

Malayaite with cobalt prepared using mechanical activation

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Abstract

In this work sphene pigments of malayaite type doped by cobalt were prepared and the mechanical activation was used as a pre-treatment of the starting materials. CaCO_3 , SnO_2 , SiO_2 and mixed Co_3O_4 were used for preparation of malayaite corresponding chemical composition $\text{CaSn}(\text{Co})\text{SiO}_{5-\delta}$, with the stoichiometric ratio of $\text{Co}/\text{Sn} = 0; 0.015; 0.058$ and 0.093 . Planetary mill Pulverisette 5 (Fritsch, Germany) was used for mechanical activation. The mechanical treated mixtures were calcinated at various temperatures (1150-1400 °C/4 hours with step 50°C) with aim to assess the effect of mechanical activation as first stage of pigment preparation with respect to their colour and optical properties. The colour properties, the particle size and the phase composition of the malayaite pigments have been investigated. Products of calcination were subjected to milling to the required particle size in order to improve optical and application properties.

Introduction

Malayaite, in the old way Tin Sphene, is nesosilicate mineral with monoclinic symmetry. Perfect chemical formulation of Malayaite can be described by the formula CaSnSiO_5 , respectively $\text{CaSnO}(\text{SiO}_4)$. Nesosilicates belong to the group of silicates and are formed by separate SiO_4 tetrahedrons, whose connection is effected by means of cations of small dimensions. High specific density, high refractive index and high hardness are characteristic properties of nesosilicates. Minerals are stable, chemically and mechanically resistant¹.

Sphene compounds can be prepared by various methods, e.g. sol-gel², precipitation³, the combustion⁴, spray pyrolysis⁵, freeze drying⁶, hydrothermal synthesis⁷ and mechanical activation⁸. Mechanical activation could be one of the possible methods that would help to improve the reactivity of the starting materials. The mechanical activation is associated with the use of external mechanical energy, usually by means of a very intensive grinding.

Mechanical treatment is possible included into as one of the first experiences of humanity, when prehistoric people found that a spark can be created by blow of suitable stones for themselves and so it can be used to start a fire. From our point of view, some chemical reactions can be triggered or accelerated already by using mechanical energy (friction and impact) which was transferred to a solid through the mill.

Normally, grinding is used to create the maximum active surface of a powder at the minimum energy consumption, whereas the aim of the activation is to accumulate energy in the form of defects or other structural modifications of a solid, which makes it possible to decrease the activation energy or improve steric conditions for its subsequent chemical transformations⁹.

Definition of mechanical activation is not precisely determined. V.V. Boldyrev proposed two distinct cases of the chemical activation. In the first case, the duration of the mechanical treatment involving the formation of a stress field and its relaxation is longer than the chemical reaction time and these processes are commonly referred to as mechanochemical. In the second case, the duration of the chemical treatment involving the formation of a stress field is shorter than the chemical reaction time or these processes take place separately. This case is associated with the chemical activation⁹.

According to P. Yu. Butyagin a classification of all mechanochemically activated solid-state reactions are divided into two groups, depending on the rate-limiting step of the overall process: either the development of contacts (where the reaction proceeds in the near-surface regions) or the mass-transfer into the bulk¹⁰.

Mechanochemistry is generally defined as the branch of chemistry dealing with chemical and physico-chemical changes of substances of latent conditions that were caused by the application of mechanical energy. Mechanical impact plays an important role especially in chemical reactions, where one of the reactants is in the solid state. The most effective the reactions are taking place during milling and friction¹⁰.

Due to the effect of mechanical energy are changed structures and these changes are most often associated with the formation of a high concentration of defects in the crystal lattice. Physical, physico-chemical and chemical properties of mechanically processed substances often are changing¹¹.

In this work sphene pigments of malayaite type doped by cobalt were prepared. Mechanical activation consisting in very intense dry milling of precursors and then their firing at the desired temperature was used for the synthesis of these compounds. Structure thus prepared pigments, their colour and optical properties were investigated.

