

The role of organosilicon polymers in the formation of hydrophobic properties of synthetic paint coatings used in building renovation

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Abstract—The article studies the structure of protective coatings containing organosilicon polymers with different chemical structure, used in the building renovation. The relation between the contact angle of the cured coating and the type of the organosilicon polymer is analyzed. It has been found that the water-repellent properties of the coatings are influenced by the composition of these polymers. Using spectroscopic studies, the mechanism of hydrophobisation of coatings was explained. The analysis of spectral maps along the cross section of the coatings has shown polysiloxane additives migration from the substrate into the coating/air interface. The arrangement of polysiloxanes in cross-section of the coatings was varied and depended on the weight fraction of organic resin in the paint formulation and the chemical composition of polysiloxanes. Tests were carried out using an IR Continuum microscope. The analysis was conducted on cured coatings derived from acrylic paints containing polysiloxanes based on: polydimethyl siloxane PDMS, polymethylvinyl siloxane PMVS and polymethylphenyl siloxane PMPS. The highest mobility was shown by PDMS and PMVS based polysiloxanes. The width of the segregation area for PMPS was greater, which confirms low migration tendency of this polysiloxane.

Keywords—Restoration of Monuments, rehabilitation of Buildings, silicone dyeing coats, silicone resin, polymer resin, IR spectroscopy, the surface properties

I. Introduction

Proper selection of paint coatings used for renovation of historic buildings ensures the efficiency and durability of conservation treatment. After the restoration of buildings, protective coatings should allow free diffusion of water vapor and protect the walls against the ingress of water from the outside. Water-repellent properties of coatings can be achieved by using different additives. Products containing organosilicon polymers, commonly known as "silicones" or "polysiloxanes," provide extensive possibilities. The essential characteristic of these compounds is assuring hydrophobic properties of the cured coatings while maintaining high water vapor permeability[1,2].

Polysiloxanes are organosilicon compounds, which consist of siloxane chains composed of alternately connected silicon and oxygen atoms. With such a skeleton organic substituents

are linked through Si-C bonds, which make these polymers unique in terms of surface properties. They make polysiloxanes widely popular in manufacturing of all kinds of protective coatings. The architectural paints they improve rheological properties, application and their fluidity, *anti-cratering*, wettability, etc. In cured coatings they improve flexibility, prevent cracking and improve resistance to weathering [3-5]. This was demonstrated in the latest method of continuous monitoring of strain developed by J. Juraszek. They consist in implementation of FBG (Fiber Bragg Grating) and OTDR (Optical Time Domain Reflectometry) in coatings made of paints containing polysiloxanes [6-11]. They are also added to paint formulations in order to obtain hydrophobic properties of the cured coatings [12]. The compounds most commonly used for waterproofing the paint coatings include silicone polymers with a linear structure, so-called. silicone oils, for example. poly(dimethylsiloxane), PDMS, and branched structure polymers, so-called silicone resins[13].

The behavior of polysiloxanes located at the interface plays a key role in shaping the properties of paints and varnishes. In anticorrosive paints, polysiloxane-based additives to perform their function only when they are transferred to the interface. The ability of the organosilicon compounds to migrate towards the border of the solid and the gas phase (*air/coating surface*) is a phenomenon known and described in the literature[14-17]. The study of this issue was the subject of the work by Hinder *et al.* [15]. They demonstrated that the migration of polysiloxanes to air-coating interface in multi-layer anti-corrosion coating systems occurred during coating curing. Horgnies *et al.* [16,17] proved that migration and segregation of polysiloxane-based additives took place in the coating also after curing. It can be assumed that the phenomenon of the organosilicon compounds migration in the direction of the interface is also present in the polymer paints used to protect the facades. However, in the literature we do not find the answer to how is this phenomenon influenced by polysiloxane structure and the presence of other ingredients of polymer paints. So far no one has analyzed where organosilicon compounds segregation occurs in the cured coatings, what it depends on, and what is the impact of segregation place on the water repellent properties of the coatings.

