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SYNTHESIS AND CHARACTERISATION OF PRECIPITATED COPPER(II) SILICATES

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The study was undertaken to obtain a blue inorganic pigment of copper(II) silicate of high degree of dispersion. The process of precipitation of synthetic copper(II) silicates was optimised. The effect of the direction of dosing, percent concentration and volume ratio of the reagents, temperature and type of copper salt used on the physico-chemical properties of the products was studied. The copper(II) silicate obtained was characterised by satisfactory parameters; bulk density of 198 g/dm³, water absorbing capacity of 225 cm³/100g and paraffin oil absorbing capacity of 300 cm³/100g. The diameters of the precipitated silicates varied from 0.955 – 120.2 µm, with a dominant presence of larger particles making secondary agglomerates.

key words: copper silicate, precipitation process, particle size distribution, wettability, colorimetric data

INTRODUCTION

Pigments are colouring inorganic or rarely organic substances in the form of fine powder, insoluble in water, oil, resins or organic solvents. Pigments added to carrier or matrix, acting as a binder, make the fundamental component of coating materials; paints and enamels (Erfutrh 1998, Xuening 2000, Yuan 2005).

Highly dispersed pigments should be characterised by low bulk density to minimise sedimentation of pigments in dispersive media. Low water absorbing

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capacity at elevated level of paraffin oil absorbing capacity is desired to permit the use of pigment in lyophilic systems, while the reverse relation of these parameters the pigments can be used in lyophobic (hydrophilic) systems (Krysztafkiewicz 1997, 1999).

Inorganic pigments, divided into natural and synthetic (Wieczorek 2003, Johnston 2004) are resistant to chemical compounds and to extreme pH values and have higher covering power than organic ones. Besides they are highly resistant to light (Werner 1985).

Highly dispersed silicates of calcium, aluminium, magnesium, zinc and aluminium-sodium are used as insoluble components of rubber blends and other organic polymers, e.g. as fillers of polyvinyl chloride (Rothe 2009, Anastasiadis 2008, Lee 2008) or rubber (Krysztafkiewicz 1998, Wang 2005, Varghese 2003). The use of silicates as fillers brings improvement in mechanical properties of the filled polymers and do not change the colour of the substance to which they are added (they belong to the so-called bright fillers).

Inorganic pigments are used in paints, varnishes and resins (El-Nahhal 2005) and they often have colour other than white: e.g. chromium silicates are green (Krysztafkiewicz 2008, Klapiszewska 2003), nickel silicates are blue-green (Klapiszewska 2005).

Recent development in production of synthetic silicates has promoted their use in many fields. Interestingly, the synthesis of silicates permits formation of more types of silicate bonds than met in nature. Synthetic silicates can have crystalline structure (as natural ones) or amorphous structure. Many of them are obtained in the form of inter-oxide systems.

EXPERIMENTAL

MATERIALS

The substances used included: 5% and 10% solution of sodium silicate (VITROSILICON S.A.); 5%, 10% and 20% solutions of copper(II) sulphate(VI) and 5% solution of copper(II) nitrate(V) or copper(II) chloride (Chempur Piekary Śląskie).

METHODS OF STUDIES

Precipitation reaction was carried out by introducing doses of sodium silicate solution by a peristaltic pump into a reactor of the capacity of 0.5 dm³ with copper(II) sulphate(VI). The reaction was also conducted in the reverse direction and by dosing the reagents into water environment. Precipitation of highly dispersed copper(II)

silicate was performed with additional use of copper(II) nitrate(V) and copper(II) chloride solutions. The conditions of precipitation were the same as for the sample characterised by the best parameters and precipitated by copper(II) sulphate(VI).

