IMPROVING DURABILITY OF THE FINISHES BY THE FILM-FORMING PRODUCTS IN AQUEOUS DISPERSION WHEN VARYING THE POLYMERIC BINDERS

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This study highlights the selection importance of the binder type used in an aqueous dispersion *film-forming product, depending on the final product desired performances. In order to obtain products which increase the durability of painted surfaces, the compositions selection take into account the external use of the products, the action of various environment factors: water, water vapors, humidity, temperature, UV radiation, dust, organic matter, fats, etc.*

Keywords: film-forming products, aqueous dispersion, durability, acrylic resins

1. Introduction

Lately, the researchers concern is to get ecological products containing a very small amount of solvent, with new or improved performances in order to maintain the painted surfaces clean and not damaged, as much as possible by the action of the environment factors, which contribute to the durability of the supports that are applied on.

After the introduction, decades ago, of acrylic polymers, they gained an important position in the coating products industry, due to its ongoing research results on improved properties, compared to polyvinyl acetate emulsions, styrene-butadiene latex products, as well as, due to the moderate production costs. In addition, their resistance to UV exposure recommends them for use in more exterior applications. Due to their importance and development, recently they are considered some of the most important synthetic resins.

After application, the film-forming products are subject to the continuous action of environmental factors. Destructive factors that lead to the painted surfaces degradation are: heat, cold, humidity, oxygen, sunlight (UV radiation), water (liquid and vapor), mechanical and thermal actions, atmospheric pollutants and various cleaning products, dust, organic matter, fats, etc. The most important

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category of exposure in environmental conditions of film-forming products is the exposure to atmospheric conditions. Effects that may occur are decreased the gloss, color changes, the appearance of cracks, blistering, peeling [1].

The acrylic resins used as a binder in the film-forming products composition present the following advantages: water resistance, alkali resistance, flexibility and good adhesion on support, and in the absence of styrene, resistance to yellowing and loss of gloss in exterior applications [2]. The disadvantage of using these polymers is the low resistance to high, as well as low temperature.

The film-forming products properties can vary depending to the composition. Various combinations of components may be selected depending on the polymer film desired properties. For instance, it is known that the optical properties are influenced by the addition of fillers and pigments (natural calcium carbonate, precipitated calcium carbonate, titanium dioxide, sodium aluminum silicate, mica, talc, kaolin, micronized barite, silicon dioxide) [3].

The silicone resin based polymers exposed to high or low temperatures present o good behavior, a very good adhesion to the support, as well as a good resistance to chemical environments. A disadvantage of these polymers is the high price compared with other types of polymers.

Due to the various advantages presented by these polymers (polymers based on acrylic resins and silicone resin), the hybrid polymer system can be produced, mixtures that will led in obtaining new products with improved properties [4], [5], [6].

The aqueous dispersion film-forming products, which were used in this study, are based on acrylic resins, silicone resins, potassium silicate solution and silica nanodispersion in acrylic resin. In order to determine the products with very good performances and to establish the application tests were performed regarding the products durability.

The film-forming products durability was studied by exposing the film-forming products applied on the concrete specimens to urban-industrial environmental conditions (natural aging), UV radiation and condensation, as well as filtered xenon arc lamp radiation (accelerated aging). The main durability criteria refer to in time color retention, adhesion to the support, the water and water-vapor permeability.

2. Experimental

There were obtained different compositions, according to Table no. 1, four types of binders being used.

