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**PREPARATION OF SURFACE MODIFIED KAOLINES
BY SILICONE HYDROPHOBIZATION**

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This work deals with preparation of silanized kaolines for application in organic coatings. Coatings have a crucial task in protection of metal materials against rust. Leafy fillers improve anticorrosive properties (they participate in barrier mechanism), stability in atmospheric influences and adhesion to base plate. Organic silicate substances are able to create hydrophobic layer on a surface of different materials. Hydrophobization reduces a possibility of osmotic blisters creation. Four samples were prepared from four types of silanes (polydimethylsiloxane, methyltrimetoxysilane, aminoalkyl siloxane and aminopropylsilane) and two different kaolines. The following samples were prepared: A- $Al_6Si_2O_{13}$ (mullite, S1), B- SiO_2 (quartz, S2), C- $Al_6Si_2O_{13}$ (mullite, S3), D- SiO_2 (quartz, S4). Properties which are important for application in coatings were estimated by means of the following tests: structure identification by X-ray diffraction analysis, determination of the specific mass, oil consumption determination, specific surface area determination, determination of particle size and distribution, determination of the morphology of particles. Determination of

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methanol (MN) and water (WN) number is very important for evaluating anticorrosion properties of silanized samples in coatings. The prepared pigments have diverse chemical composition and content of structural phase quartz and mullite. The characterization of pigments shows good properties of tested pigments for production of coatings. Mechanical and anticorrosive properties will be investigated.

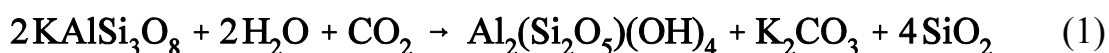
Introduction

The protection of metals against corrosion is a complicated and very expensive problem. Steel is exposed to various corrosive environments from low up to ultra-high aggressivity. The aim of paint and coating industry is to reduce the price of anticorrosive protection, which is possible by development of more efficient binders, pigments, fillers and additives.

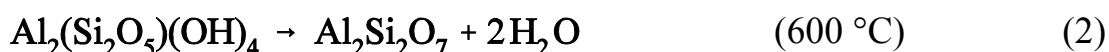
The development is influenced by ecological requirements focused on reduction of toxicity in the field of organic coatings and their applications. A strong toxicity leads to prohibition of pigments as red-lead, lead and chromate substances. These were replaced by phosphates, borates, silicates, molybdates and others which are nontoxic. Attention of this research is devoted to leafy fillers which may notably improve anticorrosive properties, stability in atmospheric influences and adhesion to base plate [1].

Pigments are basis material for production the anticorrosive coatings beside binders. They play important part in coatings and lead to paint films properties which improve their quality and field of application [2].

Fillers are compounds whose primary aim is to achieve desired pigment volume concentration of solids (fillers and pigments) in coating system. Secondary aims of fillers are optimization definite properties and specific properties of this system. Kaolines belong to fillers with non isometric (flaky, lamellar) shape of particles which participate in barrier mechanism of metals protection. Kaoline (china clay) is sedimentary mineral whose basic component is kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$, i.e. hydrated aluminosilicate [3,4]. Kaolinite is white but raw kaoline can be coloured due to foreign materials. It embodies monoclinic crystal geometry like mica. Kaolinite is made by aerating alkaline feldspar



Kaolinite loses crystal water by calcination near 600 °C and changes into kaoline [5]



At temperatures around 1,400 °C final products are cristobalite (SiO_2) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), and/or amorphous phases.

Kaoline is further used as a delusterant. Other uses of calcinated kaoline consist in application to decorative paints. Irregular shape of particles increases strength of coatings. It is also used in paint to extend titanium dioxide (TiO_2) and modify gloss levels. The largest use is in paper production, as a filler to a paper and for coating surface modifications of paper. Kaoline increases brightness and whiteness of paper and decreases its price. Another application of kaoline is in rubber and plastic industry, as a filler for cosmetics, in pharmaceuticals and in construction materials as a fire retardant. Kaolin is used in medicine, as a food additive, in toothpaste, as a light diffusing material in white incandescent light bulbs. It is generally the main component in porcelain. Porcelain is a ceramic material made by heating raw materials, generally including kaolin, in a kiln to temperatures between 1,200 °C and 1,400 °C. Kaolinite has also seen some use in organic farming, as a spray applied to crops to deter insect damage. Kaoline is a supplementary cementitious material. Metakaolin affects the acceleration of Portland cement hydration when it was added to concrete [6-9].

