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Resistance of decorative epoxy composites to sea climate

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Abstract:

The object of research is composite materials based on an epoxy binder with various pigments. The purpose of the research is to substantiate the proposed methodology for analyzing the colour change of protective coatings and to evaluate the decorative properties of epoxy composites used in marine climate conditions. **Method.** The studied composites were aged in natural and climatic conditions in the coastal strip of the Black Sea of the city of Gelendzhik (Russia) in an open area and under a canopy. Samples were scanned at control points. The resulting images were processed in a software package based on the use of the RGB colometric system, using the compiled C# programming language on the platform .NET. **Results.** As a result of the tests carried out, the dependences of changes in the RGB codes of composites were established. The compositions most resistant to colour degradation were determined, which are affected by aggressive factors, such as high humidity, ultraviolet radiation, salt fog, precipitation and seasonal temperature fluctuations.

1 Introduction

One of the main directions in modern materials science is the creation of composite materials. Polymers play a leading role due to the highest values of specific indicators of strength, stiffness, and other properties [1-3]. The increased interest in composite polymeric materials (composites) is because they help to increase reliability service life, reduce material consumption and improve other important parameters of products, assemblies, devices, thereby causing the development of scientific and technological progress in construction, mechanical engineering, aerospace and other industries [3-8]. In the construction industry, polymer composite materials are widely used as floor coverings, structural finishes, waterproofing and sealing, anti-corrosion materials, and for many other purposes. Depending on the functional purpose, such materials include frame polymer concrete floors, mastic and paint coatings. They provide reliable protection of buildings and structures when exposed to positive and negative temperatures, high humidity, seasonal temperature fluctuations, precipitation, biological chemical aggressive factors [2],[9-11]. In addition to protective properties, polymer compositions (varnish, mastic, putty) act as decorative coatings, giving structures and the building as a whole a greater aesthetic expressiveness. At the same time, the technology for installing these coatings is quite laborious, which leads to an increase in the period of work and their cost. The study of the change or preservation of the original colour of the surface of protective coatings, along with an increase in their strength properties and durability, is an important task [9],[12],[13]. The creation of coatings that are more resistant to the preservation of the appearance leads to a decrease in labor costs and the cost of current repairs to restore finishing materials during the operational life of structures and the building as a whole. Thus, the issues of increasing their durability and resistance, researching changes in decorative properties to various factors during operation are of great importance.

During operation, protective polymer coatings are exposed to heat, sunlight, moisture, oxygen and other climatic factors, causing the aging of materials [9],[14]. The ageing of paint and varnish polymer materials is a combination of physical and chemical processes occurring in polymers, leading to changes in their composition, structure, and colour characteristics under the influence of various factors [15-17]. Increased temperatures and solar radiation contribute to the acceleration of the aging of polymer materials. The latter in turn, is the most negative factor affecting the decorative properties of composites [18]. The combination of aggressive factors significantly depends on the climatic zone, and their effect is unstable during the operation time [19]. Long-term field tests make it possible to assess the intensity of destruction of polymer composites and identify the most resistant decorative compounds.

To analyze the colour of paintwork materials, visual determination, comparison with a control sample (standard), quantitative measurement, and numerical expression [9]. These methods for analyzing decorative properties require some assumptions [20]. Firstly, the expert who conducts the test must have an undistorted colour perception, upon reaching a certain age (over 40 years old) he must pass certain tests to confirm his qualifications. Secondly, eye fatigue should not be allowed when comparing colour, which leads to a decrease in work productivity. Thirdly, it is necessary to have special instruments (spectrocolorimeters) for the quantitative measurement of decorative properties. In addition, color is a characteristic that represents the highest subjectivity since it is directly related to the psychophysical sensitivity of the observer [21].

The use of simulated computer systems to assess the degradation of surface colour due to exposure to aggressive factors makes it possible to simplify the analysis of decorative properties and eliminate the human factor during the study [20],[22-24].

