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EMULSION SYSTEMS USED TO OBTAIN SYNTHETIC SILICATES BY HIGHLY DISPERSED PIGMENTS

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The studies pertained to production of highly dispersed green pigments, precipitated in the form of chromium(III) and nickel(II) silicates. The experiments were conducted at four various temperatures (20, 40, 60 or 80°C), using distinct emulsion systems and precipitating agents, so that appropriately selected parameters of the process would permit to obtain pigments of optimum utility properties.

The obtained silicates were subjected to studies on principal physicochemical properties, such as capacity to absorb water, dibutyl phthalate, paraffin oil and bulk density.

The pigments were characterised also using modern investigative techniques: SEM to study morphology and DLS (dynamic light scattering) technique to examine particle size and tendency to form agglomerates.

Key words: chromium(III) and nickel(II) silicates, DLS and SEM techniques

INTRODUCTION

Coloured chromium(III) or nickel(II) silicates represent highly dispersed pigments and fillers in dispersion aqueous and solvent paints (Klapiszewska 2003).

Inorganic pigments form valuable intermediate products used in several branches of industry, mainly in production of paints and varnishes. As compared to the share of organic pigments, their significance in the trade market grows continuously.

This is so due to, first of all, the excellent dispersion, high coating power, low bulk density, well developed outer surface of the particles, resistance to action of light, low adsorption of water and high permeability for water vapour manifested by inorganic pigments.

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Synthetic inorganic pigments obtained in processes of chemical synthesis by precipitation of sediments manifest excellent utilitarian properties, are chemically more neutral, insoluble, resistant to elevated temperatures and extreme pH of the environment (Indekin 1998, Werner 1985).

Among silicate inorganic pigments chromium(III) silicate, iron(III) silicate and nickel(II) silicate can be distinguished. They belong to pigments applicable mainly in production of silicate paints (Krysztafkiewicz 1987, 1988).

EXPERIMENTAL

The principal aim of studies on silicate production involved definition of parameters of the reaction of precipitating the product, which would warrant optimum properties of the latter.

The precipitation process was conducted in a reactor of 500 cm³ capacity, contained in a thermostate, which permitted to control temperature in a continuous manner and to change it when required. The solution, appropriately prepared and later introduced to a round bottom flask, was warmed up to a strictly defined temperature, amounting to: 20, 40, 60 or 80°C. The reactor content was intensely mixed using an overhead stirrer of the IKA WERKE EUROSTAR Digital type (Germany), fixed to a stand and revolving at the rate of 2000 rpm. In parallel, in the course of mixing the precipitating agent was dosed to the reactor using a peristaltic pump of PP1B-05 ZALIMP type (Poland), working at the constant rate of 4 cm³/min.

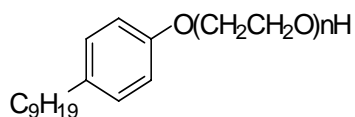
When dosing of the substrate to the reactor-contained solution was completed, the stirrer was switched off and the sample underwent stabilisation at the temperature of 80°C. In the next stage, cyclohexane was distilled off and the sample was filtered under vacuum. The sediment was additionally washed with water in order to rinse off the excess of surfactant. The obtained in this way washed sediment was dried in a stationary drier at the temperature of 105°C. Subsequently, the dried final product was subjected to grinding in an electric mill (02 type, Fritsch Pulverisette, Germany) for a period of 20 minutes, in order to secure appropriate mellowness of the product, and passed through a 0.25 mm sieve in order to appropriately equalise the product particles.

At the first stage, chromium and nickel silicates were precipitated from the solutions:

- a) from emulsion (cyclohexane, sodium metasilicate solution, emulsifier) and solution of a chromium(III) or nickel(II) salt;
- b) from emulsion (cyclohexane, solution of chromium(III) or nickel(II) salt, emulsifier) and solution of sodium metasilicate;
- c) from emulsion 1 (cyclohexane, solution of chromium(III) or nickel(II) salt, emulsifier) and emulsion 2 (cyclohexane, solution of sodium metasilicate, emulsifier).