For precipitation the solutions of Na₂SiO₃ and CuSO₄ of the following volume ratios were used 1:1, 1:2, 1:3 and 2:1, 3:1. The process was carried out at temperatures 20÷85°C. Copper silicate obtained was separated from the post-reaction mixture on a filter with the use of vacuum pump. The samples were dried at 105°C for 2h. The bulk density, absorbing capacity of water and paraffin oil were measured. In order to determine the brightness, contribution of colours, saturation and hue of colour, the colorimetric analysis was made with the CIE L*a*b* system (SPECBOS 4000 colorimeter made by Carl Zeiss Jena). With the use of a Tensiometer K100 made by Krüss, on the basis of the mass of water absorbed by the sample, the sample wettability was estimated. The size of particles was determined by Mastersizer 2000 made by Malvern Instruments Ltd. Morphology of the surface of the precipitated samples of copper silicate was analysed by the scanning electron microscopy (SEM), with a scanning microscope VO40 made by Zeiss.

RESULTS AND DISCUSSION

The blue inorganic pigment of copper(II) silicate of high degree of dispersion was obtained. The probable mechanism of its synthesis is presented in Fig. 1.

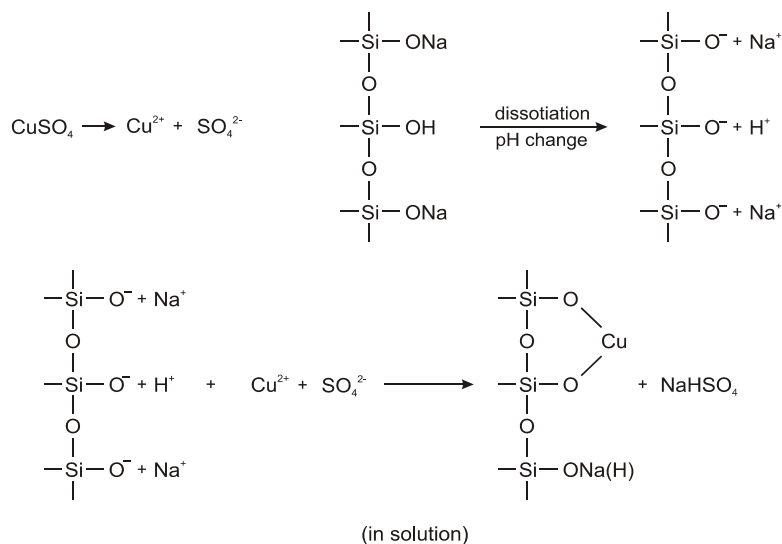


Fig. 1. Mechanism of copper silicates synteshis

Table 1 presents the method of obtaining copper silicates, while Table 2 gives their basic physico-chemical parameters and specifies the reaction systems in which they were precipitated.

Table 1. Characteristic of precipitation process

Sample No.	Precipitation direction	Solution concentration (%)		Reagents volume ratio	Temperature (°C)	
		sodium silicate	cooper salts			
1	Na_2SiO_3 to CuSO_4	5	5	1:1	20	
2	CuSO_4 to Na_2SiO_3					
3	Na_2SiO_3 and CuSO_4 to H_2O					
4	Na_2SiO_3 to CuSO_4	5	10			
5			20			
6		10	5			
7			10			
8			20			
9			5			5
10		1:3				
11		2:1				
12		3:1				
13		5	5	1:1	40	
14	60					
15	85					
16	Na_2SiO_3 to $\text{Cu}(\text{NO}_3)_2$				20	
17	Na_2SiO_3 to CuCl_2					

The lowest bulk density of 198 g/dm^3 was obtained for sample 1 that is copper silicate precipitated at the 1: 1 volume ratio of the reagents, at 20°C , by dosing a 5% solution of sodium silicate into the reactor containing a 5% solution of copper(II) sulphate(VI). The highest bulk density of 562 g/dm^3 was obtained for sample 5, that is copper silicate precipitated in the same conditions as sample 1 but with the use of a 20% solution of copper(II) sulphate(VI).

The use of another copper salt in the process of precipitation leads to an increase in the bulk density of copper(II) silicate to 220 g/dm^3 when copper(II) nitrate(V) is applied and to 456 g/dm^3 when copper(II) chloride is applied.

