THE ANTICORROSIVE CHARACTER OF MULTILAYERED SYSTEMS OF ACRYLIC PRODUCTS WITH CERAMIC MICROSPHERES AND KAOLIN ADDITION. PART 2

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ABSTRACT

The paper is the second part of the article that presents experimental results of the research developed in order to obtain innovative systems for corrosion protection of steel. There were created three recipes of an innovative type of a coating, starting from an acrylic compound in aqueous dispersion, with ceramic microspheres, in which it was introduced, in different proportions, a kaolin additive. Each product was applied on steel surfaces, in four - layered systems. There are presented results referring to the systems behavior during their exposure to corrosive environments in accelerated laboratory conditions that simulated three types of aggressive climate conditions. The adherence of the systems to the steel surface indicated a new possible merge between nanotechnology and the use of natural resources, and also a new possible direction for the use of kaolin in the coatings industry, in order to obtain a new type of coatings with a good reaction to the aggressive actions of the current climate from various countries. There are also analyzed, by comparison, the results obtained on the three and four-layered systems, respectively (the dates for the three-layered systems being initially presented in the first part of the paper).

Keywords: anticorrosion; nanotechnology; kaolin; microspheres; multilayered system.

REZUMAT

Lucrarea constituie partea a doua a articolului care prezintă rezultate experimentale ale cercetărilor efectuate cu scopul de a obține sisteme inovative pentru protecția anticorozivă a oțelului. Au fost realizate trei rețete ale unui tip de produs peliculogen inovator, pornind de la un compus acrilic în dispersie apoasă, cu microsfere ceramice, în care s-a introdus, în diferite proporții, adaos de caolin. Fiecare produs a fost aplicat pe suprafețe de oțel în sisteme de câte patru straturi. Sunt prezentate rezultate ale urmăririi comportării în timp a sistemelor pe parcursul expunerii în medii corozive în condiții accelerate de laborator, care au simulat trei tipuri de condiții climatice agresive. Aderența sistemelor la suprafața de oțel a indicat o nouă posibilă îmbinare între nanotehnologie și utilizarea resurselor naturale precum și o nouă posibilă direcție de utilizare a caolinului în industria produselor peliculogene, pentru a obține un nou tip de acoperiri cu o bună comportare la acțiunile agresive ale condițiilor climatice actuale din diferite țări. De asemenea, sunt analizate, prin comparație, rezultatele obținute pe sistemele din trei, respectiv patru straturi (datele pentru sistemele tristrat fiind prezentate inițial în prima parte a articolului)

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

1. INTRODUCTION

Experimental research works developed in order to obtain innovative systems for corrosion protection of steel are presented.

Following a similar pattern as in the first part of the paper [1], in this second part there are presented the four-layered systems obtained using the same new-created coating material, i.e. from an acrylic product in aqueous dispersion, with ceramic microspheres, after introducing, in different proportions (as presented in the first part of the paper), a kaolin additive ($Al_4Si_4O_{10}(OH)_8$) [2, 3]. After applying the four-layered systems on steel surfaces, samples were exposed to the same corrosive environments simulated in laboratory accelerated conditions, as presented in the first part of the paper.

2. EXPERIMENTAL RESEARCH. MATERIALS AND METHODS

Each product was applied on steel samples (100 x 150 x 0,6 mm) manually cleaned by a wire brush, dusted and degreased with a proper solvent. The thickness of the four-layered systems and also of the control system, with no kaolin, is presented in Table 1.

