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COMPARISON OF CARBONATE-SILICATE FILLERS MODIFIED WITH VARIOUS PROADHESION COMPOUNDS

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Studies were performed on the production of highly dispersed carbonate-silicate fillers by the precipitation procedure. The fillers were subjected to surface modification employing for this purpose either the dry or the wet technique. For the modification various acrylic derivatives and silane coupling agents were used. The obtained products showed variable hydrophobic character and particle homogeneity. The modified and the unmodified carbonate-silicate fillers were used in facade acrylic paints and in silicate paints. Application of the fillers promoted production of facade acrylic paints of properties consistent with the norms and of silicate paints of a good density in the formulation system.

Key words: carbonate-silicate fillers, silane coupling agents, acrylic derivatives, acrylic and silicate paints

1. INTRODUCTION

Despite rich deposits of natural chalk and natural limestones, the synthetic calcium carbonate is still a product which is highly required by multiple users. Also in the nature various types of calcium silicates are encountered (e.g., bentonites, montmorillonites, etc.). Co-precipitated calcium carbonate and calcium silicate should exhaust several requirements, among other high extent of dispersity, low bulk density, well developed outer surface, particle homogeneity, surface activity, defined crystallographic structure, etc.

The principal problem which still awaits solution involves selection of optimum parameters of CaCO_3 precipitation, which assure that the planned properties of the product are obtained. According to a widespread opinion, selection of raw materials from which carbonate-silicate filler is precipitated by carbonisation with gaseous CO_2

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exerts significant effect on quality of the product. Literature data permit to conclude (Domka 1979, 1995, Trypuć 1990, Sekutowski 1992) that chemical synthesis of calcium carbonate of the quality which is required by the industry is far from easy. Depending upon the precipitation process, calcium carbonate and calcium silicate form gel-like colloid sediments of carbonate-silicate fillers, which gradually transform into crystalline sediments, consisting of the grains of various polymorphic varieties of CaCO_3 , i.e., calcite, aragonite, or waterite. The type of crystallisation is determined by conditions of the precipitation (Domka 1979, Krysztafkiewicz 1998, Grodzka 1999, Grodzka 2000).

At the second stage of the process, i.e. at the stage of CaCO_3 crystal growth, undergoing when the sediment is left in the original medium, either a further increase may take place in the number and the size of grains of a given variety or the transformation of the unstable waterite crystals into thermodynamically stable varieties, i.e. calcite and aragonite (Krysztafkiewicz 1990).

EXPERIMENTAL

MATERIALS

For production of carbonate-silicate fillers, the following substrates were used:

- Sodium metasilicate (10 wt% solution of $M=3.3$ modulus)
- Calcium hydroxide (10 wt% solution)
- Carbon dioxide (gaseous).

For surface modification of carbonate-silicate fillers the following compounds were used:

- Acrylic derivatives: acrylic acid and methyl acrylate
- Silane coupling agent:
 - 3-ureidoethylaminopropyltrimethoxysilane (U-165),
 - 3-methacryloxypropyltrimethoxysilane (U-511),
 - N-2-aminoethyl-3-aminopropyltrimethoxysilane (U-15D),
 - n-octyltrimethoxysilane (U-222).

METHODS

Carbonate-silicate fillers were precipitated using 10 wt% solution of calcium hydroxide, 10 wt% solution of sodium metasilicate, the modulus of $\text{SiO}_2/\text{Na}_2\text{O} = 3.3$, and gaseous CO_2 with the flow rate equal $300 \text{ cm}^3/\text{min}$. On the other hand, modification of carbonate-silicate filler surface was performed by the following two procedures:

- *Modification in the course of precipitation (the "wet" technique)*

The modification was conducted in such a way that various amounts of an appropriate modifier (1 to 7 weight parts per 100 weight parts of the obtained filler) were added to the reactor in the course of precipitation of carbonate-silicate filler. The

reaction was conducted at 60°C. The substrates included 10% solutions and gaseous CO₂ was dosed at the rate of 300 cm³/min.