Experimental Part

The reactants used for the preparation of malayaite corresponding chemical composition $\text{CaSn}(\text{Co})\text{SiO}_{5-\delta}$ (the symbol $-\delta$ represents charge oxygen non-stoichiometry) were commercially available powders: precipitated CaCO_3 (Merck Group KGaA, Germany), SnO_2 (Alfa Aesar GmgH&KG, Germany), natural micronized SiO_2 (Sklopísek Střeleč, a.s. CZ) and mixed Co_3O_4 (The Shepherd Colour Company, USA). The purity of the starting materials ranged between 94-99%. The quantity of starting materials were weighed so as to correspond to the stoichiometric ratio of $\text{Co}/\text{Sn} = 0; 0.015; 0.058$ and 0.093 . Subsequently, all the raw materials were thoroughly homogenized in a agate mortar.

Planetary mill Pulverisette 5 (Fritsch, Germany) was used for mechanical activation. Actual process was conducted in the agate containers using agate balls of 10 mm diameter. Initiatory mixture was dosed into the grinding container in such an amount as to maintain one of the fundamental conditions of mechanical activation and that is many times greater weight of the grinding balls with compared of the weight initiatory mixture¹². In this case the mass ratio of balls to the initial mixture 10/1 was used. The mechanical activation was performed at 200 rpm for 5 hours. After that, the mechanical treated mixtures after separation of agate balls were transferred into corundum crucibles and subjected to calcination at various temperatures (1150-1400 °C/4 hours with step 50°C) with aim to assess the effect of mechanical activation as first stage of pigment preparation with respect to their colour and optical properties. After firing the calcination products were hand grinded in an agate mortar and prepared for further research.

The colour properties of the malayaite pigments have been studied as after the application of two bonding systems, namely into the transparent leadless glaze P 07410 in the weight ratio 10% (Glazura Roudnice, a.s., Czech Republic); and into the organic acrylate matrix (Parketol, Akzo Nobel Coatings CZ, a.s., Opava, Czech Republic) in the mass tone. The colour properties were measured in the visible region of the light (400-700 nm) using the spectrophotometer ColourQuest XE (HunterLab, USA). The colour was evaluated in the system CIE $L^*a^*b^*$ (1976), where the value L^* represents lightness or darkness of the pigment. The value a^* (red-green axis) and b^* (yellow-blue axis) indicate colour hue. Other colour characteristics have been calculated for better defining of the colour: the chroma C , the hue angle H° and for observing of colour changes the total colour difference ΔE^*_{CIE} . The total colour difference can be found out from formula: $\Delta E^*_{\text{CIE}} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* - brightness difference between the standard and given sample, Δa^* , Δb^* - difference of the colour coordinates a^* and b^* between the standard and the given sample. The standard sample (without the presence of chromophore, i.e. $x=0$) and the samples with the ratio $\text{Co}/\text{Sn} = 0.015; 0.058$ and 0.093) have been compared. The chroma represents saturation of the colour, ranges from 0 (gray) to 100 (pure colour) and it is possible to calculate using the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The hue angle H° is expressed in degrees and moves in the range within $0^\circ - 360^\circ$. The value of the hue angle can be found out from the formula: $H^\circ = \arctg(b^*/a^*)$. The interval H° for this studied system of malayaite pigments with cobalt is following: $195^\circ - 285^\circ$ blue hue, $285^\circ - 350^\circ$ violet hue¹³.

The particle size of prepared compounds was measured by the device Mastersizer 2000/MU (Malvern Instr., GB), which enables evaluation based on Fraunhofer bending or based on the Mie theory. In this case the evaluation has been examined based on Fraunhofer bending.

Products of calcination were subjected to milling to the required particle size in order to improve optical and application properties. Fine grinding was realized again in the planetary mill Pulverisette 5 (Fritsch, Germany). Because for mechanical activation the agate material was used, the same material (agate) was chosen for grinding due to minimize contamination of pigments. Grinding process was conducted in the agate containers and with the help of 10 the agate balls of 10 mm diameter. In this case the milling operation was carried out in environment of ethanol not only to protect the pigment particles before high shear and friction, but also for better subsequent manipulation with fine powder. The speed of rotation was 200 rpm and the grinding time 2 hours. Finally the pigment suspension was dried in a dryer and colour and application properties of milled powders were verified again via Colourquest XE and Mastersizer 2000/MU.

The phase composition was observed too. The tested powder samples were studied by the X-ray diffraction analysis using the device D8 Advance (Bruker, GB), working with radiation $\text{CuK}\alpha$ and the scintillation detector (the range 2Θ from 10° to 80°).

