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Effect of Particle Size on the Blue Chromate Pigment $CoAl_2O_4$

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Abstract

A stable ceramic ink for inkjet printing requires ultrafine pigment powders. However, the decreased particle size of the ceramic pigment has an uncertain effect on the chromate. To understand this effect, a series of $CoAl_2O_4$ powders with different particle sizes was prepared with the nitrate-glycine combustion method followed by bead milling. The results show that the average particle size (d_{50}) of the $CoAl_2O_4$ powder decreases from 6.4 μm to 0.33 μm after milling for 10 h. The particle size has a clearly negative effect on the color of $CoAl_2O_4$ pigment. The chromate value changes from $L^* = 49.82$, $a^* = 0.05$, $b^* = -50.90$ to $L^* = 56.42$, $a^* = -13.15$, $b^* = -28.02$. Accordingly, the $CoAl_2O_4$ pigment changes from dark blue into sky blue. However, this rule is weak for $CoAl_2O_4$ pigment used in transparent glaze. The chromate of glaze changes only from $L^* = 29.65$, $a^* = 25.07$, $b^* = -52.12$ to $L^* = 20.61$, $a^* = 22.28$, $b^* = -41.35$. The glaze changes from dense blue into bright blue.

Keywords: Inkjet printing, pigment, $CoAl_2O_4$, particle size, chromate

I. Introduction

Inkjet printing is now the most popular technology for the decoration of ceramic tiles because of its numerous advantages, such as non-contact direct-write, higher image definition, lower cost, and so on [1]. Ceramic inks are at the core of inkjet printing technology. The inks need micron- or nano-sized pigment to avoid clogging of the nozzles and to ensure excellent suspension stability. However, the color of the pigment changes with the particle size because the optical properties of ceramic pigments depend on the particle size [2]. Light absorption increases with a decrease in particle size until a critical value is reached, and finally it is practically constant with size. Light scattering increases with a decrease in particle size up to a maximum corresponding approximately to half wavelength. Optimum scattering occurs in the range of 200 – 400 nm as the visible region is 400 – 780 nm. Obviously, a difference in the chromate of pigments with different particle size must exist, which will have the effect on the printed patterns.

$CoAl_2O_4$ is usually applied as a primary color in ceramic pigment, which is traditionally fabricated on industrial scale with the solid-phase method. The average particle size of this type of pigment is about 1.2 – 10 μm, which is coarse for the application of ceramic ink. To obtain an ultrafine pigment, wet chemical synthesis of $CoAl_2O_4$ pigment is proposed, such as the sol-gel [3], co-precipitation [4], micro-emulsion [5], hydrothermal [6–8], and combustion methods [9,10]. However, despite having the same chemical composition, the chromate of $CoAl_2O_4$ pigments is different. This indicates that the particle size of the pigment results in chromatic aberration. This is unfavorable for the $CoAl_2O_4$ pigment used in inkjet printing because it results in a deviation between the inkjet-printed pattern and the designed pattern. To avoid or reduce this deviation by controlling the content of the blue pigment, an in-depth understanding of the relationship between the particle size of the pigment and its chromaticity is necessary.

In the present work, $CoAl_2O_4$ pigment was synthesized with the nitrate-glycine method, and then bead-milled to obtain different particle sizes. The chromates of the pigments and $CoAl_2O_4$ pigments used in the transparent glaze were measured. The relationship between the particle size and the chromate of $CoAl_2O_4$ pigment was researched.

II. Experiment

(1) Preparation of $CoAl_2O_4$ pigment

$CoAl_2O_4$ pigment was prepared with the nitrate-glycine combustion method. In a typical experiment, 6.9852 g $Co(NO_3)_2{\cdot}6H_2O$, 27.0092 g $Al(NO_3)_3{\cdot}9H_2O$ and 14.4134 g glycine were dissolved in distilled water. The solution was then heated slowly on a hot-plate with changing voltage until the mixture burned off. The combustion residues were collected and calcined in a muffle furnace at 1000 °C at a heating rate of 5 K/min. The obtained pigment was bead-milled for 1 – 10 h.

The blue $CoAl_2O_4$ pigments with different particle size were mixed with a transparent glaze, and then water was added to form a slurry. The glaze layer of a certain thickness was formed by spraying the slurry. The blue glaze was obtained after calcining at 1150 °C for 1 h.