Quantitative assessment of the weatherability of coatings can be carried out under artificially created and natural conditions. In laboratory conditions, it is difficult to simulate the whole complex of natural and climatic factors affecting building materials, products and structures during their operation. We have conducted empirical studies of colour changes in epoxy composites with various pigments due to holding samples in naturally climatic aggressive environments in Gelendzhik, Krasnodar Krai (Russia). The choice of the area for the experiment is due to the most aggressive impact of the marine climate on building structures. The test site is characterized by temperature regimes that are characteristic of a subtropical climate close to the Mediterranean. Subtropical climatic zones are characterized by the absence of a pronounced seasonal nature of meteorological indicators.

In contrast, the levels of these indicators often significantly exceed similar indicators of a temperate climate. Due to this, the aging processes of polymer materials proceed more intensively, which, in turn, allows developers of new materials to more quickly adjust their prescription composition and achieve the formation of the required operational properties of new materials [9]. The samples were placed in an open-air environment and under the canopy of the Black Sea coast. In this test, aggressive factors were: wind, high humidity, UV radiation, salt fog, biodestructors, precipitation and seasonal temperature fluctuations.

Purpose and objectives of research

The purpose of the research is to substantiate the proposed methodology for assessing the degradation of the color of protective coatings and to study the durability of epoxy composites in unfavorable aggressive environments.

Research objectives:

1. To substantiate the practicality of applying the methodology for assessing the degradation of the colour of decorative protective coatings.
2. To evaluate the influence of natural and climatic factors on the colour change of decorative composites when kept in the air environment of the Black Sea coast for a long time.
3. To consider the average values of RGB codes as controlled indicators.
4. To establish the effect of various pigments on the durability of decorative epoxy composites operated in a humid maritime climate.
5. To identify the compositions most resistant to colour degradation, which are under the influence of aggressive factors of the marine climate.

2 Materials and Methods

Studies of epoxy composites of various compositions were carried out to assess the atmospheric resistance of polymeric materials. As a binder, epoxy-diane resin of the ED-20 brand (manufactured in Russia, Dzerzhinsk) was used. Polyethylene polyamine was used in the compositions as a hardener.

The following pigments were considered as a colouring component: black S722 (Shanghai Yipin International Pigments CO LTD, China); green S5605 (Shanghai Yipin International Pigments CO LTD, China); yellow iron oxide Fepren Y-710 ocher (Precolor A.S., Czech Republic); 960 synthetic blue (ITKOR LLC, Kirov, Russia); red iron oxide (Jarkhiminvest LLC, Yaroslavl, Russia); lead crowns (LLC Yarkhiminvest, Yaroslavl, Russia). Experimental formulations are shown in Table 1.

Table 1. The content of components in the studied compositions

№ composition	The content of components, mass fraction		Pigment	Pigment content by hiding power, in % of resin weight
	epoxy resin ED-20	polyethylenepolyamine PEPA		
1	100	10	960 синий	49.3
2			yellow iron oxide Fepren Y-710	25.0
3			red iron oxide	29.5
4			lead crowns	41.8
5			green S5605	20.4
6			black S722	16.7

The analysis of colour change was carried out in a software package designed to assess changes in the decorative properties of composite materials, which is operated under the influence of physical, chemical, biological and climatic factors [22]. The method of working with this program consists in the initial scanning (or photographing) of the sample surface before and after exposure to aggressive environments to obtain a digital image in *.jpg or *.tif format and its subsequent processing using a simulated complex [22], which is based on the use of the RGB colourimetric system, with the help of the compiled C# programming language on the .NET platform. The results are presented in the form of diagrams (Fig. 1) and histograms (Fig. 2) of the brightness of the RGB codes along the length and width of the image, the geometric characteristics of the colour model, the numerical values of red, green, blue colours, the coefficients of variation and correspondence, the size of the area of the triangle of brightness required to assess the uniformity of the surface colour.

