ELSEVIER

Dyes and Pigments 50 (2001) 41–54

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Effect of surface modification on physicochemical properties of precipitated sodium–aluminium silicate, used as a pigment in acrylic dispersion paints

Radosław Werner[a], Andrzej Krysztafkiewicz[a], Aleksandra Dec[b], Teofil Jesionowski[a,*]

[a] *Poznan University of Technology, Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland*
[b] *PPW Lakma S.A., Frysztacka 173 St., 43-400 Cieszyn, Poland*

Received 20 March 2001; received in revised form 6 April 2001; accepted 10 May 2001

Abstract

Sodium–aluminium silicates of high dispersion were obtained and studies of the surface modification of the silicates using silane coupling agents are described. The best modifiers were selected, which induced a change of the silicate surface from a hydrophilic to a hydrophobic one. Physicochemical analyses of the modified silicates were performed and methods of evaluating the degree of surface modification of the silicate were presented. Near infrared spectroscopy (NIR) was used to determine the degree of condensation of the silicate surface silanol groups. The degree of hydrophobization of silicate surface was determined using a calorimetric method. Studies of morphology and microstructure were performed using transmission electron microscopy (TEM). Particle size and the tendency to form primary and secondary agglomerate structures were determined using dynamic light scattering technique (DLS). Attempts were made to apply the unmodified and modified sodium–aluminium silicates as fillers and pigments in acrylic dispersion paints. The modified sodium–aluminium silicates exerted a most pronounced advantageous effect on resistance to wet scrubbing. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sodium–aluminium silicates; Surface modification; Silane coupling agents; Acrylic dispersion paints

1. Introduction

In recent years, synthetic silicates have increasingly gained in commercial importance, finding use as inorganic pigments and as fillers. Inorganic pigments enjoy broad usage in the production of paints and varnishes [1], plastics, inks, construction materials, paper, glass and ceramic products [2]. Inorganic pigments are used in the production of varnishes due to their excellent coating power, resistance to light, good colour intensity and staining power. They are chemically neutral, insoluble, and are resistant to elevated temperatures, environmental factors, (e.g. to extreme variations of environmental pH), as well as thermal or chemical attack. Such properties of the pigments reflect, to a large extent, the chemical composition, size distribution of the particles as well as the surface properties of pigment particles [3–15].

---

* Corresponding author. Tel.: +48-61-665-36-26; fax: +48-61-665-36-49.
E-mail address: teofil.jesionowski@put.poznan.pl (T. Jesionowski).

PII: S0143-7208(01)00029-8

Dispersion of pigments and fillers in a binding material has a significant effect on the quality and properties of the finished paints. Such pigment dispersion in a binding material depends on the decomposition of primary agglomerates and on the distribution of the component particles. In the course of the process, the size of the agglomerates gradually decreases and the total surface of the pigment increases. Upon completion of the pigment dispersing process, the wetted particles may exhibit a tendency for re-agglomeration (a phenomenon termed *flocculation)*. Maintenance of a stable equilibrium between deflocculation and flocculation is important [16].

Pigment dispersion affects properties of the coating such as gloss, coating power, rheology and stability upon storage [17,18]. The fine dispersion of particles is indispensable for obtaining adequate distribution of the pigment in the coating and, thus, for most economic use of the pigment. The smaller is its dispersion particle size, the better is the pigment distribution [19]. Depending upon the application of the paints, for example in dispersion paints (for interior and exterior walls), appropriate raw materials and appropriate formulations have to be used.

The marked importance of white pigments results from the fact that white may be considered to represent a particular type of a colour, which represents a mixture of the entire spectrum of solar light; an ideal white (i.e. a white surface) fully reflects all incident light. A white pigment should exhibit maximum scattering power and low absorption of light within the visible spectrum. TiO_2 represents the most superior white pigment, and exhibits the highest refraction coefficient; such titanium "whites" is chemically inactive and, therefore, enjoys widespread application [7].

Sodium–aluminium silicates are white pigments; highly dispersed sodium–aluminium silicates exhibit advantageous properties which promote their use as fillers and pigments in dispersion paints and coating lacquers [20,21]. They are valued for their durability, rust inhibiting properties, high coating ability, ease of dispersion and relatively low cost. As their whiteness compared well with that of pigments based on TiO_2, the expensive titanium dioxide pigments can be eliminated either in part or in full. Sodium–aluminium silicate may also be used as a carrier of paints and lacquers, there by assuming the combined role of a coupling and filling agent. Paints which contain sodium–aluminium silicate display particularly advantageous sedimentation behaviour, demonstrating a low propensity to sediment and stratify. The paints also exhibit high surface coating ability and, after drying, manifest a bright white colour. In addition, paints containing sodium–aluminium silicates maintain their whiteness for a long time and do not become grey or dirty.

Sodium–aluminium silicate exhibits relatively high hydrophilicity and its surface adsorbs considerable amounts of water. This represents a significant obstacle to the use of this silicate in dispersion paints. The difficulties reflect, in particular, the low chemical affinity of the silicates for the functional organic groups present in the constituent components of multiple component paints.

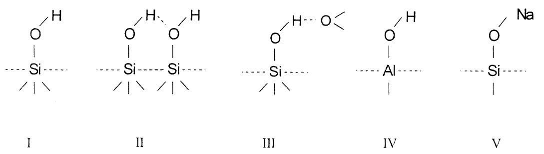
Modification of sodium–aluminium silicate surface is undertaken to improve its pigmentary properties. The principal aim of surface modification of silicate fillers is to decrease or remove their hydrophilic properties and augment their hydrophobic properties, this being conducted by introducing organofunctional groups to the pigment surface.

