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RESEARCH ON THE INFLUENCE OF COLLOIDAL SILICA ADDITION ON WATER VAPOUR PERMEABILITY OF PAINT COATING

BADANIE WPŁYWU DODATKU KRZEMIONKI KOLOIDALNEJ NA PRZEPUSZCZALNOŚĆ PARY WODNEJ POWŁOK MALARSKICH

Abstract

In the paper the influence of colloidal silica addition with different amounts of organic resin in facade paints formulations on the change of water vapour permeability of hardened coatings was researched. The results were obtained by means of experiments. To quantify the ability of paint to diffuse water vapour, S_d factor, defined as equivalent to the thickness of non-rotating air layer, was used. For the quantitative determination of the relationship between water vapour permeability and the share of analyzed components in the formulation of paint a statistical model based on multiple regression was applied. Statistical analysis of the results showed that the effect of changes in the amount of colloidal silica in the formulation of paint on S_d value is small, compared to organic resin share changes.

Keywords: colloidal silica, water vapour permeability, coating

Streszczenie

Przebadano wpływ dodatku krzemionki koloidalnej przy różnych ilościach żywicy organicznej w recepturach farb fasadowych na zmianę przepuszczalności pary wodnej przez utwardzone powłoki. Wyniki badań uzyskano na drodze eksperymentalnej. Do skwantyfikowania zdolności powłok malarskich do dyfuzji pary wodnej posłużono się współczynnikiem S_d definiowanym jako równoważna grubość nieruchomej warstwy powietrza. Do ilościowego określenia związków pomiędzy przepuszczalnością pary wodnej a udziałem analizowanych składników w recepturze farby posłużono się modelem statystycznym opartym na regresji wielorakiej. Sadystyczna analiza uzyskanych wyników wykazała, że wpływ zmian ilości krzemionki koloidalnej w recepturze farby na S_d value jest niewielki w stosunku do zmian udziałów żywicy organicznej.

Słowa kluczowe: krzemionka koloidalna, przepuszczalność pary wodnej, powłoki malarskie

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Designation

C_{PR}	–	proportion by weight of aqueous solution of colloidal silica
C_{PR}	–	proportion by weight of aqueous dispersion of organic resin
S_d	–	factor, diffusion equivalent air layer thickness [m]
V	–	coefficient of diffusion of water vapour [$\text{g}/(\text{m}^2 \cdot \text{d})$]
$m_1 - m_2$	–	the difference in mass of the container between the two measurements [g]
$t_2 - t_1$	–	the time between two consecutive measurements expressed in [h]
A	–	the surface of the tested sample expressed in [m^2]

1. Introduction

Colloidal silica is an aqueous dispersion of amorphous silicon dioxide (SiO_2) in the form of spherical, non-crosslinked particles. Surface of each such particle is fully hydroxylated, the size, as in the case of colloids, ranges from 5 to 75 nm. There are many literature references describing the possible use of colloidal silica for the manufacturing of paints for different applications. In paints containing an organic binder, the addition of colloidal silica improves the adhesion to the substrate, increases coating's hardness and resistance to weathering. Inorganic paints can be used as the main component or as the primary binder. Furthermore, the addition of colloidal silica increases the elastic modulus of the cured film, which in turn allows to reduce the amount of organic binder in paint formulations without the loss in mechanical properties of coatings. An important parameter affecting coatings' long-term functionality and enabling transport of the accumulated moisture by diffusion of water vapour is water vapour permeability. In the paper paint formulations containing various amounts of organic binder and colloidal silica in terms of water vapour permeability were tested.

2. Experimentalsection

2.1. Material

Tests were conducted on coatings made from the paint produced in laboratory scale from the formulations comprising: filler: CaCO_3 (in an amount of about 30% in comparison with all components of a formula), quartz powder (7%), thickening agent: Methyl Hydroxy Ethyl Cellulose MHEC (0.45%), Pigment: Titanium dioxide Rutil (17%), dispersing agent: sodium salt of polyacrylic acid (0.4%), silicone defoamers (0.2%) and water (qs to 100%). First the pigments, fillers and coating assistants were dispersed in water to give a base, which was then mixed in appropriate weight proportions with aqueous dispersion of a copolymer of n-butyl acrylate and styrene (incl. 50% solids) and an aqueous solution of colloidal silica (incl. 50% solids, particle size 12 nm, pH 7.5). Weight percentages of aqueous dispersion of organic resin for all ingredients of tested paints formulations (C_{PR} [%]) were: 13, 16, 19, 22 and 25% for each part of organic resin, weight shares of aqueous solution of colloidal silica (C_{SI} [%]) were 0, 3, 6, 9 and 12%. Coating thickness in the hardened state was 0.24 [mm].

