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Comparative analysis of organosilicon polymers of varied chemical composition in respect of their application in silicone-coating manufacture



Wacław Brachaczek*

Faculty of Materials and Environmental Sciences, University of Bielsko-Biala, St. Willowa 2, 43-300 Bielsko-Biala, Poland

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ABSTRACT

The present article describes the basic properties of organosilicon polymers applied in the manufacture of protective building coatings. The factors affecting the surface water absorption of silicone paint coatings were determined. It was ascertained that the types and contents of the applied hydrophobizing additives, as well as the silicone and organic resins, had a strong influence on this parameter. A comparative analysis of the recipe configurations incorporating varying amounts of silicone and organic polymers was conducted. A strong similarity was observed between the effects of organosilicon polymers of varied chemical structures on the surface water absorption of the obtained coatings. For this purpose, statistical models based on multiple regression were proposed. The dependencies of the interaction between the analysed factors were presented in the form of mathematical dependencies.

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1. Introduction

In preparation for the application of products used in the manufacture of protective building coatings, they can be divided – with respect to the applied binder – in two basic groups: polymeric (with the use of organic dispersions) and silicate (containing water glass as a binder). Further division is connected with the successive modifications of the binding systems of the above-mentioned groups [1,2,11–13]. The usage of polysiloxanes in technological recipes is an important modification. Despite the fact that their addition does not have a significant effect on the binding properties, the products of such modifications have been selected as separate groups: silicone and silicate–silicone paints, respectively. This is associated with the fact that the addition of polysiloxanes has a significant effect on the change in the physical properties of the final protective coatings [3–7].

From a chemical point of view, polysiloxanes – also known as 'silicones' – constitute a class of organosilicon polymers of the general formula $(R_{3-n}SiO_n)_x$, where n>0, x>2 and R=alkyl (usually methyl), aryl(usually phenyl) or H. The individual structures of such groups with varying R/O ratios, marked with the letters M, D, T and Q, represent the respective units R3 Si O 0.5, $R_3SiO_{0.5}$, $R_2Si(O_{0.5})_2$, $RSi(O_{0.5})_3$, $Si(O_{0.5})_4$ (see Fig. 1).

For the manufacture of facade protective coatings of polysiloxanes of a linear structure, so-called silicone oils with the inclusion of M and D units are generally used, as well as silicone resins incorporating elements of the T-type attached to their main chain, and in addition to the previously mentioned M and D units [3,4,6,8,12]. The key feature favouring the wide application of polysiloxanes in this sector of manufacture is their high permeability to water vapour, the low surface tension of silicones themselves favouring good surface wetting, high thermal and UV radiation resistance and, above all, the high hydrophobicity of the surface coated with silicone film [1,3,7,13].

The low surface tension of the silicones (around 20.4 mN/m), associated with the 50% ionic character of the Si—O bonding, facilitates both the easy wetting of various surfaces by silicones and the easy formation of silicone-containing coatings [3]. The presence of hydrocarbons – mainly methyl – oriented in the direction opposite to the wetted surface, makes the adhesive surface tension of the polyorganosiloxanes 1.5–2 times higher than their own surface tension. Consequently, they display a unique hydrophobic and anti-adhesive nature, especially when in cross-linked form [3,5,9,11].

The hydrophobizing properties of silicone compounds depend on the amount of hydrophobic substituents attached to the siloxane backbone as well as the structure of these substituents, in particular their type and spatial-orientation ability on a hydrophobic surface. Along with methyl and phenyl substituents, other aliphatic groups with longer chains (octyl) are also applied as well as aliphatic

^{*} Tel.: +48 500 030 700; fax: +48 33 496 06 10. E-mail address: wbrachaczek@ath.bielsko.pl

Fig. 1. Structural units of siloxanes.

amine groups (aminopropyl or aminoethyl–aminopropyl), alkoxy, silanol or hydrogen atoms. Higher aliphatic groups tend to lower the thermal stability of resins; however, their presence gives the applications special hydrophobic properties [1,10,11].

2. Experimental

2.1. Method

In the present study, we compared the effectiveness of the polysiloxanes of varying chemical compositions in respect of the surface water absorption of the obtained coatings. While planning the experiments, the knowledge of the subject was analysed. The shaping of the technological features of silicone paint coatings with admixtures proceeds in a highly diversified way and depends not only on the type and contents of the admixtures but also on the role they play in paint recipes. It was observed that besides the type and contents of the silicone-organic resins used in the paint recipe, the content of the organic resin also affects the analysed parameter. Owing to the interaction between the recipe ingredients, it is hard to predict their final technological properties. An analysis of each factor's influence only makes sense when it is performed in connection with the other input variables, as the risk exists that the separate investigations of the influence of the individual input variables on the analysed process or phenomenon could cause their elimination due to a lack of significance. Nonetheless, when they are considered simultaneously, they can then turn out to be crucial [13]. On the other hand, the consideration of the effects of all the factors would require many time-consuming and costly experiments, and the number of possible combinations is so large that it is, for all practical purposes, unfounded and unprofitable [14-19].

