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ПОВЫШЕНИЕ ВОДОСТОЙКОСТИ БЕССВИНЦОВОЙ ЮВЕЛИРНОЙ ЭМАЛИ

Приведены результаты разработки водостойкой эмали для золота, серебра и меди. Исследования проводились в направлении повышения устойчивости бессвинцовой стеклоосновы к действию воды. Установлено влияние Al_2O_3, TiO_2 и ZnO на основные свойства стекла. В результате проведенных исследований водостойкость исходного стекла увеличена в 10 раз.

Ключевые слова: ювелирная эмаль, бессвинцовая эмаль, водостойкость, показатель преломления стекла, золото, серебро, медь.

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ДОСЛІДЖЕННЯ АДГЕЗІЙНИХ ВЛАСТИВОСТЕЙ ГЕОЦЕМЕНТНИХ ПОКРИТТІВ БАР'ЄРНОГО ТИПУ

Наведено результати адгезійних випробувань геоцементного покриття бар'єрного типу, нанесеного на метал полімерну плівку хелатного типу, що утворилась в результаті проходження окислювально-відновних реакцій складових перетворювача іржі «Contrrust» і продуктами корозії металу. Незважаючи на діаметрально протилежний pH двох основ, не відзначено слідів відторгнення покриття від плівки, відставання і здуття, лущення та інших дефектів.

Ключові слова: *адгезія, атмосферна корозія, геоцементне покриття, металева підкладка, перетворювач іржі, система захисних покриттів.*

1. Introduction

According to statistics, atmospheric corrosion affects all metal structures, operated in the open air (about 50 % of the total available all metal structures): pipelines and containers of elevated location, the metal parts of buildings, towers, bridges, port facilities, etc. [1].

During operation the surface of the metal structures are inevitably exposed to moisture, UV radiation, temperature changes, various types of pollution, which is the root cause of the emergence and development of metal corrosion, which destroys from 10 to 12 % of the world's manufactured metal structures.

To protect against atmospheric corrosion are mainly used coatings with a lifetime of 5–10 years or more. The properties of coatings are largely determined by the properties of the film-forming substances, so considerable interest have the complex comparative study of various film-forming substances with the use of modern methods of assessment of their adaptability and resistance to corrosive factors of atmospheric conditions for developing coating systems with high protective and decorative properties.

For effectively function of corrosion protection, it must satisfy a number of requirements:

— Low moisture and oxygen permeability.
— Good mechanical properties.
— High and stable during the time the coating adhesion to steel.
— Resistance to cathode delamination.
— Good dielectric properties.
— Coating resistance to thermal aging.

According to [2–4] to the main modern anti-corrosion systems include:

1. Highly filled bicomponent system with reduced solvent content (35 %). The main advantages of highly filled systems compared to conventional — is the best corrosion resistance at comparable layer thicknesses, less material consumption and the possibility of applying a thicker

layer that provides the necessary anticorrosive protection for only 1–2 passes.

2. Single-layer anti-corrosion protection systems. The use of single-layer systems is possible in strictly defined conditions:

— For internal use or in small climatic loads.

— The exact calculation of loads, which will experience a painted structures.

— The positive experience of a similar painting for constructions or laboratory testing.

— Well-prepared surface; painting by qualified personnel in full compliance with the specifications of the supplier of the material.

— Strict enforcement of the recommended thickness.

3. The coating systems that do not require careful surface preparation.

4. Systems of water-based coatings, protective properties of which are not worse than conventional materials containing solvents.

According to the authors, more promising and environmentally friendly coatings are systems that combine, in addition to high performance adhesive properties 3 and 4 of the classification. Therefore, the creation of such coating systems is relevant and economically feasible due to the long-term protection and reduces the cost of execution of the painting works.

2. Object of research and its technological audit

The object of research is barrier-type geocement-based coatings for the protection of steel metal structures from atmospheric corrosion, as components of developed system of protective coatings ««Contrrust» rust converter + barrier-type geocement-based coating». The proposed protective coating system consists of two bases — acid and alkaline. The properties of these two substrates are separately investigated, but there are no data on the adhesive properties of geocement-based coatings to a metal surface treated with an acidic rust converter.

A positive from the use of «Contrrust» rust converter is that metal substrate corroded as a result of atmospheric corrosion doesn't require a costly and labor-intensive works aimed at preparation for painting. The disadvantage is the need to protect the metal polymer film of rust converter from moisture.

A positive from the application of barrier-type geocement-based coating is that the hardened film of alkali hydroaluminosilicates is resistant to moisture, acids and other factors due to the formation of acid-resistant potassium zeolite- and hydromicaceous compounds characterized by high durability in the structure of the protective composition. The disadvantage of the use of this composition are costly and labor-intensive work aimed at the preparation of metal structures for painting, namely premechanized cleaning of the surface to grade 3 according to GOST 9.402 (St 3 or St 2 according to ISO 8501-1).