The results and discussion

Compounds of $\text{CaSn}(\text{Co})\text{SiO}_{5.6}$ type with the ratio of $\text{Cu}/\text{Sn} = 0$; 0.015; 0.058 and 0.093 via mechanical activation and solid state reaction at the various temperatures of calcination were prepared. Calcination products were pulverized by hand in an agate mortar and applied to two bonding environment. Figure 1 shows the effect of the doped cobalt element on the colour properties of malayaites depending on firing temperature. Figure 1a demonstrates these properties after application into ceramic leadless glaze P 07410 where the pigment was added in 10 wt. %. Gradual shift to bluer shades is visible on the picture, depending on both the increasing cobalt content as well as on increasing firing temperature. From the figure it is also evident that the colour properties of pigments for adequate composition $\text{Co}/\text{Sn} = 0.058$ and $\text{Co}/\text{Sn} = 0.093$ particular for the higher firing temperatures are very similar. Therefore, it can be noted that the amount of cobalt corresponding to the ratio $\text{Co}/\text{Sn} = 0.058$ is sufficient for colouring ceramic glazes. Further increases of the cobalt would increase the cost of pigment production due to high prices of the cobalt raw material. The colour appearance of ceramic tiles was moved from white ($\text{Co}/\text{Sn} = 0$) through a gray-blue and blue-gray ($\text{Co}/\text{Sn} = 0.015$) up to blue-violet ($\text{Co}/\text{Sn} = 0.058$ and 0.093). But the tiles showed a lower covering power, which could be caused by unsuitable particle size or insufficient layout of the pigment particles in the glaze.

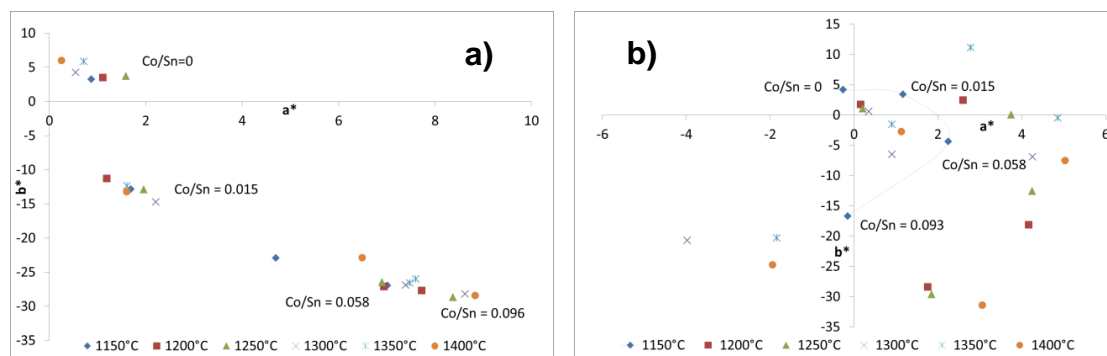


Figure 1. The effects of doped chromophore and the temperatures of calcination on the colour properties of the pigment $\text{CaSn}(\text{Co})\text{SiO}_{5.6}$ prepared with using mechanical activation and applied into: a) leadless glaze P 07410 (10 wt.%); b) organic matrix (mass tone)

Figure 1b is devoted to colour properties of the mechanically activated pigments calcined at different temperatures and applied into the organic binder. In this case, the trend obtained for glaze was different. Conversely, it seems from the first look on the colour coordinates plotted in graph, that the colour characteristics of individual samples are random. But during more careful study of this graphic presentation, it is evident that the colour properties after application show certain dependence. This trend is marked (firing temperature 1150 °C) for easier understanding. The colour coordinates are moved from the first quadrant of the colour cross ($\text{Co}/\text{Sn} = 0$) across IV. to III. quadrant with increasing of cobalt content. The U-shaped character is retained for other temperatures. However, it is necessary noted, that the paints with the dispersed pigments exhibited some transparency, i.e. lower hiding power, which was probably caused by an inappropriate particle size of the pigments. Colour shift is thus realized out from white ($\text{Cu}/\text{Sn} = 0$), through light blue ($\text{Co}/\text{Sn} = 0.015$) and blue ($\text{Co}/\text{Sn} = 0.058$) to dark blue ($\text{Co}/\text{Sn} = 0.093$).

