JET MILL VERSUS PLANETARY MILL – COMPARISON OF PROPERTIES OF MILLED $ZnFe_2O_4$ PIGMENT

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Abstract

In this study the powders of zinc ferrite obtained by milling in a planetary mill and a jet mill were compared. The spinel $ZnFe_2O_4$ was prepared by calcination of initial mixture of ZnO and Fe_2O_3 in stoichiometric ratio at 1100°C/4h. The pressures from 4 to 10 bars were used for dry milling in the jet mill Labomill (FPS, S.r.l., Italy). The next samples were prepared with using the planetary mill Pulverisette 5 (Fritsch, Germany), i.e. by wet milling in ethanol for the grinding time from 10 to 40 min. The agate balls and the zircon beads were used. Our attention was focused on determining of the fundamental pigmentary properties, which could be affected by grinding. The particle size distribution was measured by Mastersizer 2000/MU (Malvern Instr., BG). The surface area was obtained with using NOVA 1200e (Quantachrome Instruments, USA). The colour properties were studied with help of ColourQuest XE (HunterLab, USA).

Introduction

Inorganic pigments are substances derived from minerals and they impart colour or functionality to the objects in which they are applied. The inorganic pigments are exploited for not only colouring of paints, ceramics, cements, but nowadays they are used for their other properties. For example, they are required due to their resistance to the effects of radiation, temperature and chemical attack in high technology applications, such, as fibers, engineering plastics, highly durable coatings[1].

The pigments are produced as either fine powders or dispersions of the pigment particles in a carrier. The colour of supplied pigments is controlled not only by the physical properties (structure, particle size distribution, particle shape, etc.), but also their chemical properties (composition, stability, purity, ect.)[1].

Particle size distribution belongs to the most fundamental measured characteristics. Powders have the ability to form agglomerates (created by linking individual particles together by weak forces) or hard aggregates (resulting from powerful forces). Particle size is the most often modified using various types of mills. Choice of a suitable mill has a significant effect on the resulting properties of milled pigment. i.e. it is possible to influence not only the particle size distribution, their shape, surface area, but also the final colour effect.

Planetary mill is one of the most widely used laboratory mills. Planetary ball mill is a device for fast and fine grinding of dry samples or suspension. Very often it is also exploited for mixing, homogenizing of emulsions and pastes or for mechanical activation in research of materials. The planetary motion is caused by rotation of the grinding bowl about its axis and rotation of the carrier disc. A formation of centrifugal forces is the result, which they have the effect on content of the grinding bowls. Because the grinding bowls and the carrier disk are rotating in opposite direction, the centrifugal forces act alternately at regular periods agreeably and against each other. Acceleration of grinding balls in the radial direction reaches a multiple of the acceleration due to gravity. The resulting grinding effect is given by two processes: the first one - the movement of the balls and the grinded material along the inner wall of the grinding bowl and the second one – the impact of the balls on the sample and the opposing inner wall of the grinding bowl[2].

The jet mill was developed for the first time in USA in 1927 and at present, it belongs among to well known the milling systems, the most suitable for the micronizing of the chemical and pharmaceutical products. It is a mill designed for dry grinding and it utilizes the energy of compressed air, gas or steam for milling. The jet mill has no moving parts, therefore, a friction effect and thus subsequent contamination by metal are minimized. The size reduction is due collisions between particles (particle to particle) and due mechanical effect (impact of particles on the inner wall of grinding chamber)[3].

The zinc ferrite with the chemical formula $ZnFe_2O_4$ belongs to the large group of spinel pigments. Structurally they have a cubic symmetry and they are derived from natural occurring mineral the magnesium aluminate $MgAl_2O_4$. Generally, the spinels have a common chemical formula AB_2X_4. Based on the ions A, B and X, spinel can be divided into three groups: spinels of the first type (2-3) have combination of ions A and B in oxidation state II^{+} and III^{+}; the second type (4-2) have combination A^{IV+} and B^{II+} ions and the third type (6-1) A^{VI+} and B^{I+}. Only spinels with the oxygen anions are used as the inorganic pigments. The spinels are widely used by the ceramic and plastic industry. Nevertheless, $ZnFe_2O_4$ and $CaFe_2O_4$ are used as anticorrosive pigments[4].

