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HYDROPHOBICITY AND WEATHERING RESISTANCE OF WOOD TREATED WITH SILANE-MODIFIED PROTECTIVE SYSTEMS

The study presents the hydrophobic effect of silane-modified protective systems on wood resistance to aging factors (water and UV radiation). This paper is focused on conventional and low VOC emulsion systems for exterior use, which were improved with silanes such as methyltrimethoxysilane (MTMOS), aminoethylaminopropyltrimethoxysilane (AEAPTMOS) and glycidoxypropyltrimethoxysilane (GPTMOS). The performance of the new protective systems, applied on pine wood by surface impregnation, was demonstrated through an accelerated weathering test and evaluated by contact angle, colour and gloss changes. The study showed improvement in the hydrophobicity and photostability of the protective systems modified with selected silanes. The highest protection from the accelerated weathering conditions was obtained using the treatment with a solvent-borne formulation with 5% AEAPTMOS and an alkyd emulsion with 5% MTMOS.

Keywords: silanes, surface impregnation, hydrophobicity, weathering

Introduction

The weathering process is a complex combination of chemical, mechanical and biological changes, all of which occur simultaneously and affect each other. Unprotected wood exposed to atmospheric factors undergoes several modifications followed by colour change, loss of gloss, formation of cracks and staining on the surface [Chang et al. 1982; Hon et al. 1985; Dawson et al. 2008; Evans et al. 2008; Cristea et al. 2010; Saha et al. 2013]. Since wood degradation through weathering is one of the major causes of the reduction in the lifespan of wood products, proper protection should be applied. Increased wood resistance to

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the abovementioned factors might be obtained by using a specific treatment method based on hydrophobation which results in a change in the hygroscopic properties of the wood, thus reducing the negative effects of its exposure to water [Rowell, Banks 1985; Feist 1992; Donath et al. 2007]. Among hydrophobic agents such as oils and waxes, silanes comprise an important group. Their ability to impart hydrophobicity as well as improve dimensional stability have been reported [Tshabalala et al. 2003; Donath et al. 2005; Weigenand et al. 2007; Vetter De et al. 2010]. Wood treated with silanes after accelerated weathering have also revealed reduced surface erosion and enhanced colour stability [Ghosh et al. 2009; Baur et al. 2012]. Since silanes form a very thin layer on the wood surface, they exhibit low water resistance, thus effective wood protection with silane alone is only obtained in high concentrations (over 20%). However, silane as a component of the protective system for wood in use class 3 might be applied at 5%, creating a thicker coating and potentially guaranteeing low production costs. Organosilicon compounds are useful not only due to their exceptional hydrophobic properties but also to their low toxicity. Since formulating new low VOC coatings with equal or better performance than conventional systems is an important aspect, silanes can provide environmentally-acceptable protection.

In view of the abovementioned arguments, it was decided to undertake research connected with the effect of the hydrophobicity of a wood surface treated with a silane-modified protective system on its resistance against aging factors, including water and UV radiation.

Materials and methods

Composition and properties of protective systems

Tests were performed on Scots pine sapwood (*Pinus sylvestris* L.) samples with a size of 7.5 × 25 × 50 mm (the last dimension along the grain). The surfaces of the samples were sanded using 80 and 220 grit sandpaper. Before impregnation, the end-grains of the samples were also sealed with a single-component polyurethane adhesive in order to prevent penetration of the agents along the grain.

Solutions containing alkyd resin in an organic solvent (SB/resin) or in a form emulsified in water (emulsion), or a blend of natural oils (SB/oil) were used as the base system. The following silanes as modyfying agents were chosen (fig. 1): methyltrimethoxysilane (MTMOS), aminoethylaminopropyltrimethoxysilane (AEAPTMOS) and glycidoxypropyltrimethoxysilane (GPTMOS). The characteristics of the protective systems are presented in table 1. The proportion of commercial resin or oil in the formulation was 30%, while the concentration of organosilicon compounds amounted to 5.0%.

