
ANTICORROSIVE CHARACTER OF THE MULTILAYERED SYSTEMS OF ACRYLIC PRODUCTS WITH CERAMIC MICROSPHERES AND KAOLIN ADDITION. PART 1

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ABSTRACT

The paper presents some experimental results of the research works developed in order to obtain innovative systems for corrosion protection of steel. The innovative nature of the research consists in the material type and the multilayered systems created and tested in laboratory and in situ conditions. Four recipes of an acrylic compound in aqueous dispersion, with ceramic microspheres, with a kaolin addition in different proportions were created and then applied on steel surfaces in 3 - layered systems. Also, there were presented the survey results of the systems mentioned above after their exposure to corrosive environments in accelerated laboratory conditions. The results of the survey, expressed by means of the adherence of the multilayered systems to steel surface, indicated a possible new merge between nanotechnology and the use of the natural resources, and a new possible direction for the use of kaolin in paint industry, in order to obtain a new type of coatings with a good reaction to the aggressive actions of the current climate manifested in various countries.

Keywords: anticorrosive; nanotechnology, kaolin, microspheres, multilayered system.

REZUMAT

Lucrarea prezintă câteva rezultate experimentale ale cercetărilor derulate cu scopul de a obține sisteme inovative pentru protecția anticorozivă a oțelului. Caracterul inovativ al cercetării constă în tipul materialului și sistemele multistrat create și testate în laborator și in situ. Au fost create patru rețete ale unui compus acrilic în dispersie apoasă, cu microsfere ceramice, cu adaos de caolin în diferite proporții, și apoi au fost aplicate pe suprafețe de oțel în sisteme formate din 3 straturi. De asemenea, au fost prezentate rezultatele comportării sistemelor menționate anterior după expunerea lor în medii corozive în condiții accelerate de laborator. Rezultatele urmăririi în timp, exprimate prin aderența sistemelor multistrat la suprafața de oțel, au indicat o nouă posibilă îmbinare dintre nanotehnologie și utilizarea resurselor naturale și o nouă posibilă direcție de utilizare a caolinului în industria de vopsele, cu scopul de a obține un tip inovator de acoperire cu o comportare bună față de acțiunile agresive ale condițiilor climatice actuale manifestate în diferite țări.

Cuvinte cheie: anticoroziv; nanotehnologie, caolin, microsfere, sistem multistrat.

1. INTRODUCTION

Experimental results of the research works developed in order to obtain innovative systems for corrosion protection of steel are presented. The innovative character of the research is given by the material type - an acrylic compound in

aqueous dispersion, with ceramic microspheres, with kaolin addition - and the multilayered systems created with it and tested in accelerated laboratory conditions.

At international level, there is no longer a novelty the detailed research or even the use of the nano - elements, such as for

example ceramic, glass, polymeric, porous or nonporous microspheres, produced by synthesis etc., in extremely different purposes, ranging from healing in the field of biology and medicine-bone repair, absorption and release of medicinal substances in the body (1, 2) till to areas of electronics (3), architecture and sustainable construction.

Starting from the typical uses of ceramic microspheres in various technical fields, as addition in polyesters reinforced with glass fibre (to manufacture fiberglass boats), in thin ink films, blasting explosives, rubber products, up to the industry of paints and varnish, nowadays, the products with ceramic microspheres can be applied on surfaces as steel, concrete, brick, plaster and more. both on the inside and on the outside.

Currently, the areas of use of nano materials for the construction industry have diversified as a result of the findings of research and improvement of various properties of the products/results: resistance to temperature, thermal barrier, reducing heat loss, low toxicity, chemical and corrosion resistance, and others.

Although coatings with microspheres are made up, generally speaking, of two principal components, binder and microspheres (4, 5, 6), other components may enter as addition and they vary and are chosen specifically according to the field of use of the new products that are intended to be obtained: inks, varnishes, road marking paints, finishing paints, anti-corrosion paints, plasters or materials with insulation character, fire resistant, etc.

In this way, numerous examples from the literature indicate a continuous increase of the manufacture and use of ceramic or other kind of solid microspheres, in order to obtain new and more innovative, sustainable products to be used in construction.

Regarding the addition of kaolin used in this research, it is known that it is an

industrial mineral raw material and its name is the trade name used to describe white clay composed primarily of kaolinite, $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, and refers both to the raw clay and to the marketed product (7).