Organic silicate substances are able to create hydrophobic layer on a surface of different materials. This layer is in principle polymeric silicon microfilm which magnifies contact angle surface with water and decreases friction coefficient. Water cannot make up continuous film on such surface, it does not wet the surface and it easily streams down. The orientation of all organic groups of silicon chain toward material surface explains the hydrophobic effect of silicon layer. The thickness of silicon film is imperceptible (ca, 10^{-6} cm). The hydrophobic layer is of very high durability, and it is spoiled by drastic recourses which simultaneously destroy material surface. A silicone film does not block interstices of material and a hydrophobized material is able to “breathe”. Water vapour goes through its interstices, however, the water is not retained [10].

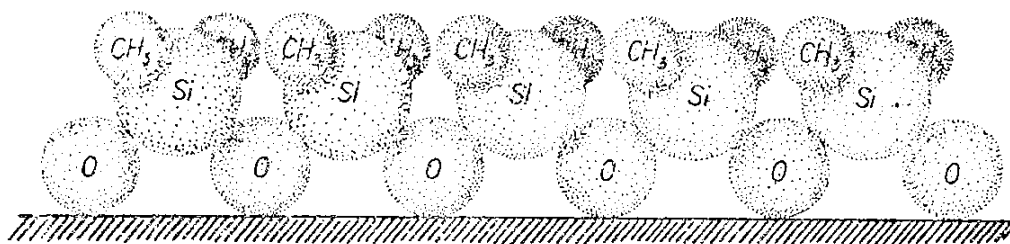


Fig. 1 Scheme of material surface which is hydrophobized by methyl silicon polymer [9]

Experimental

The prepared pigments were characterized by the following procedures. The tests, which characterize properties important for application in coatings, are described below. All the measurements were carried out under ambient conditions, i.e. 23 ± 2 °C and 50 ± 5 % relative humidity according to CSN EN 23270.

Structure Identification by X-ray Diffraction Analysis

The structure identification was performed by X-ray diffraction analysis using diffractometer X'pert PRO MPD 1880 (PANalytical, The Netherlands). When an X-ray beam bombards a crystalline lattice in a given orientation, the beam is scattered in a definite manner characterized by the atomic structure of the lattice. The Bragg law is useful for measuring wavelengths and for determining the lattice spacing of crystals. Modern X-ray crystallography provides the most powerful and accurate method for determining single-crystal structures.

Determination of Specific mass

The determination was carried out using Micromeritics AutoPyknometr 1320 (Micromeritics Instrument Corp., USA) that measures the volume of a sample based on measuring the volume of gas (helium) displaced by a measured powder pigment.

Determination of Oil Consumption

The oil consumption means the amount of flax oil in grams that makes a paste with defined properties from 100 g pigment. This determination was carried out according to CSN 67 0351 using the pestle-bowl method.

Determination of Specific Surface Area

The specific surface area of kaoline solid particles ($\text{m}^2 \text{g}^{-1}$) was determined by means of a Micromeritics ASAP 2000 Physic/chemisorption unit (Micromeritics Instrument Corp., USA). Specific surface area is a material property of solids which measures the total surface area per unit of mass. It is a derived scientific value that can be used to determine the type and properties of a material. It is defined as the by surface area divided by mass (with the units of $\text{m}^2 \text{g}^{-1}$).

Determination of Particle Size and Distribution

The size and distribution of particles was determined using Mastersizer 2000 (MALVERN Instruments Ltd, UK). Particles and size distribution means the percentages of each fraction into which a granular or powder sample is classified, with respect to particle size, by number or weight.

Determination of Morphology of Particles

The surface and shape of pigment particles were studied by means of a JEOL-JSM 5600 LV scanning electron microscope (Jeol, Japan) with accelerating voltage 15 kV. The SEM is designed for direct studying of the surfaces of solid objects by scanning with an electron beam that was generated and focused by the operation of the microscope. The SEM allows a greater depth of focus than the optical microscope. For this reason the SEM can produce an image that is a good representation of the three-dimensional sample.

Determination of Methanol Number (MN)

Methanol number is the concentration of aqueous methanol solution (in percent by wt.) in which one half of kaolin sample immerses into the liquid. The MN value reflects the strength by which silane is attached to the surface of kaolin. The higher the MN value, the stronger bond is. Procedure: 40 ml aqueous methanol of the concentration series 5, 10, 15 ...100 % MeOH is placed in a beaker, and 10 ml hydrophobized kaoline is added; The mixture is stirred at the speed of 800 rpm for 5 min. Then the mixture is transferred into a 100-ml graduated cylinder and left to stand 10 min to sediment. The proportion of sedimented and floating material is estimated on the cylinder scale. The MN value is obtained when the amounts of floating and sedimented material are equal.