The colour characteristics of the composition $\text{Co}/\text{Sn} = 0.015$ and 0.093 for both monitored applications are summarized in Table 1. The hue angle is shifted from orange region ($70\text{--}35^\circ$) with the values of $H^\circ = 70.91^\circ$ and 43.06° over red ($35\text{--}350^\circ$) $H^\circ = 0.61^\circ$ to blue (285 to 195°) for the ratio of cations of $\text{Co}/\text{Sn} = 0.015$ and application into organic matrix. Appropriate values of H° detected for temperatures $1300\text{--}1400^\circ\text{C}$ were in the range from 277.96° to 184.48° . According to this shift the calcination temperatures $1150\text{--}1250^\circ\text{C}$ probably are not sufficient for the suitable reaction of initial mixture even after mechanical activation treatment. This assumption is not supported only by H° values, but also by the saturation values which were very small and the size of brightness indicating that the compounds are after application into organic binder very light. Better results were determined for a higher ratio of cations $\text{Co}/\text{Sn} = 0.093$. For acrylic dispersion chroma ranged from 16.72 to 31.54. The values of L^* in particular from the temperature 1200°C gradually decreased towards to darker hues and according to the hue, this application can possible to place into the region of the blue ($195\text{--}285^\circ$). Colour characteristics of mentioned ratios applied into glaze are shown in Table 1 also. The hue angle values of both quantities of cobalt were very similar. But the influence of the quantity of cobalt is evident. The H° values for the ratio $\text{Co}/\text{Sn} = 0.015$ were moved in the blue area and the hue angle with increasing amounts

of cobalt up to Co/Sn = 0.093 shifted more to the region blue-violet. The chroma ranged from 12.34 to 14.88 for ratio Co/Sn = 0.015, but increasing content Co up to a ratio 0.093 is doubly changed.

Table I

The values of L*, C and H° for the pigment CaSn(Co)SiO₅₋₆ applied into leadless glaze P 07410 (10 wt. %) and organic matrix (mass tome)

Temperature calcination [°C]	The ratio of cations Co/Sn = 0.015					
	Ceramic glaze			Organic matrix		
	L*	C	H° [°]	L*	C	H° [°]
1150	77.72	12.94	277.50	86.38	3.58	70.91
1200	76.48	11.33	276.03	86.92	3.56	43.06
1250	74.24	13.05	278.64	88.70	3.75	0.61
1300	71.19	14.88	278.54	85.74	6.57	277.96
1350	71.34	12.48	277.41	78.32	20.40	185.17
1400	71.14	13.29	276.92	70.87	24.83	184.48

Temperature calcination [°C]	The ratio of cations Co/Sn = 0.093					
	Ceramic glaze			Organic matrix		
	L*	C	H° [°]	L*	C	H° [°]
1150	56.87	27.84	284.58	71.70	16.72	180.51
1200	51.47	28.76	285.57	51.59	28.42	273.55
1250	49.65	29.87	286.28	52.50	29.68	273.57
1300	45.25	29.48	287.00	48.71	21.09	190.88
1350	46.03	27.08	286.30	53.19	11.45	75.89
1400	45.67	29.75	287.27	41.93	31.54	275.57

Values of the mean particle size of mechanical activated pigments after subsequent calcination are shown in Table 2 and it is evident, that d_{50} increased both with increasing firing temperature, but also with the amount of added chromophore. Mean particle size of standard (Co/Sn = 0) by addition of the cobalt on ratio of cations 0.015 sharply changed. But the impact of the amount of cobalt for proportions of cations Co/Sn = 0.058 and 0.093 was slow. It has been found that obtained particle size was not suitable for application to the organic binder, because for this application d_{50} is recommended about around 2 μm . The optimum particle size for ceramic applications is between 5-15 μm and at respecting of this condition, pigments are usable at temperatures until 1250 °C. The pigments with higher values d_{50} were prepared via the other temperatures of calcination (1300-1400°C). These large particles probable could worsen the dispersibility of the pigments into both bonding systems and thereby to affect the resulting colour properties. Therefore, it is necessary to improve the application-optical properties, in particular in that pigments will be grinded to the desired particle size. From point of view of mechanical activation is obvious that due to intensive dry milling of the starting materials there reduction of the particle which is typical for milling operations was not realized, but the formation of larger grains and larger agglomerates after subsequent firing were registered. It is suggesting that the mechanical activation probably could promote and improve production of malayaite compounds doped with cobalt.