As structure, kaolin is a natural mineral nanomaterial emerged as a result of the increase of its crystals in various conditions of the terrestrial crust (8).

From the physical and chemical properties of kaolin can be highlighted the following aspects :

- is a variety of white clay, plastic, soft and non-abrasive, non-toxic, hydrophylic, with special optical properties;

- is characterized by fine particles with hexagonal, flat form, and confers low viscosity values when it is dispersed in water. Thus, for example, kaolin can be dispersed into water so as up to a 70% content of solid phase to be obtained a smooth, fluid, milky phase (7).

- is relatively insoluble and chemically inert to a wide range of pH values;

- depending on the quality of kaolin and especially of surface thermal treatments applied thereto, is significantly influenced the activity of kaolin particle surface, which may later lead, if necessary, at dimensional stability improvement, impact resistance, abrasion resistance, thermal stability growth of the products in which these kaolin particles are incorporated etc.

- in the field of paints, it has recognized qualities when used in different areas (7, 9), where kaolin is an extender, gives important rheological properties to the product which contribute to dispersion maintaining and also provide most of the mass of the product.

- even it has coarse particles, kaolin can be used both to reduce the amount of expensive pigments, for example titanium oxide, and to improve corrosion protection properties of alkyd paints.

With all these aspects known based on both nationally and internationally research,

there remain a number of factors still unknown: the optimum method of combining the two components, the maximum amount of kaolin in order to obtain the best combination of properties, the simulation and modeling techniques can be applied in this regard (10).

In response to all these aspects, the present research aims to verify if the use of a kaolin addition into an acrylic compound in aqueous dispersion with ceramic microspheres, generates a new product, and further, a new type of multilayered systems with anticorrosive characteristics, tough enough to resist to the actual severe climate conditions specific for our country.

2. EXPERIMENTAL RESEARCH.

MATERIALS AND METHODS

Four recipes of an acrylic compound in aqueous dispersion, with ceramic microspheres, with a kaolin addition in different proportions, were created and applied on steel surfaces in 3 - layered systems.

Each product was applied on steel samples (100 x 150 x 6 mm), manually cleaned by a wire brush, dedusted and then degreased with a proper solvent.

The thickness of the 3 - layered systems, and also of the control system, with no kaolin, are presented in table 1.

Table 1. Definition of the 3 - layered anti-corrosion systems in terms of kaolin content and average thickness

Recipes code	M	S6'	S7'	S10	S12
Kaolin content, (%)	0	12	16	28	50
Thickness, (µm)	477	559	503	480	457

The samples were exposed, in parallel, in different batches, to the action of each of the following four corrosive environments, simulating the main types of the actual severe

climate conditions specific for our country: temperature variations, high heat and humidity and respectively neutral salt fog.

The exposure conditions were:

- *High heat and humidity conditions*, according to SR EN ISO 6270-2:2018 (11), 5 days a week, 6 hours/day at $40\pm 2^\circ\text{C}$, and 18 hours/day at $T = 23\pm 2^\circ\text{C}$, $U_r = 50\pm 5\%$, then, 2 days at $T = 23\pm 2^\circ\text{C}$, $U_r = 50\pm 5\%$; one cycle/ day;

- *Temperature variations*, according to SR EN 60068-2-14:2010 (12), 5 days a week, 6 hours/day at 55°C , and 18 hours at $(-20)^\circ\text{C}$, with thermal shock; one cycle/day;

- *Natural salt fog*, according to SR EN ISO 9227: 2017 (14), 5 days at $T = 35\pm 2^\circ\text{C}$ with 5% NaCl atomized solution; continuous exposure, one cycle/day.

The experimental results during the survey were expressed by means of the adhesion to steel of the new type of protections, using the pull - of method, according to SR EN ISO 4624:2016 (15).

The durability of the multilayered protections based on the acrylic binder in aqueous dispersion with ceramic microspheres and with a kaolin addition, exposed to the action of the main severe climatic conditions specific to the Romanian territory was assessed on the basis of:

- The values of the initial adhesions of the new systems, compared to those of the control systems, with no kaolin;

- The time course of the adhesion values to steel during exposure of each system in each aggressive environment comparing to their initial adhesions.

3. EXPERIMENTAL RESULTS

In this paper is presented the first part of the experimental research - results obtained during the survey of the 3 - layered systems exposed in laboratory accelerated conditions.