Both components of the developed protective coating systems are environmentally safe for humans and the environment.

The data of components is obtained on the basis of low-power modern technologies.

Given that the basis of the action mechanism for an acid converter contains a complex of redox reactions directed to formation of chelate compounds as a metal polymer black film with a blue sheen on the reduced metal surface, the problem of adhesion for geocement-based coatings (alkaline) to such film is remained open, and, naturally, as the problem of compatibility of the two substrates in the developed protective coating system.

3. The aim and objectives of the research

The aim of research — to study the adhesive properties of the barrier-type geocement-based coating to metal polymer film formed as a result of a chemical reaction between the acid components of the rust converter and corrosion products (rust) of the metal substrate.

To achieve this aim it is necessary to perform the following tasks:

1. Make the processing of the rust products of metal substrate by acid rust converter.

2. Apply barrier-type geocement-based coating on the metal polymer film and establish their compatibility.

3. Determine the adhesive characteristics of the metal polymer film to the metal substrate and barrier-type geocement-based coating to the metal polymer film.

4. Literature review

As shown an analysis of [2–5], single/two-component protective coating and system of protective coatings based on organic binders as polyurethanes, acrylates, epoxies, fluoropolymers, polysiloxanes are used for the protection of metal structures from atmospheric corrosion. The coatings on these substrates have sufficiently high levels of adhesion (except fluoropolymer), chemical resistance, decorative and other properties. The main disadvantages of the considered protective compositions is their high cost, toxicity, vulnerability to UV action, labor input in the preparatory works of the substrate, and the performance of the painting works.

Alternative coatings are compositions based on mineral binders — phosphate, silicate and aluminosilicate. The protective phosphate-based compositions have good adhesion to metal substrates, but are quite expensive and require high temperatures for hardening. The silicate-based coatings (best known zinc silicate protective type) have a passivating properties, sufficient water and corrosion-resistant, but in their manufacture using raw materials (aerosil), which is toxic to humans and the environment. Most environmentally protective are alkaline aluminosilicate-based compositions/coatings, known as geopolymers [6–13]. However, in the given sources there is enough little information about their water and corrosion resistance to atmospheric corrosion conditions and applications. In general, the geopolymer-based compositions are used for concrete protection from the effects of acidic environment [6, 8–11] and fire [14–19]. In [7, 12, 13] the possibility of geopolymer-based coatings as protective for building metal structures is shown, but the authors pay more attention to the synthesis rather than physical and mechanical properties as a whole. There is no information about the geopolymer-based protective coating system.

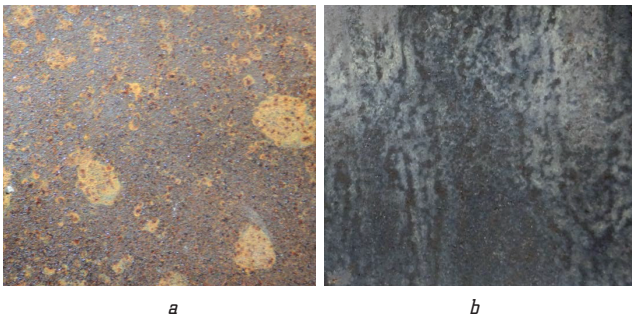
In the works of SRIBM KNUCA [20–24] protective weatherproof coating for protection of geocement-based metal structures from atmospheric corrosion (synonym of geopolymer) are developed, their basic properties are

studied and their industrial testing is carried out. Geocement-based protective coatings are characterized by high values of adhesion to the prepared metal substrate, applied without primer, but not tested as the system of protective coatings, namely adhesive properties to the film formed after the action of rust converter on corroded places of the metal substrate aren't investigated.

5. Materials and methods of research

5.1. Materials of research. For the research in this paper we were used: «Contrrust» rust converter (patent № 61544, Ukraine), acting as a primer, passivator and conservator of metal corrosion products, courtesy of G. Vysotskaya, director of PE «Ruslan and Lyudmila» (Kyiv, Ukraine); weatherproof barrier-type geocement-based coating, obtained by alkaline hydroaluminosilicates with general structural formula $K_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$, filled with functional additives.

Steel beam section with obvious signs of atmospheric corrosion (Fig. 1, *a*) was used as a metal substrate.



a *b*

Fig. 1. An exterior of the steel beam section, damaged by atmospheric corrosion before (*a*) and after treatment by «Contrrust» rust converter (*b*)

5.2. Preparation of beam section before experiment. Loose layer of rust was wiped using a damp cloth, moisten with water and applied of water rust converter solution on a damp surface.