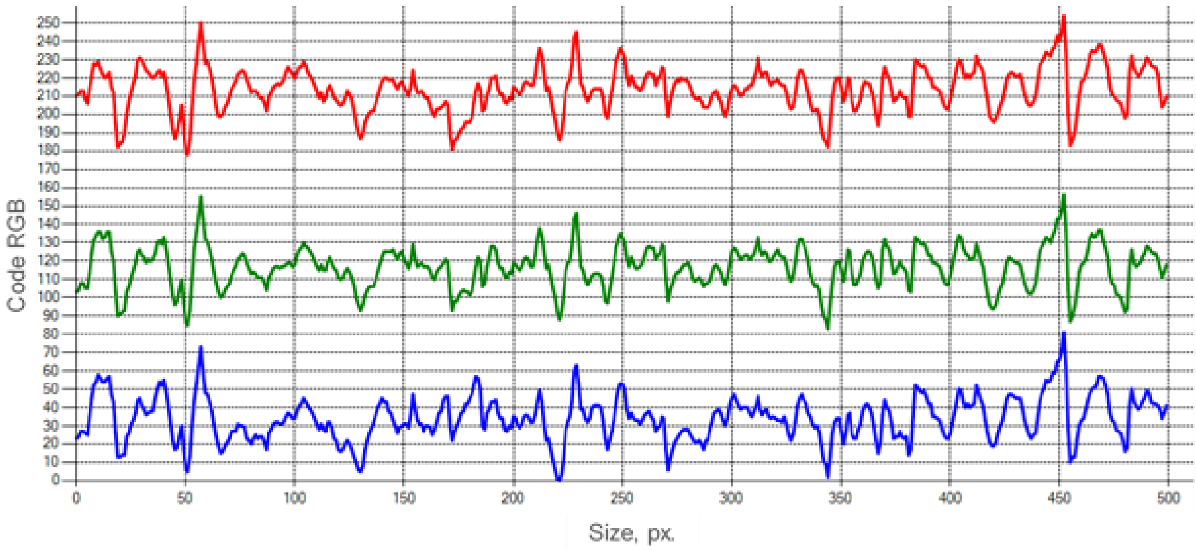

Fig. 1 - Diagram of the increase in RGB codes along the width of the image for the composition with lead crown pigment

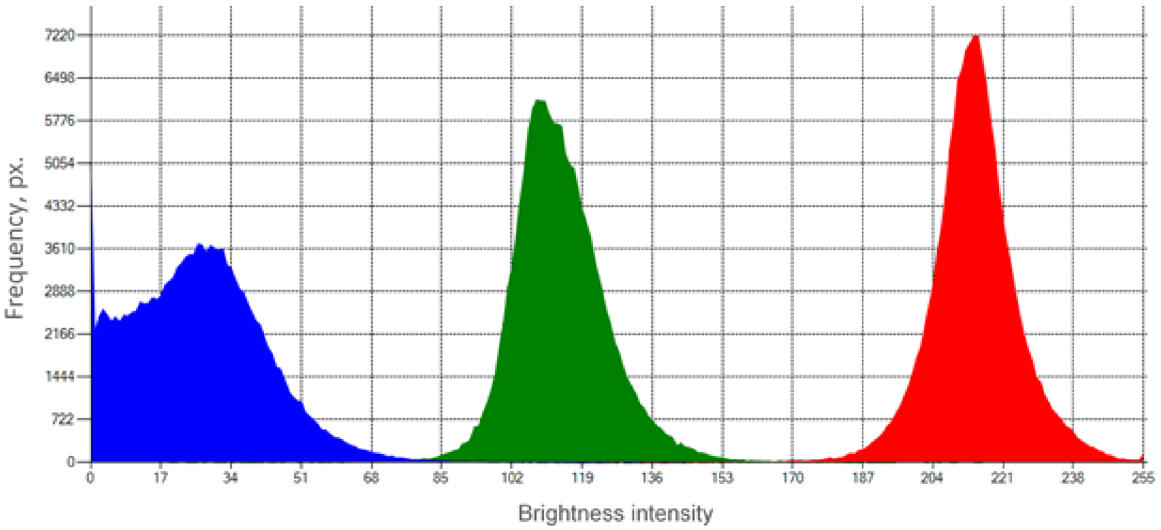

Fig. 2 - Histogram of the brightness of RGB codes for the composition with lead crown pigment

To assess the change in the decorative properties of this building material as a result of exploitation or the influence of an aggressive environment, the experimental procedure was repeated on the same sample. At the same time, the area of analysis of the scanned image is set within the same boundaries as for the original sample. Comparing the values of the colour characteristics of two photos of the model (before and after exposure to the environment), one can judge the visual and quantitative change in the decorative properties of the materials under study.