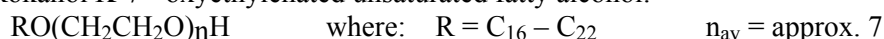
The following agents served as emulsifiers:

Rokafenol N-6 – nonylphenylpolioxyethyleneglycol ether of the following formula:



$n_{av} = \text{approx. } 6$

Rokanol K-7 - oxyethylenated unsaturated fatty alcohol:



At the final stage the obtained products were subjected to physicochemical tests. Among other, bulk density, capacities to absorb water, dibutyl phthalate, paraffin oil and particle size distribution (by DLS technique) were estimated. Surface morphology of the obtained silicates was also evaluated using for the purpose scanning electron microscopy.

RESULTS AND DISCUSSION

The obtained results permitted to conclude that pigments of a good dispersion were obtained by dosing to 5% chromium(III) sulphate solution of emulsion consisting of: 110 cm³ cyclohexane, 100 cm³ 5% solution of sodium metasilicate, emulsifier (Table 1) as well as from the system of two emulsions, in which 110 cm³ cyclohexane, 130 cm³ 5% solution of sodium metasilicate, emulsifier was dosed to emulsion composed of 110 cm³ cyclohexane, 100 cm³ 5% solution of nickel(II) chloride, emulsifier (Table 2). In both cases the sample reached the lowest values of bulk density and the highest capacity to absorb paraffin oil (at the temperature of 80°C and using Rokafenol N-6 as emulsifier).

Table 1. Principal physicochemical properties of chromium(III) silicates obtained by precipitation using sodium metasilicate solution and emulsion composed of cyclohexane, chromium(III) sulphate solution and emulsifier: 1.5 g Rokafenol N-6

Sample No.	Temperature [°C]	Bulk density [g/dm ³]	Capacity to absorb water [cm ³ /100g]	Capacity to absorb dibutyl phthalate [cm ³ /100g]	Capacity to absorb paraffin oil [cm ³ /100g]
1D	20	115	250	400	450
2D	40	134	250	300	450
3D	60	132	300	350	500
4D	80	134	200	350	600

Table 2. Principal physicochemical properties of nickel(II) silicates obtained by precipitation using two emulsion systems consisting of: Emulsion 1: cyclohexane, solution of nickel(II) chloride and emulsifier: 2.2 g Rokafenol N-6 Emulsion 2: cyclohexane, solution of sodium metasilicate and emulsifier:

2.2 g Rokafenol N-6

Sample No.	Temperature [°C]	Bulk density [g/dm ³]	Capacity to absorb water [cm ³ /100g]	Capacity to absorb dibutyl phthalate [cm ³ /100g]	Capacity to absorb paraffin oil [cm ³ /100g]
1L	20	195	100	300	350
2L	40	235	150	350	350
3L	60	217	200	400	500
4L	80	178	200	300	550

Silicates precipitated from the other systems exhibited slightly worse parameters and, thus, failed to exhaust criteria of their practical and technological usefulness (Table 3).

Table 3. Principal physicochemical properties of chromium(III) silicates obtained during precipitation using sodium metasilicate solution and emulsion consisting of cyclohexane, chromium(III) sulphate solution and emulsifier: 3.5 g Rokanol K-7

Sample No.	Temperature [°C]	Bulk density [g/dm ³]	Capacity to absorb water [cm ³ /100g]	Capacity to absorb dibutyl phthalate [cm ³ /100g]	Capacity to absorb paraffin oil [cm ³ /100g]
1C	20	274	200	300	400
2C	40	278	150	400	450
3C	60	264	100	400	500
4C	80	218	150	350	500

In the particle size distribution of chromium(III) silicate, sample 2D (Fig. 1) (precipitation temperature: 40°C), an intense band could be notified in the range of 359 – 495 nm, reflecting presence of primary particles and agglomerates (maximum intensity of 100 corresponded to the particles of 422.2 nm in diameter). In the size distribution a band of a very low density could also be observed representing secondary agglomerates in the range of 1783 – 2511 nm (maximum intensity of 8 corresponded to agglomerates of 2189.6 nm in diameter).