- *Modification of precipitated carbonate-silicate fillers (the “dry” technique)*

The carbonate-silicate filler, precipitated from solutions of sodium metasilicate and calcium hydroxide in the presence of gaseous CO₂ (Na₂SiO₃:Ca(OH)₂=2:1 (v/v), the temperature of precipitation: 60°C), was placed in a mixer, adding appropriate amounts of the modifier. The mixing was conducted for 1 h. The silanes were added at 1 to 7 weight parts per 100 weight parts of the filler and acrylic derivatives at 0.5, 1, 2, or 3 weight parts per 100 weight parts of the filler.

Selected samples of the precipitated fillers were subjected also to microscopic analysis, mainly in order to characterise the surface morphology of respective particles and their tendency to form agglomerates. For this purpose, the scanning electron microscope, Philips SEM 515 was used. Sample preparation included formation of a suspension of the filler in tertiary butanol, application of the suspension on the microscope table and 10 min coating with gold atoms on an ionisation plate.

Particle size distribution was also examined using a ZetaPlus apparatus (Brookhaven Instruments Co, USA). The particle size was measured using the dynamic light scattering (DLS) technique. The technique involved weighing out of an appropriate sample, placing it in a small amount of water (0.1 g in 200 cm³ H₂O) and stabilising it in an ultrasonic bath (50 kHz). The prepared sample was placed in a cuvette and size distribution of carbonate-silicate particles was then measured.

The unmodified carbonate-silicate filler was used as a substitute for titanium white and for the carbonate filler (chalk) in the formulation of the facade acrylic paint *AKRYL LAKMA*. In the studied paint, 10 wt% of the titanium white content in the formulation and the total amount of the chalk filler were substituted by the carbonate-silicate filler.

Carbonate-silicate fillers were used also in the anti-corrosion silicate paints. Composition of the silicate paint included:

- 50 g potassium metasilicate solution, modulus 4.0
- 25 g zinc powder
- 0.5 g pyrogenic silica, Cab-O-Sil
- 5 g carbonate-silicate filler, unmodified or modified.

Time of silicate paint densification was measured. Paint samples were observed for one week.

RESULTS AND DISCUSSION

The samples of carbonate-silicate fillers, precipitated from sodium metasilicate and calcium hydroxide solution using gaseous CO₂ at various temperatures, are listed in Table 1.

Carbonate-silicate filler of best parameters was obtained at 60°C. The product showed the lowest bulk density, the highest paraffin oil and dibutyl phthalate absorbing capacities and a high value of flow-off point.

Table 1. Physicochemical properties of carbonate-silicate fillers precipitated with calcium hydroxide and sodium metasilicate solutions as well as gaseous carbon ($\text{Na}_2\text{SiO}_3:\text{Ca}(\text{OH})_2=2:1$)

Temperature [°C]	Bulk density [g/dm ³]	Flow-off point [cm ³ /10g]	Dibutyl phthalate absorbing capacity [cm ³ /100g]	Paraffin oil absorbing capacity [cm ³ /100g]	Water absorbing capacity [cm ³ /100g]
40	243	26.5	300	400	250
60	235	26.5	300	450	200
80	282	23.0	250	300	200

Modification of carbonate-silicate filler using either the “dry” or the “wet” technique was conducted using various substances in order to obtain various physicochemical properties of the fillers.

At the first stage, acrylic derivatives, methyl acrylate and acrylic acid were used for modification. The derivatives were introduced to the system in the course of precipitation, preserving the remaining conditions of the process. Samples of carbonate-silicate fillers, precipitated in the presence of acrylic derivatives, are listed in Table 2. As compared to acrylic acid, methyl acrylate was less effective in affecting principal physicochemical properties of the carbonate-silicate fillers. Acrylic acid induced higher activity of carbonate-silicate fillers: bulk densities of the fillers decreased and the values of their flow-off point increased. The amounts of acrylic acid used for the modification of carbonate-silicate filler evidently affected parameters of the filler. Following modification of the filler with 3 weight parts of acrylic acid, bulk density decreased by more than 25% and flow-off point increased by almost 75% as compared to the unmodified filler.