The use of this technique for assessing the quality of composites by changes in their surface colour can be different. In particular, the salt formation can be detected in cement composites exposed to extreme operating conditions [25]. There are also developments of a reference assessment of the image quality of composite materials [26] and decorative properties of paint coatings [27].

In the conducted studies, to assess the quality of the regression model, a complex regression error (CRE) was used, which takes into account both standard errors and the coefficient of determination. It is proposed to define CRE in the form of the following formulas:

a) if not one of the errors of the radical expression is not equal to zero, then

$$CRE = \sqrt[4]{MaxError \cdot MeanError \cdot RMSE \cdot MedError} + \frac{1}{R^2 + eps}, \quad (1)$$

b) otherwise

$$CRE = \frac{MaxError + MeanError + RMSE + MedError}{4} + \frac{1}{R^2 + eps}, \quad (2)$$

where $MaxError$ is the maximum modulo error, $MeanError$ is the mean modulo error, $RMSE$ (Root Mean Square Error) is the root mean square error, $MedError$ is the median error, R^2 is the coefficient of determination, eps is a preassigned small positive number the order of 10^{-12}.

3 Results and Discussion

The parameters for assessing the change in decorative properties were the average values of the RGB codes. The change in the RGB codes of the surface of paint and varnish coatings on an epoxy binder as a result of keeping the samples in an open area in the coastal zone is shown in Figure 3.