The values of absorbing capacity of water and paraffin oil were similar for all samples. The exceptions are samples 9 and 10 precipitated at the 1:3 and 3:1 volume ratio of the reagents, whose absorbing capacities are much different.

Table 2. Physicochemical parameters of precipitated copper silicates

Sample No.	Bulk density (g/dm ³)	Water absorbing capacity (cm ³ /100g)	Paraffin oil absorbing capacity (cm ³ /100g)
1	198	225	300
2	447	150	250
3	508	200	300
4	399	150	250
5	562	185	250
6	413	185	250
7	376	200	250
8	553	150	200
9	365	150	185
10	440	100	150
11	307	235	300
12	537	150	200
13	247	200	350
14	330	225	250
15	238	200	350
16	220	200	300
17	456	150	250

As shown from Table 3 and on Fig. 2, the direction of dosing, concentration and temperature of the process have significant effect on the particle size of copper(II) silicate. In fact the primary particles accumulate forming aggregates and agglomerates.

Samples 4 and 11 contain the finest particles. Ninety percent of the volume of sample 4 (precipitated at the 1:1 volume ratio of reagents, at 20°C, from a 5% solution of sodium silicate and a 10% solution of copper(II) sulphate) is taken by particles of diameter smaller than 28.4 µm, 50% of sample 4 volume is taken by particles of diameter smaller than 7.1 µm, and 10% of sample 4 volume is taken by particles of diameter smaller than 2.3 µm. As to sample 11 (precipitated at the 2:1 volume ratio of reagents, at 20°C, from a 5% solution of sodium silicate and a 20% solution of copper(II) sulphate) particles of diameter smaller than 31.6 µm take 90% of its

volume, those of diameters below 9.1 μm take 50% of its volume and those of diameters below 3.0 μm occupy 10% of its volume.

According to the results, the particle size of the samples obtained depends strongly on the type of copper salt used in precipitation, Fig. 2e. In sample 16 obtained from copper(II) nitrate(V) 90% of its volume is occupied by particles of diameters smaller than 39.3 μm . In sample 17 obtained from copper(II) chloride 90% of its volume is taken by particles of diameter smaller than 32.5 μm .

Table 3. Dispersive characteristic of precipitated copper silicates

Sample No.	Diameter (μm)		
	d(0.1)	d(0.5)	d(0.9)
1	3.6	10.9	40.3
2	3.5	16.3	45.4
3	3.5	13.9	51.7
4	2.3	7.1	28.4
5	3.3	13.2	48.3
6	3.3	10.9	41.3
7	3.9	17.3	49.3
8	3.0	9.0	36.5
9	4.1	18.9	53.5
10	3.5	25.7	68.9
11	3.0	9.1	31.6
12	2.5	8.7	36.1
13	4.6	13.8	40.6
14	4.2	14.7	43.6
15	4.7	14.8	47.3
16	3.3	11.7	39.3
17	2.9	11.2	32.5

