Forecasting and Optimisation of the Waterborne Anticorrosive Paint Composition with Non-Toxic Pigments

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Summary: The investigations of the waterborne anticorrosive composition containing non-toxic pigments and binders with different chemical nature have been carried out. The effect of binders, pigments, extenders and the level of pigmentation on the structure of coatings (Hg porosity test, DMTA) and on the protective properties (corrosion chambers, EIS, SVET) were tested. The test results show that protective properties of the coatings depend on the chemical composition of binders and the mechanism of film formation. The impact of pigments on protective characteristics of the coatings is connected with their chemical composition, physical shape and the level of pigmentation. The application of the statistical analysis of the results allows to define the weight of particular components of paints in shaping protective properties of the coatings and the selection of the optimum composition.

Keywords: waterborne paints; non-toxic pigments; coatings; barrier; electrochemical properties

Introduction

A lot of research has been carried out but the formulation of anticorrosive waterborne coatings containing non-toxic pigments is still problematic. There are many controversies on efficiency and the mode of performance of this kind of pigments. These problems come from the lack of the explicit laboratory method that would enable forecasting of the resistance of coatings and the differentiation of their protective capacity. [1]

The aim of the project was to determine the effect of main paint components – binders and

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pigments/ extenders – on shaping of protective properties of waterborne coatings. The using of test methods, including both the physical structure and protective efficiency of coatings, has allowed to forecast protective properties and to optimise the paint composition.

Paint formulation

The components used in paint formulations are characterised in Table 1.

Table 1. Components and the level of pigmentation of paints

Binder	Urethane dispersion modified by fatty acids „A”	Alkyd emulsion (ok. 46% plant oils) „B”	Epoxy-ester dispersion „C”	Styrene-acrylic dispersion „D”	
Pigment	Zinc phosphate „2”	Zinc calcium phosphate „3”	Zinc ferrite „4”	Micaceous iron oxide „5”	Jon-exchanged pigment „6”
Extender	$CaCO_3$ „a”	$BaSO_4$ „b”			
Λ (Reduced Critical Pigment Volume Concentration)	Λ=0,45 „I”	Λ=0,6 „II”	Λ=0,8 „III”		

The paints contained the same amount of red iron and microtalc.

Adopted marking consists of four variable elements:

binder/ pigment extender/ Λ

for example: A/2a/I – urethane dispersion/ zinc phosphate, $CaCO_3$/ Λ=0,45

The coatings to be tested were formulated with possibly best packing of pigments and extenders which means their best compatibility in the area of the lowest CPVC identical with the efficiency of the anticorrosive performance in water dispersion.

Test methods

The following test methods were carried out for the paint compositions:

- Hg porosity test – at the apparatus constant of 21,63 μF / pF, max. pressure of 4,680 psi and wet angle Hg of 130 deg,
- dynamic-mechanical analysis (DMTA) – at the frequency of 1 Hz and the tension amplitude of 16 μm,
- salt spray test according to PN ISO 7253,
- *Prohesion* test: 1 h of spraying with electrolyte solution 0,5 g NaCl + 3,5 g $(NH_4)_2SO_4$/ l, temp. 25 ^{0}C/ 1 h of dry conditions, temp. 35 ^{0}C,
- humidity test according to ISO 6270,
- electrochemical impedance spectroscopy (EIS) at the amplitude of the measuring signal of 10 mV and the frequency of 0,01 Hz to 100 kHz, using as the electrolyte 3 % NaCl,
- scanning vibrating electrode technique (SVET) – at the frequency of 80 Hz and the amplitude of 50 μm, using as the electrolyte 10^{-3} M NaCl with complexing agent 10^{-3} M EDTA.

The paints were tested either as free film with the mean thickness of 70 μm or coatings with the mean thickness of 50 μm applied on steel plates of 70 x 150 mm.