The hydrophilic character of sodium–aluminium silicate reflects its structure: the siloxane groups (≡Si–O–Si≡) are nonpolar and constitute a hydrophobic portion of the silicate surface. On the other hand, the isolated hydroxyl groups and hydrogen bonds formed due to the close proximity of hydroxyl groups, bound to the neighbouring silicon atoms, comprise the hydrophilic portion of the surface. The surface of silica and of silicates has been shown to carry three types of hydroxyl groups, namely:

I. free (isolated) hydroxyl groups (silanol groups);
II. paired hydroxyl groups, belonging to neighbouring silicon atoms;
III. bound hydroxyl groups, with two to four hydroxyl groups in their vicinity.

Moreover, the surface of sodium–aluminium silicate carries the following structures [20–22]:

IV. aluminol groups (Al–OH);
V. silanolan groups (Si–O–Na);



The free (isolated) hydroxyl groups or silanol groups (≡Si–OH), represent the most reactive groups within the surface.

The introduced groups can provide sites for the physical adsorption of organic particles and, in addition, they can react with multiple substituents such as surface active agents [23,24], hydrophobicity-inducing agents or adhesion stimulating compounds (e.g. silane coupling agents) [25–27]. For the surface modification of silicas and silicates, several silane coupling agents have been used, including: vinyltrimethoxysilane, vinyltriethoxysilane [28] and γ-methacryloxypropyltrimethoxysilane [29,30]. By selecting an appropriate silane coupling agent that contains not only groups able to react with the silicate surface (alkoxy groups), but also functional groups showing chemical affinity towards the functional groups of organic compounds, it should be possible to modify the surface of sodium-aluminium silicate. This modification results in a change in the surface properties from hydrophilic (silanol groups on the surface of unmodified silicate) to hydrophobic [31, 32]. The application of, for example, methacryloxysilane or vinylsilane for modification, should result in the potential reaction at the functional methacryloxy or vinyl groups with methyl methacrylate or vinyl polyacetate, the basic components of dispersion paints.

The main objective of our studies was to obtain hydrophobic sodium–aluminium silicates that would exhibit properties permitting their application as an active filler and paint pigment.

Table 1
Properties of applied sodium–aluminium silicates

Parameter	Unit	Value	
		P-01 (precipitated)	P-820 (Degussa)
Weight loss on drying (2 h/105 °C)	%	7.3	7.0
SiO_2 content	%	79.6	82.0
Al_2O_3 content	%	10.6	9.6
Na_2O content	%	9.4	8.0
Fe_2O_3 content	%	0.06	0.03
Bulk density	g/dm^3	100.2	93.3
pH of 5 wt.% water dispersion	–	9.7	10.4
Specific surface area (BET)	m^2/g	95	100
Degree of whiteness	%	97	98

2. Experimental

2.1. Materials

Sodium–aluminium silicate P-820 (Degussa, Germany) and sodium–aluminium silicates precipitated in our laboratory (by our own method) were used, which exhibited the properties shown in Table 1.

For surface modification of sodium–aluminium silicate, the silane coupling agents listed in Table 2 (produced by Witco Co.), were used.

2.2. Procedures and methods

Sodium–aluminium silicate was obtained by precipitation from solutions of sodium metasilicate and aluminium sulphate as described earlier [21,33]. The modification reaction was carried out during the precipitation process in which the silicate surface was modified by mixing the post-reactive mixture, containing the precipitated sodium–aluminium silicate, with a minimum amount of the appropriate silane coupling agent solution. The duration of the reaction was 20 min. The ensuing

Table 2
List of silane coupling agents used for sodium–aluminium silicate surface modification

Symbol	Nomenclature	Formula
A-172	Vinyltris(β-methoxyethoxy)silane	$CH_2{=}CHSi{-}(OCH_2CH_2OCH_3)_3$
A-174	γ-Methacryloxypropyltrimethoxysilane	$CH_2{=}CCH_3COO(CH_2)_3Si{-}(OCH_3)_3$

modified sodium–aluminium silicate was separated from the post-reactive mixture by filtration under reduced pressure; the prepared sample was then dried at 105 °C for 8 h [33].

Following modification, the silicates were subjected to physicochemical tests, their bulk densities were estimated, as well as their water, dibutyl phthalate and paraffin oil absorbing capacities.

The heat of immersion of the silica surfaces (both modified and unmodified) in water (H_i^w) and in benzene (H_i^B) were determined by calorimetry. Ampoules of a silica sample were carefully evacuated for 6 h at 110 °C, sealed under vacuum, and then transferred to a KRM-type differential calorimeter [34].

To quantify the extent of modification, the degree of condensation of silanol groups on the silicate surface was estimated using near infrared spectroscopy (NIR), permitting control of the decrease in silanol groups at the silicate surface after modification with various proadhesive compounds. NIR spectra were recorded for silicates both prior to and after modification using a Acta Beckman UV–visible–NIR spectrophotometer [35,36].

Studies of the morphology and microstructure of the silicates were performed to obtain data on the dispersion and morphology behaviour of the granules, as well as the structure of individual particles and also silicate agglomeration following modification. These studies were conducted using transmission electron microscopy, in a JEM 1200 EX II electron microscope. The samples were examined using an indirect single stage replica technique, characterized by high fidelity of reproduction, high resolving power, and high transparency of the electron beam [37].

The size distribution of the silica particle agglomerates and aggregates was estimated using a dynamic light scattering technique (DLS) on a ZetaPlus instrument (Brookhaven Instruments Co.) [33].

To define the suitability of the modified sodium–aluminium silicate as an active filler and as a white pigment in acrylic dispersion paints, application studies were performed using selected samples of sodium–aluminium silicate in three acrylic paint systems destined for exterior and interior applications (Table 3).