Table 2. Physicochemical properties of carbonate-silicate fillers precipitated with calcium hydroxide and sodium metasilicate solutions as well as gaseous carbon in presence of acrylic derivatives

Amount of modifying agent [w/w]	Methyl acrylate		Acrylic acid	
	Bulk density [g/dm ³]	Flow-off point [cm ³ /10g]	Bulk density [g/dm ³]	Flow-off point [cm ³ /10g]
0.5	296	28.0	263	26.0
1.0	205	32.0	238	30.0
2.0	224	29.0	174	36.5
3.0	236	29.0	175	36.0

Modification with the silanes was conducted both by the “dry” and the “wet” technique. Principal physicochemical parameters of carbonate-silicate fillers following their modification are presented in Tables 3 and 4.

Table 3. Physicochemical parameters of chose sample of carbonate-silicate fillers modified with silane coupling agents („wet method”)

Amount of modifying agent [w/w]	Bulk density [g/dm ³]	Flow-off point [cm ³ /10g]	Dibutyl phthalate absorbing capacity [cm ³ /100g]	Paraffin oil absorbing capacity [cm ³ /100g]	Water absorbing capacity [cm ³ /100g]
U-165 silane					
1	251	20.5	300	250	350
2	289	20.0	200	200	300
5	248	21.0	250	250	300
U-511 silane					
1	296	18.0	200	200	250
2	305	17.5	200	250	200
5	279	23.5	250	250	250
U-15D silane					
1	217	21.5	336	253	275
3	221	26.0	325	276	306
5	231	28.5	277	280	310
7	245	29.0	223	292	320
U-222 silane					
1	216	*	390	210	*
3	255	*	260	216	*
5	270	*	210	235	*
7	265	*	200	250	*

*non-wettable

Following modification with ureidosilane and with aminosilane in particular the capacity of carbonate-silicate fillers to absorb water increased markedly. The respective value reached even 360 cm³/100g. This proved that the adsorption of silanes with the amino group increased hydrophilic character of the modified fillers. Similar relations could be observed (Tables 3 and 4) whether the “wet” or the “dry” technique of modification was applied. Surface modification of carbonate-silicate fillers with octylsilane was most effective in altering surface of the filler from a typically hydrophilic to a hydrophobic one. This was shown by the measurements both the water absorbing capacity and the flow-off point. The surface was demonstrated to be completely unwettable with water.

Size distribution of agglomerates of carbonate-silicate filler, precipitated at 60°C, at the Na₂SiO₃:Ca(OH)₂, v/v ratio = 2:1, is presented in Fig.1. Mean diameter of agglomerates was 1,772.4 nm and the polydispersity value amounted to 0.011. As demonstrated by the presented agglomerate size distribution, the unmodified carbonate-silicate filler was characterised by the presence of two agglomerate bands of various intensities.

Table 4. Physicochemical parameters of chose sample of carbonate-silicate fillers modified with silane coupling agents („dry method”)

Amount of modifying agent [w/w]	Bulk density [g/dm ³]	Flow-off point [cm ³ /10g]	Dibutyl phthalate absorbing capacity [cm ³ /100g]	Paraffin oil absorbing capacity [cm ³ /100g]	Water absorbing capacity [cm ³ /100g]
U-165 silane					
1	296	18.0	200	200	250
2	305	17.5	200	250	300
5	279	23.5	250	250	350
U-511 silane					
2	356	19.5	250	320	250
5	367	*	150	300	*
U-15D silane					
1	217	25.5	240	225	290
3	247	29.0	230	243	350
5	267	32.5	203	276	360
7	282	33.0	200	296	360
U-222 silane					
1	215	*	380	200	*
3	239	*	265	193	*
5	267	*	260	156	*
7	296	*	250	136	*