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II. Experimental section

A. Measurement methods

The samples were studied using a Thermo Continuum IR microscope equipped with a MCT (Mercury Cadmium Telluride) detector cooled with liquid nitrogen. The microscope was coupled to a “Nicolet 6 700” spectrophotometer. A reflexion method was used for the study. The measurement area was $20 \times 160 \mu\text{m}$, where the dimension of $160\text{-}\mu\text{m}$ was parallel to the coating cross-sectional surface for better spectral averaging. The measurement step was $10 \mu\text{m}$ and the number of scans per measurement 1024. Scanning was performed perpendicularly and at a 45° to the substrate. The scanning slope was designed to calculate the average of spectra recorded on the coating cross-section length afterwards.

In order to determine the hydrophobicity of the coating, the water contact angle WCA θ , specifying the ability of a paint coating surface to create water-beading effects, was used. It is defined as an angle between the surface of the paint coating and the plane tangent to the surface of the water bordering the paint coating at the contact point of the solid, liquid and gas phases. The angle θ was measured with a goniometer by observing the contact point of the phases at high magnification.

B. Subject of research

The subject of research covered architectural paint coatings based on organic resin: styrene-acrylic copolymer, containing the following polysiloxane hydrophobising admixtures with diversified chemical structure:

- SR1: poly(dimethyl)siloxane (PDMS) resin incorporating T, M and D units, 50% solid content;
- SR2: poly(dimethyl-co-methylvinyl)siloxane (PMVS) resin, additionally substituted with octyl groups D^{Oc} and hydroxyl groups D^{OH} , 50% solid content,
- SR3: poly(dimethyl-co-methylphenyl)siloxane (PMPS) resin containing, besides methyl groups, approximately 20% of phenyl groups with DPh units, 50% solid content.

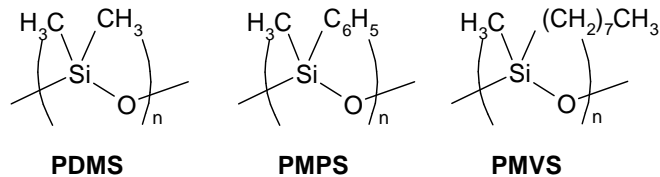


Fig. 1. Surface-active polysiloxanes used for hydrophobisation of paint coatings: PDMS – poly(dimethyl)siloxane, PMPS - poly(dimethyl-co-methylphenyl)siloxane, PMVS - poly(dimethyl-co-methylvinyl)siloxane.

The other ingredients of the paints included: thickening agent: methyl-hydroxy-ethyl cellulose (MHEC), rheology modifier: xanthan gum, titanium dioxide, rutil, dispersing agent: sodium salt of polyacrylic acid, defoamers, fillers: Plastorit 0 (mica / quarto / chlorite filler), talc, Sachtleben

micro (synthetic barium sulfate) and Celatom MW-25 (Diatom).

Figure 2 presents spectra of silicone resins, modified and non-modified, recorded in the medium IR range between $4000\text{--}400 \text{ cm}^{-1}$. Structure of all polymers is similar to that of poly(dimethylsiloxanes). There are absorption bands characteristic for silicones visible here, the most important of which are [19]:

- 2967 cm^{-1} and 2909 cm^{-1} , derived from stretching vibration of the C-H bond in CH_3 group
- 1414 cm^{-1} , derived from asymmetric deformation vibration of Si-CH_3 group,
- 1267 cm^{-1} , derived from the symmetric deformation vibration of Si-CH_3 group,
- 1111 cm^{-1} and 1036 cm^{-1} , derived from asymmetric stretching vibration of Si-O-Si group,

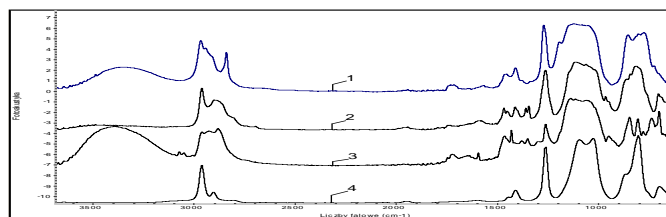


Figure. 2. Summary of photoacoustic FTIR spectra for the analyzed silicone resins: 1 – SR1: PDMS resin, 2 –SR2: PMVS resin with octyl substituents, 3 – SR3: PMPS resin, and 4 - the silicone oil spectrum.

Using these components, 30 different variants of paints were prepared. Paint formulations differed in the mass ratio of the C_{PR} [%] organic resin dispersion to the C_{SR} [%] polysiloxane dispersion. The C_{PR} [%] to C_{SR} [%] ratios in different variants are presented in table 1.