The aim of this work was to compare the properties of the samples grinded in a planetary and a jet mill with regard to their particle size distribution, shape, surface area and colour characteristics.

Experiment

The commercially available powders Fe_2O_3 (Precheza a.s., Přerov) and ZnO (SlovZink, a.s., Košeca) were used for preparation of the spinel compound. The purity of used staring raw materials was about 99%. The zinc ferrite $ZnFe_2O_4$ was prepared by calcination of homogenised initial mixture in stoichiometric ratio. The calcination was performed at 1100°C with the duration 4 hours on maximum temperature[5]. For fine milling the planetary mill Pulverisette 5 (Fritsch, Germany) and the jet mill Labomill (FPS, S.r. I., Italy) were used.

The jet mill Labomill belongs in to group of spiral jet mills operating on the principle of dry intensive milling using compressed air. The samples of the zinc ferrite were dosed into mill by feed rate 0.0045 $g.s^{-1}$. For operation the pressures 4-10 bars were used.

The samples of $ZnFe_2O_4$ processed on the planetary mill Pulverisette 5 were milled for 10 – 40 minutes. The agate bowls of 80 ml were used. The agate balls of diameter 10 mm and the zircon beads of 1.1-1.2 mm were selected as grinding material. A ball-to-powder weight ratio was 8:1. The samples were milled in ethanol by speed 250 rpm. The suspensions of ethanol and the zinc ferrite were dried in an electric dryer and after cooling were ready for analysis.

The particle size distribution of all samples was measured with using the Mastersizer 2000/MU (Malvern Instr., Ltd.). It is the highly integrated laser measuring system (He-Ne laser, λ=633 nm) for analysis of the particle size distribution. The equipment uses scattering of the incident light on particles. The samples were before own measuring ultrasonically homogenised in $Na_4P_2O_7$ solution (c=0.15 $mol.dm^{-3}$) for 90 s. The signal was evaluated on basis of Fraunfofer bending.

For study of morphology and shape of milled samples the field emission scanning microscope JEOL JSM-7500F was also used. The JSM-7500F (JEOL, Ltd., Japan) features an optical system that includes a semi-in-lens objective lens, which can collimate the electron beams at low accelerating voltages. For these materials 1kV accelerating voltage was applied. The resulting images were obtained by the detection of backscattered along with secondary electrons. Materials were observed at magnifications from 2000 to 50000x.

The measurement of the specific surface area was carried out on the equipment NOVA 1200e (Quantachrome Instruments, USA). All samples were degassed at 300°C for 3 hours. The relative pressure p/p_0 of all analyses was in range 0.05-0.25. Next conditions determinations of surface area were: pressure tolerance – 0.2 mm Hg; equilibration time – 120 s; equilibration timeout – 480 s. The measurement was performed in 9 mm cuvette at 77 K using N_2 (adsorptive) and He (non-adsorptive) gases. The surface area was calculated with using multipoint BET statistical method (seven points).

The main attention was focused on comparison of colour properties of the samples milled at different mills. The colour parameters were studied for the powdered samples and for samples applied into 2 binding systems – organic matrix in mass tone (Parketol, Akzo Nobel Coatings CZ, a.s., Opava, Czech Republic) and the middle-temperature transparent leadless ceramic glaze P 07410 in the weight ratio 10% (Glazura Roudnice, a.s., Czech Republic). 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). In this system, the L* represents lightness or darkness of the pigment. The values a* and b* indicate the direction of the colour; +a - the red colour; -a – the green colour and similarly +b – the yellow colour; -b – the blue colour. Next colour characteristics have been calculated for better description 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: $\Delta E^{*}_{CIE}=[(\Delta L^{*})^2+(\Delta a^{*})^2+(\Delta b^{*})^2]^{1/2}$, 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 (unmilled zinc ferrite) and the samples milled in different mills at different conditions 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°- 360°C. The value of the hue angle can be found out from the formula: H°=arctg(b*/a*). The interval H° for this studied system of studied pigments is following: 350°-35° red hue, 35°-70° orange hue, 70°-105° yellow hue[6].