*non-wettable

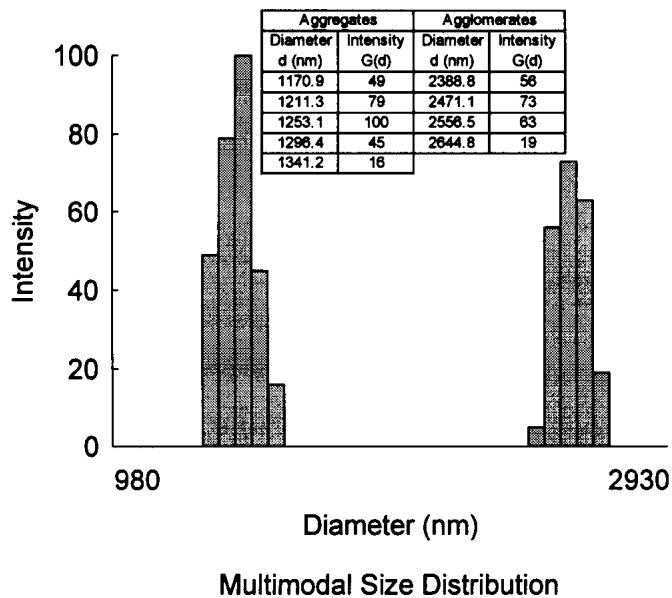


Fig. 1. Particle size distribution of unmodified carbonate-silicate filler

The primary agglomerate (aggregate) band exhibited higher intensity than that shown by the secondary agglomerate band. The primary agglomerate band fitted the agglomerate range of 1,170-1,350 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 1,253.1 nm). On the other hand, the band of secondary agglomerates occupied the diameter range of 2,300 to 2,650 nm (maximum intensity of 73 corresponded to the agglomerate diameter of 2,471.1 nm). Thus, the unmodified sample of carbonate-silicate filler showed low homogeneity.

Following modification with ureidosilane (U-165), conducted in the course of precipitation of the carbonate-silicate filler, more extensive secondary agglomerates formed than those of the unmodified filler. Following modification with 2 weight parts of U-165 silane, mean diameter of agglomerates was 4,878.8 nm and polydispersity value was 0.250. The particle size distributions for the carbonate-silicate filler, modified with 2 weight parts of ureidosilane, is presented in Fig.2. In the distribution, two primary agglomerate bands of lower intensity are present together with a secondary agglomerate band of a higher intensity. The primary agglomerate band is noted within the range of small diameters (340 to 610 nm) and maximum intensity of 80 corresponded to agglomerate diameter of 482.6 nm. On the other hand, the band of secondary agglomerates fitted the range of 7,900 to over 10,000 nm.

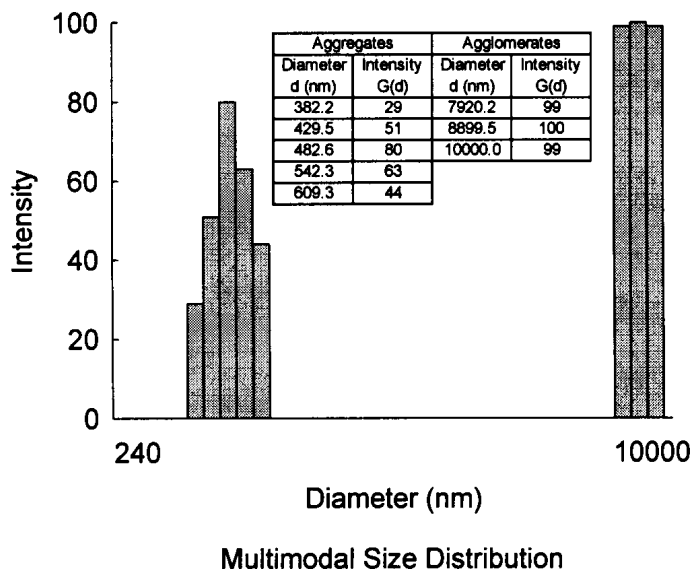


Fig. 2. Particle size distribution of modified carbonate-silicate filler with 2 w/w of U-165 silane

Most important parameters of facade acrylic paints are presented in Table 5. In the table, the parameters of the standard paint were compared with the parameters of the paint in which 10% of titanium white in the formulation and the complete amount of chalk filler were substituted by the precipitated unmodified carbonate-silicate filler (the sample was precipitated at 60°C at Na₂SiO₃:Ca(OH)₂, v/v ratio = 2:1).