The studies were conducted as specified earlier [38,39]. In each of the examined paints, 10% by mass of the titanium white pigment, defined by formulation, was substituted by the

Table 3
Systems of acrylic paints for interior and exterior use selected for studies on application of selected samples of sodium–aluminium silicate

	Amount (wt. %)
1. TOP AKRYL LAKMA W	
Acrylic dispersion single layer paint, white, water soluble, for indoor use	
Acrylic–styrene dispersion (acrylic–styrene polymer, 50 wt.% in water)	20–25
Carbonate fillers	30–35
Titanium white	20–22
Dispersing agents, wetting agents, densifiers	18–30
2. AKRYL LAKMA	
Acrylic dispersion paint, white, water soluble, for outdoor use	
Acrylic–styrene dispersion (acrylic–styrene polymer, 50 wt.% in water)	20–25
Carbonate fillers	30–35
Titanium white	15–17
Dispersing agents, wetting agents, densifiers	23–35
3. AKRYBET	
Acrylic dispersion paint, white, organic solvent soluble, for outdoor use	
Acryl resin in a solvent (whitespirit)	20–25
Carbonate fillers	30–35
Titanium white	15–17
Dispersing agents, wetting agents, densifiers	23–35

sodium–aluminiumsilicate pigment. For this purpose, sodium–aluminium silicate P-820 (Degussa), unmodified sodium–aluminium silicate (P-01), sodium–aluminium silicate which had been modified with A-174 silane (P-02) as well as sodium–aluminium silicate which had been modified with A-172 silane (P-03) was used.

3. Results and discussion

The basic physicochemical parameters of the sodium-aluminium silicates, as imparted by modification with the applied silane coupling agents, are presented in Table 4.

The unmodified silicate P-820 exhibited low bulk density (93.3 g/dm^3), resembling that of the unmodified silicate, P-01, obtained in our laboratory (100.2 g/dm^3). Surface modification induced an evident increase in bulk density. The results presented in Table 4 reveal that the optimum amount of applied silane coupling agents, at which the effect of the silane on the physicochemical parameters of sodium–aluminium silicate proved significant, was 2 parts by mass.

The relationship between the bulk density of both the unmodified and modified sodium–aluminium silicates and the type of silane coupling agent used is presented in Fig. 1.

The heats of immersion in both water and benzene for the surfaces of silicates unmodified and modified with the silane coupling agents as well as the calculated degrees of silicate surface hydrophobization are presented in Table 5.

The heats of immersion in water and benzene of the modified silicates are also presented in Fig. 2. The relationship between the degree of silicate surface hydrophobization and the amount of modifying agents used is given in Fig. 3.

Table 4
Physicochemical properties of unmodified and modified sodium–aluminium silicates

Sample No.	Modifying agent	Amount of modifying agent (w/w)	Water absorbing capacity (cm^3/100 g)	Dibutyl phthalate absorbing capacity (cm^3/100 g)	Paraffin oil absorbing capacity (cm^3/100 g)	Bulk density (g/dm^3)
P-820	–	–	250	750	1150	93.30
P-01	–	–	250	650	1050	100.22
P-02	A-174	2	200	600	950	141.83
P-03	A-172	2	200	600	900	135.72

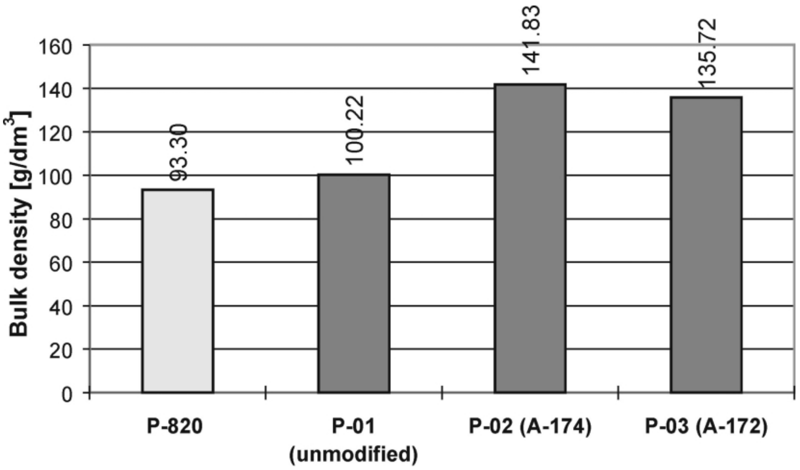


Fig. 1. Relation between value of bulk density and the type of silane coupling agent used (2 parts by mass of silane coupling agents were applied).

Table 5
Heats of immersion in water and benzene and calculated degrees of silicate surface hydrophobization (by calorimetric method), peak area and calculated degrees of condensation of surface silanol groups (by NIR spectroscopy) of unmodified and modified sodium–aluminium silicates

			Calorimetric method			Spectrophotometric method	
Sample No.	Modifying agent	Amount of modifying agent (w/w)	Heat of immersion in water H_i^W (J/g)	Heat of immersion in benzene H_i^B (J/g)	Degree of hydrophobization N (%)	Peak area (cm^2)	Degree of condensation η (%)
P-820	–	–	23.0	23.7	–	2.90	–
P-01	–	–	22.9	23.8	–	2.70	–
P-02	A-174	2	10.4	33.1	28.09	2.32	14.07
P-03	A-172	2	10.6	32.7	27.21	2.42	10.37

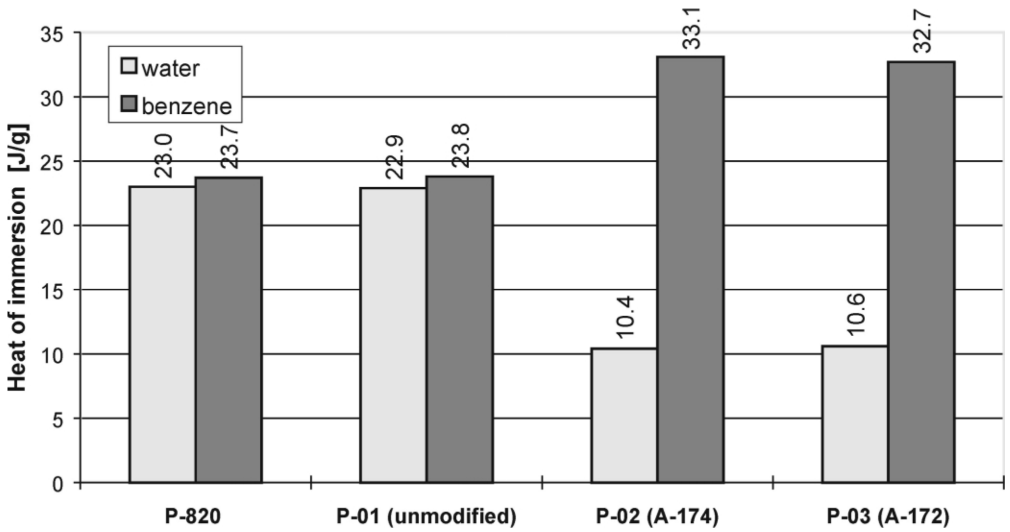


Fig. 2. Relation between heats of immersion in water and benzene for surface of unmodified and modified sodium–aluminium silicates and type of modifying agent used (2 parts by mass of silane coupling agents were applied).