Discussion and result analysis

The first was determined the particle size of the milled samples and they were compared with the values obtained for unmilled zinc ferrite. The following values were measured for unmilled $ZnFe_2O_4$: d_{10}=0.50 μm, d_{50}=2.04 μm and d_{90}=46.92 μm. This result indicated the presence of larger particles and in the case of next applications, it is necessary to improve the particle size of the spinel compound. The obtained values of milled samples are summarized in Table I. The recommended the mean particle size for application to organic matrix is around 2 μm. The optimum particle size for ceramic applications is between 5-15 μm. Table I shows that in the case of the jet mill using 4 bars the reduction of initial d_{90} from 46.92 μm to 10.53 μm was recorded. The particles of very similar size were obtained when using compressed air from 6 to 10 bars. It is evident from the table that the width of the distribution curve is tapering with increasing pressure of the compressed air. For more radical improvement in the particle size of the original zinc ferrite was obtained using the planetary mill and zircon beads. The initial d_{50} (decreased to 1.04 μm) and even the d_{90} (to 2.69 μm) were reduced after 10 minutes of grinding. More intensive milling brought further particle size reduction. Pigments having the d_{50} below 1 μm were prepared using the planetary mill, the zircon beads and the grinding time 20 - 40 minutes. The worst, but still satisfactory results were obtained for milling of the zinc ferrite in the planetary mill and using the agate balls. The values of the mean particle size obtained for this set are similar to the d_{50} for jet mill. However, the biggest values d_{90} were recorded for this series.

Table I
The particle size distribution of studied samples

The jet mill				The planetary mill – the agate balls				The planetary mill – the zircon beads			
Press. of air [bars]	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	Time of milling [min]	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	Time of milling [min]	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
4	0.55	1.48	10.53	10	0.50	1.53	11.04	10	0.41	1.04	2.69
6	0.54	1.23	2.57	20	0.47	1.46	8.83	20	0.34	0.86	2.07
8	0.53	1.13	2.16	30	0.44	1.33	5.83	30	0.34	0.77	1.60
10	0.55	1.20	2.26	40	0.44	1.32	5.38	40	0.34	0.74	1.53

Table II
The results of the surface area analysis

The jet mill				The planetary mill – the agate balls				The planetary mill – the zircon beads			
Press. of air [bars]	sample weight [g]	C const.	Surface area [m^2/g]	Time of milling [min]	sample weight [g]	C const.	Surface area [m^2/g]	Time of milling [min]	sample weight [g]	C const.	Surface area [m^2/g]
4	1.98	79.82	1.79	10	2.22	87.81	1.85	10	2.59	87.03	2.45
6	2.12	84.10	1.95	20	2.53	91.56	2.07	20	2.59	98.37	3.55
8	2.16	66.45	2.14	30	2.26	102.47	2.45	30	2.50	88.17	4.70
10	2.22	82.30	2.06	40	2.89	103.84	2.72	40	2.64	95.04	5.49

The specific surface area belongs to the group of basic variables that can be used for characterize of the powder material. Determined values of specific surface area, together with the values of the constant C and weight of the samples are summarized in Table II. The value of specific surface area of unmilled zinc ferrite was very small and for the unmilled pigment following data were observed: sample weight - 3.04 g, C - 141.08 and surface area - 1.24 m^2/g. Generally known fact, increasing of the surface area with growing grinding time and while decreasing the particle size is visible. The growth of surface area in depending on the particle size reduction is probably related to the kinds of the mills and the forces through which the particles are reduced. Compounds are in the jet mill grinded at the expense of mutual collisions of particles and impacts of the particles to the chamber wall and the friction effect is minimized. The values of the specific surface area of samples milled in the jet mill had slow growing nature. In contrast, in the planetary mill, where the effect of friction and impact of the balls on wall of the bowl are preferred, larger values of specific surface area were recorded. This hypothesis is even better visible from the values of specific surface area obtained for the samples micronized in planetary mill using zircon beads. The zircon material has a higher density (5.7 g/cm^3) than the agate (2.7 g/cm^3) and the size of beads is more suitable for fine grinding, and therefore, the frictional effect was more intensified in the case of this grinding process. The BET constant C is related to the interaction of adsorbate and adsorbent and their values correspond to the values of typical oxidic inorganic materials, for which well-defined monolayer was formed.