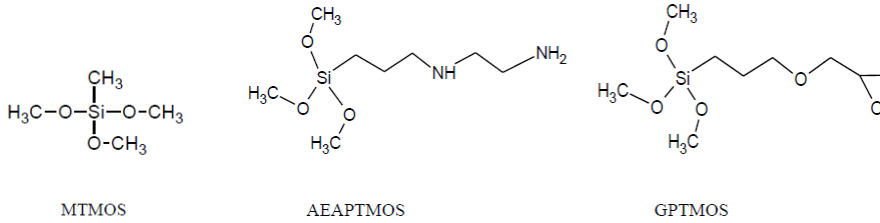

Fig. 1 Chemical structure of silanes

The wood samples were treated by immersion or brushing. For the SB systems the immersion method was applied, while for the emulsion the brushing method was used due to the higher viscosity and density of the solution. 5 replicates were used for each treatment variation.

In order to assess the applicability of the proposed protective systems, retention of solutions, preliminary technological tests of the product (colour, the presence of sediment, skinning and gelation) as well as density, viscosity and fluidity, were conducted. 14 days after their preparation the tested solutions were characterized by uniform colour, absence of sedimentation, skin or gelation. Analysis of the recorded data (table 1) showed that the addition of silanes to the protective systems slightly reduced the retention rate. In addition, the density of the SB/resin and oil systems was 0.821 and 0.832 g/cm^3, meeting the limits specified by the respective standards (0.810–0.875 g/cm^3) for such products. The values of relative viscosity fluctuated between 11 s for the alkyd products and 14 s for the oil products, meeting the standard requirements (11–18 s). The introduction of the silanes to the solutions resulted in a slight increase in the density and viscosity. The alkyd emulsion exhibited a slightly higher density and viscosity (0.888 g/cm^3 and 18 s). The addition of MTMOS and GPTMOS caused a decrease in the viscosity to 13 and 14 s, respectively, while the addition of AEAPTMOS resulted in its increase to 19 s. The tested systems were characterized by very good fluidity, receiving a score of 10 on the adopted scale.

Table 1. Summary of the protective systems' variants

Variants	Mean retention [g/m^2]	Properties		
		density [g/cm^3]	viscosity [s]	fluidity [rating scale 0–10]
SB/resin	125	0.821	11	10
SB/resin/AEAPTMOS	120	0.826	12	
SB/oil	135	0.832	14	
SB/oil/AEAPTMOS	135	0.835	15	
Emulsion	105	0.888	18	
Emulsion/MTMOS	105	0.894	13	
Emulsion/AEAPTMOS	101	0.898	19	
Emulsion/GPTMOS	94	0.897	14	

Accelerated aging test

Artificial weathering was performed following the methodological assumptions specified in the standard EN 927-6. An assessment of the resistance of the treated wood to the action of atmospheric factors was conducted in a SOLARBOX chamber (M/S Erichsen, model 522). During the aging procedure a temperature of 70ºC and a wavelength of 280 nm were applied, corresponding to direct solar irradiation. The samples in the chamber were periodically wetted to simulate precipitation. The samples were exposed to the accelerated aging test for a total of 20 cycles, with one continuous light cycle amounting to 102 min with UV-radiation and water spray of 18 min. An evaluation of the exposed specimens was done after every 5 cycles by contact angle, colour and gloss measurements.

The contact angle [Θ] test was performed according to PN-EN 828 using a biological microscope equipped with a goniometer attachment. Drops of 3.5 µl redistilled water with a surface tension of $\gamma_L = 72.9$, ($\gamma_L^d = 23.6$; $\gamma_L^p = 49.3$) mN/m, were transferred with a chromatographic injector. The value of the contact angle was determined at 5 selected points perpendicular to the grain. Based on the value of the contact angle, the values of free surface energy [γ_S], work of adhesion [W_a] and surface tension at the interface [γ_{SL}] were calculated together with their dispersion (^{d}) and polar (^{p}) components, according to formulas given in literature [Kloubek 1974; Neumann et al. 1974; Nguyen, Johns 1978; Liptáková 1980].

The colour of the finished surface was determined using a Datacolor colorimeter (Model 600) equipped with a UV lamp EMITA WT 410. Measurements were made using a D65 illuminant and 10-degree standard observer. The value of the colour was analysed after each cycle, at 3 selected points perpendicular to the grain. The values of coordinates L^*, a^* and b^* were measured and the differences in colour were calculated in relation to the reference standard (1).

$$\Delta E_{ab} = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

where: ΔL, Δa, Δb denote differences in parameters of compared colours

L^* – axis defining lightness (values from 0 to 100%)

a^* – axis running from the red colour ($+a^*$) to the green colour ($-a^*$)

b^* – axis running from the yellow colour ($+b^*$) to the blue colour ($-b^*$).