In sample 4D (Fig. 2), an accumulation of primary agglomerates (the so called aggregates) was present in the range of 507 to 616 nm (maximum intensity of 100 corresponded to aggregates of 559.8 nm in diameter). In turn, primary particles were represented by the band span 192 to 245 nm (maximum intensity of 57 corresponded to particles of 222.5 nm in diameter). Mean particle diameter in the silicate amounted to 428 nm, and the polydispersity of 0.224 indicated low homogeneity of the sample.

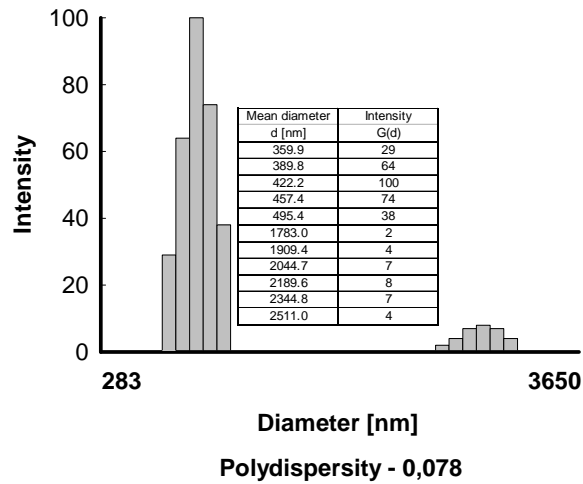


Fig. 1. Particle size distribution in chromium(III) silicate (sample 2D)

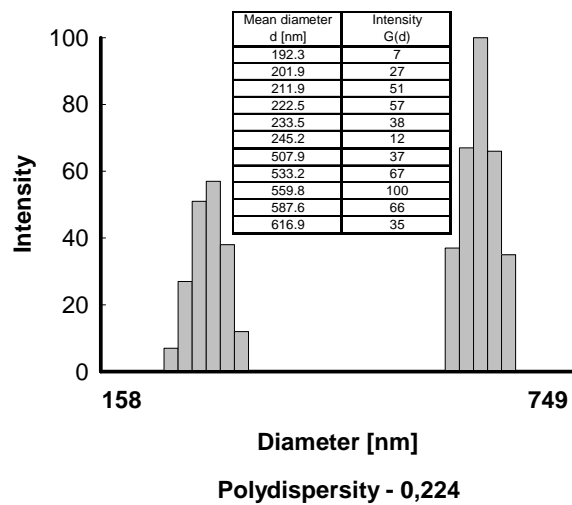


Fig. 2. Particle size distribution for chromium(III) silicate (sample 4D)

In the particle size distribution of nickel(II) silicate, sample 2L (Fig. 3a) an accumulation of primary agglomerates was noted in the range of 190 to 254 nm (maximum intensity of 93 corresponded to agglomerates of 214.3 nm in diameter) and a band of secondary agglomerates in the range of 608 to 812 nm (maximum intensity of 100 corresponded to agglomerates of 682.7 nm in diameter). This was confirmed by the excellent SEM microphotograph (Fig. 3b) of the nickel(II) silicate sample.