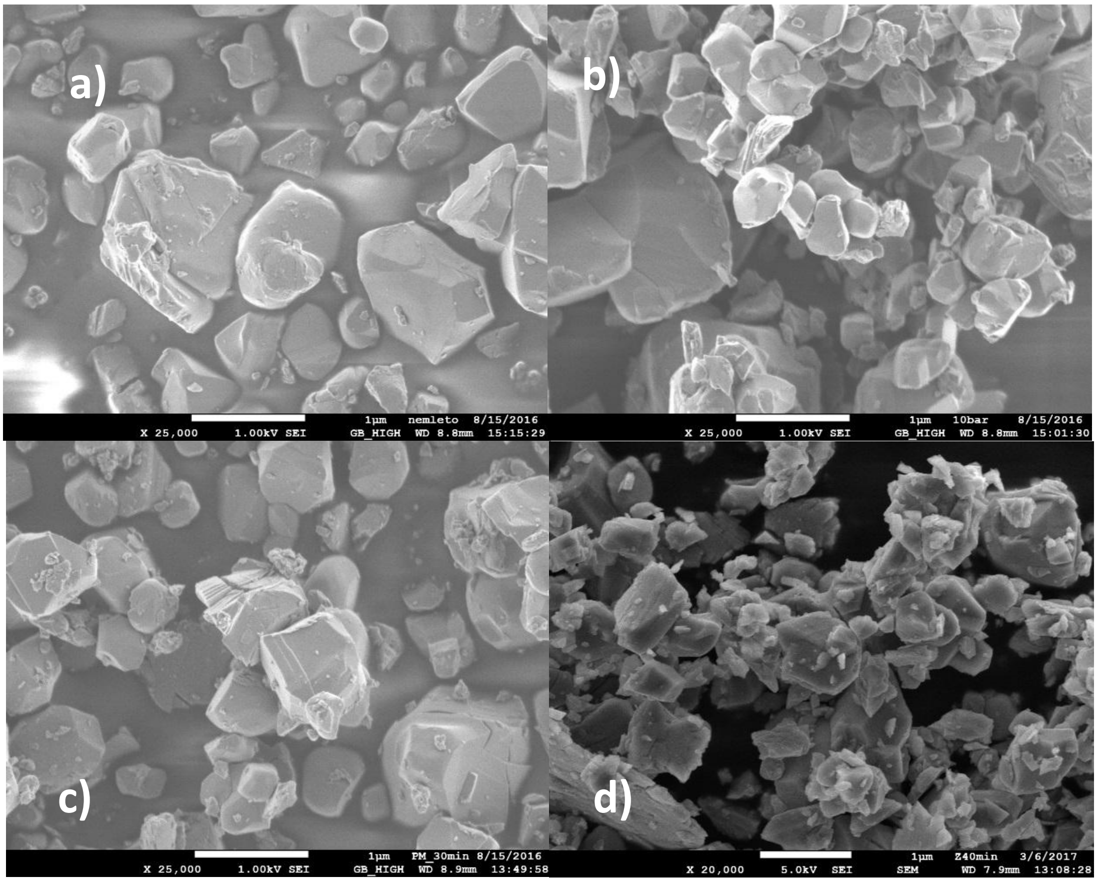

Figure 1. SEM images of $ZnFe_2O_4$: a) unmilled; b) milled in the jet mill 10 bars; c) milled in the planetary mill – the agate balls - 30 min; d) milled in the planetary mill – the zircon beads – 40 min

The particle shape is an additional attribute of powdered materials, which can be influenced by the grinding process. Therefore, the shape, particle morphology and homogeneity were studied by SEM analysis. Images for selected samples are shown in Fig. 1. The cubic structure having Fd-3m space group, which is typical for zinc ferrite, is not visible clearly. From the viewpoint of homogeneity, it is evident, that although the sample from the jet mill (Fig. 1 b) contained a very small amount of bigger grains, homogeneous product was prepared with help the planetary mill using zircon beads. By monitoring the shape of particles after grinding has been found that pigment grains with rounded polished edges are produced by milling in the jet mill. Conversely, the planetary mill, where it occurs rather the frictional effect, produced particles with sharp edges in the shape of plates or flakes. Fractures generated during very intensive milling under the effect of friction forces are very well visible in Fig. 1 c).