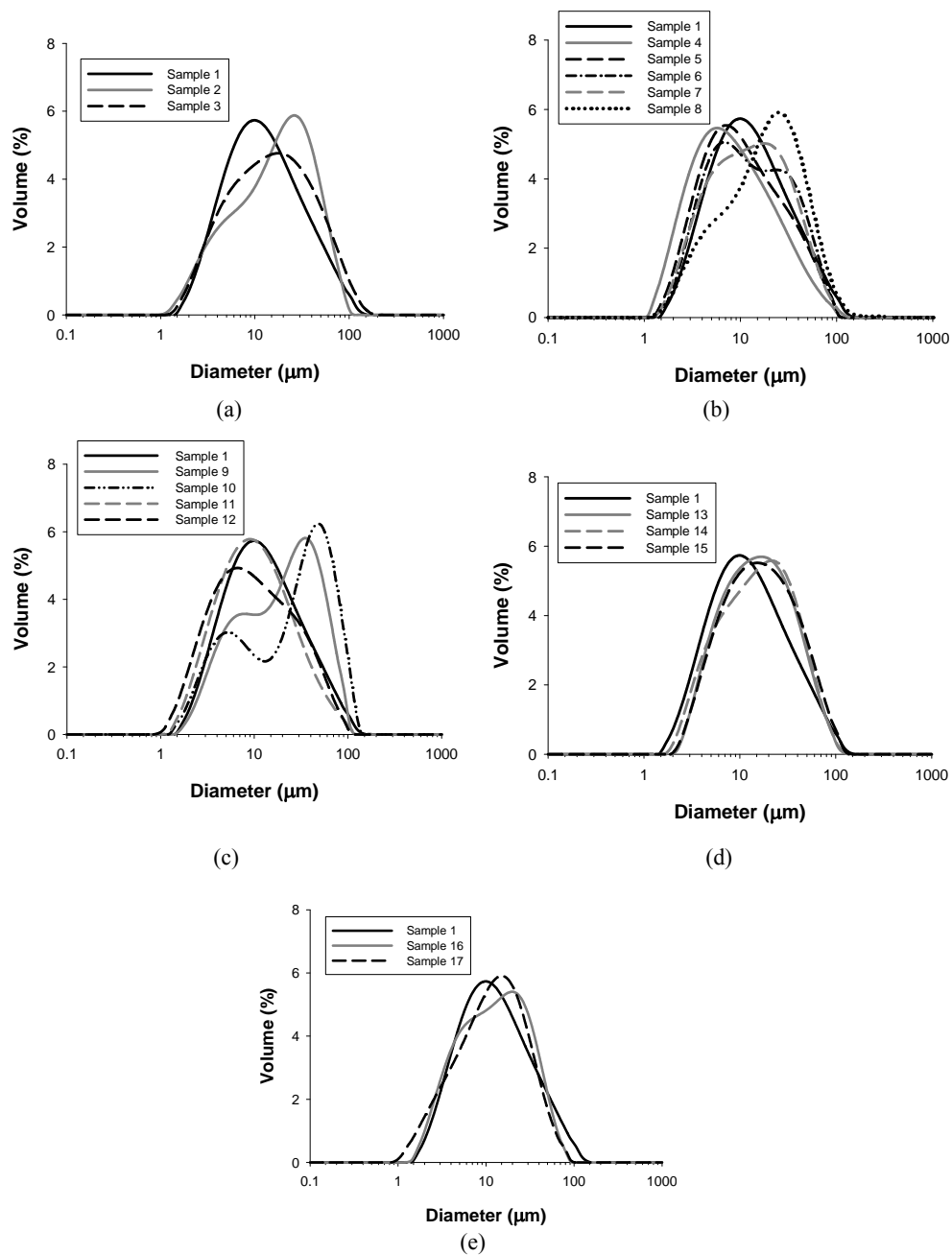


Fig. 2. PSD of copper silicates precipitated (a) at different precipitation direction (b) at different reagents concentration (c) at different reagents volume ratio (d) at different temperatures (e) using different copper salts