Tabel 1

Composition of the studied film-forming products

Raw materials that were used / Product chemical composition	Composition, %				
	C1	**C2**	**C3**	**C4**	**C5**
Soft water	34.5	29.5	29.5	34.5	44.5
Dispersing Agent / Sodium polymetaphosphate $Na_6O_{18}P_6$	0.1	0.1	0.1	0.1	0.1
Antifoaming / Mineral oil	0.1	0.1	0.1	0.1	0.1
The cellulosic thickener / Hydroxyethyl cellulose (HEC)	0.2	0.2	0.2	0.2	0.2
*p*H regulator / The aqueous solution of the sodium salt of the copolymer of maleic acid diisobutylene	0.15	0.15	0.15	0.15	0.15
Dispersing Agent / The aqueous solution of the sodium salt of the copolymer of maleic acid diisobutylene	0.9	0.9	0.9	0.9	0.9
Dispersing Agent (surfactant) / The ammonium salt of polyacrylate	0.7	0.7	0.7	0.7	0.7
Coalescing Agent / Monopropylenglicol	0.6	0.6	0.6	0.6	0.6
Pigment /TiO_2	10.0	10.0	10.0	10.0	10.0
Filler/ $CaCO_3$	32.0	32.0	32.0	32.0	32.0
Resin 1/ Acrylic	**15.0**	**15.0**	**8.0**	**0**	**5**
Resin 2/ Silicone resin emulsion	**0**	**5**	**0**	**0**	**0**
Resin 3/ Potassium silicate solution	**0**	**0**	**12**	**0**	**0**
Resin 4/ Silica nanodispersion in acrylic resin	**0**	**0**	**0**	**15**	**0**
Solvent /White spirit	1.0	1.0	1.0	1.0	1.0
Antifoaming / Mineral oil	0.1	0.1	0.1	0.1	0.1
Biocide / 5 chloro - 2-methyl-4 isothiazolinone	0.4	0.4	0.4	0.4	0.4
HASE rheology modifiers /Hydrophobically modified alkali soluble emulsion	0.8	0.8	0.8	0.8	0.8
HEUR rheology modifiers /Hydrophobically modified ethoxylated urethane emulsion	0.5	0.5	0.5	0.5	0.5
TOTAL	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

Note: C 1= paint based on acrylic resin;
C 2 = paint based on silicone resin;
C 3 = paint based on acrylic resins and potassium silicate solution dispersion;
C 4 = paint based on silica nanodispersion in acrylic resin.
PVC (pigment volume concentration) =60-70%.

The materials used in obtaining the film-forming products are: dispersing agent, Calgon N - Aako, Netherlands; Antifoam, Antifoam W-Quinitécnica; Thickener cellulosic MHBR Natrosol 250, Ashland Inc.; pH regulator, AMD 95;

dispersing agent, MD 20 - BASF the Chemical Company; dispersing agent Coatex P 90, Arkema; coalescing agent, MPG - Chemical Plus; Pigment - TiO_2, DELTIO 81x-HUNTSMAN; Filler - Ca CO_3, 15C-Ionian Kalk; Resin, Acronal 290D - BASF the Chemical Company; Silicone resin, potassium silicate solution, Silica nanodispersion in acrylic resin - Wacker; Solvent - (white spirit), Shersol D 40 - Shell Chemicals; Biocide, PARMETOL DF 35 - Schülke & Mayr GmbH Germany; HASE rheological modifiers, Latekoll DS 6269 - BASF The Chemical Company; HEUR rheological modifiers, Colacral PU 85 - BASF The Chemical Company.

The product obtaining procedure was as follows:

- the cellulosic thickener and the antifoam were mixed in water using a Cowless type mixer, with a speed of 400 rpm;
- the mixing time was of 10 minutes, till the thickening was observed;
- the other ingredients: *p*H regulator, dispersing agent and coalescing agents were then added, each at a period of 5 minutes to each other and were mixed with a speed of 400 – 500 rpm;
- the dispersion was then finished by adding the TiO_2 pigment and mixing for 10 minutes at a speed of 800-1000 rpm;
- $CaCO_3$ was added and mixed for 10-15 minutes at a speed of 1000 to 1200 rpm; at this time was checked the grinding fineness degree or the dispersion grade that has to be maximum 35 µm;
- the resin latex was added and mixed for 10 minutes at a speed of 700 rpm;
- the HASE / HEUR rheology modifiers were added dissolved in water, in order to avoid the formation of agglomerates, together with the biocide and mixed for 15 minutes at a speed of 1000 to 1200 rpm.

The products application was performed on the concrete support that was prior correspondingly prepared by brushing, dusting and degreasing, taking into account that this has a decisive influence on the paints coverage and durability quality.

