INFLUENȚA PIGMENTULUI NANOMETRIC FOTOCATALITIC DE TiO_2 ASUPRA PROPRIETĂȚILOR PRODUSELOR PELICULOGENE PE BAZĂ DE LIANȚI ORGANICI ÎN DISPERSIE APOASĂ

THE INFLUENCE OF TiO_2 NANOMETRIC PHOTOCATALYTIC PIGMENT ON THE PROPERTIES OF THE FILM-FORMING PRODUCTS BASED ON ORGANIC BINDERS IN AQUEOUS DISPERSION

MIRELA LAZĂR[1*], DANIELA FIAT[1], GHEORGHE HUBCĂ[2]

[1] Institutul de Cercetări pentru Echipamente şi Tehnologii în Construcții - ICECON S.A., Şos. Pantelimon, nr.266, Sector 2, Bucureşti, România

[2] Universitatea POLITEHNICA Bucureşti, Str. Gheorghe Polizu, Sector 1, Bucureşti, România

In the recent years, the film-forming products obtained by adding a nanometric photocatalytic titanium dioxide pigment into their composition have drew the attention of both researchers and manufacturers.

The purpose of this paper is the development of new compositions based on organic binders in aqueous dispersion with different contents of nanometric photocatalytic titanium dioxide pigment and novelty lies in the study of their influence on the film-forming products properties. The study performed on these products revealed self-cleaning effect of the films after exposure to UV radiation and natural aging in urban-industrial environment and the improvement of certain properties, such as: coating power, adherence to support, water and watery-vapours permeability.

Pe parcursul ultimilor ani, produsele peliculogene obținute prin adăugarea în compoziție a pigmentului nanometric fotocatalitic de dioxid de titan, au atras considerabil atenția atât a cercetătorilor cât şi a producătorilor.

Scopul lucrării constă în elaborarea unor noi compoziții pe bază de lianți organici în dispersie apoasă cu conținut diferit de pigment nanometric fotocatalitic de dioxid de titan iar noutatea constă in influența acestora asupra proprietăților produselor peliculogene. Studiul efectuat asupra acestor produse a evidențiat efectul de autocurățare al peliculelor după expunere la radiații UV şi condensare şi după expunere la îmbătrânire naturală în mediu urban-industrial precum şi îmbunătățirea anumitor proprietăți precum: puterea de acoperire, aderența la suport, permeabilitatea la apă şi a vaporilor de apă.

Keywords: *titanium dioxide, self-cleaning, photocatalysis, film-forming product, aqueous dispersion.*

1. Introduction

Titanium dioxide is the most important pigment and it is widely used in the industrial film-forming products manufacturing. Introduced in the film-forming products composition its effect is to efficiently disperse the visible light, assuring white, brightness and opacity. In the paint industry two polymorphic forms of the titanium dioxide are used: anatase and rutile. As anatase crystalline form, titanium dioxide can be used as a photocatalyst material, in the presence of UV radiation. When TiO_2 nanoparticles used as photocatalyst absorb ultraviolet (UV) from sunlight or light sources, they will produce pairs of excited electrons. The electrons are promoted from the valence band (VB) to the conduction band (CB). This creates an area of positive charge (H+), voids in the valence band and a free electron in the conduction band. These charge carriers can either, recombine, or migrate to the surface. The positive charge area reacts with the hydroxyl groups, or with the water molecules adsorbed on the surface. Following this reaction different radicals are produced, such as hydroxyl radicals (-HO·) and hydroperoxy radicals ($-HO_2\cdot$). The free electron from the conduction band is combining with the atmospheric oxygen and super oxide radicals are produced. These radicals produce powerful oxidizing processes and can cause the deterioration of the organic contaminants existing on the films surface [1].

Another feature of the nanometric photocatalytic titanium dioxide pigment present in a film-forming composition is the super-hydrophilic behavior of the film formed on the support. The contact angle between the titanium dioxide particle surface and the water molecules surface is substantially reduced and this allows the easy removal of contaminants, by the water [2].

The properties of film-forming products

* Autor corespondent/*Corresponding author*,
E-mail: mirela.lazar@icecon.ro

based on organic binders in aqueous dispersion are influenced by the nature of used pigments and the intensity of the interactions, of type particles - particle and particle - polymer.

The TiO_2 nanometric photocatalytic pigment can not be incorporated into to the film-forming products based on organic binders in aqueous dispersion, because they can oxidize the polymer matrix and thereby contribute to the degradation of the binder. Thus, there were used mixtures of TiO_2 nanometric photocatalytic pigment with tetraethyl orthosilicate (TEOS) [3,4].

By adding TiO_2 pigment, having nanometric dimensions and due to the photocatalysis process, many advantages may be achieved on the long term, conferring the film-forming products: self-cleaning properties, environment cleaning by removing nitrogen compounds and volatile organic compounds and increasing the durability of the support surfaces [5-8].

The basic composition of the film-forming products under study was carefully selected in order to obtain products with superior performances, for indoor and exterior use and having good resistance to environmental factors. Thus, the values of the application efficiency, adhesion to support, permeability to water and watery-vapours and the self-cleaning effect have to be superior compared to the products available on the market.