The paint coating were prepared for the tests in the following way: the paint was applied to poly(vinylidene chloride) PVDC foil with a $240 \mu\text{m}$ thick applicator and then, after drying, it was subject to seven cycles of alternate soaking in a water bath with water circulation for 24 h and drying for 24 h.”

C. Measurement results

In order to determine the areas in which polysiloxanes are located in cross-sections of cured coatings, spectral mapping was carried out. Scanning was completed along a line perpendicular to the surface of the test samples. Since the observation of the whole spectrum of the coating was difficult, or even impossible, to interpret, the observation of changes in the chemical composition of the coating was limited to a wave number range of $1100\text{--}1250 \text{ cm}^{-1}$, where absorption bands characteristic for silicones, derived from asymmetric stretching vibrations of Si-O-Si groups occur. Figure 3 shows the IR absorption spectrum of the silicone paint coating with a clearly visible band corresponding to the Si-O-Si group.

To determine the size of the area in which the absorption band, characteristic of Si-O-Si groups, was observed in the

cured coating cross-section, the S [μm] parameter, called "width of polysiloxane placement in the coating," was used.

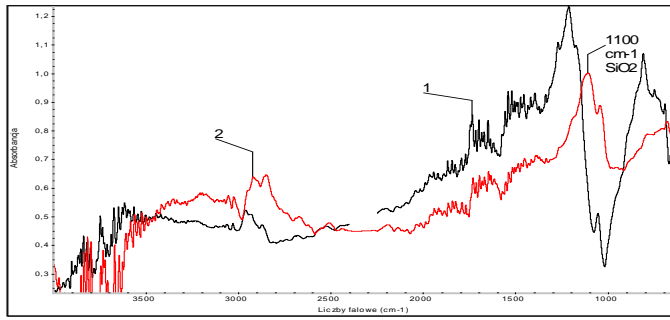


Fig. 3. Spectrum for the paint coating 90 μm from the substrate after the Kramers – Kroning correction – 1 and the same spectrum, wherein the characteristic silicone band Si–O–Si was observed – 2.

Figure 4 shows the spectral map of the coating containing PDMS (SR1), in which the organic to silicone resin ratio $C_{PR}:C_{SR}$ was 8:8. The analysis of spectral maps in the wave number range of 1100-1250 cm^{-1} has shown that absorption bands characteristic of Si-O-Si groups are present in the cross-section of the coating at a distance of 70-113 μm from the substrate, and throughout the rest of the coating thickness no such bands were found. The S for this coating was 43 μm .

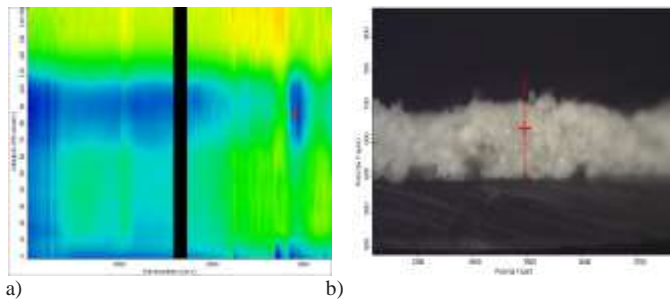


Fig. 4a. A spectral map of the silicone paint coating that includes the PDMS resin SR1 with a $C_{PR}:C_{SR}$ ratio at 8:8.

Fig. 4b. A microscopic cross-sectional image of the silicone paint coating with the line of mapping marked.

Similar results were obtained by analyzing the spectral maps of a coating containing PMVS resin. At an identical C_{PR} to C_{SR} ratio, absorption bands characteristic of Si-O-Si groups are present in the cross-section of the coating at a distance of 71-110 μm from the substrate.

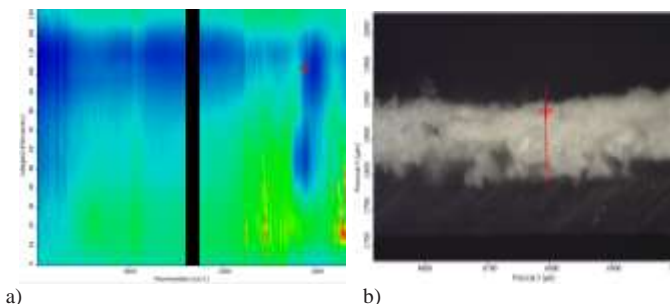


Fig. 5a. A spectral map of the silicone paint coating that included PMPS resin, with $C_{PR}:C_{SR}$ ratio at 8:8.