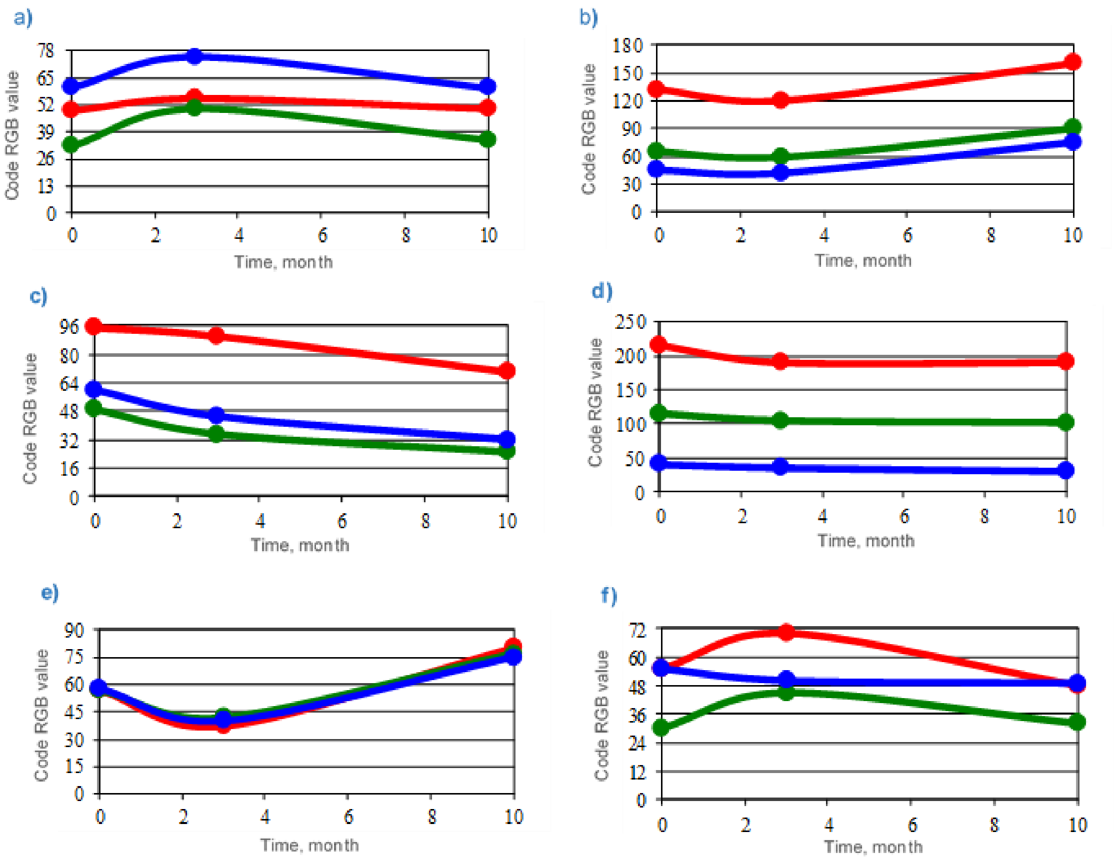

Fig. 3 - Changing the RGB codes of epoxy composites with pigments blue 960 (a), yellow Fepren Y-710 (b), red w/o (c), a lead crown (d), S5605 green (e), S722 black (f), aged on the Black Sea coast in an open area

These changes in the RGB code of the surface of decorative composites with pigment 960 blue (composition No. 1) show an increase in RGB codes for all colour components of the material surface after 3 months of exposure to an aggressive environment. After 10 months, there is a decrease in the red, green, blue codes relative to the previous values obtained after 3 months of exposure (Fig. 3 a).

According to fig. 1 b for composites with the Fepren Y-710 yellow pigment at the first stage of the experiment after 3 months of testing, a slight decrease in the colour components (red, green, blue) relative to the control indicators is characteristic. After 10 months of keeping the samples in an open area, the RGB values of the scanned surface of the given composition increased (Fig. 3b). Lightening of the surface of samples of composition No. 2 as a result of atmospheric influences was visually detected.

The impact of aggressive factors (natural-climatic and bi-destructors) on samples of composition No. 3 with iron oxide red pigment leads to a significant decrease in the values of RGB codes relative to the initial values (Fig. 3c).

Evaluation of the decorative qualities of samples of composition No. 4 with lead crown pigment showed slight changes in the colour of the samples. It is evidenced by the dependences obtained, shown in Fig. 1 g. The difference in the values of RGB codes for colour components is: for red - from 220 to 195; green - from 120 to 105; blue - from 40 to 35 (Fig. 3d).

Analyzing the dependencies of the RGB codes for composition No. 5 (Fig. 3e) as a result of exposure to atmospheric factors, we see that after 3 months of testing, the values of the RGB codes are less than the initial values by 25%. At the next exposure point (after 10 months), the indicators of the colour components increased (Fig. 3e). On visual inspection, a lightening of the surface is observed.

For an epoxy composite with w / o black pigment exposed in an open area, it was established:

a) red and green colour components after 3 months. Aggressive impact increased, and then there was a decrease in these indicators relative to control samples (Fig. 3f);

b) Code B (blue) has had a downward trend throughout.

The experiment revealed that epoxy composites with lead crown pigment are the most resistant in terms of their decorative properties to weathering in an open area. When keeping the samples in an open space on the coast of the Black Sea, the maximum change in the colour of the surface was found in compositions No. 2 and 5. Tests of samples in the open area after 10 months of exposure revealed that ultraviolet radiation leads to color fading of composites stained with iron oxide yellow and green pigments. The surface color of the samples of these compounds has become lighter relative to the original color.

The dependences of the change in the RGB codes of the surface of pigmented epoxy composites as a result of keeping the samples in the coastal zone under a canopy for 2 years are shown in Fig. 4.