After completion of the redox reaction between the metal corrosion products and «Contrrust» components (within 2 hours) blue-black metal polymer film was formed on the surface of a metal beam (Fig. 1, *b*).

Weatherproof barrier-type coating was applied on metal polymer film using a spatula.

After hardening for 24 hours, its surface and surface of the metal polymer film using a two-component epoxy adhesive Sikadur®-52 were pasted metal defining points 50×50×10 mm size.

5.3. Materials of research. The thickness of the metal polymer film and geocement coating was determined using NOVOTEST CT-1 (coating thickness; Russia) thickness gauge. This unit is included in the State Register of measuring instruments of Ukraine Y3380-1 and corresponds to DSTU 4219-2003 (Fig. 2).

Adhesion (traction), point was measured by incision method (parallel or cross) with thicknesses of films and coatings up to 200 microns using multiblade knife-adhesion tester NOVOTEST CT-1 according to GOST 15140, ISO 2409, ISO 16276-2, ASTM B 3359 (Fig. 3, *a*).

Adhesion, MPA was measured by normal force separation method with film and coating thickness using instrument of TCBC KNUCA design according to GOST 28574 and DSTU B V.2.7-126: 2011 (Fig. 3, *b*).

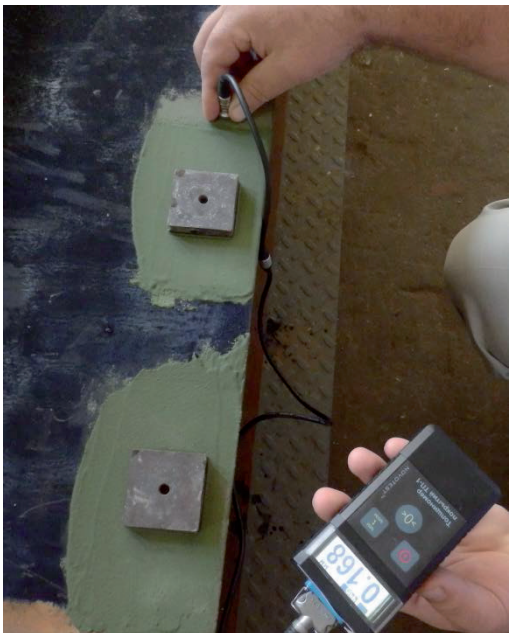


Fig. 2. Thickness measurements of metal plastic film and protective coating using NOVOTEST CT-1 device

a

b

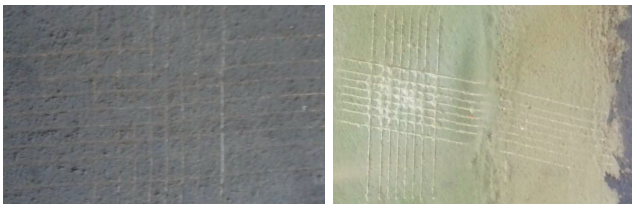
Fig. 3. Adhesion measuring by the methods: cross cuts (*a*) and the normal force separation (*b*)

Mechanical compression load cell model 3 tons 30 kN (pilot plant «IMPULSE», Ivanovo, Russia) was used as a measuring-load device. According to the requirements of these regulations, the amount of adhesion of the film/coating to the metal substrate should be at least 0,6 MPa.

6. Research results

According to the measurement by NOVOTEST CT-1, average metal polymer film thick is 116–118 microns and coating — 550 microns and 168 microns.

The adhesion of the metal polymer film to the metal substrate is 1 point (Fig. 4, *a*), which corresponds to the declared value of the rust converter manufacturer.

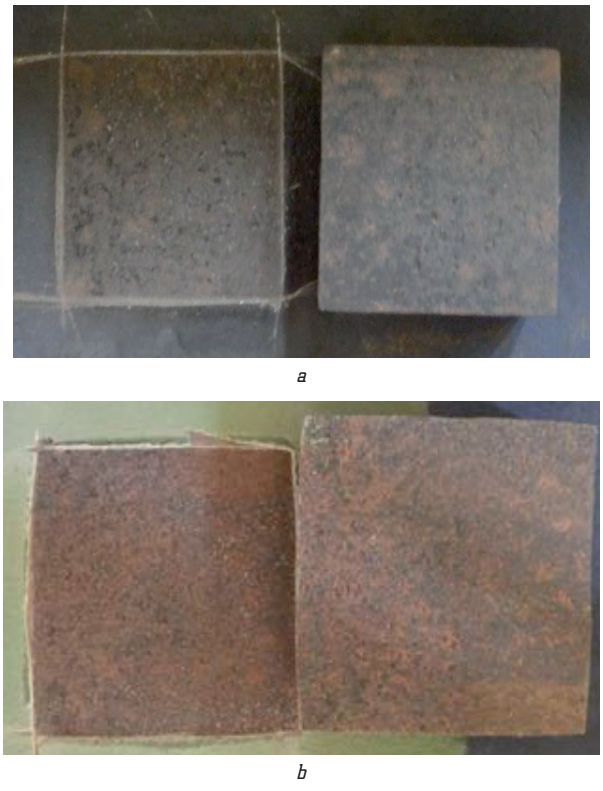


a *b*

Fig. 4. Results of the adhesive test by the methods of metal polymer film incisions (*a*) and a protective coating (*b*)