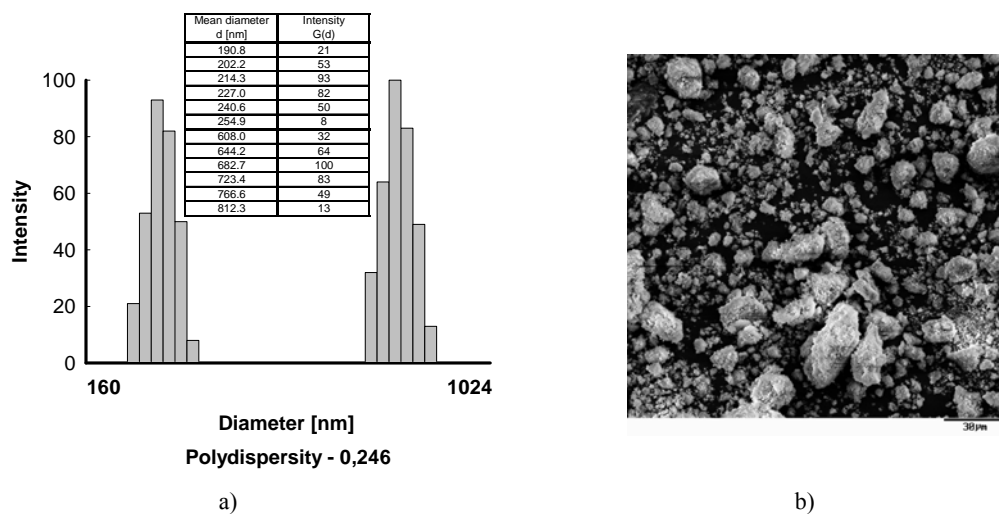


Fig. 3. Particle size distribution a) and SEM microphotograph b) of nickel(II) silicate (sample 2L)

Sample 4L demonstrated presence of two bands of different intensities (Fig. 4). The band of higher intensity could be ascribed to aggregates or primary agglomerates and it spanned the range of 288 – 368 nm (maximum intensity of 100 corresponded to primary agglomerates of 326.1 nm in diameter). Secondary agglomerates, on the other hand, formed a band of lower intensity in the range of 982 – 1334 nm (maximum intensity of 28 corresponded to secondary agglomerates of 1110.5 nm in diameter). Mean diameter of the particles amounted to 533 nm and proved to be very advantageous. The sample was also more uniform, as documented by polydispersity value of 0.156.

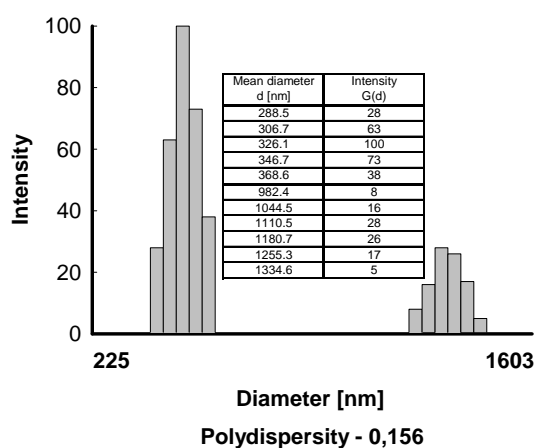


Fig. 4. Particle size distribution in nickel(II) silicate (sample 4L)

In sample 2C (chromium silicate obtained in the presence of another emulsifier, Rokanol K-7) secondary agglomerates formed a band spanning the range of 583 – 713 nm (maximum intensity of 73 corresponded to agglomerates of 632.4 nm in diameter). On the other hand, primary agglomerates were represented by a band in the range of 260 – 305 nm (maximum intensity of 100 corresponded to aggregates of 282.2 nm in diameter) Fig. 5.

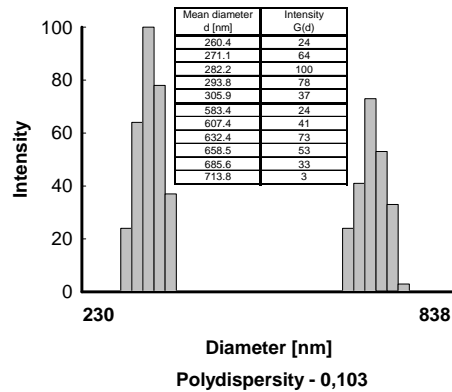
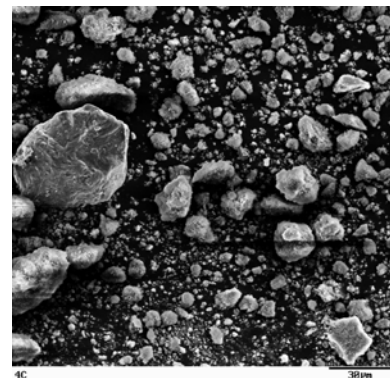
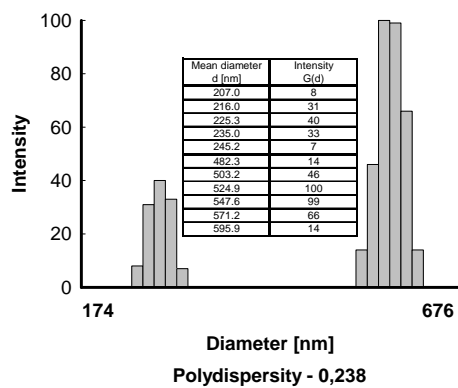