The characteristics that must be carry out by the film-forming products based on organic binders in aqueous dispersion having in their composition nanometric photocatalytic titanium dioxide pigment are: coating power, self-cleaning effect, color maintaining, good adhesion to the support, low permeability to water, high permeability to watery-vapours, better behavior after exposure to accelerated aging (UV radiation from light sources) and natural aging in urban-industrial environment, compared to conventional products.

2. The experimental part

2.1. Materials

In this study four film-forming products compositions R1, R2, R3, R4. based on organic binders in aqueous dispersion having in their composition nanometric photocatalytic pigment of titanium dioxide were used. In addition, the behavior of four conventional film-forming products (without nanometric photocatalytic pigment of titanium dioxide), R5, R6, R7, and R8 was studied.

The used materials in the film-forming products compositions were: dispersing agent, sodium polymetaphosphate, $Na_6O_{18}P_6$ (Calgon N - Aako) 0.1%, aqueous solution of sodium salt of the maleic acid diisobutylene (MD 20 - BASF) copolymer, 0.9%; ammonium polyacrylate (Coatex P 90 - Arkema) 0.7%; anti-foaming agent, mineral oil, (Antifoam W - Quimitécnica) 0.1%; cellulosic thickener, hydroxyethyl cellulose HEC (Natrosol 250 MHBR - Ashland Inc.) 0.2%; pH regulator, 2-amino-2-methyl-1-propanol (AMP 95 - The Dow Chemicals Company) 0.15%; coalescing agent, monopropylene glycol (MPG - Chemical Plus) 0.6%; pigment TiO_2 (DELTIO 81x-250 nm - HUNTSMAN); filler Ca CO_3 (15C - Ionian Kalk); acrylic resin (Orgal P 850 W - CRAY VALLEY) 32%; silicon resin - nano TiO_2 dispersion and in tetraethoxysilane, in a molar ratio of 1% of acrylic resin, Wacker; solvent - white spirit (Shersol D 40 - Shell Chemicals) 1%; biocide - 5 chloro - 2-methyl - 4 isothiazolinone (PARMETOL DF 35 - Schülke & Mayr GmbH) 0.4%; rheology modifiers, hydrophobically modified alkali soluble emulsion HASE (Latekoll DS 6269 - BASF) 0.8%; hydrophobically modified ethoxylated urethane emulsion HEUR (Colacral PU 85 - BASF) 0.5%.

The content of pigment, resin and water are presented in Table 1.

Table 1

The content of pigment, resin and water in the composition of the studied products
Conținutul de pigment, răşină şi apă din compoziția produselor studiate

Raw materials *Materii prime*	Composition, % / *Compoziția, %*							
	Paint *Vopsea* *R 1*	Paint *Vopsea* *R 2*	Paint *Vopsea* *R 3*	Paint *Vopsea* *R 4*	Paint *Vopsea* *R 5*	Paint *Vopsea* *R 6*	Paint *Vopsea* *R 7*	Paint *Vopsea* *R 8*
Softened water *Apă dedurizată*	42.5	37.5	25.5	2.5	42.5	25.5	37.5	2.5
Pigment TiO_2 *Pigment TiO_2*	**10.0**	**10.0**	**10.0**	**10.0**	**10.0**	**27.0**	**15.0**	**50.0**
Nanodispersion TiO_2 and tetraethoxysilane in acrylic resin *Nanodispersie de TiO_2 şi ortosilicat de tetraetil în răşină acrilică*	**10.0**	**15.0**	**27.0**	**50.0**	**0**	**0**	**0**	**0**
Acrylic resin *Răşină acrilică*	**0**	**0**	**0**	**0**	**10.0**	**0.0**	**10.0**	**10.0**
Silicone resin *Răşină siliconică*	**0**	**0**	**0**	**0**	**0**	**10**	**0**	**0**