The concrete mix design for the support is presented in Table no. 2:

Tabel 2

The concrete mix design for the substrate

Component	**Dosage**
Cement 42.5R	13.4 kg/m^3
Water (water / cement ratio = 0.4)	5.37 l
Aggregate size: 0-4	22.3 kg
Aggregate size: 4-8	25.1 kg
Super plasticizer additive	25 ml
Density	2320 kg/m^3

The layers application sequence on the concrete surface was as follows: first layer - primer 1 is applied diluted with water in a ratio of 1:4; second layer -

film-forming product (C1-C5) is applied diluted 10% with water; third layer - film-forming product (C1-C5), is applied undiluted.

The film-forming products were applied to a specific consumption of 180-250 g/m^2/layer and a application efficiency of 6-8 m^2/l/layer.

The (C1-C5) obtained products were characterized using the test methods specific for film-forming products, both on liquid products, as well as on products applied on the mineral support.

The liquid products characterization was performed by determining the following properties: density, according to SR EN ISO 2811-1:2011, time flow, according to SR EN ISO 2431:2007, non-volatile-matter content, according to SR EN ISO 3251:2008, the size of the largest particles, according to SR EN ISO 1524:2002, hiding power, according to SR EN ISO 6504-3:2007.

The products applied on support characterization was performed by determining the following properties: wet film thickness, according to SR EN ISO 2808:2007, pull-off test to the support, according to SR EN ISO 4624:2003, specular gloss of non-metallic paint, according to SR EN ISO 2813:2003, impact resistance, according to SR EN ISO 6272-1:2004, water permeability, according to SR EN ISO 1062-3:2008, water-vapor permeability, according to SR EN ISO 7782:2012.

The determination of wet-scrub resistance, according to SR EN ISO 11998:2007, is performed using the Wet Abrasion Scrub Tester, type Byk-Gardner, PB 5002 equipment, that features two brush holders for side by side testing.

The film-forming products behavior determination to natural aging in urban-industrial environment was performed in exposure stations. The exposure stations consist of a number of stands on which the samples to be studied are mounted. The samples were positioned in such a way that they are oriented towards south and under an angle of 45^0 to the horizontal [7]. The examination of samples from the exposure stations was performed every month, in an exposure period of 12 months.

The film-forming products applied on mineral support were tested for artificial aging, as it follows:

- 1000 hours to UV radiation exposure and 1000 hours condensation, for 250 cycles, one cycle consisting in 4 hour exposure to UV radiation at a temperature of 60 ± 3^0C, followed by 4 hours condensation at a temperature of 60 ± 3^0C, method A [8]; the used apparatus is Q-UV type, Accelerated Weathering Tester, with QVB-313 EL type lamps;
- the exposure to radiation of a filtered xenon arc lamps including water and water-vapor, for 500 exposure cycles (one exposure cycle consisting in: 18 minutes moistening, 102 minutes drying); the test condition in testing chamber are: temperature (38 ± 3) ^{0}C and relative humidity (40-60) % during the drying;

the exposure is performed using equipment fitted with the xenon arc lamps, Q-SUN type, method 1, cycle A [9].

The exposed products properties are compared with unexposed products (standard witness samples), prepared from the same material, at the same time and in the same way.

The test result was recorded, taking into account the changes in appearance or other signs of coating deterioration: discoloration, blisterings, crackings, according to SR EN ISO 4628-1-8:2004 and some properties variation (specular gloss of non-metallic paint, pull-off test for adherence, water permeability, water-vapor permeability) after 1000 hours exposure to UV radiation and 12 months exposure to urban-industrial conditions.

3. Results and discussion

The products characterization was performed and the obtained results are presented in Table no. 3.