Gloss was measured by the photoelectric method according to ISO 2813, using a PICOGLOSS gloss meter (Erichsen, Model 503), at 5 selected points along the grain at a light incidence angle of 60º. The percentage change in the gloss of the specimen during accelerated weathering relative to its initial gloss value was calculated and defined as gloss retention.

Results and discussion

Wetting characteristics

The differences in the wetting characteristics of the selected systems are presented in fig. 2. During the course of the impregnation process, the surface protected with silanes achieved a contact angle in the range of 72º18' to 84º42' receiving a similar or higher contact angle to the surface when protected only with resin or oil. The exception was the emulsion with AEAPTMOS which showed the most hydrophilic nature compared to all the other formulations.

The contact angle decreased as the aging time increased for all the systems. Emulsion modification with the use of MTMOS at a concentration of 5% made it possible not only to obtain a surface with enhanced hydrophobicity (angle Θ 82°12'), but also showing the highest resistance to the aging conditions (after 20 cycles, angle Θ of 69°42'). The combination of AEAPTMOS with a solvent-borne oil-based system was also effective in protecting the wood surface (final angle Θ 65°54').

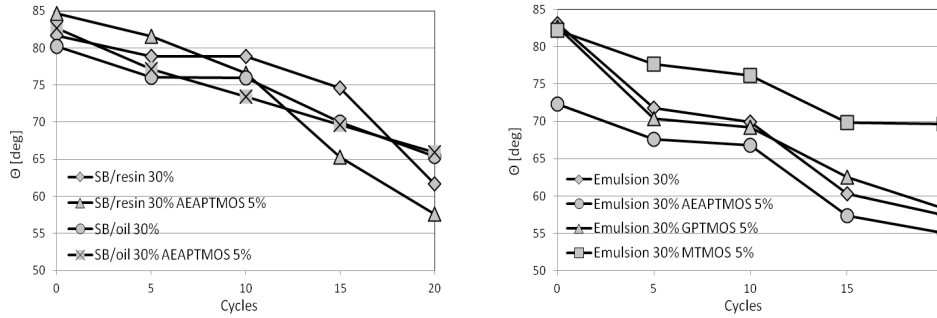

Fig. 2. Values of angle Θ in the function of the number of aging cycles for wood surface treated with selected systems

Based on measurements of the contact angle, the parameters γ_S, W_a and γ_{SL} were determined together with their components (fig. 3–5). The values of γ_S (below 50 mJ/m^2) obtained for all the systems should be considered advantageous from the point of view of the assumed criteria of the adsorption theory of polymer adhesion to wood. The level of adhesion effects is determined by the γ_S ratio of the materials in contact. In order to provide effects of high quality, γ_S of the formed coating has to be lower than that of the protected wood. According to literature data [Liptáková 1987] these values for pine wood are as follows: γ_S = 67.6, (γ_S^d = 24.7; γ_S^p = 42.9) mJ/m^2. The values of γ_S for all the tested systems increased in the function of the number of aging cycles, caused by an increase in the polar component. The values of component γ_S^d were almost constant and fell within the range of 30–33 mJ/m^2. An increase in the values of com-

ponent γ_S^p resulted in a reduction in the hydrophobic properties of the treated wood surface.

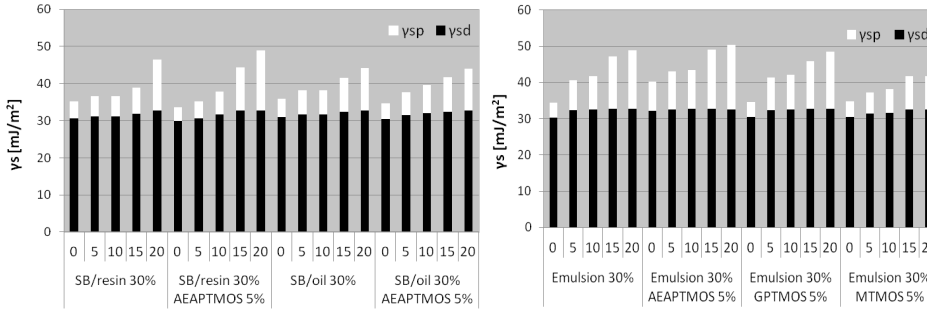

Fig. 3. Values of γ_S and its components in the function of the number of aging cycles (0–5–10–15–20) for wood surface treated with selected systems