In Table 5, similar parameters were obtained for both studied acrylic paints. Moreover, the acrylic paints containing precipitated carbonate-silicate filler manifested coat quality, coat adherence to the base, water solubility, coating ability and the resistance to flowing off vertical surfaces consistent with appropriate norms. Effect of modified carbonate-silicate fillers on time of densification of silicate paint. The unmodified and the aminosilane-modified carbonate-silicate fillers were found to form a stable suspension of a silicate paint. This consistency persisted for over a week (in line with expectations).

Table 5. Physicochemical parameters of acrylic paint

Parameter	Norm requirement [PN-C-81914: 1998]	TOP AKRYL LAKMA W	AKRYL LAKMA with modified carbonate-silicate filler
Density, [g/cm ³]	1.45-1.55 [≤ 1.6]	1.48	1.48
Viscosity KW10 estimated by time of dripping, [s]	Drips after 10-30"	Drips after 23"	Drips immediately
Viscosity acc. to Brookfield, [cP] (S05, 20RPM)	-	82.5% 16520	16 180
Drying time		(20°C, 58% air humidity)	20°C, 64% air humidity)
1° [min.]	-	23'	13'
5° [min.]	[≤ 5h]	28'	18'
Resistance to wet scrubbing	[≥ 750 advances]	Base exposure after 800 advances	Base exposure after 10,000 advances
Quality coating of white paint	≤ III	I	III

On the other hand, the fillers modified with methacryloxysilane and, first of all, those modified with octylsilane promoted rapid gelation and densification of the paint. Thus, in silicate paints the best effects were obtained using fillers of a hydrophilic character. Following application on metal plates, the obtained silicate paints, containing aminosilane-modified carbonate-silicate fillers, were noted to form ideal coats of the surfaces.

CONCLUSIONS

- Modification of carbonate-silicate filler with acrylic acid promoted increased activity of the surface (flow-off point elevated by 75% as compared to the unmodified filler)
- Following modification with octylsilane (U-222), independently of the applied modification technique, the carbonate-silicate filler exhibited highly hydrophobic character.

- Following modification with ureidosilane (U-165), conducted in the course of precipitation, secondary agglomerates of carbonate-silicate filler were formed and the effect was more pronounced than in the case of the unmodified filler.
- Unmodified and aminosilane-modified carbonate-silicate fillers form stable suspensions of silicate paints.

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J. Grodzka, A. Krysztafkiewicz, T. Jesionowski, *Porównanie napelniaczy węglanowo-krzemianowych modyfikowanych różnymi czynnikami wiążącymi*, *Fizykochemiczne Problemy Mineralurgii*, 35, 2001, 73-81, (w jęz. ang.)

Przeprowadzono badania nad otrzymywaniem metodą strącania wysoko zdyspergowanych napelniaczy węglanowo-krzemianowych. Napelniacze te poddawano powierzchniowej modyfikacji, wykorzystując w tym celu metodę „mokrą” i „suchą”. Do modyfikacji zastosowano pochodne akrylowe oraz silanowe związki wiążące. Otrzymano produkty o różnym stopniu hydrofobowości oraz jednorodności cząstek. Modyfikowane i niemodyfikowane napelniacze węglanowo-krzemianowe zastosowano w farbách akrylowych fasadowych oraz w farbách krzemianowych. Aplikacja tych napelniaczy przyczynia się do uzyskania farb fasadowych akrylowych o właściwościach zgodnych z normami oraz farb krzemianowych o dobrym stopniu ząęszczenia w układzie recepturowym.