Tabel 3

The studied film-forming products characteristics

Characteristics	**Obtained value / film-forming product**				
	C1	**C2**	**C3**	**C4**	**C5**
Density, 20^0C, g/cm^3	1.522	1.540	1.720	1.484	0.960
Flow time, flow cups with 6 mm diameter, (seconds)	30	55	89	31	98
Non-volatile-matter content, %	61.15	63.98	75.95	65.50	45.15
Hiding power, m^2/l	5.31	8.98	3.4	7.15	4.23
Largest particles size, µm	40	30	45	30	40
Type MC (40) applied on concrete support products characterization					
Impact resistance, cm	90 mark without changes	100 mark without changes	100 mark without changes	100 mark without changes	20 mark with cracks
Wet-scrub resistance after 200 washing cycles - loss of weight, g/m^2 - loss of thickness, µm	 30.69 31.76 Class 3	 18.16 19.22 Class 2	 36.75 19.47 Class 2	 8.20 3.150 Class 1	 270.80 120 Class 5
Specular gloss of non-metallic paint, at 85^0 - initial - after aging • UV exposure (1000 hours) • Xenon exposure (1000 hours) • urban-industrial environment exposure (12 months)	 2.3 G 3 1.5 1.8 1.7	 2.5 G 3 1.9 1.7 1.5	 3.2 G 3 3.1 2.9 2.7	 1.5 G 3 1.2 1.1 1.0	 2.8 G3
Pull-off test, adherence to the support, N/mm^2					

- initial - after aging • Xenon exposure (1000 hours) • urban-industrial environment exposure (12 months)	2.25 2.26 2.27	2.46 2.47 2.48	1.84 1.89 1.79	0.74 0.79 0.82	0.25
Water permeability, W, kg/m^{2}x h^{0,5} - initial - after aging • Xenon exposure (1000 hours) • urban-industrial environment exposure (12 months)	 0.064 W_3 0.111 0.189	 0.059 W_3 0.107 0.115	 0.046 W_3 0.112 0.191	 0.168 W_2 0.199 0.184	 0.507 W_1
Water-vapor permeability, V, g/m^{2}x h -initial -after aging • Xenon exposure (1000 hours) • urban-industrial environment exposure (12 months)	 1.26 V_2 3.21 3.092	 1.40 V_2 2.80 3.058	 0.89 V_2 2.36 2.040	 3.84 V_2 3.71 3.767	 6.930 V_1

The experimental results highlight the following:

- the density values (fig. 1), non-volatile-matter content (fig. 2), flow time (fig. 3), hiding power (fig. 4) and the size of the largest particles (fig. 5) are similar to the products C1 - C4 and are usual for aqueous dispersion film-forming products;
- the product C5 presents low values in comparison to other products for density, non-volatile-matter content, while the flow times is much higher and the hiding power and the size of the largest particles are similar to other products;

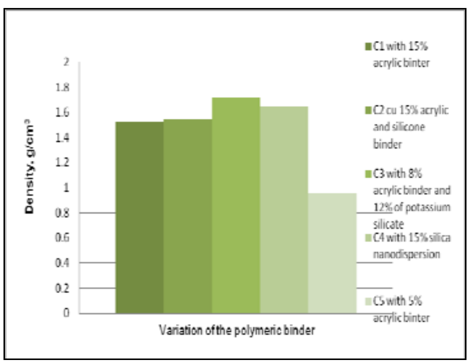

Fig. 1 Variation of the density depending on the nature of the polymeric binder (C1-C5)

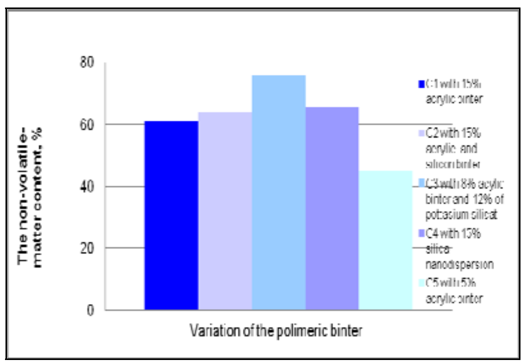

Fig. 2 Variation of the non-volatile-matter content depending on the nature of the polymeric binder (C1-C5)

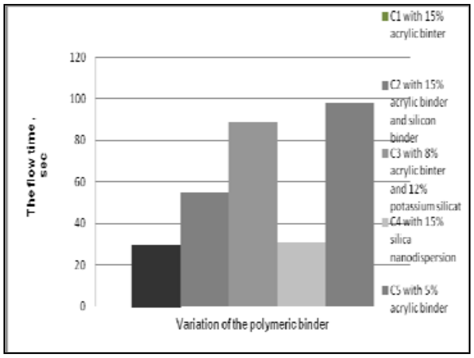

Fig. 3 Variation of the flow time depending on the nature of the polymeric binder (C1-C5)