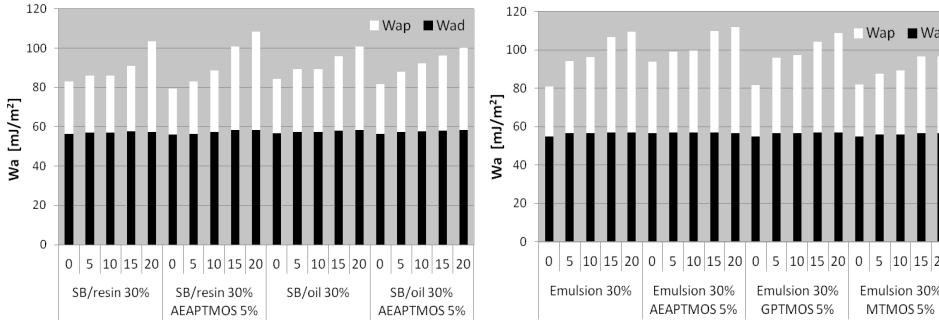

Fig. 4. Values of W_a and its components in the function of the number of aging cycles (0–5–10–15–20) for wood surface treated with selected systems

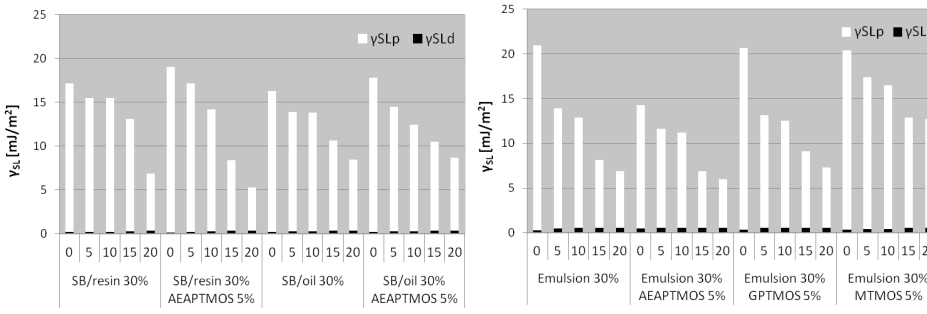

Fig. 5. Values of γ_{SL} and its components in the function of the number of aging cycles (0–5–10–15–20) for wood surface treated with selected systems

In accordance with literature data [Liptáková, Kudela 1994] for a wood-coating system, a linear dependence is found between the adhesion work W_a and

surface tension γ_{SL} on the layer interface. The higher the W_a value, the lower the γ_{SL} level. For all the analysed systems, the value of W_a at the initial stage of aging was below 100 mJ/m^2, while for the parameter γ_{SL} it was at least 4 times higher than 3 mJ/m^2. In view of the above, the systems did not meet the criterion of energy minimization (0–3 mJ/m^2) at the interface of the materials in contact [Pirmasens 1983; Paprzycki 1991]. The aging cycles had a significant effect on the fluctuations in W_a and γ_{SL} values. The adhesion work showed slight upward trends. When analysing the data concerning γ_{SL}, a considerable reduction was recorded, amounting to 4.3 mJ/m^2. Such considerable changes in W_a and γ_{SL} occurring during the course of aging were influenced first and foremost by the polar components of these parameters.

Colour changes

The artificial weathering resulted in photodegradation of the wood surface, which affected the colour of the surface (table 2). After 20 cycles the non-treated wood was characterized by the parameter ΔE amounting to 14.80 units. The colour changes in the untreated wood were mainly attributable to the high Δb value, which showed a yellowing of the surface caused by carbonyl-groups forming due to lignin degradation and photo-oxidation of the cellulose [Pandey 2005]. Comparable behavior was observed in the samples treated with the SB/resin and oil systems. The emulsion displayed lower ΔE values than the SB systems, amounting to 10.51 units.