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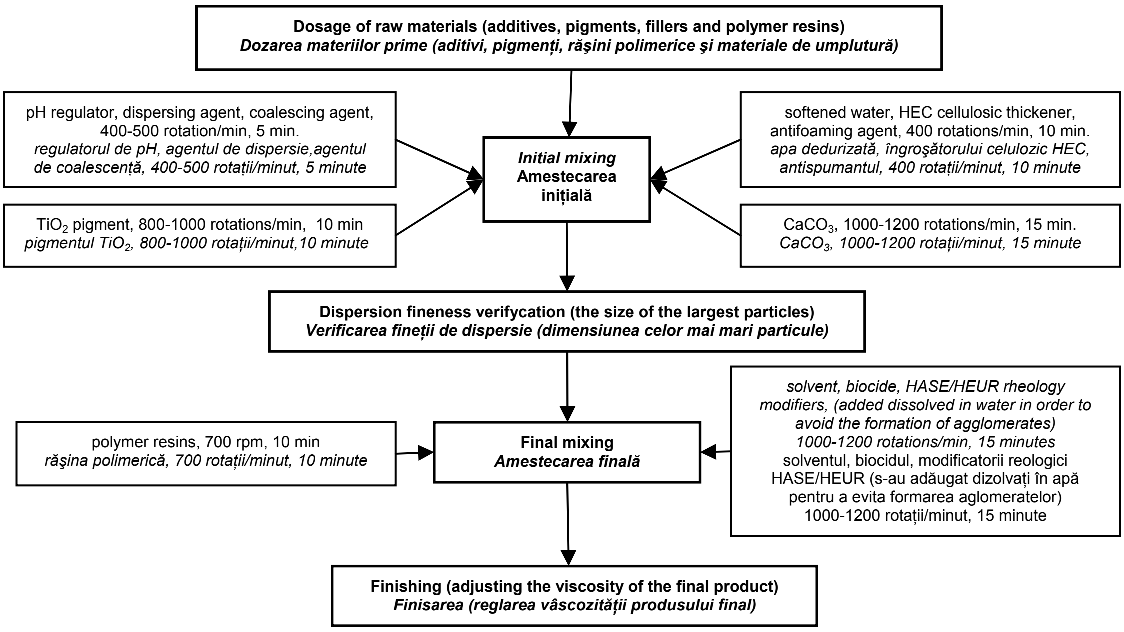

Fig. 1 - *The technological process stages for obtaining of the film-forming products/* Etapele procesului tehnologic de obținere a produselor peliculogene.

2.2. The work procedure

The products were obtained using a Cowles type mixer.

Figure 1 presents the technological process stages for obtaining of the film-forming products.

In order to characterize the obtained film-forming products, there were determined: density, flow time, non-volatile-matter content, coating power, dispersion fineness (size of the largest particles), adherence to support (pull-off test), specular gloss of non-metallic paint films (gloss film), impact resistance, water permeability, watery-vapours permeability, according to the valid standards [9-19].

The influence of TiO_2 nanometric photocatalytic pigment on the film-forming products, film structure and morphology were performed using a QUANTA F INSPECT electronic microscope, equipped with X-ray detector with an energy dispersive (EDX), with an operating voltage of 30 KV. The analyzed samples were covered with a thin layer of gold using a metal spraying system.

The film-forming products were applied on mortar cement supports, in the following manner: the first layer was composed of 50% water diluted product, the second layer was composed of 10% water diluted product and third layer was composed of the undiluted product. After the products application, the support samples were dried for 7 days at a temperature of $(23 \pm 2)^0$ C and (50 ± 5)% relative humidity.

In order to determine the photocatalytic activity, the self-cleaning effect was performed, after the exposure of film-forming products to UV radiation. Before the exposure, on the surfaces of the samples a methylene blue solution was applied [20].

The method principle is the following: the film-forming products are applied on the test supports and dried for 24 hours, after the last layer application; a solution of 1% methylene blue is sprayed on the surfaces covered with the products to be tested; the products are exposed either to UV radiation in a special exposure equipment or to sunlight, in weather conditions; after the exposure period, the surfaces are examined in order to determine the film aspect; based on the methylene blue removing degree, the self-cleaning power of the products films is assessed. Table 2 presents the grading of the self-cleaning effect.

Table 2

The code of the grading of the self-cleaning effect
Modul de notare a efectului de autocurățare

Self-cleaning degree of methylene blue *Grad de autocurățare al albastrului de metilen*	Self-cleaning effect *Efect de autocurățare*
Total self-cleaning *Autocurățare totală*	High / *Puternic*
Partial self-cleaning *Autocurățare parțială*	Average / *Mediu*
No self-cleaning *Autocurățare nulă*	None / *Nul*

The self-cleaning effect of the obtained products was determined by exposing them to UV radiation and condensation (accelerated aging), as well as to climatic conditions specific for urban-industrial environment (natural aging) and the product properties after exposure were determined.

The accelerated aging was performed by exposing the obtained film-forming products, applied on the support (which were sprayed with a 1% solution of methylene blue), to the combined action of UV radiation (4 hours) and condensation (4 hours) [21]. The equipment used in the tests for artificial aging determination, by exposure to fluorescent UV radiation and water, was QUV type equipment, UVB-313 EL type lamp, with adjustable temperature indicator, 100^0C, class 1 of accuracy and working thermoresistance, class B precision.

The natural aging was carried out by exposing the obtained film-forming products applied on a concrete wall to an urban-industrial environment [22].

The exposed surfaces examination was performed by visually inspection in order to determine the changes in appearance or other coating deterioration signs: colour modifications, blistering and cracking. The changes due to exposure to environmental factors were evaluated by determination of the properties variation (adherence to support - pull-off test, water permeability, and watery-vapours permeability) and assessing the self-cleaning effect [23].

3. Results and discussions

The experimental results regarding the characteristics of the obtained film-forming products are presented in Tables 3, 4 and 5.

The characteristics of products influenced by the presence of TiO_2 nanometric photocatalytic pigments are presented below.