Determination of Water Number (WN)

Water number is the amount of pigment that is wetted by water and immerses. The proportion of kaolin that is not coated with silane can be estimated from WN. Thus, the proportion of non-silanized kaolin can be deduced. The lower the WN, the better the silanization is. Procedure: 40 ml water and 10 ml pigment suspension are placed in a beaker. The mixture is stirred at the speed of 800 rpm for 5 min and then transferred into a 100-ml graduated cylinder and left to sediment for a period of 24 hours. The proportion of sedimented and floating material is estimated on

a cylinder scale. The WN is the amount of the sedimented part in ml.

Results

The preparation of these types of pigments can be divided according to the way of their origin and a type of used silicone and kaoline. The temperature of preparation was 1,150 °C. Two types of kaolines were chosen for preparing the samples. Kaoline K1 is composed mainly of mullite, kaoline K2 is quartz. A summary of prepared hydrophobized kaolines is given in Table I.

Table I Summary of prepared kaolines modified by silane hydrophobization

	Sample	Kaoline	Silane
A	$\text{Al}_6\text{Si}_2\text{O}_{13}$ (S1)	K2	S1*
B	SiO_2 (S2)	K2	S2*
C	$\text{Al}_6\text{Si}_2\text{O}_{13}$ (S3)	K1	S3*
D	SiO_2 (S4)	K2	S4*

* The codes of silanes are explained below

Hydrophobization by Polydimethylsiloxane

Silane S1 is a polysiloxane emulsion containing 60 % by wt. poly(dimethylsiloxane) $[(\text{CH}_3)_2\text{SiO}]_n$ and 1-3 % by wt. Decylvinylether, the rest being water. Procedure: 83 g of this polysiloxane emulsion and 1670 g kaoline K2 are mixed in 4,170 ml water, and this mixture is heated at the temperature of 60 °C with vigorous stirring for a period of 4 hours, whereupon the suspension is filtered on a Büchner funnel. The filter cake is dried in hot-flue drying kiln at the temperature of 105 °C for a period of 24 hours. The dried material is homogenized in a grinding mortar and reduced to a fine powder. Sample A – $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite, S1) was prepared in this way.

Hydrophobization with Methyltrimethoxysilane

The starting materials: isobutyl alcohol, ethanol, kaoline K2 and silane S2-methyl-trimethoxysilane $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ were placed into a sulphonation flask of capacity 2.5 l with a stirrer, two thermometers and a reflux condenser. Reaction proceeded 4 hours in a heating mantle at the temperature of 60 °C. The suspension was filtered on a Büchner funnel. The filter cake was dried at the temperature of

100 °C for a period of 6 hours. The mixture was comminuted in a mortar and mixed to fine powder. Sample B - SiO₂(quartz, S2) was prepared in this way.

Hydrophobization with Aminoalkyl Siloxane

Silane S3 is aminoalkyl siloxane [H₂N(CH₂)RSiO_{0.5}]_n. Only the technology of preparing differs: sample C- Al₆Si₂O₁₃ (mullite, S3) and sample D- SiO₂ (quartz, S4).

Silane S3, distilled water, kaoline K1, HCl for acidification were placed into a sulphonation flask with a stirrer and a thermometer. The mixture was kept at the temperature of 80 °C for 2 hours. The suspension was filtered, and the thixotropic filter cake was dried at the temperature of 105 °C for 24 hours. The mixture was grounded to fine powder.

Hydrophobization by Aminopropyl Silane

Distilled water, aqueous solution Silane S4- [H₂NCH₂CH₂CH₂SiO_{0.5}]_n and kaoline K2 were placed into 10-l pot and everything was fully mixed. The suspension was dried in a spray drier which was heated by burned charges of natural gas. The suspension was disintegrated to small droplets by means of a rotary reel (atomizer) at a speed 30 000 rpm. The droplets came into contact with drying medium — burned charges of natural gas and hot air. Water was quickly evaporated from the surface of the droplets, and the suspension was transformed to dry powder. The dried material was separated from drying medium in a cyclone separator and the burned charges left to a chimney. Sample D- SiO₂(quartz, S4) was prepared in this way.