The second part of this research - results obtained during the survey of the 4-layered systems exposed in the same aggressive environments - will be presented in a future paper.

The experimental results obtained for each 3 - layered system during the exposure in each of the three corrosive environments are presented in tables 2, 3 and 4.

Table 2. Adhesion to steel of the 3 – layered systems exposed to high heat and humidity environment

Exposure duration System	Adhesion to the steel surface, (MPa)						
	0 days	5 days	14 days	21 days	25 days	30 days	35 days
M/3	0,90	1,05	1,00	1,10	1,20	1,20	1,27
S6`	1,41	1,41	1,42	1,50	1,50	1,60	1,62
S7`	1,34	1,34	1,22	1,23	1,23	1,32	1,30
S10/3	1,67	1,22	1,22	1,16	1,06	1,07	1,01
S12/3	1,50	1,50	1,55	1,55	1,49	1,27	1,39

Table 3. Adhesion to steel of the 3 – layered systems exposed to temperature variations

Exposure duration System	Adhesion to the steel surface, (MPa)						
	0 days	5 days	14 days	21 days	25 days	30 days	35 days
M/3	0,90	1,50	1,77	1,56	1,93	1,93	1,75
S6`	1,41	1,41	1,86	2,03	2,03	2,12	2,00
S7`	1,34	1,34	1,97	2,14	2,14	2,08	2,06
S10/3	1,67	2,06	1,66	1,66	1,50	1,50	1,85
S12/3	1,50	0,93	1,49	1,49	1,49	1,27	1,39

Table 4. Adhesion to steel of the 3 – layered systems exposed to natural salt fog

Exposure duration System	Adhesion to the steel surface, (MPa)		
	0 days	5 days	14 days
M/3	0,90	-	0,66
S6`	1,41	-	0,42
S7`	1,34	-	0,79
S10/3	1,67	0,44	-
S12/3	1,50	1,11	0,80

4. DISCUSSION

Analizing the experimental results presented in the tables 1 – 4, the following aspects are outlined:

- Against expectations, it was observed that higher kaolin addition generated lower total average thickness of the 3 – layered systems. The explanation stays in the peculiarities of the new created material. Taking into account that kaolin, in contact with the humidity contained in the acrylic base compound generates plenty of agglomerations in the mass of the mixture, the application of the product on the surface of the steel requires a greater insistence, through pressing and repetitive motions of the brush on the surface, in order to obtain plain and smooth layers.

- Before exposing the protections to the aggressive environments, the adhesion of the systems to the steel generally grew with the increasing content of kaolin, and were higher than those of the control system, with no kaolin.

- After exposing the protections to the aggressive environments, the following observations were done:

- After 35 days of exposure to high heat and humidity conditions, systems S6` and S7`, having small contents of kaolin (12% and 16%), had the best evolution of the adhesion to steel, with an ascendant trend and with the highest values;

- After 35 days of exposure to temperature variations, the same systems, S6` and S7`, had also the best evolutions of the adhesion to steel;

- The other systems than M/3, S6` and S7` had a descendent trend of the adhesion because of the high content of kaolin and its unfavorable interaction with the acrylic component.

- The adherence of the coatings to the steel rapidly decreased during the exposure to the neutral salt fog. Thus, after only 5 days,

the experimental results indicated that, after five days of exposure, the adherences of all the systems (with or without kaolin) to the steel surface were lower than 1MPa.

5. CONCLUSIONS

The main conclusions of this first part of the experimental research are the following:

- 1). The presence of the kaolin addition led to a better adhesion to steel comparing to the no kaolin system;

- 2). The thickness of the multilayered systems decreased with the increase of kaolin content;

- 3). Depending on the kaolin content introduced in the acrylic aqueous dispersion with ceramic microspheres, experimental results indicated that 3 - layered systems with a thickness of approx. 500 microns, with 12% or 16% kaolin addition had the best behaviour to the aggressive climate conditions simulated by the corrosive environments and a good cohesion between the layers.

- 4). The anti - corrosive character of the 3-layered systems decreased in the following order of the environments: *Temperature variations* > *High heat and humidity* > *Neutral Salt Fog*;

- 5). The atypical evolution of the durability vs. the thickness of the new type of the systems is considered to be specific for the nanomaterials, whose characteristics are manifested at thicknesses lower than those of the traditional similar coatings.

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