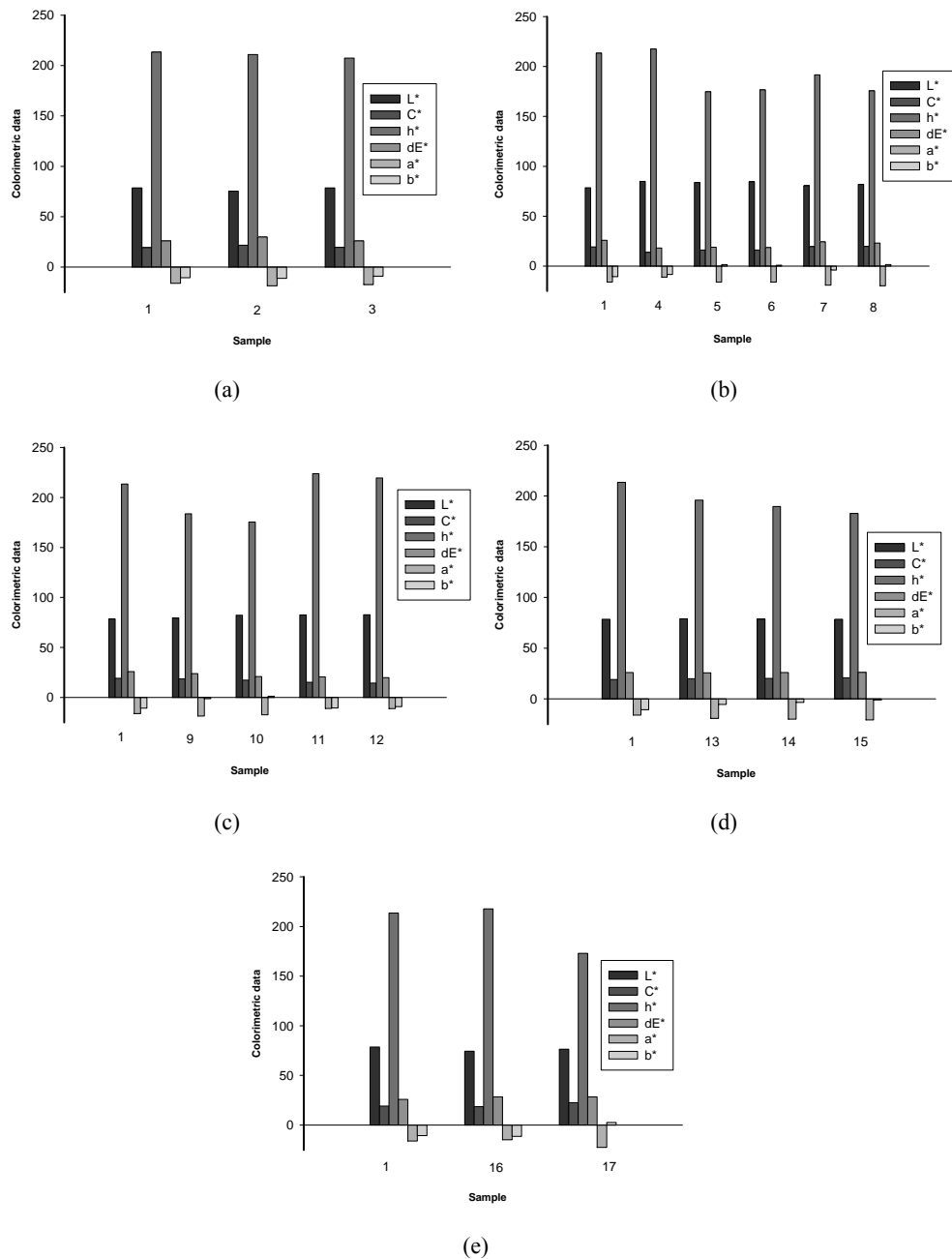


Fig. 3. Colorimetric parameters of copper silicates precipitated (a) at different precipitation direction (b) at different reagents concentration (c) at different reagents volume ratio (d) at different temperatures (e) using different copper salts

Colorimetric analysis in the CIE $L^*a^*b^*$ system provides the information on the pigment colour, Fig. 3. The greatest contribution of blue colour ($-b^*$) was found for samples 1 and 2, their blue contributions were similar; of -10.57 and -11.12, respectively. The contribution of green ($-a^*$) in these samples was also similar of -16.02 and -18.59, respectively.