The evaluation of ΔE values (fig. 6) revealed that the use of silanes significantly improved the colour stability of the wood surface. The most effective formulations were the SB/oil/AEAPTMOS and the emulsion/MTMOS, which obtained ΔE amounting to 5.19 and 5.81 units, respectively. The enhanced colour stability of those systems was evident from minor changes in the values of the chromaticity coordinates ΔL, Δa and Δb.

Gloss retention

The results of gloss retention at an angle of 60º in the function of the number of aging cycles are given in fig. 7. The tested systems demonstrated a loss of gloss retention with the final gloss values slightly lower than those of the untreated wood, with one exception. The gloss of the emulsion 30%/GPTMOS 5% amounted to 38% during the artificial aging. A lack of pronounced changes in the gloss retention indicated the stability of the aesthetic-decorative features of the treated wood surfaces.

Table 2. Changes in colour components for wood surface treated with selected systems after 20 cycles of exposure to UV irradiation and water

Variants	Changes in colour components			
	ΔL	Δa	Δb	ΔE
Untreated wood	−6.87	4.78	12.21	14.80
SB/resin	−4.35	4.15	11.62	13.08
SB/resin/AEAPTMOS	−8.96	5.02	6.46	12.13
SB/oil	−8.02	4.28	8.75	12.62
SB/oil/AEAPTMOS	−2.53	1.70	4.20	5.19
Emulsion	−5.90	3.94	7.76	10.51
Emulsion/MTMOS	−4.87	3.13	0.51	5.81
Emulsion/AEAPTMOS	−3.43	2.54	7.86	8.94
Emulsion/GPTMOS	−6.84	3.23	4.79	8.95

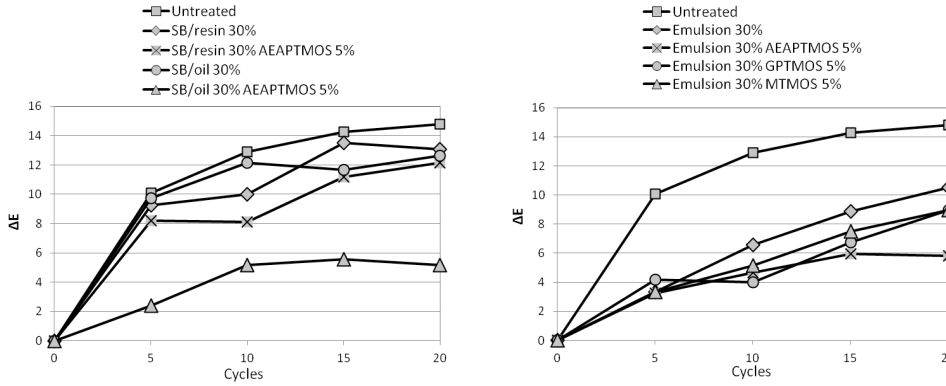

Fig. 6. Fluctuations in Δ*E* in the function of the number of aging cycles for wood surfaces treated with selected systems

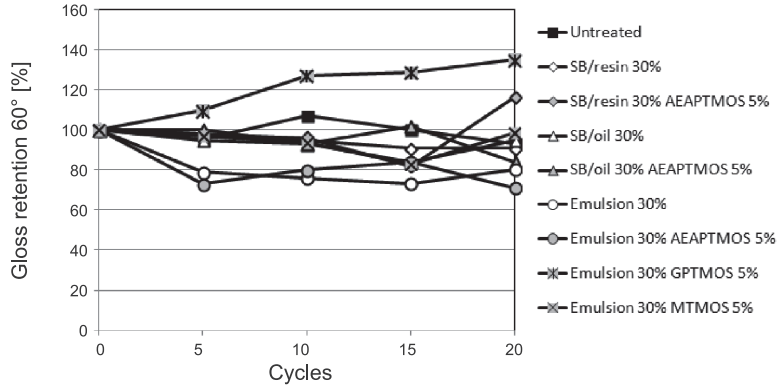

Fig. 7. Changes in gloss retention in the function of the number of aging cycles for wood surfaces treated with selected systems

Conclusions

The addition of silanes improved the hydrophobic properties of the systems based on alkyd resin and a blend of natural oils. The emulsion modified with the use of MTMOS at a concentration of 5% showed the highest hydrophobicity and resistance to the aging conditions. Amongst the solvent-borne systems, protection to the accelerated weathering conditions was obtained through treatment with the SB/oil with 5% AEAPTMOS share. The developed systems met the requirements of the criteria concerning the adsorption theory of polymer adhesion to wood in relation to the parameters γ_S and W_a, which showed adequate adhesion to form coatings of a good quality.