2.2. Measurement of S_d [m] factor, diffusion equivalent air layer thickness by Wet-Cup scale method

The ability of diffusion of water vapour of the decorative and protective coating is determined by the value of diffusion-equivalent air layer thickness S_d . It means that the thickness of the stationary air layer [m], under the same measurement conditions has the same coefficient of diffusion of water vapour V [g/(m²·d)] as the tested coating. The study was conducted on a sample of paint that had a thickness of 180 μm, using a Wet-Cup method. The equipment and materials for the study were prepared in accordance with PN-EN ISO 7783-2: 2001 [8]. For this purpose glass pans were used which, after filling with a saturated solution of ammonium dihydrogen phosphate were sealed with a porous material made of porous polyethylene PE-HD, at which the tested coating was previously applied by brush. The space between the wall of the capillaries and the sintered disc was sealed. Thus prepared dish was weighed on an analytical scale and placed in a climate chamber (see Fig. 1).

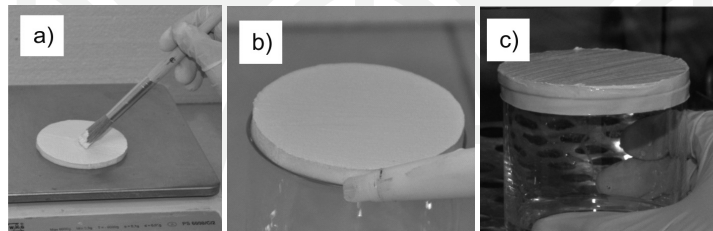


Fig 1. Preparation of the samples to determine the water vapour transmission rate

The amount of steam, which diffused through the tested coating was determined by measuring the weight. The change in mass of water, on the basis of which the S_d value was determined, was calculated as the average value of three successive measurements at subsequent intervals after equilibrium was achieved, and it was carried out on three separate coatings of the same material. For each tested sample, the values of diffusion equivalent air layer thickness S_d according to the formula (1), were determined:

$$S_d = \frac{20 \cdot A \cdot (t_1 - t_2)}{24 \cdot (m_2 - m_1)} \quad (1)$$

where:

$m_1 - m_2$ – the difference in mass of the container between the two measurements expressed in [g],

$t_2 - t_1$ – the time between two consecutive measurements expressed in [h],

A – the surface of the tested sample expressed in [m²].

The S_d value of diffusion equivalent air layer thickness of the coating was calculated as the difference of the substrate S_d with a coating without substrate $S_{d'}$

$$S_d(\text{coating}) = s_d(\text{substrate with coating}) - S_d(\text{substrate}) \quad (2)$$

3. Results and discussions

The results of studies on permeability of water vapour through the coating containing various amounts of colloidal silica and organic resin were presented in graphic form in Figure 2.

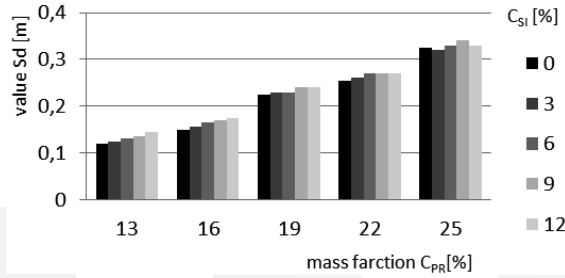


Fig. 2. Results of studies on permeability of water vapour through the coating, where: S_d – factor, diffusion equivalent air layer thickness [m], C_{PR} – proportion by weight of aqueous solution of colloidal silica, C_{Si} – proportion by weight of aqueous dispersion of organic resin

3.1. Analysis of variance according to a double classification (ANOVA)

In order to check whether simultaneous changes in the mass fraction of the analysed ingredients have a statistically important impact on the value S_d , a correlation matrix allowing for the calculation of Pearson's coefficients of correlation and assessment of their significance was developed. With this purpose in view, statistical inference with the use of ANOVA analysis of variance according to a double classification was conducted [4, 5].