Fig. 5b. A microscopic cross-sectional image of the silicone paint coating with the line of mapping marked.

For coatings containing PMPS (Figure 5), with identical C_{PR} to C_{SR} ratio, absorption bands characteristic of Si-O-Si groups were present in the cross-section of the coating at a distance of 40-112 μm from the substrate. The S for this coating was 72 μm .

It was also found that the width of the S placement in the hardened paint coating is also affected by the presence of C_{PR} organic resin in paint formulation. Figure 6 shows the spectral map of the coating containing PDMS, in which the organic to silicone resin ratio $C_{PR}:C_{SR}$ was 16:8. The width of S for this coating was 76 μm .

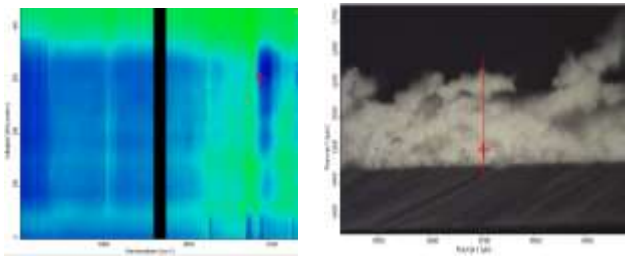


Fig. 6a. A spectral map of the silicone paint coating that includes PDMS resin with a $C_{PR}:C_{SR}$ ratio at 8:8.

Fig. 6b. A microscopic cross-sectional image of the silicone paint coating with the line of mapping marked.

In order to determine the effect the width of S polysiloxane locating on the hydrophobicity of the cured coatings in each case, contact angle θ [$^{\circ}$] was measured. It was found that in each of the analyzed cases θ has different values, which depend on the type of polysiloxanes used in the formulation and the mass fractions of C_{PR} and C_{SR} .

The detailed values of S [μm] and θ contact angles in the respective coating variants are presented in table 1.

TABLE I. The width of S polysiloxane locating and θ contact angle in the tested coatings

Mass fractions		Silicone additive					
C_{PR} [%]	C_{SR} [%]	PDMS		PMVS		PMPS	
		θ [$^{\circ}$]	s [μm]	θ [$^{\circ}$]	s [μm]	θ [$^{\circ}$]	s [μm]
6.0	0.0	43.4	–	41.3	–	44.6	–
6.0	2.0	64.8	28	68.4	33	52.5	49
6.0	4.0	92.2	31	86.4	34	58.4	58
6.0	6.0	92.9	34	102.1	37	48.8	63
6.0	8.0	102.9	41	106.6	46	59.7	64
8.0	0.0	61.3	–	62.1	–	59.8	–
8.0	2.0	82.4	31	78.6	36	61	39
8.0	4.0	94.3	33	98.6	43	64	64
8.0	6.0	97.4	36	107.1	42	68	69
8.0	8.0	103.2	43	106.5	39	72	71
10.0	0.0	78.2	–	83	–	81.5	–
10.0	2.0	86.9	36	88.1	44	85.1	59
10.0	4.0	93.7	41	97.5	46	87	69
10.0	6.0	102.6	44	102.4	48	86	66
10.0	8.0	104.4	48	106.5	52	89	78
12.0	0.0	91	–	89	–	88	–

12.0	2.0	98.3	49	88.4	56	78.6	65
12.0	4.0	102.1	49	96.4	54	97.4	61
12.0	6.0	104.6	56	103.7	63	83.2	78
12.0	8.0	104.5	54	104.9	59	93	82
14.0	0.0	97	–	98.1	–	102.3	–
14.0	2.0	93.4	59	97.3	63	104	72
14.0	4.0	102.3	64	101.3	67	102.3	69
14.0	6.0	104.6	59	103.8	59	104.6	78
14.0	8.0	104.1	61	104.8	68	104.1	88
16.0	0.0	92.1	–	97.1	–	94.1	–
16.0	2.0	103.2	66	102.3	69	102.6	87
16.0	4.0	102.1	66	103.1	71	103.5	79
16.0	6.0	103.8	71	102.3	69	102	79
16.0	8.0	102.1	76	103.1	78	104.4	89

D. Analysis of results and discussion

Statistical methods were used for the interpretation of dependencies presented in Table 1. The mathematical relationship between mass fractions of organic resin and silicone resin and the contact angle θ [°] and the width of the locating S [μm] was obtained by approximating the dependencies using linear-square polynomials with the general formula:

$$\hat{y} = B_0 + B_1 \cdot x_1 + B_2 \cdot x_2 + B_{11} \cdot x_1^2 + B_{22} \cdot x_2^2 + b_{12} \cdot x_1 \cdot x_2$$

The values of the regression coefficients are presented in Table 2.