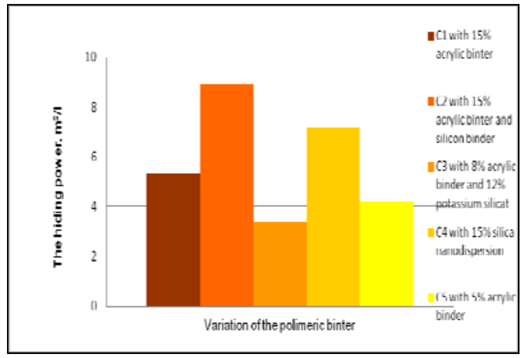

Fig. 4 Variation of the hiding power depending on the nature of the polymeric binder (C1-C5)

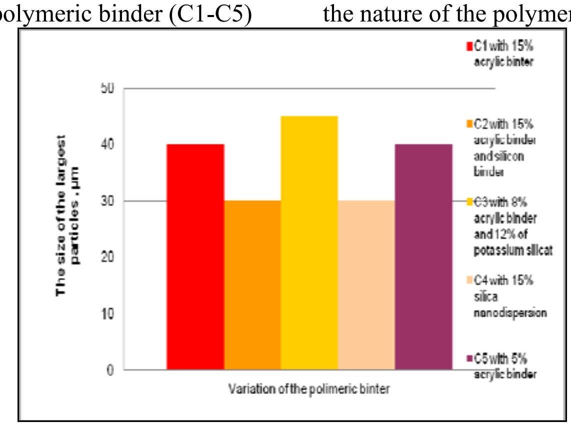

Fig. 5 Variation of the largest particles size depending on the nature of the polymeric binder (C1-C5)

- the values for impact resistance, in cm (fig. 6) are similar for products C1 - C4, accordingly; the product C5 presents very low resistance to impact, impression with cracks, improper value;

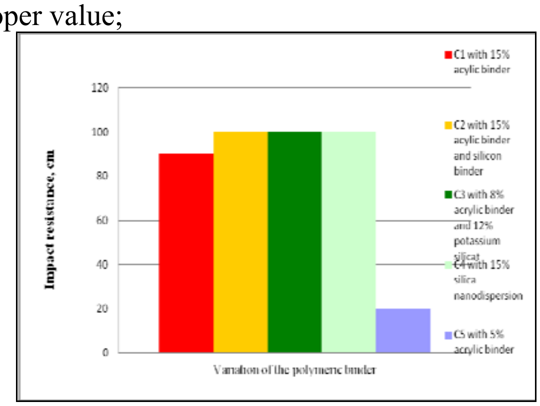

Fig. 6 Variation of the impact resistance depending on the nature of the polymeric binder (C1-C5)

- the values of wet-scrub resistance (fig. 7), after 200 washing cycles, expressed by the thickness loss, in µm, classifies the C4 product in Class 1 (presenting the lowest values and best washability), the classification for the C1 product is in Class 3, while and the C3 and C2 products is classified in Class 2;
- the value for wet-scrub resistance expressed by the mass loss, in g/m^2 (fig. 8), presents the lowest values and best wet-scrub for the C 4 product, followed by C2, C1 and C3 products with good wet-scrub, the product C5 presenting the highest value and being classified in Class 5.

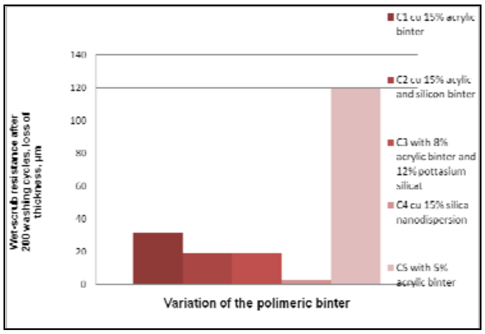

Fig. 7 Variation of the wet-scrub resistance expressed by the loss of thickness depending on the nature of the polymeric binder (C1-C5)