Fig. 5. Particle size distribution in chromium(III) silicate (sample 2C)

Similarly to the sample 2C, in the sample 4C particle size distribution (Fig. 6a) of precipitated chromium(III) silicate demonstrated two bands, of which one should be ascribed to primary agglomerates in the range of 207 – 245 nm (maximum intensity of 40 corresponded to agglomerates of 225.3 nm in diameter) while the other represented secondary agglomerates in the range of 482 – 595 nm (maximum intensity of 100 corresponded to agglomerates of 524.9 nm in diameter). Presence of such particles was confirmed by respective SEM microphotograph (Fig.6b).



a)

b)

Fig. 6. Particle size distribution a) and SEM microphotograph b) of chromium(III) silicate (sample 4C)

4. CONCLUSIONS

Highly dispersed green pigment in form of chromium(III) silicate, exhibiting the lowest value of bulk density (1.34 g/dm^3) and the highest capacity to absorb paraffin oil ($600 \text{ cm}^3/100\text{g}$) was obtained at the temperature of 80°C (sample 4D) in the precipitation process in which emulsion contained: cyclohexane, solution of chromium(III) salt and Rokafenol N-6. Sodium metasilicate served as a precipitating agent. Mean particle diameter in the silicate amounted to 428 nm, and polydispersity value was 0.224, pointing to low homogeneity of the sample.

Nickel(II) silicate of the best utilitarian properties (sample 4L) was precipitated in the process of dosing emulsion 1 (cyclohexane, solution of nickel(II) salt, Rokafenol N-6) to emulsion 2 (cyclohexane, sodium metasilicate solution, Rokafenol N-6). The results have confirmed studies on particle size distribution and SEM patterns. Mean particle diameter of the pigment amounted to 533 nm and was most advantageous. In this case also uniform character of the sample was satisfactory as proved by the low value of polydispersity (0.156).

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Klapiszewska B., Krysztafkiewicz A., Jesionowski T., *Systemy emulsyjne używane do otrzymywania krzemianów syntetycznych – wysoko zdyspergowane pigmenty*, Physicochemical Problems of Mineral Processing, 39 (2005) 141-148 (w jęz. ang).

Przeprowadzone badania dotyczyły otrzymywania wysoko zdyspergowanych zielonych pigmentów strąconych w postaci krzemianów chromu(III) oraz niklu(II). Próby prowadzone były w czterech różnych temperaturach ($20, 40, 60$ i 80°C), przy użyciu odmiennych układów emulsyjnych i czynników strącających, tak aby odpowiednio dobrane parametry prowadzenia procesu pozwoliły pozyskać pigmenty o optymalnych właściwościach użytkowych. Otrzymane krzemiany i tlenki poddano badaniom podstawowych właściwości fizykochemicznych, takich jak chłonność: wody, ftalanu dibutyłu oraz oleju parafinowego, a także gęstość nasypowa. Pigmenty te analizowano także poprzez wykorzystanie nowoczesnych metod badawczych – techniki SEM do badania morfologii oraz techniki DLS (dynamicznego rozpraszania światła) do badania struktury wielkości cząstek i ich tendencji do tworzenia aglomeratów.