The coating power represents the film-forming product capability to cover the white or black color of a contrast cards and it is expressed by the application efficiency (m^2/l). For a 150 µm wet film thickness, similar for all products, the obtained application efficiency values for R1-R4 products with TiO_2 nanometric pigment are better compared to R5-R8 conventional film-forming products. The values of the application efficiency for R1-R4 film-forming products with TiO_2 nanometric photocatalytic pigment are 1.45 times higher that obtained for the R5-R8 conventional film-forming products.

The films formation mechanism is a physical drying process by the gradual evaporation of the solvent, the particles ordering, particles coalescing and the inter-diffusion with the polymer.

The coating power is influenced by the nature of the used pigments. Due to the nanometric size of TiO_2, a large contact surface between the polymer and particle, as well as a good cohesion of the interface is achived. The polymer - particle interactions are favored in comparison with the particle - particle interactions. To support this reasoning the structure and morphology of the nanoparticles contained in the obtained the films of the R1 and R5 products were analyzed by electron microscopy (SEM). There were observed a compact structure with nanometric particle, as is presented in Figures 2, 3 and 4.

Table 3

The studied film-forming products characteristics / *Caracteristicile produselor peliculogene studiate*

Film forming product / ***Produs peliculogen***							
R1	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Density, 20^0C, g/cm^3 / *Densitate, 20^0C, g/cm^3*							
1.42	1.67	1.58	1.55	1.67	1.57	1.59	1.60
Flow time, bucket diameter = 6 mm, sec / *Timp de curgere, cupa cu diametrul 6 mm, sec*							
70	75	54	53	56	68	90	58
Non-volatile matter content, % / *Conținut de substanțe nevolatile, %*							
52.65	72.98	64.45	63.20	67.34	63.98	62.95	63.04
Coating power, expressed by application efficiency, m^2/l, for wet film thickness 150 µm / *Putere de acoperire, exprimată prin randamentul de aplicare, m^2/l/ pentru grosimea filmului uscat de 150 µm*							
8.28	8.98	9.00	8.20	6.25	6.20	6.17	5.09
Dispersion fineness, µm / *Finețe de dispersie, µm*							
30	20	20	20	60	60	50	50
Rapid-deformation (impact resistance) / *Rezistența la şoc (impact), cm*							
80	100	80	90	70	90	90	90
Specular gloss of non-metallic paint films (class G_3 - mat) at 85°≤ 10 / *Reflexia regulată a peliculei (luciu peliculă clasa G_3 – mat) la 85^0 ≤ 10*							
2.1	1.1	4.5	4.4	8.2	4.2	6.2	4.9

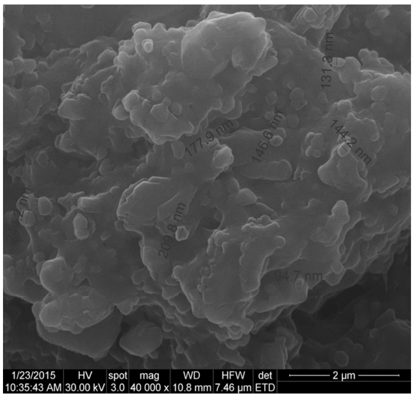

Fig. 2 - SEM image for R5 section product without TiO_2 nanometric pigment / *Imagine SEM pentru secțiune produs R 5 fără pigment nanometric TiO_2.*

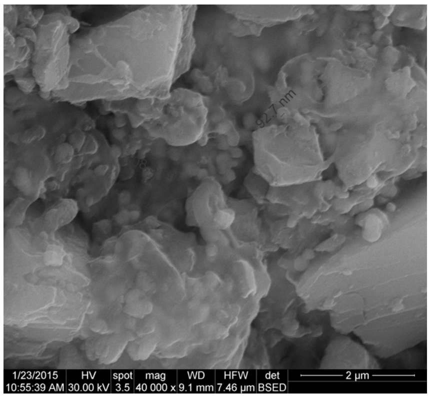

Fig. 3 - SEM image for R1 section product with 10% TiO_2 nanometric pigment / *Imagine SEM pentru secțiune produs R 1 cu 10% pigment nanometric de TiO_2.*

After the SEM analysis, it can be seen easily that the TiO_2 particles are quite dispersed, even if the percentage of used nanoparticles is high. This fact supports the coating power increase, in the case of the R1-R4 products.

The results presented in Table 4 highlight that the photocatalytic and conventional products characteristics - adhesion to support, water permeability and watery-vapours permeability are not significantly changed after artificial and natural aging.