Main attention of this contribution was focused on the monitoring of colour properties of the zinc ferrite, which has been milled to various types of mills. Fig. 2 shows the dependence of the colour coordinates for powder pigments (a)) and after their application to the organic binder in masstone (b)). In the case of the powders, the loss of both chromaticity coordinates without significant dependence it is visible for the pigment grinded in the jet mill. In contrast, the samples milled to the planetary mill using the agate balls demonstrated growth of both coordinates against the unmilled sample. Although this increase is very small, it is apparent shift to the higher values, namely with the increasing milling time. The largest changes in colour properties have been recorded in case of the zinc ferrite grinded in the planetary mill using zircon beads. From Fig. 2a it is evident significant growth of coordinates a * and b * after 10 minutes of grinding, but further intensive milling revealed a loss of red colour (decline of a* values) with growing grinding time. Very similar trends of the shifts in the colour coordinates of studied mills as in the case of powders were recorded for application in organic binder (Fig. 2b).

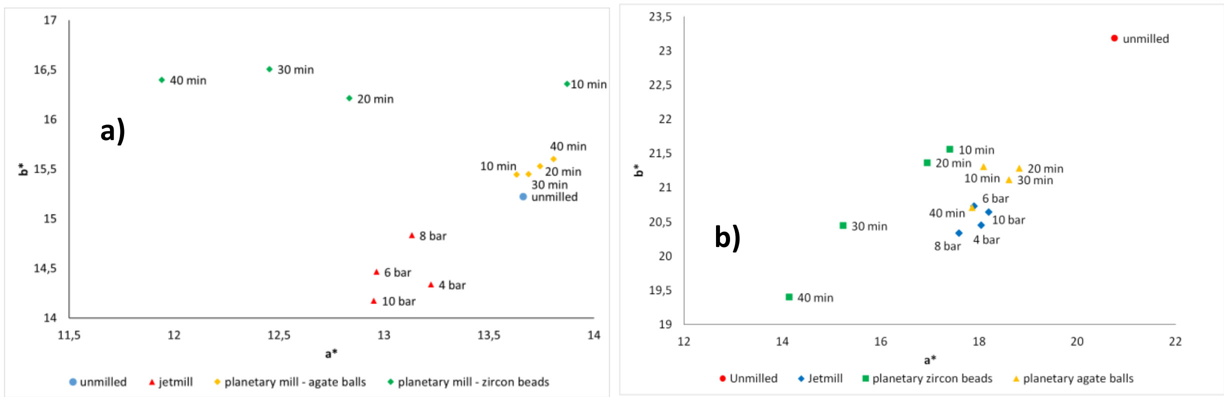

Figure 2. The colour properties of studied unmilled and milled $ZnFe_2O_4$ determine for: a) powder; b) after application into the organic matrix in masstone

Table III

The values of L*, C, H° and ΔE_{CIE}^* for the powdered pigment $ZnFe_2O_4$ a for pigments applied into the leadless glaze P 07410 (10 wt. %) and the organic matrix (mass tome)

Powdered pigments														
The jet mill					The planetary mill – the agate balls					The planetary mill – the zircon beads				
Press. of air [bars]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*
4	48.6	19.5	47.3	1.0	10	49.1	20.6	48.6	0.4	10	49.8	21.5	49.7	1.6
6	48.8	19.4	48.1	1.0	20	49.1	20.7	48.5	0.5	20	49.9	20.7	51.6	1.7
8	48.4	19.8	48.5	0.8	30	49.4	20.6	48.5	0.7	30	50.3	20.7	53.0	2.3
10	48.5	19.2	47.6	1.3	40	49.4	20.8	48.5	0.7	40	50.4	20.3	53.9	2.6
Application – organic matrix														
The jet mill					The planetary mill – the agate balls					The planetary mill – the zircon beads				
Press. of air [bars]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*
4	40.3	27.3	48.6	3.9	10	40.8	28.0	49.7	3.3	10	41.0	27.7	51.1	3.8
6	40.6	27.4	49.2	3.8	20	40.9	28.4	48.5	2.8	20	41.5	27.3	51.6	4.4
8	40.5	26.9	49.2	4.3	30	41.0	28.1	48.6	3.1	30	41.3	25.5	53.3	6.3
10	40.4	27.5	48.6	3.6	40	40.6	27.3	49.2	3.8	40	40.2	24.0	53.9	7.6
Application – ceramic transparent leadless glaze P 07410														
The jet mill					The planetary mill – the agate balls					The planetary mill – the zircon beads				
Press. of air [bars]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*	Milling Time [min]	L*	C	H° [°]	ΔE_{CIE}^*
4	34.5	15.8	48.6	6.8	10	33.4	14.3	47.2	5.1	10	34.7	16.2	48.6	7.2
6	35.4	18.1	47.4	9.3	20	34.3	16.1	46.4	7.1	20	35.6	18.6	47.7	9.8
8	35.2	18.0	47.1	9.1	30	34.3	16.9	46.7	7.8	30	36.2	19.0	49.1	10.3
10	36.4	18.9	49.6	10.3	40	34.2	15.8	45.6	6.8	40	36.7	20.4	49.1	11.8