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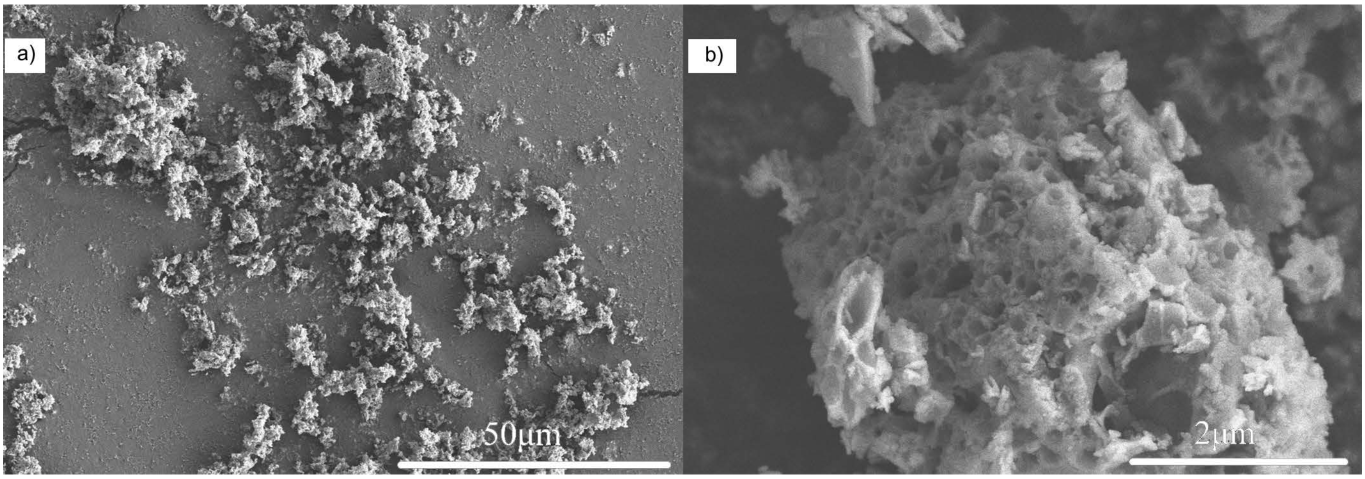

Fig. 1 : SEM images of $CoAl_2O_4$ pigment prepared with the combustion method: a) Low magnification, b) Large magnification.

(2) Characterization of $CoAl_2O_4$ blue pigment

The pigments were observed with a scanning electronic microscope (SEM, JSM-6700F, Japan). UV-visible spectroscopy was performed with diffuse reflectance and with integrating sphere (Perkin-Elmer, USA) in the 200 – 900 nm range, step 0.3 nm, using $BaSO_4$ as a reference. The CIE LAB parameters L^*, a^*, b^* were measured with a spectra-photometer (HunterLab Miniscan MSXP4000, 400 – 700 nm, white-glazed tile reference x =31.5, y =33.3). L^* is the lightness axis (black (0) ~ white (100)), a^* is the green (-) ~ red (+) axis, and b^* is the blue (-) ~ yellow (+) axis. The particle size distributions of the pigments after milling for different times were measured with a laser scattering particle size analyzer (Bettersize2000, Dandong, China).

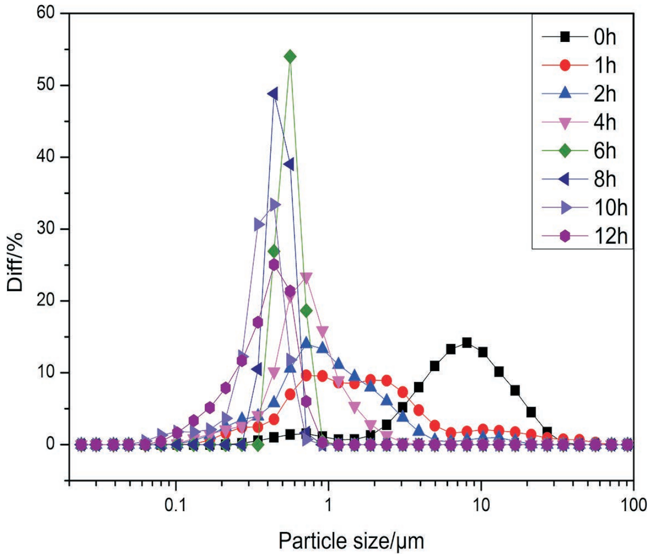

Fig. 2: Particle size distribution of $CoAl_2O_4$ pigments after different milling times.