Table II

The values of the mean particle size of mechanical treatment CaSn(Co)SiO₅₋₆ pigment before grinding on the required particle size (BG) and after grinding operation (AG)

Co/Sn	Calcination temperature [°C]/ d_{50} [μm]											
	1150		1200		1250		1300		1350		1400	
	BG	AG	BG	AG	BG	AG	BG	AG	BG	AG	BG	AG
0	4.50	1.68	5.35	1.95	5.86	1.89	7.92	2.45	10.19	2.20	13.25	2.50
0.015	5.45	1.86	9.17	2.17	10.95	2.30	14.93	2.74	19.40	2.47	20.04	2.55
0.058	7.05	2.02	11.54	2.74	13.68	2.80	18.25	3.31	24.03	3.12	41.04	3.38
0.093	8.24	2.31	13.92	2.40	13.25	2.32	17.24	2.81	14.05	2.37	29.32	3.05

Determined particle size after grinding (marked AG) is also summarized in Table 2. From table is evident, that plan to gain a particle about size close to 2 μm , i.e. to improve the dispersibility of pigments in an organic binder, was fulfilled. Particles with appropriate sizes for applicability to the organic binder were obtained after 2 hours of wet grinding. Different grinding material can be used to shorten the milling time and even greater

reduction of particle size. Zirconia balls of diameter 1.6 to 1.8 mm could be another alternative for grinding of materials, for example. This possibility was not used, due to a possible increase contamination of the pigment by grinding material.

The applicability of grinded pigments into organic matrix was improved, but at the expense of the covering power of studied pigments. The intensity of the blue colour fundamentally decreased after adjustment by grinding. In terms of evaluation of application to the organic binder, the malayaite pigments are not suitable for this application. Coatings with pigments had little intense colour which were not able to cover a whole substrate and pigments had only a blue turbidity. This property is from the perspective of producer of paints totally inadequate. Colour and optical properties of the ground pigments are shown in Figure 2. The first one (2a) is dedicated to monitoring of the colour properties after the application in organic binder in mass tone and it is apparent that the trend observed for unmilled particles is remained even after grinding.

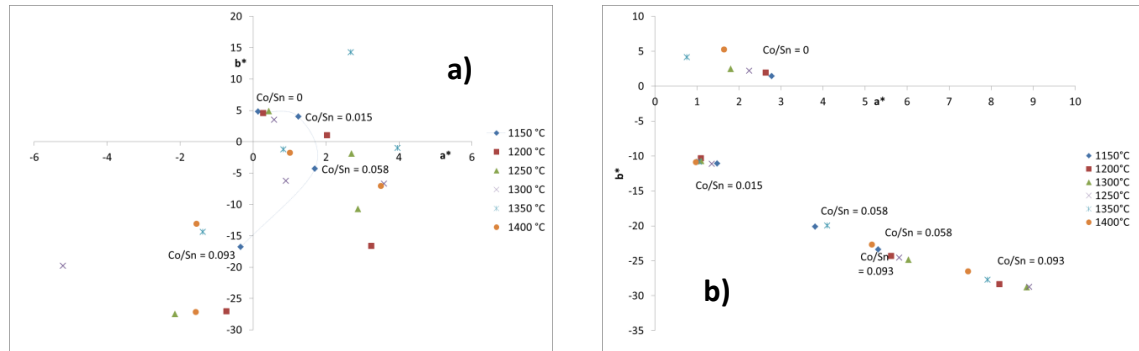


Figure 2. The influence of doped chromophore and the temperatures of calcination on the colour properties of the pigment $\text{CaSn}(\text{Co})\text{SiO}_{5-6}$ after grinding: a) application - organic matrix in mass tone; b) application - leadless glaze P 07410 (10 wt.% of pigment)

Conversely, a radical improvement of dispersibility of pigment particles was achieved for the application of glaze. Reducing of the particle size allowed a better spreading of the pigment particles in the molten glaze and therefore hiding power of pigments was increased. Ceramic tiles showed very interesting blue shades that ranged in pastel colours. Colour properties of the malayaite pigments after grinding are illustrated in Figure 2b. There is a shift toward bluer shades depending on rising the firing temperature and the amount of doped cobalt. In terms of assessing of the cobalt amount, the content of $\text{Co}/\text{Sn} = 0.058$ for coloring of malayaite lattice is sufficient and further increasing of cobalt is unnecessary, because the difference between the color characteristics of the sample $\text{Co}/\text{Sn} 0.058$ and 0.093 is negligible.

Phase composition of the mechanical treated pigments have been investigated too. The results of this analysis are summarized in Table III.