TABLE 2. The results of summary statistics

Analyzed function	Regression function coefficients						Regression param.		
	B ₀	B ₁	B ₂	B ₁₁	B ₂₂	B ₁₂	R	R ²	p
SR1: PDMS resin									
$\theta_1 = f(C_{SR}; C_{PR})$	-4.68	10.75	13.58	-0.27	-0.42	-0.63	0.97	0.92	0.00
$S_1 = f(C_{SR}; C_{PR})$	15.79	0.19	1.95	0.19	0.08	0.12	0.99	0.97	0.00
SR2: PMVS resin									
$\theta_2 = f(C_{SR}; C_{PR})$	-4.68	10.75	13.58	-0.27	-0.42	-0.63	0.97	0.93	0.00
$S_2 = f(C_{SR}; C_{PR})$	15.99	2.01	0.76	0.09	0.1	-0.07	0.97	0.94	0.00
SR3: PMPS resin									
$\theta_3 = f(C_{SR}; C_{PR})$	-27.02	14.59	2.24	-0.41	-0.05	-0.08	0.97	0.92	0.00
$S_3 = f(C_{SR}; C_{PR})$	23.98	2.3	4.41	0.06	0.1	-0.24	0.91	0.78	0.00

Graphic image of the designated statistical functions is presented in graphs 6-10. Figure 7 shows the simultaneous effect of PDMS resin and the organic resin in the paint formulations on the contact angle of the cured coatings. It was found that the greatest impact of the PDMS resin on values θ occurs at mass fractions of an organic resin $C_{PR} \in (6-10)\%$. In the case of coatings for which the percentage concentration by weight of an organic resin was between $C_{PR} \in (10-16)\%$, the effect of the PDMS resin on the value θ is negligible.

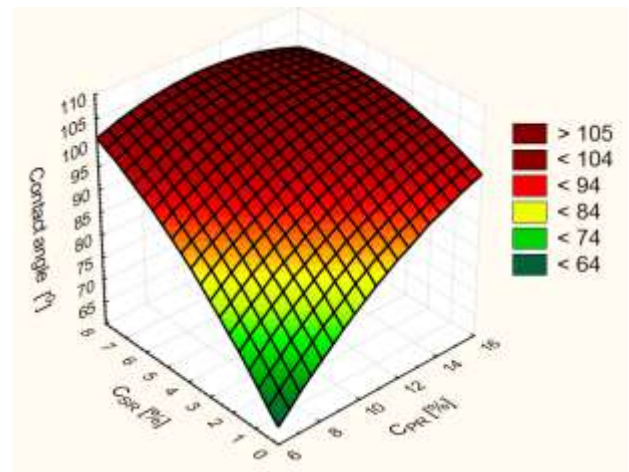


Figure 7. A surface chart of the regression function $\theta_1 = f(C_{SR}; C_{PR})$

Figure 8 shows the simultaneous effect of the PDMS resin and the organic resin on the segregation width S [μm]. A clear impact of changes in the fractions of an organic resin on the segregation width S was found. With mass fractions of organic resin $C_{PR} \in (6-10)\%$ the segregation width was the lowest and ranged between 30-40 μm. The highest S parameter value of 70-94 μm was determined for $C_{PR} \in (14-16)\%$.