Table III summarizes the values of colour characteristics for all studied systems. Colour characteristics of unmilled zinc ferrite were as follows: the powder: L*= 48.8; C=20.5; H°=48.1°; the organic matrix: L*= 40.2; C=31.1; H°=48.2°; the glaze: L*=32.6; C=9.3; H°=51.6°. Powder samples milled in the jet mill exhibited the same values of brightness and hue angle as the unmilled sample. The chroma C decreased slightly. The values of the total colour difference ranged from 0.8 to 1.3 and they fell into the area barely noticeable difference. The brightness increased for samples milled on the planetary mill in both compared cases, for the agate balls slightly and for the zircon beads shift about 2 units was recorded. The C values were unchanged. The H° for the agate balls was with no significant changes, but for the zircon beads shifted to higher values towards yellower orange hue. The total colour difference increased with milling time, for the agate balls the values were very smallest (imperceptible to the colour difference) and for the zircon the ΔE_{CIE}^* values were the highest (barely noticeable difference) from all compared mills. A similar trend in characteristics L* and H°, as it was for powder pigments, was found for the samples applied to the organic binder too. However, an exception was the decline of C recorded for all investigated systems, which it agrees with Fig. 2b, where the shift is visible towards lower values of colour coordinates in comparison with unmilled sample. All the ΔE_{CIE}^* values were in the area of large colour differences. Colour characteristics determined for samples applied to the glaze were for all studied systems very similar. The brightness grew with the grinding time, which was recorded by lighter surface of the ceramic tile. Significant changes were detected in the case of the C, because doubling values in comparison with unmilled pigment were observed in the majority of the samples. This increase manifested itself a significant improvement in the colour properties of the samples applied to ceramic glazes. The ΔE_{CIE}^*-values grew with time of grinding.

Conclusion

The $ZnFe_2O_4$ products, which were obtained by milling in two different types of mills, were compared in this work. The particle size, shape, surface area of the powders and finally their colour properties were studied. Powders gained from the jet mill and the planetary mill were investigated, while the agate balls and the zircon beads were used as the grinding materials for this type of mill. When evaluating of results of the particle size it was possible to conclude that the best results were obtained from the planetary mill and zircon beads. But also the jet mill produced particles of the zinc ferrite with a very narrow distribution curve indicating the production of powdered $ZnFe_2O_4$ about suitable particle size distribution for the following applications. No significant change in particle shape was detected during milling. Conversely, surprising results were found in monitoring of the surface area depending on the type of grinding. Although the better results of the particle size distribution were measured for the samples milled in the jet mill in comparison with the planetary mill and agate balls, it was found, that the powders prepared by the jet mill had a much smaller surface area in compared to the other samples. The frictional forces emerging in a planetary mill probably play a major role at increasing of the surface area. When studying the influence of the grinding kind on the colour properties of investigated zinc ferrite it turned out, that the order of the type mill is as follows: the planetary mill - agate balls, the jet mill, the planetary mill - zircon beads. The maximum pressures of compressed air, that they can be used in the jet mill Labomill, had resulted in the production of powdered pigment, which it is in terms of the colour properties approaching to the samples grinded to planetary mill with using the zircon beads for 20-30 minutes. Therefore, selection of the type mill depends on the further application of powdered pigment. The grinding on the jet mill is sufficient for ceramic applications, but the planetary mill can be recommended for the paints.

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