The protective systems, in terms of their applicability, showed:

- advantageous properties in the liquid state and for coatings in terms of the preliminary technological tests, density, relative viscosity and fluidity;
- enhanced resistance to the weathering process;
- enhanced colour stability of the wood surface in relation to AEAPTMOS.
- stable aesthetic-decorative value under the aging conditions as evident from the gloss changes.

The accelerated aging test showed that silanes, due to their hydrophobic properties, inhibit the weathering process. Therefore, it is suggested that silanes might be used in combination with suitable coatings for the treatment of wooden elements, such as garden furniture.

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List of standards

EN 927-6:2006 Paints and varnishes. Coating materials and coating systems for exterior wood. Exposure of wood coatings to artificial weathering using fluorescent UV lamps and water

PN-EN 828:2000 Adhesives – Wettability – Determination by measurement of contact angle and critical surface tension of solid surface

PN-EN ISO 2813:2001 Paints and varnishes. Determination of specular gloss of non-metallic paint films at 20, 60 and 85 degrees

HYDROFOBOWOŚĆ I ODPORNOŚĆ NA CZYNNIKI STARZENIOWE DREWNA IMPREGNOWANEGO SYSTEMAMI OCHRONNYMI MODYFIKOWANYMI ZWIĄZKAMI KRZEMOORGANICZNYMI

Streszczenie

Celem pracy było zbadanie wpływu związków krzemoorganicznych wprowadzonych do modelowych systemów impregnacyjno-ochronnych na hydrofobowość i odporność powierzchni drewna na abiotyczne czynniki niszczące.

Badania przeprowadzono na drewnie bielu sosny zwyczajnej (*Pinus sylvestris* L.). Próbki drewna poddano impregnacji metodą powierzchniową wybranymi systemami impregnacyjno-ochronnymi bazującymi odpowiednio na żywicy alkidowej oraz mieszaninie olejów naturalnych z udziałem silanów w postaci metylotrimetoksysilanu (MTMOS), aminoetyloaminopropylotrimetoksysilanu (AEAPTMOS) oraz glicydoksypropylotrimetoksysilanu (GPTMOS).

Zakres pracy obejmował ocenę właściwości fizykochemicznych opracowanych kompozycji, charakterystykę zwilżania oraz badania odporności na procesy starzeniowe zabezpieczonych powierzchni drewna. Do oceny jakości wyrobów i wymalowań zastosowano oznaczenie gęstości, lepkości i rozlewności. W celu określenia wpływu promieniowania UV i wody na badane systemy porównano takie właściwości jak zwilżalność, barwę oraz połysk przed i po ekspozycji na czynniki niszczące. Pomiarów dokonano odpowiednio po 5, 10, 15 i 20 cyklach starzeniowych.

Na podstawie analizy wyników przeprowadzonych badań stwierdzono, że powierzchnia drewna sosny zabezpieczonego systemami impregnacyjno-ochronnymi z udziałem związków krzemoorganicznych (MTMOS, AEAPTMOS, GPTMOS) wykazała podwyższone właściwości hydrofobowe, a przez to zwiększoną odporność na promieniowanie UV i wodę. Powierzchnię drewna o najwyższej hydrofobowości oraz odporności na czynniki starzeniowe uzyskano poprzez impregnację systemem SB/olej z udziałem 5% AEAPTMOS oraz emulsją alkidową z udziałem 5% MTMOS. Opracowane systemy spełniały również wymagania kryterialne adsorpcyjnej teorii adhezji polimerów do drewna w odniesieniu do parametrów γ_S i W_a. Systemy pod względem aplikacyjnym wykazywały

zwiększoną odporność na procesy fotodegradacji oraz stabilne walory estetyczno-dekoracyjne w warunkach starzenia.

Słowa kluczowe: związki krzemoorganiczne, impregnacja powierzchniowa, hydrofobizacja, starzenie