III. Results and Discussion

Fig. 1 shows SEM images of the $CoAl_2O_4$ pigments prepared with the nitrate-glycine method [11]. It can be seen the $CoAl_2O_4$ pigment is loose and the particles have an irregular shape. The interior of the particles presents a honeycomb-like porous structure produced during the combustion process. This porous structure contributes to obtaining a smaller size of the milled particles.

Fig. 2 shows the particle size distributions of the $CoAl_2O_4$ pigments after different milling times. It can be seen that the untreated $CoAl_2O_4$ pigment has a bimodal particle size distribution with a mean particle size of 6.4 μm. As shown in Fig. 1, the primary crystals are in a soft-aggregation state. The mean particle sizes decrease and the particle size distributions change sharply with the prolonged milling time. Under the given milling conditions, there is a grinding limit and the particle size reaches the minimum value when the milling time is 10 h. However, the particle size of $CoAl_2O_4$ pigment increases again if the milling time exceeds 12 h owing to increased surface energy.

Fig. 3 shows the XRD patterns of $CoAl_2O_4$ pigments after different milling times. The XRD patterns suggest that the majority phase of the pigment is $CoAl_2O_4$, and the minority phase is Al_2O_3. The existence of Al_2O_3 is due to the super-stoichiometric aluminum nitrate in the experiment, which makes the $CoAl_2O_4$ pigment brighter [11]. It also can be seen that the intensity of the peaks decreases with the particle size, which indicates that the longer milling time leads to amorphization. However, no new peaks appear, although the diffraction peaks broaden. It can be deduced that the milling does not result in new material generation in the $CoAl_2O_4$ pigment. In this sense, it could exclude the possibility that the color change is related to the crystal structure besides the light scattering and light absorption. The chromate change just depends on the particle size of $CoAl_2O_4$ pigment itself.

Table 1 lists the chromate of the $CoAl_2O_4$ pigments with different particle size. As can be seen, the brightness (L^*) of the pigment first increases and then decreases with the decrease in particle size. When the pigment particle size (d_{50}) is 0.607 μm, the brightness reaches the maximum of 59.44, indicating the pigment is at its brightest.

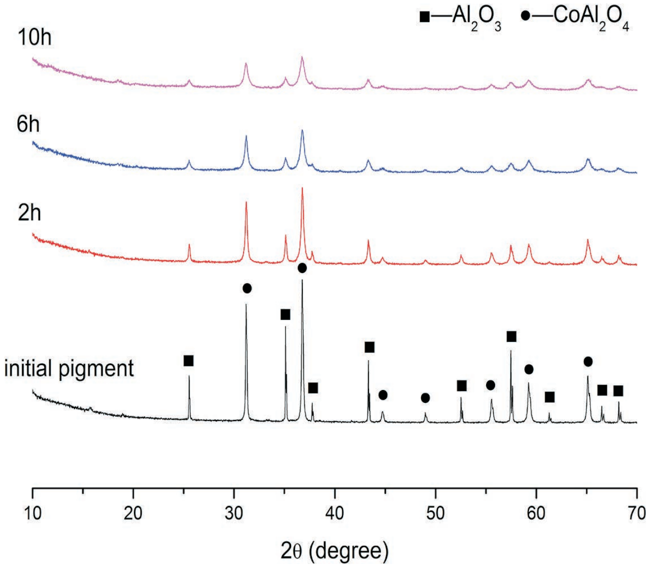

Fig. 3 : XRD patterns of the pigment after different milling times.