Test results

Physical and mechanical properties of coatings, such as tightness, flexibility, homogeneity, often decide of their long-time durability, thus efficient corrosion protection. The type of binder and the way and level of pigmentation as well as the interaction of pigment/ pigment and pigment/ binder determine these properties in pigmented paint compositions. [2,3] It is especially important for waterborne paints in which the mechanism of acting of non-toxic anticorrosive pigments is still not fully recognised.[4]

The investigations of the effect of main paint components on the coating structure connected with anticorrosive properties have allowed both to explain the mechanism of pigment acting and to give guides to paint formulation.

The test results show that protective properties of the waterborne coatings depend on the chemical composition of binders and the mechanism of film formation reflected by cross-linking density and glass transition temperature T_g. Fatty-acid modified urethane dispersion (A) has the best barrier properties.

The impact of pigments on protective properties of the coatings is connected with their chemical composition (interaction with the binder), with their physical nature (size and particle size distribution) and the level of pigmentation (PVC/CPVC). [5-8]

The combining barrier- electrochemical acting has been found out for zinc calcium phosphate (3) and zinc ferrite (4). These pigments show better protective properties than others. Other tested pigments participate in barrier protection only.

Taking into account all the test results the binders can be ranked according to their decreasing protective properties as follows: A > B > C > D and the pigments: 4 > 3 > 2 = 6 > 5.

As an example, Figure 1 shows changes in impedance data depending on the kind of binder and Figure 2 - depending on the kind of pigment.

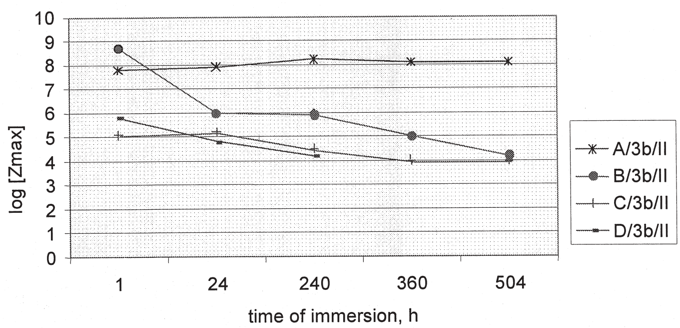

Figure 1. Changes of $[Z_{max}]$ in the time of immersion in 3% NaCl depending on the kind of binder.

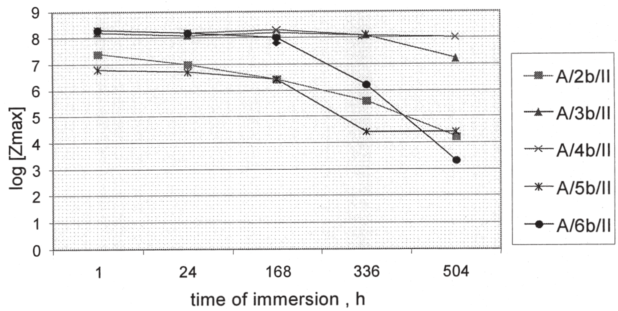

Figure 2. Changes of $[Z_{max}]$ in the time of immersion in 3% NaCl depending on the kind of pigment.

Forecasting and optimisation of the composition

Analysed data obtained from the test chambers comprised the factors of corrosion changes, such as blistering size (S) and density (D) and corrosion of substrate (C). These factors were determined in arbitrary range 0 – 5 (0-without changes, 5 – maximum changes). The mean values, including all the factors, were calculated for each sample. They have been given in the range 0 – 100% and marked respectively: Sm for salt spray test, Wm for water condensation test and Pm for *Prohesion* test.

The base of electrochemical data were the mean values of impedance modulus determined after 1 h immersion and total mean values.

The comparison of test results obtained by EIS, salt spray test, water condensation test and *Prohesion* test is given in Table 2.