Table 1. *Definition of the four - layered anticorrosion systems in terms of kaolin content and average thickness*

Recipes code	M	S10	S11	S12
Kaolin content, (%)	0	28	32	50
Thickness, (μm)	885	748	585	508

The samples were exposed, in parallel, in different batches, to the action of each of the following three corrosive environments, created in accelerated laboratory conditions, simulating the main types of the actual severe climate specific for our country: temperature variations, high heat and humidity and neutral salt fog, the last one being specific for the coastal areas. The exposure conditions were:

- *High heat and humidity conditions,* according to SR EN ISO 6270-2:2018 [4], for 5 days a week, 6 hours/day at 40±2˚C, 100% humidity, and 18 hours/day at a temperature T = 23±2˚C, relative humidity Ur = 50±5%, followed by 2 days at T = 23±2˚C, Ur = 50±5%, one cycle / day;
- *Temperature variations,* according to SR EN 60068-2-14:2010 [5], for 5 days a week, 6 hours / day at 55 ºC and 18 hours / day at (-20)ºC, with thermal shock, one cycle / day;
- *Neutral salt fog,* according to SR EN ISO 9227: 2017 [6], for 5 days at T = 35±2˚C with 5% NaCl atomized solution, continuous exposure, one cycle/day.

The experimental results during the survey were expressed by means of the adhesion of the new type of protections to steel, using the pull-of method, according to SR EN ISO 4624:2016 [7].

The survey of the multilayered protections based on the acrylic binder in aqueous dispersion with ceramic microspheres and kaolin additive exposed to the action of the mentioned severe conditions was assessed on the basis of the: initial adhesions of the control system (with no kaolin), compared to those of the four-layered systems, and also, on the trend of the adhesion during the exposure of each system in each aggressive environment.

3. EXPERIMENTAL RESULTS

The experimental results obtained for each four-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 for the four - layered systems exposed to high heat and humidity* environment

System \ Exposure duration	Adhesion to the steel surface, (MPa)					
	0 days	5 days	21 days	25 days	30 days	35 days
M/4	0,90	1,50	1,34	1,31	1,17	1,92
S10/4	1,34	1,47	1,67	-	1,50	1,34
S11/4	2,09	1,89	1,41	-	1,36	1,36
S12/4	1,37	1,47	1,47	1,30	1,38	0,97

Table 3. *Adhesion to steel for the four - layered systems exposed to temperature variations*

System \ Exposure duration	Adhesion to the steel surface, (MPa)					
	0 days	5 days	21 days	25 days	30 days	35 days
M/4	0,90	1,50	2,22	2,09	1,96	2,06
S10/4	1,34	1,37	1,84	1,96	1,53	1,96
S11/4	2,09	2,46	2,19	2,64	1,61	2,68
S12/4	1,37	1,56	1,88	1,80	-	1,82

Table 4. *Adhesion to steel for the four - layered systems exposed to neutral salt fog*

Exposure duration / System	Adhesion to the steel surface, (MPa)	
	0 days	5 days
S10/4	1,34	0,81
S11/4	2,09	0,74
S12/4	1,37	0,82

4. DISCUSSION

Analyzing the experimental results presented in Tables 1 - 4, the following aspects could be outlined:

- For the four-layered systems, as in the case of the three-layered ones, it was observed that a higher kaolin content generated a lower total average thickness of the coating. The explanation, also mentioned in Part 1 of the paper, still 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 thickness of each layer gets lower because the application of the product on steel requires pressing and repetitive motions of the brush on the surface, in order to obtain smooth layers;
- In the case of the three-layered systems, before their exposure to the action of the aggressive environments, the adhesions to steel generally grew with the content of kaolin and were higher than those of the control system. In the case of the four - layered coatings, before the exposure, the adherence had a similar trend comparing to the control system but, after the kaolin content was increased, the adherence got higher, corresponding to a certain kaolin content (a *threshold content)*, or remained relatively stationary while this component was further added. It has also to be mentioned that for the latter systems, the adherence values characterized the cohesion between the layers, mainly between the third and the fourth one, and was not the adhesion of the system to the steel. A possible explanation is the presence of kaolin agglomerations in the coating layers and that was probably why, as the kaolin content was higher, the pull - of test showed a preponderant cohesive character of the tear and not an adhesive one, as in the case of the three - layered coatings. Even so, we assume that the best adhesion to steel for the four-layered systems depends mainly on the acrylic component: kaolin content ratio, and not on the number of the layers;
- After the exposure of the protections to the aggressive environments, the following observations were done:

\- In the case of the three-layered systems, after 35 days of exposure to high heat and humidity conditions, the adherences to steel of S6\` and S7\` systems, with 12% and 16% kaolin, respectively, were generally higher (between 1,62MPa and 1,30MPa) than those of S10/3 and S12/3 systems, with 28% and 50% kaolin, respectively (between 1,01MPa and 1,39MPa). In the case of the four - layered systems, after 35 days of exposure, for the products having 28% and 50% kaolin, respectively, adherences to the steel reached slightly lower or equal values (between 0,97MPa and 1,34MPa), comparing to the initial ones (between 1,34MPa and 1,37MPa). It was also observed that excepting systems S6\` and S7\`, where adherence had an ascendant trend, for all the other systems, with higher kaolin content (28% and 50% kaolin), whether with three or four layers, adherence had first an ascendant and then a descendant trend, meaning that increasing the amount of kaolin in such kind of coating material has a positive effect on the adhesion to the steel, but mainly for a specific acrylic component: kaolin ratio, effect most visible at the systems with four layers. In the case of the three - layered systems, after 35 days of exposure to temperature variations, both systems S6` and S7` with relatively low kaolin content (12% and 16% kaolin) had the best evolutions regarding the adhesion to steel (between 1,99MPa and 2,06MPa), comparing to the adherences (1,85MPa and 1,39MPa) of the other systems of the group, S10/3 and S12/3, with a higher kaolin content (28% - 50% kaolin). In the case of the four - layers systems, mainly for those with a high kaolin content, after the same exposure period, the adherences were higher (1,96MPa and 1,82MPa) than of those of the three - layered systems (1,85MPa and 1,39MPa) at the same kaolin contents. System S11/4 is an exemption because its adherences were the highest of the group, probably because of another acrylic component: kaolin ratio considered as a new *threshold content* of kaolin, another one than that characteristic for the system S6`.

Thus, it is taken into account the possible existence of more than one *threshold content* of kaolin, meaning a specific acrylic component: kaolin ratio, respectively, generating a certain structure for the resulting material. This could be possible if we consider: the complex structure of the basic component - the acrylic compound in aqueous dispersion with ceramic microspheres, the specific structure of kaolin and also the particularities of its interaction with humidity.

- If in the case of all the three-layered systems, with or without kaolin, the adherence of the coatings to the steel rapidly decreased (bellow 1MPa) during the 14 days of exposure to the neutral salt fog chamber, in the case of the four-layers systems, the same situation appeared after only 5 days of exposure in the same conditions.

5. CONCLUSIONS

The main conclusions of this experimental research are the following:

1. The presence of the kaolin addition led to a better adhesion to steel comparing to the control system, with no kaolin;
2. The thickness of the 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 the three - 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 in the laboratory and also, had a good cohesion between the layers;
4. By means of the adherence values to the steel surface, resulted that the three - layered systems had a protective, anti - corrosive character when they were exposed to temperature variations or to high heat and humidity conditions;
5. The evolution of the durability vs. thickness for the new type of the systems can be considered as specific for nanomaterials, whose characteristics are manifest at thicknesses that are much lower than those of the traditional similar coatings.
6. The multi - layered systems tested in this research behaved differently to each aggressive environment, depending on three main aspects: kaolin content, acrylic component: kaolin content ratio and the number of the layers in the system.
7. Taking into account the experimental results obtained, it can be concluded that the use of a kaolin addition into an acrylic compound in aqueous dispersion with ceramic microspheres can generate a new product, a new type of multilayered systems with anticorrosive characteristics, tough enough to resist to the severe climate conditions of Romania.

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