Table 1 presents the results of the analysis of variance in the aspect of the assessment of impact of the change in the fraction of the analysed ingredients on the value of S_d . The calculated values of statistics $F(C_{PR})$ and $F(C_{Si})$ were compared with the critical values of $F(C_{PR}, \alpha)$ and $F(C_{Si}, \alpha)$ read in the Fisher-Snedecor distribution table [5].

Table 1

The results of a test based on analysis of variance according to a double classification ANOVA

Value S_d [m]						
	SS	dg. of freedom	MS	F	F_{crit}	p
free term	1.111	1	1.111	16832.06		0.000000
C_{PR} [%]	0.159	4	0.039	601.3	3.49	0.000000
C_{Si} [%]	0.004	4	0.0011	16.61	3.26	0.000015
error	0.0011	16	0.00007			

where:

- F – computational value of F -Snedecor statistics,
- F_{Crit} – critical value read from F -Snedecor distribution tables at the significance level $\alpha = 0.05$ and the number of the degrees of freedom $(w - 1)$ and $(z - 1)$,
- SS – total of squares of differences in the dependent variable and its mean,
- MS – mean square,
- C_{PR} – mass fraction of polymer resin [%],
- C_{SI} – mass fraction of colloidal silica [%].

Having analysed the results of ANOVA tests, it can be stated, that the simultaneous impact of changes in the values of C_{PR} % and C_{SI} %, d_s depends on the change in the fraction of both ingredients.

3.2. Calculation of substitute characteristics, assessment of the significance of the identified regression functions

In order to quantify the relationship between simultaneous influence of the shares of the analyzed components C_{SI} [kg/t], C_{PR} [kg/t] in the formulation and S_d [m], a linear multiple regression model was established. In this case, the shares of the analyzed components were correlated with S_d by equation:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + \dots + b_k x_k + \varepsilon \quad (3)$$

where:

- b_i – model parameters (regression coefficients) describing the impact of the i -th variable,
- ε – error factor.

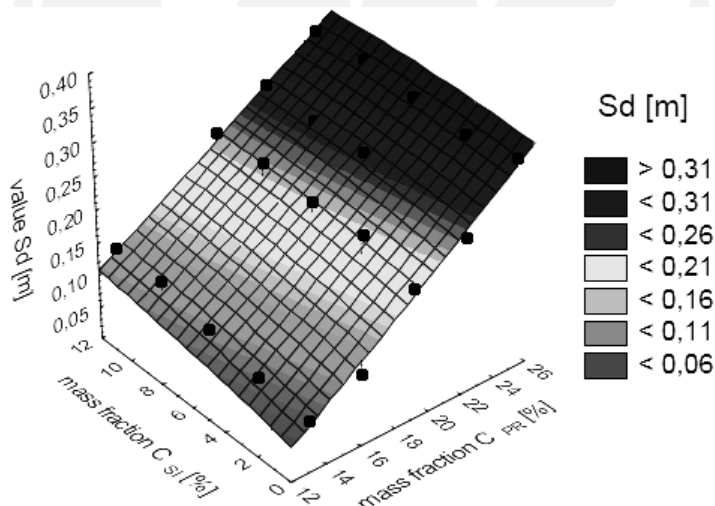


Fig. 3. Surface chart of the regression function $\hat{d}_s = f(C_{SI}; C_{PR})$

Values of statistics summarising regression functions

N = 25	Summary of dependent variable regression: ds [m] R = 0.9834709 R ² = 0.96720752 corrected: R ² = 0.96422639 F(2.22) = 324.44 p < 0.00000 Standard error of estimation: 0.015					
	b*	St. Error of b*	b	St. Error Of b	t(22)	p
free term			-0.15973	0,015023	-10.6325	0.000000
C _{PR} [kg/t]	0.970274	0.038608	0.018533	0.000737	25.1315	0.000000
C _{SI} [kg/t]	0.160549	0.038608	0.003067	0.000737	4.1585	0.000000

Table No. 2 shows that the model is linear with respect to the ds parameter. Linearity was checked by test F . The p level for this test is 0.000, the R correlation factor was 0.98347 which means that there is a strong linear relationship between the variables. The standard error of estimate is 0.015. This means that the predicted values of the ds variable differ from empirical values on average by 0.015 m.