Table 2. Comparison of test results

Symbol	Logarithm of impedance modulus Mean values		Unified factors of corrosion changes											
			Salt spray test				Humidity test				*Prohesion* test			
	after 1 h	total	S	D	C	Sm	S	D	C	Wm	S	D	C	Pm
A	7,83	6,27	2,6	3,0	2,0	50	2,6	4,3	0,0	47	0,4	0,5	0,7	10
B	8,10	6,47	4,0	4,5	3,0	77	3,5	4,0	0,0	50	2,0	2,5	2,8	49
C	5,30	4,61	3,5	4,3	4,2	80	2,6	2,9	0,0	37	3,4	2,2	2,8	56
D	5,64	4,72	4,0	4,3	4,2	84	1,3	1,7	0,0	20	3,0	3,2	3,6	66
2	6,53	5,36	3,6	4,0	3,6	75	2,8	3,8	0,0	44	1,5	2,0	2,6	41
3	7,08	6,09	3,3	3,7	2,5	63	2,5	3,6	0,0	41	2,1	2,0	2,3	43
4	7,03	6,43	2,1	2,4	1,1	37	2,4	4,2	0,0	44	0,8	0,5	1,1	16
5	5,75	5,02	3,7	4,1	4,3	80	2,8	3,1	0,0	39	1,8	2,3	2,5	43
6	7,02	5,68	3,1	4,1	2,5	64	1,4	2,1	0,0	23	1,8	0,9	0,9	24
a	7,78	7,11	2,4	3,0	1,5	46	2,8	4,7	0,0	49	0,3	0,3	0,7	9
b	6,59	5,48	3,4	3,8	3,2	69	2,3	3,2	0,0	37	1,8	1,9	2,2	39
I	7,31	6,49	3,0	3,5	2,5	60	2,5	4,0	0,0	43	1,1	1,4	1,8	28
II	6,06	5,18	3,5	4,0	3,5	73	2,3	2,9	0,0	35	2,1	1,9	2,2	42
III	6,75	5,16	3,3	3,6	2,8	65	2,4	3,2	0,0	37	1,8	1,7	2,0	37
Optimum	A(B)/3a/I A(B)/4a/I		A/4a/I				D/6b/II				A/4a/I			

From the data given in Table 2 it is evident, that the test results obtained by salt spray and *Prohesion* methods point clearly at paint formulation containing fatty acid modified urethane dispersion (A), zinc ferrite (4), $CaCO_3$ (a) with Λ=0,45. Furthermore electrochemical test results show, that the good corrosion protection can be obtained by paints basing on urethane dispersion (A) or alkyd emulsion (B) pigmented with zinc calcium phosphate (3) or zinc ferrite (4).

In case of humidity test the results are different from mentioned above. These results are not representative enough, because the most essential factor C – corrosion of substrate – has the value

0 and the assessment has been based on other factors only.

Taking into consideration the test results from salt spray, *Prohesion* and EIS methods the optimum paint composition should be as follows:

A/4a/I

The statistical analysis shows, that the salt spray, *Prohesion* and EIS methods are a good tool for the forecasting and optimisation of paint composition containing waterborne binders and non-toxic pigments. The more clearly results can be obtained in corrosion chambers. In the case of EIS it is very important to find more representative criterion for an analysis than a measurement after 1 h of immersion (i. e. time in deflection point of curve).

Conclusions

• The test results show that protective properties of the waterborne coatings depend on the chemical composition of binders and the mechanism of film formation reflected by cross-linking density and glass transition temperature T_g. Fatty-acid modified urethane dispersion has the best barrier properties and styrene acrylic dispersion – the worse protective efficiency.

• The impact of pigments on protective properties of the coatings is connected with their chemical composition (interaction with the binder), with their physical nature (tightness and homogeneity of coatings) and the level of pigmentation.

• Combining barrier-electrochemical acting has been found for zinc calcium phosphate and zinc ferrite. These pigments present better protective features. Other tested pigments participate in barrier protection. The more evident it is the more the coating is.

• The application of the statistical analysis of the test results allows to define the weight of particular components of paints in shaping protective properties of the coatings and to select the optimum composition as well as the correlation between the methods which have been used. Basing on the comparison of correlation coefficient *Prohesion* method has been chosen as the most compatible with electrochemical methods. The humidity chamber was eliminated because the test results do not completely reflect protective properties of the coatings.

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