The comparison of the impact of resins with varied chemical composition on surface absorbability was made by comparing the results of four complete experiments. The impact on water permeability of one of the analysed silicone resins was tested in each experiment. The experiment involved conducting the measurements of the water absorption coefficient w_{24} , which was the output value for the acquired model for L arbitrarily selected input values x and for determining the approximating function y = f(x). The experimental tests were carried out as follows:

- (a) For the input variable x_1 corresponding to the percentage concentration of organic resin C_{PR} (%) in the formula of silicon paint, six values within the following range were selected [C_{PR} min = 6 (%), C_{PR} max = 16 (%)];
- (b) For the input variable x_2 corresponding to the percentage concentration of organic resin C_{SR} (%) in the formula of silicon paint, seven values within the following range were selected $[C_{SR} \min = 0 \text{ (\%)}, C_{SR} \max = 8 \text{ (\%)}];$
- (c) A single measurement was made for each combination of the input values;
- (d) Based on the conducted measurements, the approximating function $f(\cdot)$ was determined.

To reduce the number of measurements, it was assumed that the values of the other input values – such as the kinds and quantities of the fillers and auxiliary agents and the thickness of the coats used for the tests – were constant (it was assumed that the analysed silicone paint coatings would be formed from the same resource base, that is: the same pigments, fillers and other admixtures in the form of skimmers, thickeners and coalescents).

The determined 180 μ m thickness of the coatings would remain intact. Also, the impact of the changes in the parameters for mixing and dispersing the paints would not be considered. The types and the contents of the hydrophobizing admixtures in the form of silicone-organic polymers of varying chemical compositions would be subjected to change in separate experiments. The values of the random variable parameters were determined independently of the experimental schedule as a result of repeating the arbitrarily selected values of $C_{\rm PR}$ and $C_{\rm SR}$. The results of the measurements were analysed mathematically only after conducting the experiment. To present the model of the subject of the tests in a form of mathematical relationships, statistical models based on multiple regression were proposed for the comparative analysis.

2.2. The subject of the research

The subject of the research was paint coatings obtained from paints containing silicone-organic polymers that are available on the market and widely used by the manufacturers of silicone paints:

- SR1: polydimethylsiloxane of a linear structure incorporating units: M and D = Me₂SiO (reduced record);
- SR2: methylsiloxane resin incorporating the units T, M and D;
- SR3: methylsiloxane resin incorporating the units T, M, D, D^{OH} and D^{Oc} (the top index signifies substituents attached to silicone atoms other than Me: D^{OH} = MeOHSiO, D^{Oc} = MeOcSiO; Oc-octyl group);
- SR4: methylphenylsiloxane resin incorporating the units M, T and D^{Ph} = MePhSiO.

The above-mentioned components were applied in the form of water dispersions (50% solid content). The presence of the functional groups was confirmed by means of a spectrophotometric analysis with the application of a Perkin Elmer 1720X Fourier Transform Infrared Spectrophotometer. With the above in mind, minor samples were collected from each of the analysed silicon resins. The samples were spread on aluminium foil and left to dry under ambient conditions for 48 h. Next, 5×5 mm sections of the foil with a silicon film were cut out and placed in a measuring holder. Photoacoustic spectra of the silicon film were made, on average, from five foil fragments. The bands in the spectrum were described with the use of George Socrates' "Infrared and Raman Characteristic Group Frequencies Tables and Charts" Third edition, Wiley 2004 [12]. Fig. 2 presents the obtained spectra with the frequency of vibration characteristics of the mentioned functional groups.

The other ingredients of the recipe were: styrene-acrylic copolymer (50% solid content); a thickening agent, methyl hydroxyethyl cellulose (MHEC); a rheology modifier, Xanthan gum (a polysaccharide of microbiological origin); a pigment, titanium dioxide rutile; a dispersing agent, sodium salt of polyacrylic acid; silicone deformers and fillers, Plastorit 0 (a natural mineral composed of chloride/mica/quartz), precipitated barium sulphate and diatomaceous earth (Tables 1–3).

The paints containing the above-mentioned components were produced at a laboratory scale using a laboratory mixer (a power of $0.37-2.2\,\mathrm{kW}$; a working chamber volume of $1000\,\mathrm{ml}$; a maximum spindle speed of $11\,\mathrm{m\,s^{-1}}$; a dispersing disc diameter of $50\,\mathrm{mm}$).

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