From the data presented on sodium–aluminium silicate surface hydrophobization, it is clear that modification of the surface induced marked changes in wettability. Modification resulted in augmented values for the heat of immersion in benzene and, in parallel, in markedly decreased values of the heat of immersion in water. Modification with each of the applied silane coupling agents led to hydrophobization of the silicate surface, the extent of which depended on the type of the modifying compound. Comparing the degrees of hydrophobization of the silicate surfaces obtained after modification, the most pronounced hydrophobization was found to have been imparted by silane A-174. The calculated degrees of hydrophobization provided information on the progress of modification.

The relationship between the degree of condensation of surface silanol groups for those silicates which had been modified with the chosen proadhesive compounds and the amount of modifying substances used are shown in Fig. 4.

Evidently, the degree of condensation of silanol groups on the surface of sodium–aluminium silicate increased as a result of modification with the proadhesive compounds, particularly when 2 parts by mass of the compounds were used. This provided a convenient way of obtaining the optimum

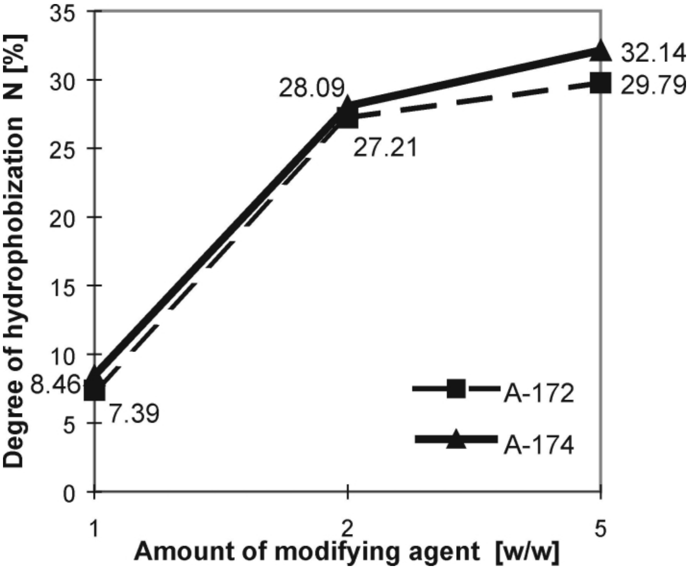


Fig. 3. Effect of amount of modifying agent on the degree of silicate surface hydrophobization.

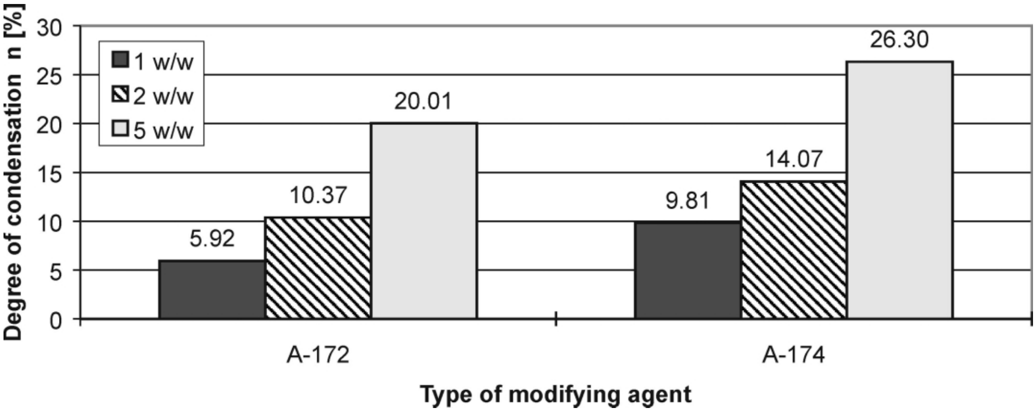


Fig. 4. Relation between degree of condensation of surface silanol groups and the type and amount of silane coupling agent used.

supplementation with the modifier, (i.e. the minimum amount of modifier at which the condensation effect was still significant). The results of the modification of the sodium–aluminium silicate with the various coupling compounds indicated that peak degrees of condensation were achieved using silane A-174 (2 parts by mass of A-174 resulted in 14.07% condensation); the application of silane A-172 induced 10.37% degree of condensation.

NIR spectroscopy confirmed that modification of the sodium–aluminium silicate surface with the silane coupling agents resulted in a significant reduction in the surface silanol groups content, which was in parallel with the amount of the modifying agent used.

Electron microscopic examinations of the surface of selected samples of the sodium–aluminium silicates are presented in Figs. 5–8; the patterns were obtained after the partial solubilization of the objects in hydrochloric acid solution.

The surface of the sodium–aluminium silicate P-820 is shown in Fig. 5 which documents the uneven character of the particle surface. Unfortunately, these particles manifest a tendency to form agglomerates.

The surface of the sodium–aluminium silicate, P-01, precipitated according to our own technique, is displayed in Fig. 6. Sample P-01 demonstrated outer surface particulate development, similar to that of P-820, and exhibited a particle size comparable to that of silicate P-820. The particles showed only a slight tendency to form agglomerates. The surface properties displayed by P-01 appear beneficial for its potential use as a pigment and an active filler of paints.