Table II

The phase composition of studied mechanical treatment compounds based on $\text{CaSn}(\text{Co})\text{SiO}_{5-6}$ pigments

Mass ratio Co/Sn	Composition/Temperature [°C]		
	1300	1350	1400
0	Malayaite, Cassiterite, Calcium Tin Oxide, Wollastonite	Malayaite, Calcium Tin Oxide, Cassiterite	Malayaite, Cassiterite
0.015	Malayaite, Cassiterite	Malayaite, Cassiterite	Malayaite
0.058	Malayaite, Cassiterite	Malayaite	Malayaite
0.093	Malayaite, Cassiterite	Malayaite, Cassiterite	Malayaite, Cassiterite

The powder pigments prepared at 1300-1400°C were subjected to the X-ray analysis. Malayaite sample with a mass ratio $\text{Co}/\text{Sn} = 0$, which was prepared at 1300°C contained four compounds: Malayaite- $\text{CaSn}(\text{SiO}_4)\text{O}$, Cassiterite- SnO_2 , Calcium Tin Oxide- CaSnO_3 and Wollastonite- CaSiO_3 . Based on this information it can be stated that the temperature of 1300°C is not sufficient for complete reacting of the starting compounds in case of standard. Phase composition changed after increasing the calcining temperature on 1350°C and three compounds were identified, namely Malayaite, Cassiterite and Calcium Tin Oxide. A further increase of temperature promoted the reaction so that the pigment prepared in 1400°C was diphasic (Malayaite and

Cassiterite). Considerable better results were obtained in the case of pigments doped by Co. It is possible that the doping element cobalt has probably an effect on the better reactivity of the starting materials, if we compare samples without and with Co. All assessed samples prepared at 1300°C were diphasic and contained Malayaite as a major phase and a Cassiterite as a minor phase. The X-ray pattern obtained for the compound with the ratio Co/Sn = 0.058 prepared at 1350°C pointed that only one compound in this case has been identified and corresponded to Malayaite. Single-phase compound was also founded for the same sample prepared at 1400°C. The compound containing Co/Sn = 0.093 was two-component for all studied temperatures and included Malayaite and Cassiterite. In none of the patterns compounds related with cobalt have been recorded, so that it can be assumed that chromophore cobalt was incorporated into the crystal lattice of Malayaite. Better results of mechanochemical treated samples were obtained if these powders were compared with the samples of the same proportions Co/Sn, but which were prepared by only once calcining at 1350°C¹⁴. Improvement of the pigment composition relating to the samples Co/Sn = 0.015 and also Co/Sn = 0.058 was detected, because in case of samples of the same ratio, but without mechanical treatment, two compounds (Malayaite and Cassiterite) for Co/Sn = 0.058 and three compounds for Co/Sn = 0.093 were indentified, namely Malayaite (CaSn(SiO₄)O), Cassiterite (SnO₂) and Co-akermanite (Ca₂Co(Si₂O₇)).

Conclusion

The results of the evaluation of colour and application properties of malayaite pigments doped by cobalt which were prepared using mechanical activation as pre-treating were summarized in this contribution. Compounds CaSn(Co)SiO_{5-δ} with the mass ratios of cations Co/Sn = 0; 0,015; 0.058 and 0.093 were investigated. Initiatory mixtures were at first subjected to mechanical activation in the planetary mill and subsequently calcined in the temperature range 1150-1400°C/4 hours. Colour and application properties of the pigments were observed after the dispersion into ceramic leadless transparent glaze P 07410 and organic acrylic binder. Colour of studied pigments was ranged from white to blue-violet depending on the cobalt amount and the temperature of calcination. Calcines, which were manually crushed, were characterized by a lower hiding power in the glaze and organic matrix, which was caused by unsuitable particle size. The mean particle size was ranged from 4.50 to 41.04 μm. Therefore it was necessary to include grinding operation on required particle size which improved quality of pigment product. The values d₅₀ of milled pigments were about 2 μm. It was showed by improvement hiding power in both of assessed applications. X-ray diffraction analysis confirmed that malayaite compound was prepared in all investigated ratios of cations Co/Sn, but only in two cases, Co/Sn=0.058-1350 and 1400°C and Co/Sn=0.015-1400°C, the compound was monophasic. For viewpoint of the assessment of mechanical activation it can be stated this pre-treatment brought quality improvement of preparation of malayaite pigments with cobalt even though it is a very energy intensive process.

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