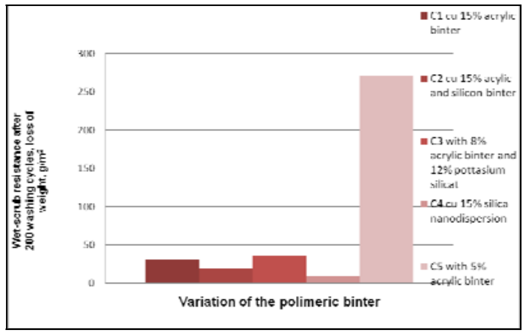

Fig. 8 Variation of the wet-scrub resistance expressed by the loss of weight depending on the nature of the polymeric binder (C1-C5)

The products characteristics studied after the exposure to aging were the following: specular gloss of non-metallic paint (film gloss), pull-off test (adhesion to the support), water permeability and water-vapor permeability.

The experimental results highlight the following aspects:

The specular gloss of non-metallic paint (film gloss)

- initially, the studied film-forming products present a gloss degree at $85^0 \leq 10$, result which classifies them in Class G3 - matte surface;
- after aging under UV radiation, the exposure to the xenon arc lamp filtered radiation and aging in the urban-industrial environment, the obtained values are slightly lower than the initial values (Fig. 9), and the classification being similar Class G3 - matte surface, the change is observed visually by comparing the exposed samples to unexposed witness samples.

Pull-off test (adherence to the support)

- the initial values of adherence are > 0,5 N/mm^2, for C1 - C4 products, good adherence to the support;
- after aging under a xenon arc lamp filtered radiation and aging in urban-industrial environment, the obtained values are slightly higher than the initial values (fig. 10), the adherence to support being considered as appropriate.

The water permeability

- the initial values of the water permeability classifies the C1 - C3 products in Class W_3, low permeability, the C4 product is classified in Class W_2, average permeability;
- after aging under a xenon arc lamp filtered radiation and aging in urban-industrial environment, the obtained values are higher than the initial ones (fig. 11);
- after aging, the water permeability is higher and the products are classified in Class W_2, average permeability, specific for film-forming products used in exterior coatings.

The water-vapors permeability

- the water vapor permeability initial values classify the C1 - C4 products in Class V_2, (average permeability);
- after aging under a xenon arc lamp filtered radiation and aging in urban-industrial environment, the obtained values are slightly higher than the initial ones (fig. 12);
- the water-vapor permeability is slightly higher after aging, the products maintain the Class W_2 (average permeability) classification, specific for film-forming products used in exterior coatings.

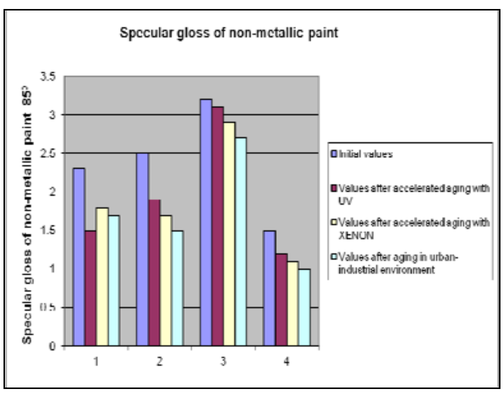

Fig. 9 Specular gloss of non-metallic paint (gloss film) after exposure to accelerated and natural aging