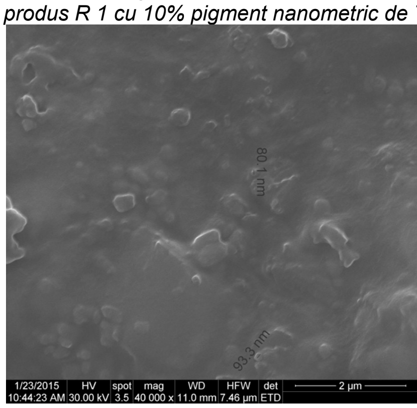

Fig. 4 - SEM image for R1 surface product with 10% TiO_2 nanometric pigment / *Imagine SEM pentru suprafața produsului R 1 cu 10% pigment nanometric TiO_2 .*

Table 4

Characteristics of the products applied on ciment mortar, initial and after aging
Caracteristicile produselor aplicate pe suport de mortar de ciment, inițiale şi după îmbătrânire

Film forming product / Produs peliculogen							
R1	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Adhesion on support (pull-off test) / *Aderența la suport,* N/mm²							
- initial/ *inițial*							
1.45	1.49	1.15	1.96	0.79	0.86	0.95	0.62
- after artificial aging, UV exposure (1000 hours) / *- după îmbătrânire artificială expunere UV (1000 ore)*							
1.42	1.50	1.12	1.85	0.75	0.81	0.92	0.59
- after natural aging exposure in urban industrial environment (one year) / *- după îmbătrânire naturală expunere mediu urban-industrial (12 luni)*							
1.39	1.48	1.13	1.92	0.72	0.85	0.93	0.60
Water permeability / *Permeabilitatea la apă W, kg/m²xh^0,5*							
- initial/ *inițial*							
0.096	0.089	0.086	0.059	0.131	0.120	0.191	0.670
- after artificial aging, UV exposure (1000 hours) / *- după îmbătrânire artificială expunere UV (1000 ore)*							
0.094	0.080	0.085	0.050	0.129	0.115	0.180	0.662
- after natural aging exposure in urban industrial environment (one year) / *- după îmbătrânire naturală expunere mediu urban-industrial (12 luni)*							
0.090	0.078	0.081	0.053	0.125	0.112	0.184	0.640
Watery -vapours permeability / *Permeabilitatea la vaporii de apă, V, g/m²xh*							
- initial/ *inițial*							
5.347	5.766	5.399	6.028	2.556	1.400	2.040	2.030
- after artificial aging, UV exposure (1000 hours) / *- după îmbătrânire artificială expunere UV (1000 ore)*							
5.320	5.640	5.215	6.002	2.348	1.395	2.015	2.029
- after natural aging exposure in urban industrial environment (one year) / *- după îmbătrânire naturală expunere mediu urban-industrial (12 luni)*							
5.331	5.655	5.244	6.010	2.351	1.397	2.032	2.024

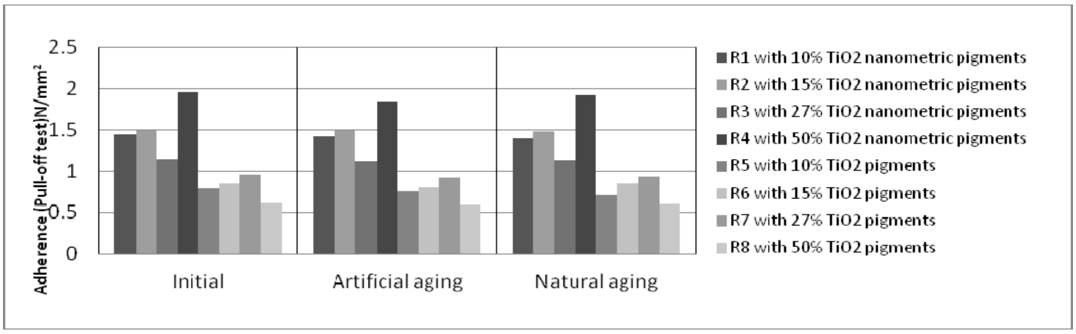

Fig. 5 - The adherence to support (Pull-off test), initial and after aging / *Aderența la suport inițială şi după îmbătrânire.*

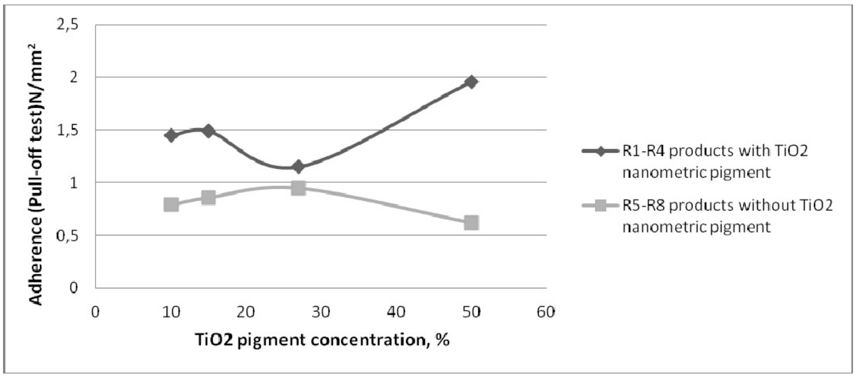

Fig. 6 - *The adherence to support (Pull-off test) according to the concentration of TiO_2 pigment* / Aderența la suport funcție de concentrația de pigment TiO_2

The adherence to support (pull-off test) values, obtained for R1 – R4 film-forming products with TiO_2 nanometric pigment are approx. of 2 times higher than the values obtained for R5 - R8 conventional products (Figure 5 and Figure 6), what explains a better cohesion of the film interface - test support. The highest value 1.94 N/mm^2, was obtained for R 4 product, which contains in the composition 50% nanometric TiO_2 pigment and the lowest value 0.62 N/mm^2, was obtained for R 8 product with the same TiO_2 content. For all R1-R8 products, the values obtained for the adherence to support, both initially and after exposure to UV radiation and condensation (accelerated aging) and exposure in urban-industrial environment (natural aging) are greater than 0.5 N/mm^2, a performance level allowed for film-forming protective products, according to the Romanian construction standard [24].

