free films were obtained by laying a paint and varnish composition on a fluoroplastic substrate (coating formation time up to 7 days at (20 ± 2) °C) and controlling their formation by changing the state of the surface to “stick” and then removing the films.

The aggressive environment is known for affecting the change in the geometric dimensions of film samples. In this regard, before the exposure the linear dimensions and thickness of the free films were identified using a Condrlt CoF (FN) device that operates on the principle of magnetic induction.
The possible microcracks and defects on the surface of paint coatings were spotted using an M10M light microscope (magnification x280).

The color characteristics of free films were changed according to GOST 52490-2005, using the CIELab system widely used for polymer materials [22-25]. In the graphic light model “lightness” is specified by the L coordinate and the chromatic component of the color is specified by the two Cartesian coordinates a and b. The elaboration of the data obtained when measuring the coordinate data of the comparison samples and the tested coatings and subsequent calculation of the parameters of the difference in their color characteristics was carried out according to the formulas (2-9):

- total color difference:

\[
\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}
\]  

(2)

\[
\Delta L^* = L_T^* - L_R^*
\]  

(3)

\[
\Delta a^* = a_T^* - a_R^*
\]  

(4)

\[
\Delta b^* = b_T^* - b_R^*
\]  

(5)

\[
\Delta L_{ab}^*, \Delta a_{ab}^*, \Delta b_{ab}^* - color coordinates of the test sample;
\]

\[
\Delta L_R^*, \Delta a_R^*, \Delta b_R^* - color coordinates of the comparison sample.
\]

- color purity differences:

\[
\Delta C_{ab}^* = C_{ab,T}^* - C_{ab,R}^*
\]  

(6)

\[
\Delta C_{ab,T}^* = (a_T^{*2} + b_T^{*2})^{1/2}
\]  

(7)

\[
\Delta C_{ab,R}^* = (a_R^{*2} + b_R^{*2})^{1/2}
\]  

(8)

\[
\Delta C_{ab,T}^* - color purity for the test sample;
\]

\[
\Delta C_{ab,R}^* - color purity for comparison sample.
\]

- differences in color tone:

\[
\Delta H_{ab}^* = k_H\{(\Delta E_{ab}^*)^2 - (\Delta L_{ab}^*)^2 - (\Delta C_{ab}^*)^2\}^{1/2}
\]  

(9)

\[
k_H = +1 \text{ for } (a_R^* b_T^* - a_T^* b_R^*) \geq 0,
\]

\[
k_H = -1 \text{ for } (a_R^* b_T^* - a_T^* b_R^*) < 0.
\]

2.3 Testing in model media

The biostability of coatings was tested in a laboratory kinetic plant [26]. The tests were carried out for 8 days at an ambient temperature of 40±2 °C, which according to the Van't Hoff rule is equivalent to 28 days at 20±2 °C through the automatic control of the main parameters of the medium - temperature and pH (3.45).

The laboratory plant [27] consists of a test vessel in which the test samples are immersed in the simulated medium, a support, drain tank and also a measuring tank for determining the pH of the simulated medium and calibration of the pH electrode, an electronic control unit that measure pH, temperature of the simulated medium and maintaining them at a given level.

A mixture of carboxylic acids was used as a simulated medium: acetic, oxalic, malic and citric acids, they were chosen due to their presence in the metabolites of bacteria isolated in public and residential buildings [28, 29].

3 Results and discussion

It is known [30, 31] that one of the stages during the exposure in liquid medium is sorption. In this regard the water absorption coefficient of free films was determined and it amounted to 6% which is an acceptable value for coatings based on acrylic copolymers [20, 30, 32].

In order to carry out the experiment 4 samples of free films were prepared in which the initial geometric dimensions, thickness and mass were evaluated (table 1), and the surface appearance was recorded (figure 1).

A visual examination of the surface of coatings (samples of free films) revealed the absence of defects (microcracks) in them, as well as the smooth distribution of the composition components in volume and the absence of aggregates which excludes the possibility of obtaining incorrect results.
Table 1. Initial characteristics of free films.

| Parameter name | Sample number |
|----------------|---------------|
|                | 1  | 2  | 3  | 4  |
| Weight, g      | 0.161 | 0.181 | 0.182 | 0.179 |
| Thickness, mm  | 136 | 123 | 130 | 166 |
| Length, mm     | 47  | 47  | 47  | 47  |
| Width, mm      | 15  | 15  | 15  | 15  |

Figure 1. The surface of the original samples of free films (magnification ×280).