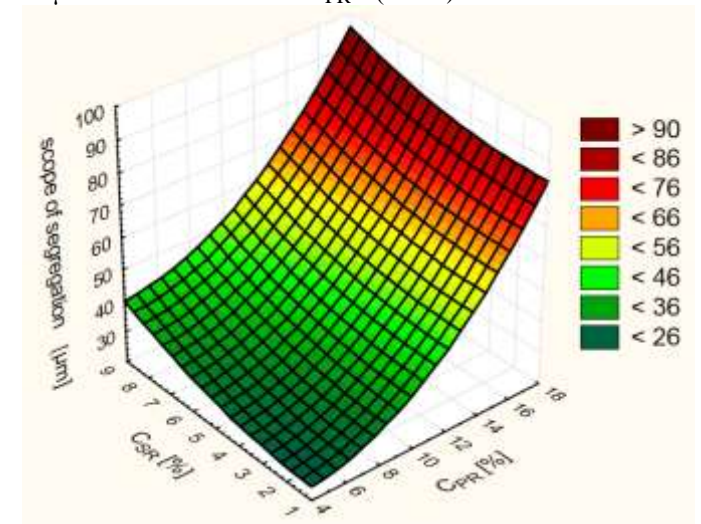


Figure 8. A surface chart of the regression function $S_1 = f(C_{SR}; C_{PR})$

In order to verify whether the locating width S influences the contact angle θ , the statistical analysis the correlation between these variables was conducted. Visual evaluation of the chart (Figure 9) shows that the relationship is linear. The value of the correlation coefficient was 0.65, indicating a high linear dependence of the contact angle θ and the location width S . The level of significance p for the t statistic was less than 0.05, which means that the θ variability may be described by location width S with high statistical probability.

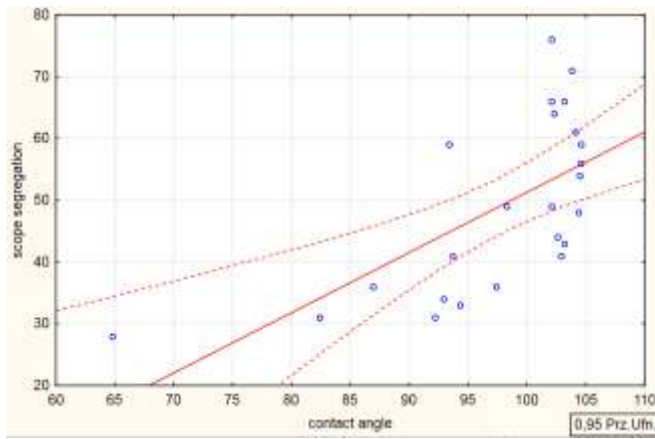


Figure 9. A scatterplot of the location width S against the contact angle θ

A similar analysis was performed for PMVS resin. It was found that also in this case, the greatest impact of the PDMS resin on values θ occurs at mass fractions of an organic resin $C_{PR} \in (6-10)\%$. When examining the correlation between variables θ [$^\circ$] and S [μm], the determination coefficient was 0.66, which means that θ variability is explained by the location width S variation in 66%.

Figure 10 shows the simultaneous effect of PMPS resin and the organic resin in the paint formulations on the contact angle of the cured coatings. It was found that the effect of the PMPS resin θ value is small in the whole range of variation of the mass fractions of organic resin C_{PR} .

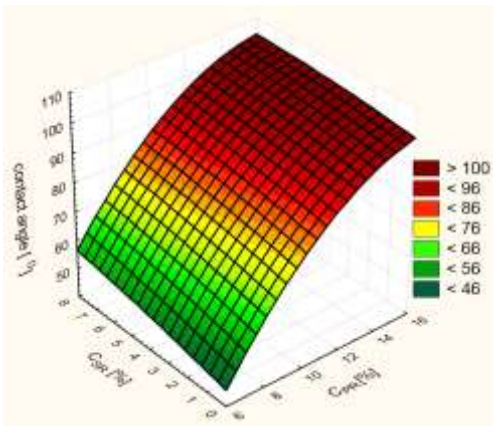


Figure 10. A surface chart of the regression function $\theta_3 = f(C_{SR}; C_{PR})$

After analyzing all of the regression functions it was found that at fixed C_{PR} to C_{SR} ratios, the location widths S [μm] vary depending on the chemical composition of polysiloxanes. The smallest area of the coating cross-section was occupied by PMVS and MDMS, and the largest location width was noted for PMPS. It was also found that, irrespective of chemical composition, the location width S of polysiloxanes increased

with the increase in the mass fraction of the organic resin in the paint formulation.