Water permeability (W) (Figure 7) present the following results (according to classification standard): R1-R4 film-forming products with TiO_2 nanometric pigment have the values W ≤ 0.1 kg/ (m^{2}xh^{0,5}), corresponding to the W3 class - low permeability; R4-R7 film-forming products have the values W = 0.1 ÷ 0.5 kg / (m^{2}xh^{0,5}), corresponding to W_2 class - average permeability; R8 film-forming product without TiO_2 nanometric pigment have the value W > 0.5 kg/(m^{2}xh^{0,5}), corresponding to the class W1 - high permeability [25]. The low water permeability (Figure 8) is due to presence the well dispersed TiO_2 nanoparticles.

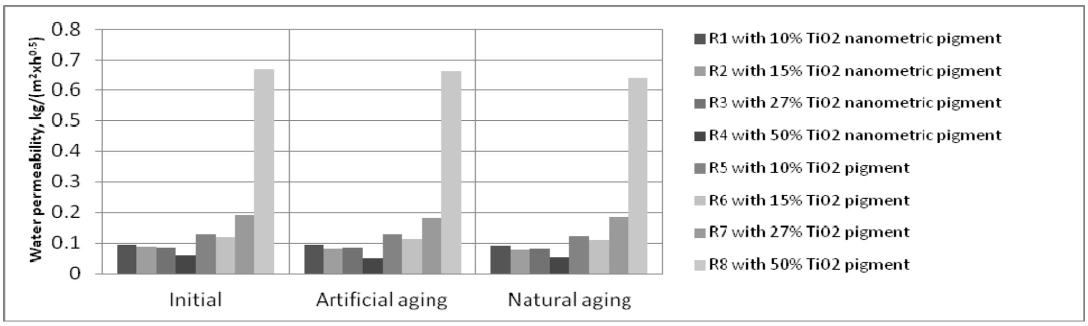

Fig. 7 - *Water permeability* (W), *initial and after aging* / Permeabilitatea la apă (W), inițială şi după îmbătrânire.

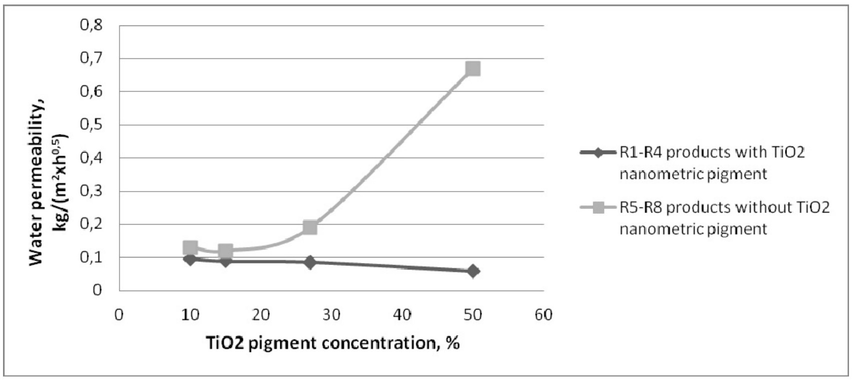

Fig. 8 - Water permeability according to the concentration of TiO_2 pigment / *Permeabilitatea la apă funcție de concentrația de pigment TiO_2.*

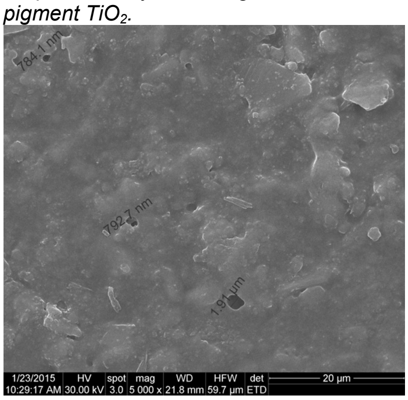

Fig. 9 - SEM image for R 5 surface product without TiO_2 nanometric pigment / *Imagine SEM pentru suprafața produsului R 5 fără pigment nanometric TiO_2.*

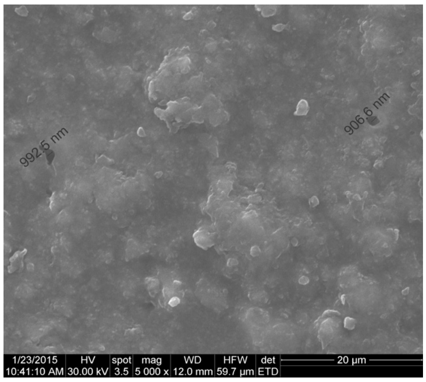

Fig. 10 - SEM image for R 1 surface product with 10% TiO_2 nanometric pigment / *Imagine SEM pentru suprafața produsului R 1 cu 10 % pigment nanometric TiO_2 .*

The analysis performed by SEM electron microscopy for the products without nanometric pigment (Figure 9) and for the products with TiO_2 nanometric pigment (Figure 10) showed the presence of pores with small sizes, on the film surface of the products containing 10% TiO_2. Due to the presence of small size pores, the water permeability of the R1-R4 products is reduced compared to R5-R7 products, which have a medium permeability and the R8 product which has a high permeability.