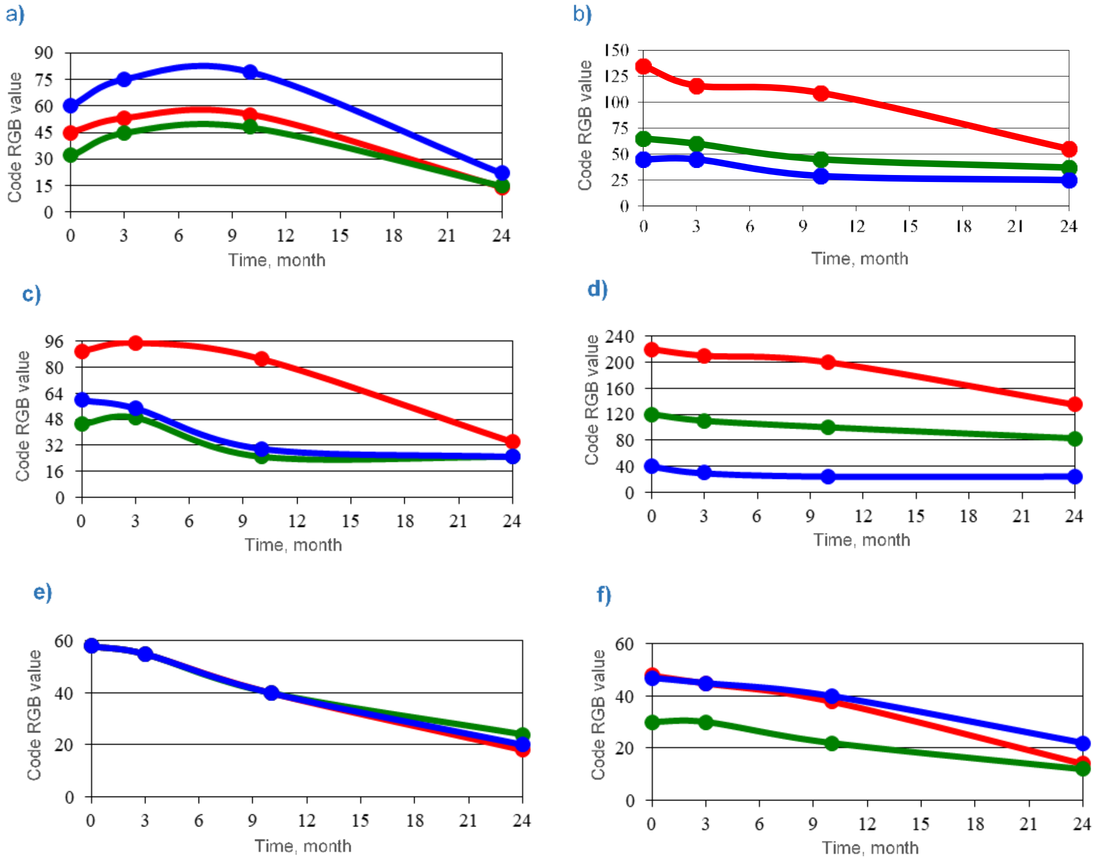

Fig. 4 - Changing the RGB codes of epoxy composites with pigments blue 960 (a), yellow Fepren Y-710 (b), red w/o (c), a lead crown (d), S5605 green (e), S722 black (f), aged on the Black Sea coast under a canopy

When testing samples of decorative purposes under canopies, a general trend was revealed to reduce the values of RGB codes relative to the control (initial) characteristics, this indicates a darkening of the surface colour of the composites as a result of natural and climatic factors, such as wind, temperature and air humidity. Analyzing the changes in the RGB codes for composition No. 1 due to the impact of aggressive factors, we see that after 10 months. Aging, the indicators were taken into account relative to the control samples. However, after 2 years of testing, the colour indicators (RGB codes) decreased and began to vary in the range of values from 13 to 22. Analyzing the RGB codes of the composite with Fepren Y-710 yellow pigment (Fig. 4 b), there is a decrease in the values of all components, a decrease in the importance of the red component of the colour after 2 years of exposure to an aggressive environment by more than 2.5 times. At the endpoint of exposure, the surface colour of compositions No. 3, 5, 6 is close to black (RGB codes are in the range of 10-20). This is also visually identified. After 2 years of testing, the colour of composites with lead crown pigment changed from orange-yellow to light brown.

4 Conclusions

1. The analysis of the assessment of the colour of materials and products based on them made it possible to identify promising methods in the field of direct scanning and computer processing of the obtained images.

2. The use of the method of direct scanning of the surface of finishing coatings and computer processing of these images on the same analyzed areas through interval time sections makes it possible to establish quantitative dependences of colour degradation as a result of various aggressive influences,

and this, in turn, determines the need application and selection of protective composites of specific compositions.

3. The conducted studies have shown that the oxidative degradation processes taking place in the composite as a result of UV radiation, positive temperatures, high humidity, and wind lead to a change in the color of epoxy composites. The most preferred, from the point of view of preserving the decorative properties of protective coatings, are compositions containing lead crown as a pigment.

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