The adhesion of the protective coating 550 microns thick to metal polymer film is 3–4 points, and a thickness of 168 microns thick — 1 point (Fig. 4, *b*).

When using the method of normal force separation, the average value of the adhesion of the metal polymer film to the metal substrate is from 1,7 to 6,1 MPa (Fig. 5, *a*). The range of values of adhesion variables associated with the chemical processes of interaction of «Contrrust» rust converter components: at lower values of adhesion occurs preservation of corrosion products to form on the surface of the barrier metal polymer film at large — complete binding of iron corrosion products in water-resistant chelate complexes. As seen in Fig. 4, metal polymer film is completely detached from the metal substrate.



a

b

Fig. 5. Results of the adhesive test by the method of normal force separation: metal polymer film (*a*) and a protective coating (*b*)

Adhesion of the protective coating 550 microns thick to metal polymer film is 1,68–1,71 MPa in the case of normal force separation. During the test (Fig. 5, *b*) there was a joint separation of two metal structures from metal substrate surface, indicating that a substantial adhesion strength barrier-type geocement-based coating 550 microns thick to metal polymer film.

When thinner thicknesses geocement coating, adhesion value was not determined for thinner thicknesses of geocement-based coating.

7. SWOT-analysis of research results

Strengths. Adhesive bond of barrier-type geocement-based coating (alkaline reaction) to metal polymer film formed as a result of chemical reactions between components of acidic converter and corrosion products (rust) is so large that facilitates the joint separation of the two protective compositions from the surface of the metal substrate. Test results aren't observed rejection of geocement-based coating from the metal polymer film in spite of their different substrates; applying the complex in the form of protective coating systems — «Contrrust» rust converter + barrier-type geocement-based coating — significantly reduced the costs of preparing metal surfaces for painting, work time and environment is not polluted.

Weaknesses. The negative effect of the object of research on its internal factors has not yet been found.

Opportunities. Prospects for future research will be focused on the creation of protective coating systems ««Contrrust» rust converter + barrier-type geocement-based coating» and research of its basic physical, mechanical, special properties and durability.

Threats. External factors such as chlorine, petroleum, oil and other aggressive environments and compounds can have a negative effect on the object of research that will be the object of further research.

8. Conclusions

As a result of the research there are following conclusions:

1. After processing centers of rust by «Contrrust» composition it was confirmed the formation of the blue-black metal polymer film that is due to the chemical reaction products of corrosion of the metal substrates are converted into water-resistant chelate complexes.

2. After applying and hardening the barrier-type geocement-based coating on the metal polymer film the «Contrrust» rust converter, despite the diametrically opposite pH of the two substrates, traces of rejection coating on the film, detachment and blistering, peeling and other defects weren't observed.

3. The adhesive characteristics of the compositions included in the developed system of protective coatings: ««Contrrust» rust converter + barrier-type geocement-based coating»:

— Adhesion for incision method of metal polymer film 117 microns thick to metal substrate is 1 point, and geocement coating to metal polymer film 550 and 168 microns thick is 3–4 and 1 point.

— Adhesion for normal force separation method of metal polymer film 117 microns thick to the metal substrate is 1,8–6,1 MPa and barrier-type geocement-based coating applied to metal polymer film 550 microns thick is 1,7 MPa, which respectively in 3–10,2 and 2,83 times higher than regulations.

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ИССЛЕДОВАНИЕ АДГЕЗИОННЫХ СВОЙСТВ ГЕОЦЕМЕНТНЫХ ПОКРЫТИЙ БАРЬЕРНОГО ТИПА

Приведены результаты адгезионных испытаний геоцементного покрытия барьерного типа, нанесенного на металл полимерную пленку хелатного типа, образованную в результате прохождения окислительно-восстановительных реакций составляющих преобразователя ржавчины «Contrrust» и продуктами коррозии металла. Несмотря на диаметрально противоположный pH двух основ, не отмечено следов отторжения покрытия от пленки, отставания и вздутий, шелушения и прочих дефектов.

Ключевые слова: адгезия, атмосферная коррозия, геоцементное покрытие, металлическая подложка, преобразователь ржавчины, система защитных покрытий.

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