Characterization of Prepared Kaolines

A – Al₆Si₂O₁₃(mullite, S1)

Structural phases:	mullite (Al ₆ Si ₂ O ₁₃), quartz (SiO ₂)
Specific mass:	2.68 g cm ³
Oil consumption:	34.5 g/100 g pigment
Specific surface area:	BET-isotherm 0.84 m ² g ⁻¹
D ₁₀	2.89 μm
D ₅₀	7.07 μm
D ₉₀	31.21 μm
MN	50
WN	0

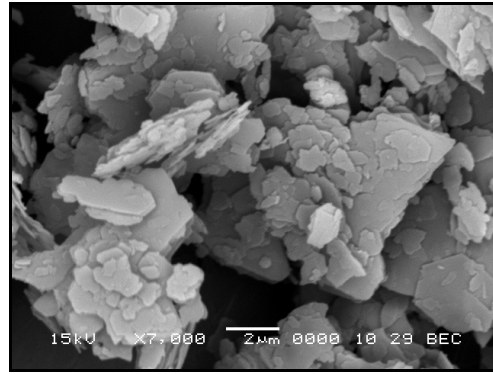
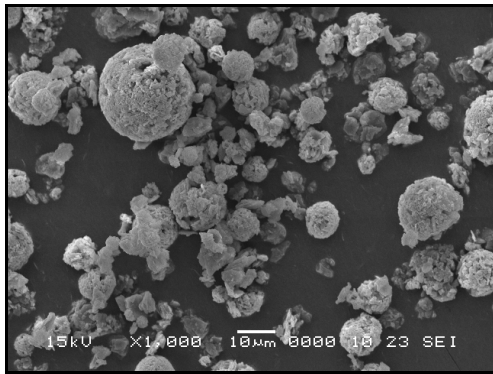


Fig. 2 SEM micrographs of sample A

B – SiO₂(quartz, S2)

Structural phases:	quartz (SiO ₂), mullite (Al ₆ Si ₂ O ₁₃)
Specific mass:	2.72 g cm ³
Oil consumption:	37.3 g/100 g pigment
Specific surface area:	BET-isotherm 0.68 m ² g ⁻¹
D ₁₀	2.31 µm
D ₅₀	3.19 µm
D ₉₀	6.46 µm
MN	40
WN	0

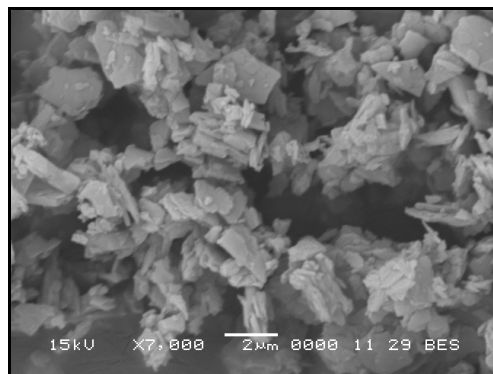
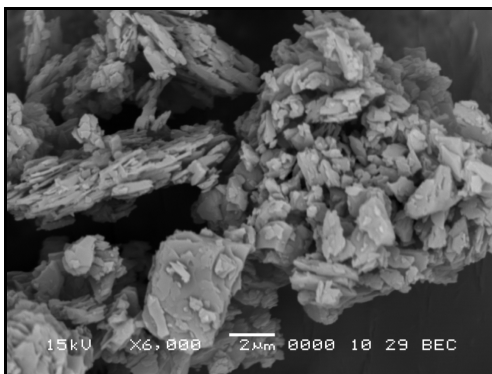


Fig. 3 SEM micrographs of sample B

C – Al₆Si₂O₁₃(mullite, S3)

Structural phases:	mullite (Al ₆ Si ₂ O ₁₃), quartz (SiO ₂)
Specific mass:	2.74 g cm ³

Oil consumption:	47.4 g/100 g pigment
Specific surface area:	BET-isotherm 2.63 m ² g ⁻¹
D ₁₀	0.95 μm
D ₅₀	3.46 μm
D ₉₀	30.34 μm
MN	0
WN	Everything was dipped