Fig. 7 shows the surface of a sample modified with 2 parts by a mass of methacryloxysilane (A-174). The pattern of the sample surface clearly indicates that the modification favourably affected development of the outer surface and significantly restricted the tendency to particle agglomeration. This tendency is particularly evident in Fig. 8. In this case, a tendency has been noted for the manifestation of primary particles: the obtained sodium–aluminium silicate shows a highly dispersed character.

The effect of modification may also be judged from Fig. 8, which shows the surface of sodium–aluminium silicate which was modified with 2 parts by mass of vinylsilane (A-172). The surface micrograph clearly shows the advantageous effect of modification on surface structure and an increased tendency for the presence of numerous primary particles of small diameter. Modification with silane A-172 completely restricted the tendency

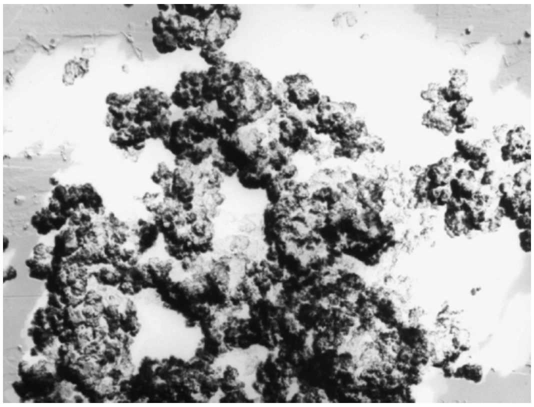


Fig. 5. Electron micrograph of unmodified silicate P-820 (Degussa) (magnification ×20,000).

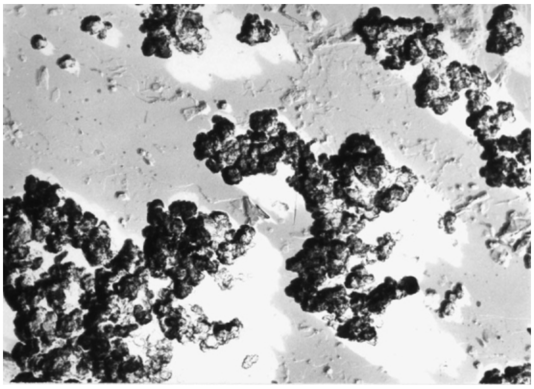


Fig. 7. Electron micrograph of silicate P-01, modified with 2 parts by mass silane A-174 (magnification ×20,000).

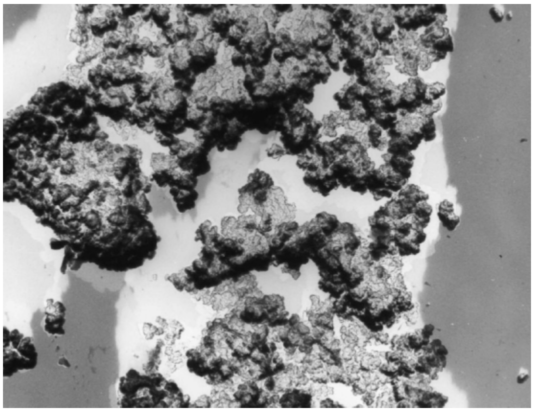


Fig. 6. Electron micrograph of unmodified silicate P-01 (precipitated by our own method) (magnification ×20,000).

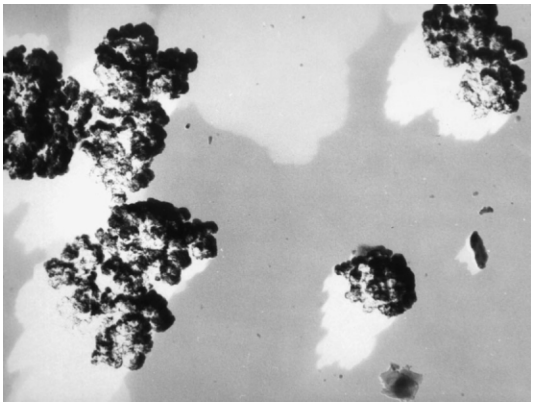


Fig. 8. Electron micrograph of silicate P-01, modified with 2 parts by mass silane A-172 (magnification ×20,000).

for particle agglomeration. Thus, application of vinylsilane (A-172) at 2 parts by mass was even more advantageous with respect to the morphology and microstructure of the sodium–aluminium silicates when compared to the use of silane A-174

Microscopic studies confirmed that modification with 2 parts by mass of both A-172 and A-174 silane coupling agents was sufficient to correct the morphology and outer surface of the sodium–aluminium silicates.

To corroborate the results obtained using transmission electron microscopy (TEM), the size distribution was determined and the tendency to form aggregates and agglomerates was examined using a dynamic light scattering (DLS). The particle aggregate and agglomerate size distributions obtained for the precipitated sodium–aluminium silicate samples, and unmodified silicates are shown in Figs. 9–12. The size distributions of the unmodified sodium–aluminium silicate (P-820) and the precipitated P-01 silicate are shown in Figs. 9 and 10, respectively.

In the cases of both P-820 and P-01, the presence of similar primary structures (particle aggregates) was noted. The size distribution of aggregates in the P-820 silicate was 524.3–681.3 nm (a size of 597.7 nm corresponded to an intensity of 100) and in the P-01 silicate it was in range of 361.8–499.2 nm (a size of 425.0 nm corresponded to an intensity of 100). For each of the silicates, the tendency to form secondary agglomerate structures of low intensities was observed, the intensity of which was somewhat higher for the precipitated silicate P-01 (within the relatively broad range of agglomerate sizes of 1688.2–2513.5 nm their maximum intensity was 10) while in the case of the P-820 silicate in the range of agglomerate sizes of 2471.1–2761.9 nm maximum intensity of secondary agglomerate structures was as low as 2. The mean diameter of the P-820 silicate was 646.3 nm and that of the P-01 silicate was 647.2 nm.