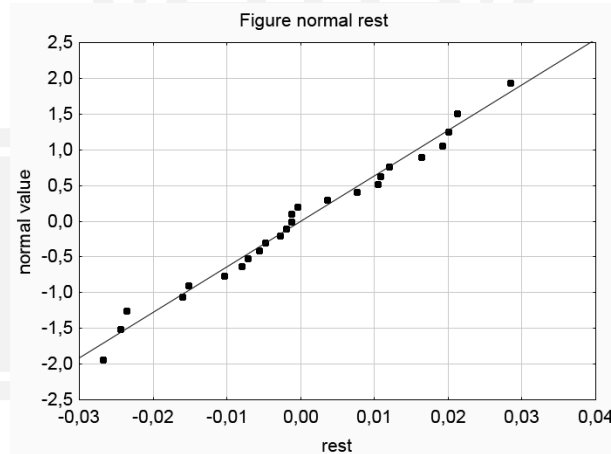


Fig. 4. Normality residues chart

In order to verify whether the residues have a normal distribution, normality residues chart was created, Fig. 4. The analysis of residuals was based on Cook's distance measurement. It was found that all the statistic values are of the same order, and there is no different case affecting the load of the regression equation. On the basis of the analysis of the residuals, the correlation factor and determination, it can be assumed that the adjustment of the model to empirical data is proper. The multiple regression equation calculated in this way is:

$$d_s = 0.018533 \cdot C_{PR} + 0.003067 \cdot C_{SI} - 0.15973 \pm 0.015 \quad (4)$$

This means that if the C_{Si} increases by 1 kg, d_s will then rise by about 0.018533 [m]. Similarly, if the amount of colloidal silica is increased by 1 kg, d_s will increase by 0.003067 [m]. The relatively large error of the free term indicates that it should be used with caution when predicting random variable.

Changes in proportion by weight of organic resin and colloidal silica affect the size of S_d with varying intensity. The change of share of organic resin has greater influence on the analyzed parameter than the change in the quantity of colloidal silica. The observed dependences can be explained by a difference in binding the mineral components of the coating by organic resin and colloidal silica. The aqueous dispersion of a copolymer of n-butyl acrylate and styrene used in the paint formula, is undergoing a film-forming material pervious to coalescence by evaporation of water. Thus obtained film is flexible, durable and resistant to water, with high adhesion to mineral surfaces as well as surfaces made of plastics and non-metals. The colloidal silica that is involved in the binding process, binds the mineral components as a result of silicification reaction. The active functional groups of colloidal silica are involved in the reaction: $-\text{Si}(\text{OH})_2$, mineral components of the coating and the substrates, mainly calcium carbonate and silica sand. Thus formed structure is an open-porous one, of high permeability with respect to water vapour. Large diffusivity in relation to water vapour was obtained for the coatings for which the weight fraction of aqueous organic resin does not exceed 13%. In that case, irrespective of the content of colloidal silica, the range of changes in S_d equivalent air layer does not exceed 0.14 [m]. Such coatings, due to the volume of water vapour permeability factor, according to DIN EN 1062-1: 2005 [7] are classified as Class I: high diffusivity of water vapour. Application of colloidal silica in the recipes will also have a positive impact on other properties of cured coatings. Chemical bonding method of colloidal silica will exert a positive impact on the stability and adhesion of coatings to mineral substrates. Together with a decrease in the share of organic resin, the coating's tendency to soiling will be reduced. When designing paint, one should consider the fact that reduction of the share of polymer resin will be connected with an increase in the surface absorption of coatings for water and it may be necessary to use hydrophobicizing agents, which may have an impact on the value of S_d factor.

The applied statistical method, that is based on multiple regression can be a useful tool to quantitatively assess the relations between the simultaneous influence of paints' ingredients and other parameters of coatings, such as surface water absorption, abrasion resistance, etc. A well designed program of studies however will reduce the number of time-consuming research, and thus the time of developing the technology of new products will be reduced, which will bring tangible economic benefits.

4. Conclusions

On the basis of experimental research it was estimated that there is a correlation between the change in the quantity of organic resin and colloidal silica in the formulation of paints and water vapour permeability quantified by relative diffusion resistance S_d of cured coatings. Based on statistical analysis it can be concluded, that this relationship is of a positive character, statistically highly linear.

The effect of changes in the amount of organic resin in a formulation is greater than the effect of changes in the amount of colloidal silica on water vapor permeability.

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