The values obtained for watery-vapours permeability of the paints based on organic binders in aqueous dispersion with TiO_2 nanometric pigment (V) (Figure 11) are of approximately 5 g/(m^2xh) compared to products without nanometric pigment, which are approximately 2 g/(m^2xh). For all R1 – R8 film-forming products, the values V=0.6÷6 g/(m^2xh) are corresponding for the class V_2 – medium permeability, according to the standard classification [25]. The pores with small sizes, on the film surface of the products with TiO_2 nanometric pigment, increase the watery-vapours permeability (Figure 12).

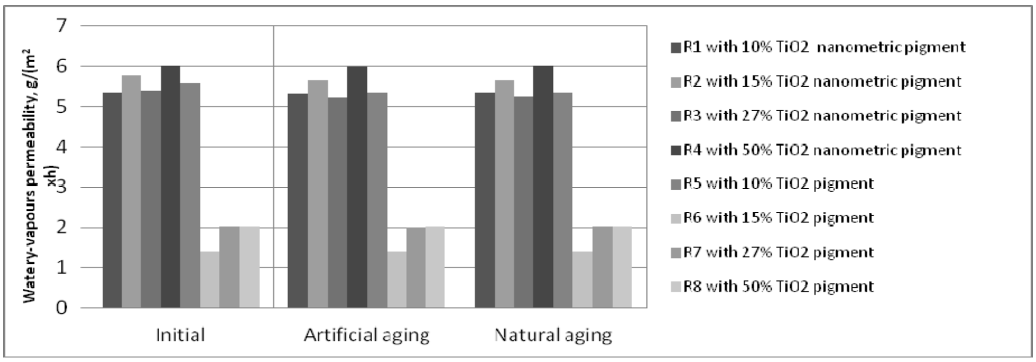

Fig. 11 - Watery-vapours permeability (V), initial and after aging / *Permeabilitatea la vapori de apă (V), inițială şi după îmbătrânire.*

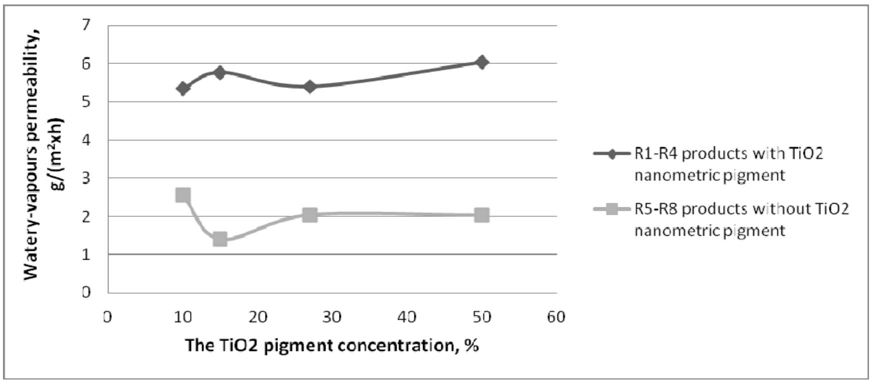

Fig. 12 - Water permeability according to the concentration of TiO_2 pigment / *Permeabilitatea la apă funcție de concentrația de pigment TiO_2.*

Table 5

Characteristics of the products applied on a concrete wall, after aging
Caracteristicile produselor aplicate pe un perete de beton, după îmbătrânire

Film forming product *Produs peliculogen*							
R1	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Estimate of the self-cleaning effect / *Evaluarea efectului de autocurățare*							
- after artificial aging, UV exposure *- după îmbătrânire artificială, expunere UV*							
7 days high self-cleaning effect *7 zile efect de autocurățare puternic*	32 days average self-cleaning effect *32 zile efect de autocurățare mediu*	32 days average self-cleaning effect *32 zile efect de autocurățare mediu*	32 days average self-cleaning effect *32 zile efect de autocurățare mediu*	32 days average self-cleaning effect *32 zile efect de autocurățare mediu*			
- after natural aging exposure in urban industrial environment *- după îmbătrânire naturală, expunere în mediu urban-industrial*							
90 days high self-cleaning effect *90 zile efect de autocurățare puternic*	180 days high self-cleaning effect *180 zile efect de autocurățare puternic*	180 days average self-cleaning effect *180 zile efect de autocurățare mediu*	180 days average self-cleaning effect *180 zile efect de autocurățare mediu*	180 days average self-cleaning effect *180 zile efect de autocurățare mediu*			
240 days without color change, blistering, cracking, peeling *240 zile fără modificare de culoare, fără bășicare, fisurare, exfoliere*				240 days dirt on the surface, without color change, blistering, cracking, peeling *240 zile murdărirea suprafeței, fără modificare de culoare, fără bășicare, fisurare, exfoliere*			