The size distribution of the particle aggregates and agglomerates following surface modification with 2 parts by mass of A-174 methacryloxysilane are shown in Fig. 11.

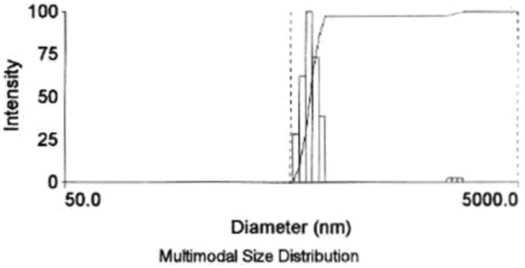


Fig. 9. Aggregate and agglomerate size distribution of unmodified sodium–aluminium silicate P-820.

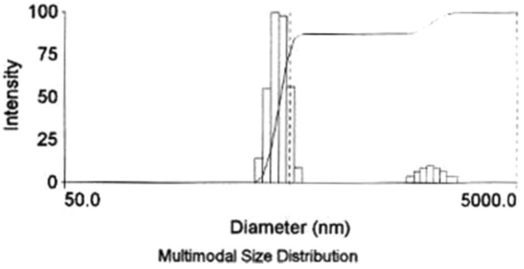


Fig. 10. Aggregate and agglomerate size distribution of unmodified sodium–aluminium silicate P-01.

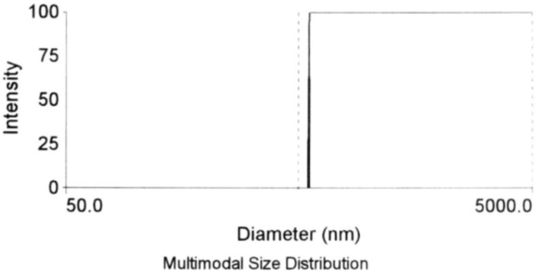


Fig. 11. Aggregate and agglomerate size distribution of sodium–aluminium silicate modified with 2 parts by mass of A-174 silane.

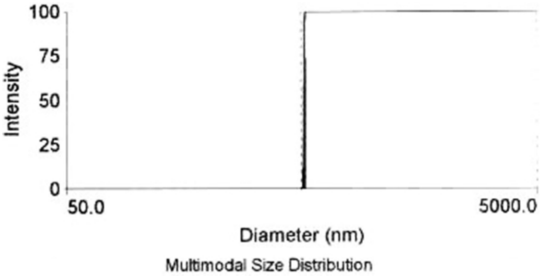


Fig. 12. Aggregate and agglomerate size distribution of sodium–aluminium silicate modified with 2 parts by mass of A-172 silane.

The surface modification with A-174 fully abrogated the tendency to form secondary agglomerate structures. Thus, modification during the precipitation of the sodium-aluminium silicate results in complete decomposition of secondary agglomerate structures. The advantageous effects of the A-174 silane also related to the size distribution of the silicate primary structures (particle aggregates). Following surface modification with A-174, the intensity of the latter structures resembled that observed for the unmodified P-820 silicate and the precipitated P-01 silicate.

In contrast, significant differences in particle aggregate size distributions were observed as a result of modification of the silicates. As can be observed in Fig. 11, application of 2 parts by mass of A-174 silane resulted in the silicate particles being markedly more uniform, lowering the range of the aggregate sizes; the silicate aggregates ranged in size between 545.6 and 554.7 nm (551.3 nm had an intensity of 100) and the mean diameter of the silicate was 550.7 nm.

A similar effect of surface modification on the size distribution of the aggregate and agglomerate structures was observed when the vinylsilane A-172 (Fig. 12) was used instead of the A-174 silane.

In a manner similar to the A-174 silane, the use of A-172 completely eliminated the presence of secondary agglomerates. In this case the intensity of the primary structures resembled those achieved for silicates which had been modified with A-174 or the unmodified silicates. Also, in this case, modification made the silicate particles much more uniform, this particular effect being even more pronounced than that observed using A-174. Modification with A-172 reduced the aggregate size to 504.9–515.0 nm (a size of 512.9 nm corresponding to an intensity of 100). Thus, following surface modification with A-172 silane, the range of aggregate sizes was narrower than those obtained for silicates modified with the A-174 silane or unmodified silicates P-820 and P-01. The mean diameter of the former silicate particle aggregates was 511.8 nm.

The studies of the particle size distribution of sodium–aluminium silicates confirmed that surface modification using the A-174 or A-172 silanes completely eliminated silicate agglomerates (so called secondary structures). The ensuing surface modification was also advantageous due to narrowing of the so called primary structure size range which resulted in greater homogeneity of the sodium–aluminium silicate particles.

To define the suitability of the modified silicates as active fillers and white pigments in acrylic dispersion paints, studies were performed on three selected samples of silicate in three acrylic dispersion paints, diluted using either water or organic solvents. In each of the paints 10% by mass of the original amount of the titanium white pigment was substituted by the sodium-aluminium silicate pigment (Tables 6–8).

The data in Tables 6 and 7 reveal that the densities of the studied water soluble paints, including both the *TOP AKRYL LAKMA W* paint for indoor use and the *AKRYL LAKMA* paint for outdoor use, produced using either the unmodified silicates P-820 and P-01 or the surface modified silicates P-02 and P-03, fitted the required range of 1.45–1.55 g/cm^3. As shown by the data in Table 8, the density of the exterior *AKRYBET* paint produced using application sodium–aluminium silicates, fitted the required range of 1.35–1.50 g/cm^3.

Moreover, exterior paint (Table 6), obtained using the modified sodium–aluminium silicates, exhibited very short drying time, which ranged between 25 and 30 min (normal requirements being not more than 5 h). As demonstrated by the data of Table 6, in the case of this paint, the use of P-02 or P-03 sodium–aluminium silicate, premodified with A-174 or A-172 silane, as a filler, shortened the drying time (to 25–27 min), compared to the paints in which the unmodified sodium–aluminium silicates, P-820 or P-01, were used as fillers; in the cases of the latter paints, the drying time was 30 min.