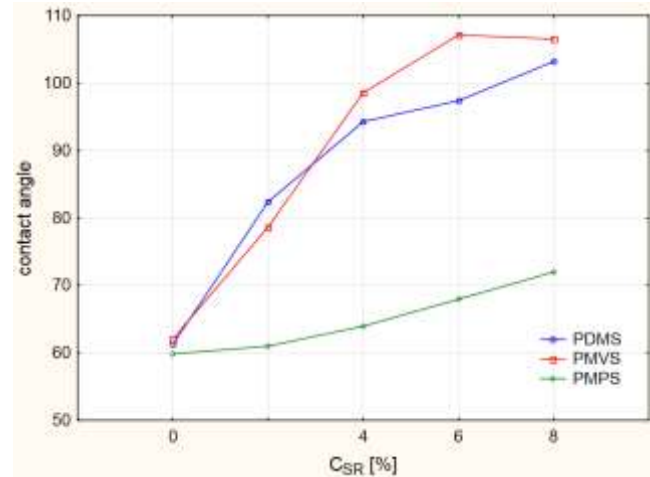


Figure 11. Changes in the contact angle depending on the mass fraction of the polysiloxanes resin C_{SR} [%], $C_{PR} = 8\%$.

The effect of the analyzed silicone resins on the change of the contact angle θ for individual polysiloxanes was compared using the same fraction of the organic resin of $C_{PR} = 8\%$. Because of the impact of polysiloxane resin on θ , such amount of C_{PR} is optimum. Higher fractions of the organic resin affect the θ value to a small extent. The analysis of measurement results has shown the greatest impact of PDMS and PMVS resins fraction on the θ parameter. Change in PMPS resin fraction in the paint formulation alters the contact angle to the lowest degree (Figure 11). Figure 12 shows changes in the location width of polysiloxanes depending on the mass fraction of the organic resin C_{PR} [%].

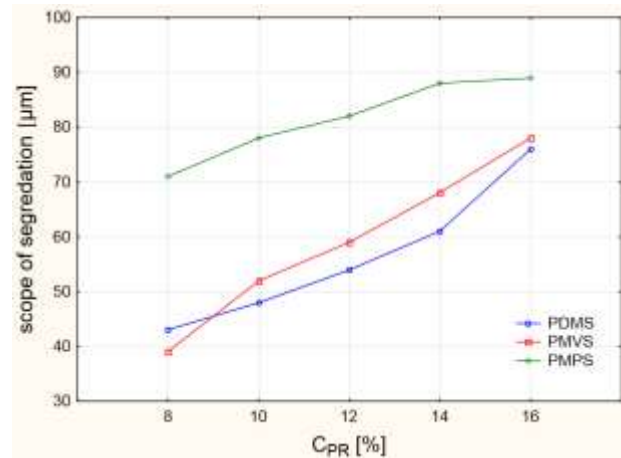


Figure 12. Changes in the location width of polysiloxanes depending on the mass fraction of the organic resin C_{PR} [%], $C_{SR}=8\%$

E. Application significance of the study

Using modern research methods it has shown that the polysiloxanes are segregated and migrate in the direction from the substrate to the air-coating interface. This phenomenon is

of key importance to a series of recommendations to be put into practice:

- in the narrowest cross sectional area of the coating, near the air-coating interface. resins containing aliphatic methyl or octyl substituents were segregated. PDMS and PMVS organosilicon polymers form some of the most flexible and mobile polymer chains. wherein the side chains, especially methyl groups, can easily rotate around Si-O bond [5, 6]. The change in mass fraction of these resins was the greatest influence on the water-repellent properties of the cured coatings;
- the optimum mass fraction of the polymer resin in the formulation of a paint containing polysiloxanes should not exceed $C_{PR} = 8\%$. and silicon resin - not less than $C_{SR} = 4\%$;
- the use of a silicone resin with higher fractions of an organic resin is economically unjustified. Too low C_{PR} fractions can cause the polysiloxane to be located too close to the outer surface of the coating. As a result of the natural aging of the coating under the influence of external factors, they may soon be removed from the shell.

III. Conclusions

The article analyzes the impact of polysiloxanes of different chemical structure on the changes in the chemical composition of a cross-section of cured coatings. The study was conducted on the example of facade paints containing an organic styrene-acrylic binder. Knowledge of the mechanisms in paint coatings allows to avoid mistakes in developing paint formulations based on polysiloxanes, used in the restoration of monuments. The determined fractions of organic and silicone resin may provide a valuable prerequisite for optimizing production formulas.

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