The products behaviour study regarding to the self-cleaning effect, after different time periods of aging exposure (Table 5), highlights the film-forming products with TiO_2 nanometric photocatalytic pigment which after exposure to UV radiations and condensation present total self-cleaning - high self cleaning effect, after 7 days (R1 product) and partial self-cleaning - average self-cleaning effect, after 32 days (R2, R3 and R4 products).

R5, R6, R7 and R8 conventional products, after exposure to UV radiations and condensation, present partial self-cleaning - average self-cleaning effect, after 32 days.

After exposure to natural aging in urban-industrial environment conditions, the film-forming products with TiO_2 nanometric photocatalytic pigment were assessed as follows: R1 product presents total self-cleaning – high self cleaning effect, after 90 days, R2 product presents total self-cleaning - high self cleaning effect, after 180 days, and R3 and R4 products, partial self-cleaning - average self-cleaning effect, after 180 days.

After 240 days of exposure to natural aging in urban-industrial environment conditions, the conventional products without TiO_2 nanometric photocatalytic pigment present changes of the films aspect - surfaces dirtying (grey colouring), compared to the film-forming products with TiO_2 nanometric photocatalytic pigment, which present clean surfaces due to the self-cleaning effect.

4. Conclusions

The experimental results presented in this paper highlight the influence of TiO_2 nanometric photocatalytic pigment in the film-forming products composition based on organic binders in aqueous dispersion, the proprieties of the obtained film-forming products with TiO_2 nanometric pigment being superior compared to the conventional products without TiO_2 nanometric pigment.

The increase of the coating power is 1.45 times higher than the values obtained for the conventional products, due to the enlargement of the contact surface between the polymers -particle, as well as due to the better dispersion of the TiO_2 nanometric photocatalytic pigment, as presented in Table 3, fact supported by the SEM analysis (Figures 2 - 4).

The adherence to support values obtained for the film-forming products with TiO_2 nanometric pigment are about 2 times higher than the values obtained for the conventional products, which explains the better cohesion of the film – test support interface. The highest value (1.94 N/mm^2) was obtained for the product which has in its composition 50% of TiO_2 nanometric pigment, and the lowest value (0.62 N/mm^2) was obtained for the conventional product with 50% of TiO_2 pigment (Figures 5 and 6).

It can be noticed the decrease of the water permeability, due to the presence of TiO_2 nanoparticles in a good dispersion, and of the pores having smaller dimensions, on the surface of films with 10% TiO_2 nanometric photocatalytic pigment, as assessed by the analysis performed using SEM electronic microscopy (Figures 9 and 10).

The watery-vapours permeability of the products based on organic binders in aqueous dispersion with TiO_2 nanometric photocatalytic pigment is two times higher compared with products without nanometric pigment. Due to a better dispersion of the TiO_2 particles and the small dimensions of the pores from the film surface of the products with TiO_2 nanometric photocatalytic pigment, it is favoured the increase of the watery-vapours permeability.

The assessment of the self-cleaning effect, after exposure to UV radiation and condensation, highlights the product having 10% TiO_2 nanometric photocatalytic pigment, product presenting total self-cleaning - high self-cleaning effect (after 7 days), compared to the other products which present partial self-cleaning - average self-cleaning effect (after 32 days).

After exposure to natural aging in urban-industrial environment, the products with a 10% concentration of TiO_2 nanometric photocatalytic pigment present the best self-cleaning effect (total self-cleaning - high self-cleaning effect), performed in half a time compared with the other products, i.e. 90 days instead of 180 days.

The films surface of the products containing TiO_2 nanometric photocatalytic pigment remain clean after 240 days of exposure to natural aging in urban-industrial environment due to the photocatalysis process, compared to the films surfaces of products without TiO_2 nanometric photocatalytic pigment which present colour changes, as a result of surface dirtying under the action of the impurities present in the atmosphere (CO_2, SO_2, dust).

The TiO_2 nanometric photocatalytic pigment used with a 10% concentration in the film-forming products composition based on organic binders in aqueous dispersion confers the new obtained products additional fields of application, such as: the interior use in rooms with high humidity (bathrooms, kitchens), or the exterior use due to the good resistance to urban-industrial environment conditions and the high self-cleaning effect of the films.

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Contact:

Dr. habil. **Leon Mishnaevsky Jr**.,
Senior Scientist, Symposium Chairman
Technical University of Denmark,
Roskilde, Denmark
lemi'@'dtu.dk

Professor **Shinji Ogihara,**
Symposium Chairman,
Tokyo University of Science
Chiba 270-1153, Japan
ogihara'@'rs.noda.tus.ac.jp

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