Similarly, all of the exterior paints, including both the water soluble *AKRYL LAKMA* paint and *AKRYBET* paint using an organic solvent (Tables 7 and 8), exhibited very short drying times (16.3–26 min for the former and 35–58 min for the latter type of paint; normal requirements being no more than 3 h).

In the case of the water-dilutable exterior *AKRYL LAKMA* paint (Table 7), use of P-01 or P-03 sodium–aluminium silicate as a filler, following its surface modification with A-174 or A-172 silane, did not elongate drying times (21 and 26

Table 6
Parameters of *TOP AKRYL LAKMA W* acrylic dispersion single layer, water soluble paint for interior use

Parameter	Norm requirement (PN-C-81914: 1998)	*TOP AKRYL LAKMA W*	*TOP AKRYL LAKMA W* containing:			
			P-820	P-01	P-02	P-03
Density (g/cm^3)	1.45–1.55 (⩽ 1.6)	1.48	1.46	1.45	1.45	1.47
Viscosity, KW10 estimated by time of dripping (s)	Drips after 10–30″	Drips after 23″	Drips after 19″	Drips after 14″	Drips after 22″	Drips after 14″
Viscosity according to Brookfield (cP) (S05, 20RPM)	–	82.5% 16,520	42.8% 8560	67.9% 13,560	54.3% 10,860	67% 13,400
Drying time		(20 °C, 58% air humidity)	(20 °C, 58% air humidity)	(24 °C, 65% air humidity)		
1° (min)	–	23′	25′	15′	13′	15′
5° (min)	(⩽5 h)	28′	30′	30′	25′	27′
Resistance to wet scrubbing	(⩾750 advances)	Base exposure after 800 advances	Base exposure after 1450 advances	Slight base exposure after 3000 advances	Slight base exposure after 3500 advances	No base exposure after 5000 advances
Quality coating of white paint	⩽III	I	II	I	I	I

Table 7
Parameters of *AKRYL LAKMA* acrylic dispersion white, water soluble paint for exterior use

Parameter	Norm requirements (PN-91/B-10102)	*AKRYL LAKMA*	*AKRYL LAKMA* containing:			
			P-820	P-01	P-02	P-03
Density (g/cm^3)	1.45–1.55 (⩽1.6)	1.48	1.48	1.41	1.42	1.43
Viscosity, KW10 estimated by time of dripping (s)	Drips after 17–24″	Drips after 17″	Drips after 17″	Drips immediately	Drips after 5″	Drips immediately
Viscosity according to Brookfield (cP) (S04, 5RPM)	–	46% 18,480	41.6% 16,680	73% 29,600	67% 26,840	74.5% 29,760
Drying time		(20 °C, 58% air humidity)	(20 °C, 58% air humidity)	(24 °C, 75% air humidity)		
1° (min)	–	13′	13′	15′	13′	15′
5° (min)	(⩽3h)	20′	16′30″	25′	21′	26′
Resistance to wet scrubbing	(⩾1500 advances)	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances
Quality coating of white paint	⩽III	III	III	III	III	III

Table 8
Parameters of *AKRYBET* acrylic white, organic solvent soluble paint for exterior use

Parameter	Norm requirements (PN-91/B-10102)	*AKRYBET*	*AKRYBET* containing:			
			P-820	P-01	P-02	P-03
Density (g/cm^3)	1.35–1.50 ($\leqslant$1.6)	1.39	1.39	1.36	1.38	1.37
Viscosity, KW4 estimated by time of dripping (s)	Drips after 50–150″	Drips after 136″	Drips after 137″	Drips after 115″ (slight amount remained in the cup)	Drips after120″ (slight amount remained in the cup)	Drips after 120″ (slight amount remained in the cup)
Viscosity according to Brookfield (cP) (S04, 5RPM)	–	60.3% 3020	63.1% 3160	74.9% 3740	73.5% 3670	70.4% 3515
Drying time		(20 °C, 58% air humidity)	(20 °C, 58% air humidity)	(24 °C, 75% air humidity)		
1° (min)	–	30′	43′	27′	45′	35′
5° (min)	($\leqslant$3 h)	35′	54″	35′	58′	43′
Resistance to wet scrubbing	($\geqslant$1500 advances)	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances	No base exposure after 10,000 advances
Quality coating of white paint	$\leqslant$III	III	III	III	III	III

min, respectively), compared to the paint in which the P-01 unmodified sodium–aluminium silicate had been used as a filler (drying time of 25 min). Only in the case of *AKRYBET*, an organic solvent paint for outdoor use (Table 8) did the use of P-02 or P-03 sodium–aluminium silicate premodified with the A-174 or A-172 silanes, slightly extend the drying time (to 43 min and 58 min, respectively), compared to the paint in which the P-01 unmodified silicate had been used (drying time of 35 min). The slight elongation of the drying time of the exterior *AKRYBET* remained, however, unimportant since drying time achieved was within that required of no more than 3 h.

The use of both the unmodified or the surface modified sodium–aluminium silicates as a pigment increased the resistance of the paint to wet scrubbing. In the case of the *TOP AKRYL LAKMA W* water soluble paint (Table 6), which contained a modified sodium–aluminium silicate (P-02 or P-03) filler, the base under the paint coat was not even exposed until, respectively, 3500 and 5000 advances were performed. The results appeared very satisfactory, compared to paints which contained the unmodified silicate P-820 (1450 advances) or P-01 (3000 advances) and, in particular, compared to the original *TOP AKRYL LAKMA W* paint, based on a traditional formulation using TiO_2 (800 advances). The observed enhanced resistance of the former paint to wet scrubbing, exceeded many times the normal requirements (at least 750 advances), obtained after painting with *TOP AKRYL LAKMA*, in which modified sodium–aluminium silicate was used as a co-filler.