After the exposure of the samples in a laboratory kinetic plant it was established (table 2) that the influence of the model medium causes a change in the geometric dimensions of free films by ~ 12%, thickness by ~ 14%, and the average weight loss was ~ 36%. Besides, a comparative analysis of the mass samples after exposure and drying, showed an increase in the absorption of the solution by an additional 7%, and in total with the value of the rate of water absorption it ended up at 14%.

Table 2. Characteristics of Exposed Free Films.

| Parameter name | Sample number |
|----------------|---------------|
|                | 1  | 2  | 3  | 4  |
| Weight, g:     |    |    |    |    |
| - after exposure | 0.11 | 0.128 | 0.138 | 0.129 |
| - after drying  | 0.097 | 0.111 | 0.116 | 0.112 |
| Thickness, mm  | 121 | 117 | 113 | 133 |
| Length, mm     | 44  | 45  | 45  | 45  |
| Width, mm      | 14  | 14  | 14  | 14  |

It is known [20, 32] that the film agent is the main component that largely determines the biostability of the polymer composite. It may be estimated indirectly through the indicators of water absorption, chemical structure and hardness. The action of the simulated medium can contribute to the enlargement of mineral particles and their partial leaching from the bulk of the film, this is indirectly confirmed by microphotographic images of their surface (figure 2) and mass after exposure (table 2). In addition, the impact of the mixture of acids may lead to the chemical degradation and oxidation of the film agent [33, 34] which cause a change in the color of free films (figure 3a) in favor of the yellow tones (figure 3b).

Figure 2. The surface of exposed free films in a simulated medium (magnification ×280).
One of the quality indicators of polymer coatings during their destruction is color. In this regard, a calculation was made to determine the change in the color characteristics of the exposed films. It is the calculation of following indicators: lightness ($\Delta L^*$), color purity ($\Delta C_{ab}^*$), color tone ($\Delta H_{ab}^*$) and full color difference ($\Delta E_{ab}^*$). In this regard, it was necessary to determine the color coordinates of the original and exposed samples according to the chromaticity coordinates (table 3). In the graphic light model lightness is specified by the L coordinate, and the chromatic component of the color is specified by the two Cartesian coordinates a and b (figure 4).

| Sample Number | Coordinate value | | |
|---------------|------------------|---|---|
|               | L base values | a | b |
| 1             | 96 | 2 | 4 |
| 2             | 97 | 2 | 4 |
| 3             | 97 | 1 | 3 |
| 4             | 97 | 2 | 4 |
|               | values after exposure | | |
| 1             | 94 | 5 | 11 |
| 2             | 96 | 4 | 9 |
| 3             | 94 | 4 | 11 |
| 4             | 92 | 2 | 12 |
When analyzing the results of calculations (table 4), it was found that exposure of samples in the simulated medium contributes to the destruction of the film agent. The significant change in the Δb* parameter represented by the shift in the color coordinate towards yellow tones indicates the chemical aging processes of the styrene component of the binder [35-37]. In addition, there is a change (up to 10%) in the indicators of color purity and color tone. However, in general, exposure in a simulated medium at 40 °C for 8 days does not significantly affect the color characteristics of free films.

| Table 4. The results of calculating the parameters of the difference in color characteristics. |
|---------------------------------------------------------------|
| Sample Number | ΔL* | Δa* | Δb* | ΔE* | ΔC* | ΔH* |
|----------------|-----|-----|-----|-----|-----|-----|
| 1              | -2  | 3   | 7   | 7.87| 7.61| 0.27|
| 2              | -1  | 2   | 5   | 5.47| 5.37| 0.30|
| 3              | -3  | 3   | 8   | 9.05| 8.54|-0.16|
| 4              | -5  | 0   | 8   | 9.43| 7.69| 2.19|

It should be noted that during testing samples in a 4-acid simulated medium, a slight change in the color characteristics of coatings occurs due to chemical degradation of the film agent, and in the aqueous medium the level of intermolecular interactions between the filler particles and the polymer matrix is weakened which contributes to the process of aggregation and their partial washing out of film volume. Therefore the result indicates a loss of ~ 10-15% of the physic-mechanical properties of the films.

4 Conclusion
In summing up, it was found that the exposure of the styrene-acrylic coatings in a laboratory kinetic plant causes a change in their structure: the enlargement and leaching of mineral components occur (decrease in the level of film reinforcement) confirmed by the microphotographic images of the surface and the decrease in the mass of coatings. In addition, during the washing out of the solid particles an increase in the elasticity of free films is observed, which is caused by the sorption of water and the destruction of the network of physical bonds between the film agent and the filler.

It is shown that the simulated medium, which is a mixture of carboxylic acids, promotes the degradation of the film agent which manifests itself in a change in the color characteristics of the coatings, as it is evidenced by the shift in the color coordinate (b) towards the yellow tones.

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