As follows from Fig. 3e, the type of copper salt used in precipitation of copper silicate also influenced the colour of the pigment. When copper(II) sulphate(VI) (sample 1) or copper(II) nitrate(V) (sample 16) were used, the contributions of blue ($-b^*$) and green ($-a^*$) were comparable and equalled -10.57 and -11.38 (blue) and -16.02 and -14.73 (green). When copper(II) chloride was used (sample 17), no contribution of blue was observed, while the contribution of green ($-a^*$) was -22.40.

Fig.4 presents the SEM photograph of copper(II) silicate precipitated from copper(II) sulphate(VI), sample 1. The material has complex structure of particles showing relatively high tendency towards formation of aggregates and agglomerates. The structure of this type has been earlier described when determining the sizes of particles. The particle diameters in micrometers indicate that the particles in this sample of copper silicate form agglomerate structures.

The wettability curves of the copper silicates studied are presented in Fig. 5. The greatest mass increase in time was found for sample 1, precipitated from copper(II) sulphate(VI). The mass increase in sample 16 – precipitated with the use of copper(II) nitrate(V) - and in sample 17 – precipitated with the use of copper(II) chloride – is much smaller.

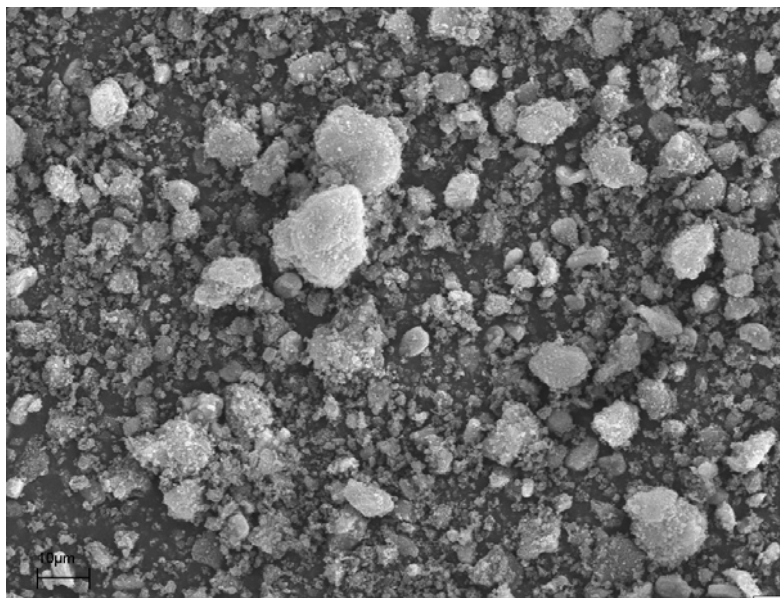


Fig. 4. SEM photograph of copper silicate – sample no. 1

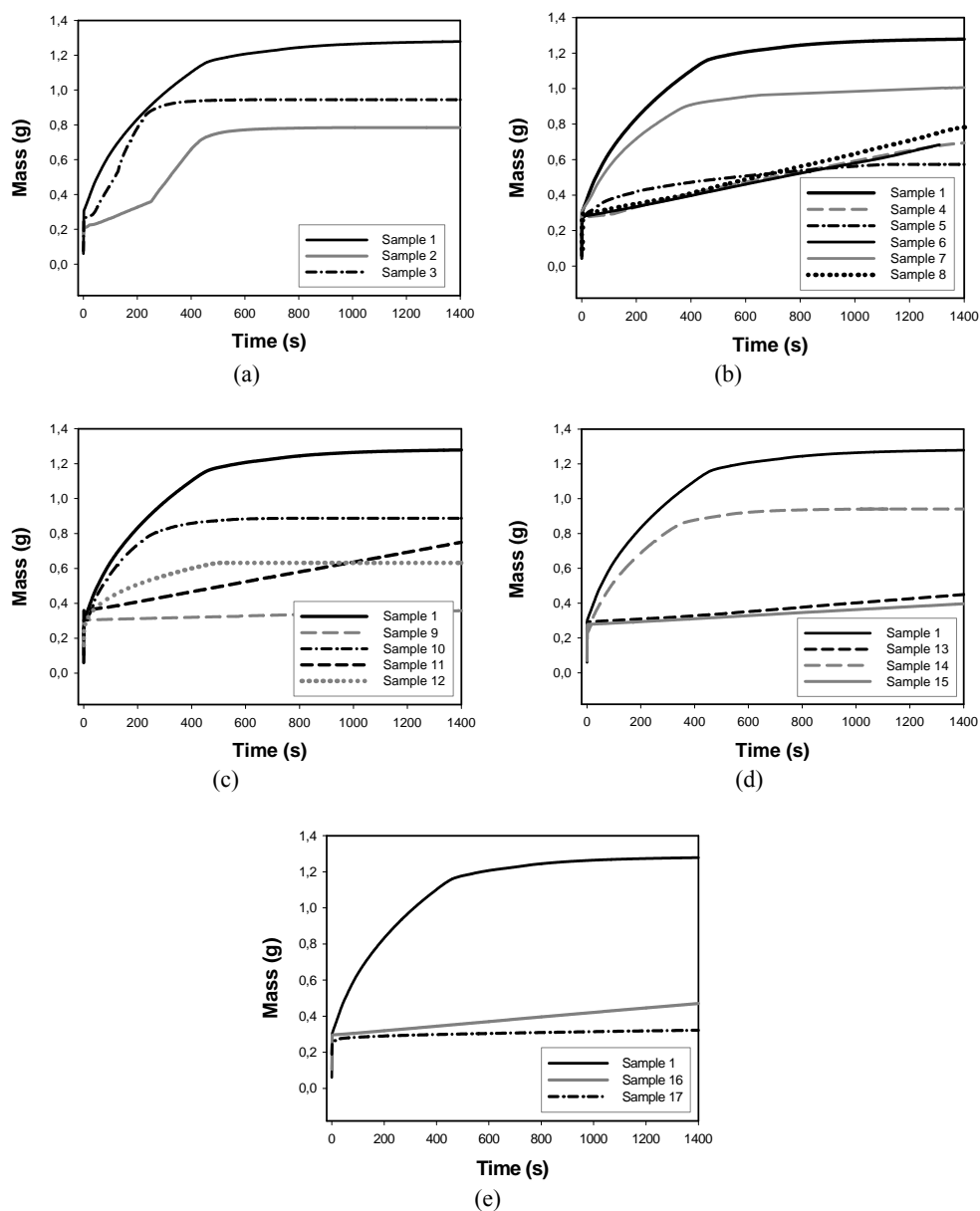


Fig. 5. Wettability of synthetic copper silicates samples precipitated (a) at different precipitation direction (b) at different reagents concentration (c) at different reagents volume ratio (d) at different temperatures (e) using different copper salts

CONCLUSIONS

As follows from the above presented and discussed results, the direction of dosing, concentration and volume ratio of the reagents, temperature of the process and type of the copper salt applied have significant effect on the physico-chemical properties of the final products.

The physico-chemical parameters most beneficial from the point of view of the desired applications were obtained when the copper silicates were precipitated with the use of copper(II) sulphate (VI) (sample 1) and copper(II) nitrate(V) (sample 16). The parameters of these two samples are similar, although sample 1 has lower bulk density.