An even better effect on paint resistance to wet scrubbing was obtained using either the unmodified or modified sodium–aluminium silicate as a filler of the exterior paints *AKRYL LAKMA* water soluble (Table 7) and the organic solvent soluble *AKRYBET* paints (Table 8). In each case (i.e when both the unmodified sodium–aluminium silicate P-820, P-01 or its modified equivalent P-02, P-03 was used), the paint base was not exposed following 10,000 advances, the normal requirement being more than 1500 advances.

Each of the acrylic paints studied exhibited very high quality parameters which easily met appropriate requirements of advance to base and coating of white.

Surface painting with the different types of dispersion paints, including those containing unmodified or modified sodium–aluminium silicate, resulted in smooth coats of good quality that were free of craters and pits, with no foreign inclusions or filler grains.

All the obtained coats of acrylic paints exhibited good adherence to the base. On the margin of the surface cuts the paint coat did not chip off.

All of the acrylic dispersion paints, including both the water soluble and organic solvent soluble types, created no problems upon brush, roller, or spray application and did not run off vertical surfaces.

4. Conclusions

The sodium–aluminium silicates obtained are characterized by parameters comparable to those of the commercial sodium–aluminium silicate P-820 (Degussa).

Surface modification changed the surface properties from hydrophilic to hydrophobic. Modification of the sodium–aluminium silicate increased its chemical affinity towards organic groups and promoted transformation from a hydrophilic to hydrophobic silicate. The use of γ-methacryloxypropyltrimethoxysilane (A-174) or vinyltris(β-methoxy–ethoxy)silane (A-172) for modification introduced functional methacryloxy or vinyl groups which were capable of reacting with methyl methacrylate or vinyl polyacetate, the basic components of acrylic dispersion paints.

Modified sodium–aluminium silicates may be used as valuable fillers and pigments in acrylic dispersion paints. Acrylic paints containing unmodified (P-820, P-01) or modified (P-02, P-03) sodium–aluminium silicates which were used as a substitute for 10% by mass TiO_2 content, exhibited excellent quality and resistance. The use of the modified sodium–aluminium silicate as both white pigments and fillers of acrylic dispersion paints, both water and organic solvent soluble types, for interior or exterior use, well appear promising.

Acknowledgements

The work was supported by the research grant No. BW 32/001/2001.

References

[1] Krysztafkiewicz A, Michalska I, Jesionowski T, Bogacki M. Fizykochemiczne Problemy Mineralurgii 1999;33:83.
[2] Endriss H. Inorganic coloured pigments today. Hannover: Curt R. Vincentz; 1998.
[3] Fryer JR. Surface Coatings International 1997;9:421.
[4] Glausch R. Farbe & Lack 1992;98:98.
[5] Indeikin EA, Zvonkina IJ. Eur Coat J 1998;9:639.
[6] Novak K. Paint and Ink International 1995;3-4:2.
[7] Article supplied by Bayer Leverkusen A.G. Paint and Ink International 1997;3-4:16.
[8] Schroder J. Eur Coatings J 1998;5:334.
[9] Boxall J. Pigment Resin Technol 1985;20:18.
[10] Muller B, Kientiz P. Farbe & Lack 1995;101:919.
[11] Wold CR, Soucek M. J Coatings Technol 1998;70:43.
[12] Muller B, Schubert M, Kinet G. Pigment Resin Technol 1990;28:279.
[13] Amirudin A, Barreau C, Hellouin R, Thierry D. Progress in Organic Coatings 1995;25:339.
[14] Muller B, Klager W. Corros Sci 1996;38:1869.
[15] Muller B, Forster I. Corros Sci 1996;38:1103.
[16] Kobayashi T. Progress in Organic Coatings 1997;28:79.
[17] Paper R. Progress in Organic Coatings 1996;28:79.
[18] Gesenhues U. Farbe & Lack 1999;3:151.
[19] Brown RFG, Carr C, Taylor ME. Progress in Organic Coatings 1997;30:185.
[20] Werner R, Krysztafkiewicz A, Jesionowski T. Pigment Resin Technol 2000;29:281.
[21] Jesionowski T, Krysztafkiewicz A, Werner R. Modified sodium–aluminium silicates—polyurethane fillers and paint pigment, International Symposium EUROFILLERS'99 (Villeurbanne, France), extended abstract.
[22] Jesionowski T, Krysztafkiewicz A. Pigment Resin Technol 1996;3:5.
[23] Szanto F, Dekany I, Patzko A, Varkonyi B. Colloids SurfA 1986;18:359.
[24] Patzko A, Dékany I. Colloids Surf A 1993;71:299.
[25] Mittal KL. Silane and other coupling agents. Utrecht: VSP; 1992.
[26] Plueddemann EP. Silane coupling agents. New York: Plenum Press; 1992.
[27] Pizzi A, Mittal KL. Handbook of adhesive technology. New York: MDI; 1994.
[28] Li Ou D, Seddon AB. Journal of Non-Crystalline Solids 1997;210:188.

[29] Isoda K, Kuroda K. Chem Mater 2000;12:1702.
[30] Husing N, Schwertfeger F, Tappert W, Schubert U. J Non-Crystalline Solids 1995;186:37.
[31] Dekany I, Szanto F, Nagy LG. J Colloid Interface Sci 1985;103:321.
[32] Dekany I, Szanto F, Nagy LG. J Colloid Interface Sci 1986;109:376.
[33] Krysztafkiewicz A, Werner R, Lipska KL, Jesionowski T. Colloids Surf A 2001;182:65.
[34] Zielenkiewicz W, Kurek T. Przemysł Chemiczny 1968; 45:247.
[35] Krysztafkiewicz A, Rager B. Colloid Polym Sci 1998; 266:485.
[36] Fink P, Mueller B. Wiss Ztschr dFSU Jena, Math Nat R 1981;30:589.
[37] Bradley DE. Br J Appl Phys 1965;5:165.
[38] PN-C-81914 Polish Norm, 1998.
[39] PN-91/B-10102 Polish Norm, 1991.