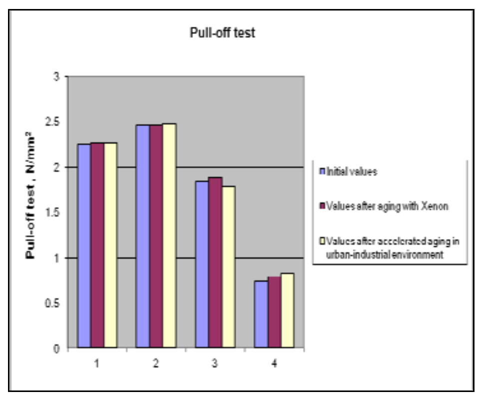

Fig. 10 Pull-off test after exposure to accelerated and natural aging

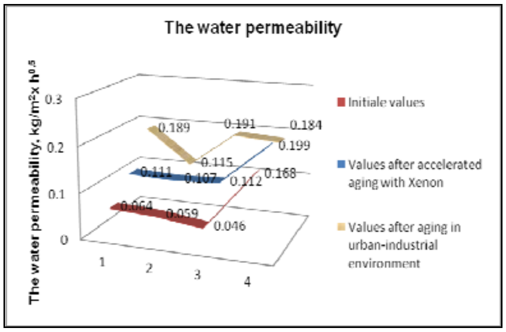

Fig. 11 The water permeability after exposure to accelerated and natural aging

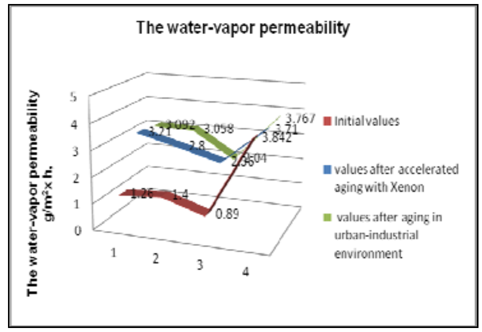

Fig. 12 The water-vapor permeability after exposure to accelerated aging and natural aging

Color and aspect film changes

- after 12 months exposure to natural aging are noticed: dirt deposit on the surfaces applied with the C1 and C3 products, a slightly dirt deposit on the surfaces applied with the C2 product and unmodified surfaces covered with C4 product.

4. Conclusions

Analyzing the experiments obtained for the studied products, several results can be highlighted:

- there is a product (C5) containing 5% acrylic resin which presents:
  - for density, values < 1 g/cm^3, the non-volatile-matter content < 50 %, the impact resistance - mark with cracked surface, Class 5 wet-scrub resistance, the pull-off test result (adherence) is < 0,3 N/mm^2;
  - for the water permeability, according to SR EN 1062-1:2004, Class W_1 - high permeability (W > 0,5 kg/m^{2}x h^{0,5});
  - for the water-vapors permeability, according SR EN 1062-1:2004, Class V_1 - high permeability (V > 6 g/m^{2}x h).

The C5 product characteristics recommend its use as a primer, not as a top coat in a coating system, having the role of preparing the concrete support for the C1 - C4 film-forming products following layers application.

- other C1-C4 film-forming products present values corresponding for the outdoor use, both for the initial characteristics, as well as after the exposure to natural aging, urban-industrial environment and accelerated aging by exposure to UV lamp and an arc xenon filtered radiation;
- the C4 product based on silica nanodispersion in acrylic resin has the best behavior after natural aging; the covered surfaces presenting suitable characteristics and remaining clean after the exposure period.

R E F E R E N C E S:

[1]. *A.R. Marrion*, ed. The Chemistry Of Physics And Coatings. 2nd Edition, The Royal Society of Chemistry,2004, p 84;

[2]. *T. Brock, M. Groteklaes, P. Mischke*, Brock/European Coatings Handbook, Vincentz Network GmbH & Co KG, 2000, p 66;

[3]. *P. Dumitru, I. Jitaru*, "Improving Hiding Power Obtained by Variation of Fillers for Interior Emulsion Paints", Rev. Chem.(Bucharest), 61.5, 2010, p 479-483;

[4]. *Y. Liu, N.J. Dayton*, Silicon-acylic copolymer, US Patent Application Publication, US 2013/0012653 A1, 2013;

[5]. *P. Hong-Soo, et al.,* “Synthesis of silicone-acrylic resins and their applications to superweatherable coatings”, Journal of Applied Polymer Science, Volume 81, Issue 7 (2001), p 1614-1623;

[6]. *Park H-S. et al.* "Preparation and characterization of weather resistant silicone/acrylic resin coatings." Journal of coatings technology, Volum 75, Issue 936, (2003), p 55-64;

[7]. SR EN ISO 2810:2005 “Paints and varnishes - Natural weathering of coatings - Exposure and assessment”;

[8]. SR EN ISO 11507:2007 ”Paints and varnishes - Exposure of coatings to artificial weathering - Exposure to fluorescent UV lamps and water”;

[9]. SR EN ISO 11341:2005 ”Paints and varnishes - Artificial weathering and exposure to artificial radiation - Exposure to filtered xenon-arc radiation”.