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REFERENCES

- ANASTASIADIS S., CHRISOPOULOU K., FRICKC B., 2008, *Structure and dynamics in polymer/layered silicate nanocomposites*, Materials Science and Engineering B, 152, 33–39.
- EL-NAHHAL Y.Z., LAGALY G., 2005, *Salt effects on the adsorption of a pesticide on modified bentonites*, Colloid Polym. Sci., 283, 968–974.
- ERFURTH U., 1998, *Farby na bazie żywic silikonowych – mity i rzeczywistość*, Renowacje, 3, 17–23.
- JOHNSTON J., MCFARLANE A., BORRMANN T., MORAES J., 2004, *Nano-structured silicas and silicates – new materials and their applications in paper*, Current Applied Physics, 4, 411–414.
- KLAPISZEWSKA B., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2003, *Highly dispersed green silicate and oxide pigments precipitated from model systems of postgalvanic waste*, Environ. Sci. Technol., 37, 4811–4818.
- KLAPISZEWSKA B., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2005, *Nickel(II) silicates and oxides – highly dispersed green pigments*, Pigment Resin Technol., 34, 139–147.
- KRYSZTAFKIEWICZ A., RAGER B., JESIONOWSKI T., 1997, *Otrzymywanie barwnych krzemianów – pigmentów o dużym stopniu rozdrobnienia*, Fizykochemiczne Problemy Mineralurgii, 31, 165–173.
- KRYSZTAFKIEWICZ A., MICHALSKA I., JESIONOWSKI T., BOGACKI M., 1999, *Highly dispersed synthetic zinc silicates as future pigments for ecological silicate paints*, Physicochemical Problems of Mineral Processing, 33, 83–92.
- KRYSZTAFKIEWICZ A., MICHALSKA I., JESIONOWSKI T., WIECZOREK W., 1998, *Odpady chromowe i żelazowe – potencjalne źródło do otrzymywania pigmentów*, Fizykochemiczne Problemy Mineralurgii, 32, 77–85.
- KRYSZTAFKIEWICZ A., KLAPISZEWSKA B., JESIONOWSKI T., 2008, *Precipitated green pigments: Products of chromate postgalvanic waste utilization*, Environ. Sci. Technol., 42, 7482–7488.

- LEE S., YOUN J., 2008, *Properties of polypropylene/layered-silicate nanocomposites and melt-spun fibers*, Journal of Applied Polymer Science, 109, 1221–1231.
- ROTHER B., ELAS A., MICHAELI W., 2009, *In situ polymerisation of polyamide-6 nanocompounds from caprolactam and layered silicate*, Macromol. Mater. Eng., 294, 54–58.
- VARGHESE S., KARGER-KOCSIS J., GATOS K.G., 2003, *Melt compounded epoxidized natural rubber/layered silicate nanocomposites: Structure-properties relationships*, Polymer, 44, 3977–3983.
- WANG Z., WANG B., QI N., ZHANG H., ZHANG L., 2005, *Influence of fillers on free volume and gas barrier properties in styrene-butadiene rubber studied by positrons*, Polymer, 46, 719–724.
- WERNER J., *Podstawy technologii malarstwa i grafiki*, 1985, PWN, Warszawa
- WIECZOREK M., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2003, *Comparative characteristics of local and foreign bentonites*, Macromolecular Symposium, 194, 345–350.
- XUENING F., TIANYONG Z., CHUNLONG Z., 2000, *Modification study involving a naphthol as red pigment*, Dyes and Pigments, 44, 75–80.
- YUAN J., ZHOU S., GU G., 2005, *Encapsulation of organic pigment particles with silica via sol-gel process*, Journal of Sol-Gel Science and Technology, 36, 265–274.

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Przeprowadzone badania miały na celu otrzymanie niebieskiego nieorganicznego pigmentu krzemianu miedzi(II). Badano wpływ sposobu dozowania, stężenia procentowego, stosunku objętości reagentów, temperatury procesu oraz rodzaju użytej soli miedzi na fizykochemiczne właściwości otrzymywanych produktów końcowych. Otrzymany krzemian miedzi charakteryzował się zadawalającymi parametrami, takimi jak: gęstość 198/dm³, pojemność absorbowanej wody 225 cm³/100g, pojemność absorbowanego oleju parafinowego 300cm³/100g. Średnice wytrąconych cząstek krzemianów zmieniały się od 0,55 do 120,2 μm, z dominacją dużych cząstek tworzących wtórne agregaty.

słowa kluczowe: krzemian miedzi, precypitacja, skład ziarnowy, zwilżalność, dane alometryczne