Fig. 4 shows the UV – vis absorption curves of the $CoAl_2O_4$ pigments after different milling times. It can be seen that the $CoAl_2O_4$ pigments have stronger absorption in the wavelength range of 570 nm – 620 nm. The light in the range of 570 nm – 620 nm is yellow and orange light. According to the color principle, the $CoAl_2O_4$ pigment absorbs the yellow and orange light and shows the color of blue, cyan and violet. The pigments are still blue after milling because the absorption wavelength range has not changed. After milling, the light absorption intensity by the $CoAl_2O_4$ pigment only attenuates. When the pigment particle size is further reduced, the light absorption coefficient of the pigment gradually increases, at this time, the color brightness decreases gradually. With the decrease in the pigment particle size, the particle scattering shifts gradually from red to blue, the red and orange light scattering on the pigment is weakened. Correspondingly, the light absorption by the pigment gradually increases. In summary, the particle size of the $CoAl_2O_4$ pigment changes the light absorption and scattering of the pigment particles, which also changes the pigment color.

As discussed above, the chromate of $CoAl_2O_4$pigment has no relationship to the new phase. The effect of the particle size on the chromate of pigment can be explained by the light scattering and the light absorption [2]. According to the measurement principle of the colorimeter, the reflection and scattering of light are detected. When the pigment particle size is down to 0.607 μm, the particle size is similar to the wavelength of the red and orange light. Now, the pigment particles have a strong light scattering effect on red and orange. The pigment shows the complement light, which is bright blue. When the pigment particle size is further reduced, the light absorption of the pigment gradually increases, at this time, the color brightness decreases gradually.

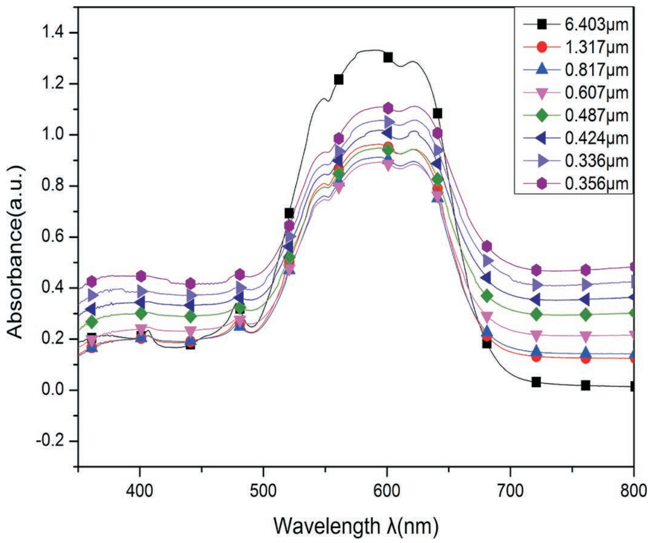

Fig. 4: UV – vis absorption curves of the $CoAl_2O_4$pigment with different particle sizes.

With the decrease in the particle size, the light scattering by the particles gradually shifts from red to blue. But at the same time, the light absorption of the pigment gradually increases. With combination of the two effects, the b^* value of $CoAl_2O_4$ decreases, and the color gradually changes from dark blue to light blue.

Table 2 shows the effect of the particle size on chromate of the $CoAl_2O_4$ pigment in transparent glaze. The

Table 1: Effect of particle size on the chromate of the $CoAl_2O_4$ pigment.

Milling	Particle size/μm					
time/h	d10	d50	d90	L^*	a^*	b^*
0	2.173	6.403	14.92	49.82	0.05	-50.90
1	0.422	1.317	7.846	55.74	-10.12	-40.27
2	0.308	0.817	2.380	58.33	-11.06	-35.17
4	0.327	0.607	1.153	59.44	-11.12	-31.57
6	0.400	0.487	0.600	58.10	-12.56	-30.07
8	0.343	0.424	0.505	57.48	-12.98	-29.02
10	0.200	0.336	0.450	54.62	-13.77	-27.51
12	0.163	0.356	0.531	56.42	-13.15	-28.02

Table 2: Effect of the particle size on the chromate of the $CoAl_2O_4$ pigment in transparent glaze.