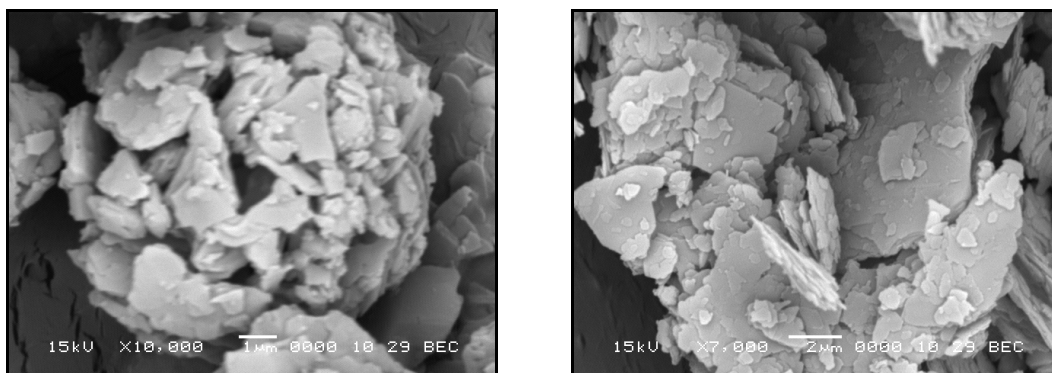


Fig. 4 SEM micrographs of sample C

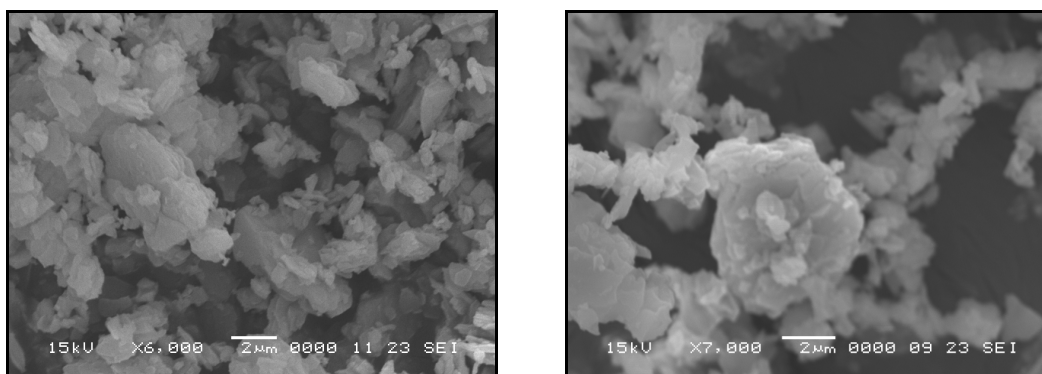


Fig. 5 SEM micrographs of sample D

D – SiO₂(quartz, S4)

Structural phases:	quartz (SiO ₂), mullite (Al ₆ Si ₂ O ₁₃)
Specific mass:	2.71 g cm ³
Oil consumption:	52.7 g/100 g pigment
Specific surface area:	BET-isotherm 0.29 m ² g ⁻¹
D ₁₀	2.60 μm
D ₅₀	8.82 μm
D ₉₀	18.37 μm

MN	0
WN	Everything was dipped

Discussion and Conclusion

Samples A – $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite, S1) and C – $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite, S3) have the same chemical composition, i.e. they contain mainly mullite. Samples B – SiO_2 (quartz, S2) and D – SiO_2 (quartz, S4) are predominantly composed of quartz. Chemical composition was determined by RTG analysis. The highest value of oil consumption was measured with sample D – SiO_2 (quartz, S4) – 52.7 g/100 g of pigment. The largest value of specific surface area was found in the case of sample C – $2.63 \text{ m}^2 \text{ g}^{-1}$, which is perceptible from SEM micrograph in Fig. 4. SEM micrographs (Figs 2-4) show lamellar shape of particles. All the samples had similar sizes and distribution of particles. Sample A – $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite, S1) had higher abundance of large particles, so there are clumps of particles in the SEM micrograph Fig. 2.

The highest value of methanol number was measured in the case of samples A – $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite, S1) and B – SiO_2 (quartz, S2) which were silanized with silane S1 and S2. These samples had simultaneous low value of water number. High degree of silanization predestines samples A and B to good anticorrosive properties because hydrophobization declines the possibility of osmotic blisters creation. Sample A is mainly composed of mullite in contrast to sample B which is formed by quartz. Anticorrosion tests are being carried out to show, if the degree of silanization or the chemical composition is crucial for anticorrosive protection. The characterization of pigments reveals good properties of the tested pigments to create coatings. The prepared pigments are going to be applied to alkyd resin. Mechanical and anticorrosive properties will be investigated.

Acknowledgments

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