Milling	Particle size/μm					
time/h	d10	d50	d90	L^*	a^*	b^*
0	2.173	6.403	14.92	29.65	25.07	-52.12
1	0.422	1.317	7.846	29.57	26.86	-51.11
2	0.308	0.817	2.380	27.01	26.97	-50.64
4	0.327	0.607	1.153	29.24	26.05	-50.53
6	0.400	0.487	0.600	29.54	25.52	-50.20
8	0.343	0.424	0.505	27.11	25.05	-48.32
10	0.200	0.336	0.450	23.43	24.33	-47.06
12	0.163	0.356	0.531	20.61	22.28	-41.35

pigment particle size has less effect on the L^* and a^* value of $CoAl_2O_4$. The b^* value increases slightly with the decrease in the particle size. This is caused by the special color mechanism of the $CoAl_2O_4$ pigment in glaze. Al^{3+} in $CoAl_2O_4$ pigment integrates into the glaze caused by the strong erosion at high temperature melt. In this process, the Co^{2+} is free. The color of $CoAl_2O_4$ pigment in glaze depends mainly on the content of Co^{2+}. Therefore, the fine $CoAl_2O_4$ pigment contributes to the dissolution of Co^{2+}, but has less effect on the color of the pigment in glaze.

Fig. 5 shows the UV – vis absorption curves of the $CoAl_2O_4$ pigments with different particle sizes in glaze. It can be seen that the decrease in the particle size does not change the light absorption of the glaze. So, the different size of $CoAl_2O_4$ pigment particles used in the transparent glaze is still blue. The absorption intensities change slightly. It is clear that the UV-visible light absorption intensity decreases slightly with the decrease in the particle size. The glaze changes gradually from dark blue to sapphire blue. In inkjet printing, the ultrafine $CoAl_2O_4$ pigment is usually used as the primary color and mixed with other primary pigments to obtain the designed patterns. The final color can be adjusted depending on the amount of the primary pigments. It is possible to increase the coloring ability of the $CoAl_2O_4$ pigment by increasing the amount of the pigment when the $CoAl_2O_4$ pigment is weakened owing to the reduced particle size. For example, in order to obtain a deeper blue color, the particle size of the $CoAl_2O_4$ pigment is increased within the allowable range of the inkjet printing apparatus or the solid content of the cobalt blue ink is increased. If a brighter sapphire is required, the fine pigment can be chosen.

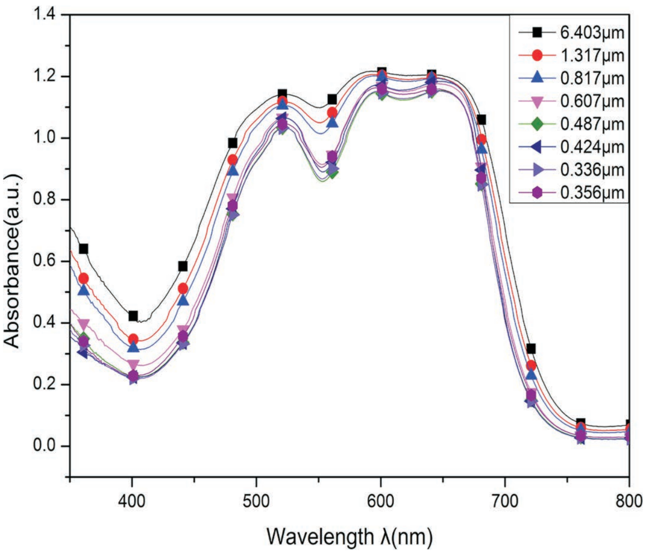

Fig. 5: UV – vis absorption curves of the $CoAl_2O_4$ pigment used in a transparent glaze after different milling times. .

IV. Conclusions

The particle size has a clearly negative effect on the color of $CoAl_2O_4$ pigment. The chromate value changes from L^* =49.82, a^* =0.05, b^* =-50.90 to L^* =56.42, a^*=-13.15, b^* =-28.02. The L^* value of the $CoAl_2O_4$ pigment gradually increases with the decrease in particle size. However, both a^* value and b^* value have the opposite tendency to that of the L^* value. The color change of the pigments with different particle size in the transparent glaze is smaller. The color mechanism of $CoAl_2O_4$ pigment used in transparent glaze is "ion coloring", the color performance is related to the cobalt ion content.

According to the above relationship between the chromate and the particle size, the chromatic aberration can be reduced by adjusting the content of $CoAl_2O_4$ pigment based on the particle size.

Acknowledgments

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