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Study on the Coloration and Acid Resistance of Cobalt Blue Pigments on Ceramic Glazes

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The solid phase method was used to synthesize spinel $CoAl_2O_4$ and willemite (Co, Zn) $2SiO_4$ cobalt blue materials, and their color rendering and acid resistance were compared. The SiO_2 and MgO were introduced to modify the Co_2O_3-Al_2O_3 system and the finely ground $CoAl_2O_4$ was taken as crystal nucleus to investigate its effect on the color rendering of the pigment and acid resistance. The on-glaze cobalt blue pigment with bright color rendering, high color saturation and good acid resistance was developed. The solid phase method was used to synthesize willemite cobalt blue material and then the lead-free flux with strong acid resistance was selected and mixed with the pigment in a certain proportion. The cobalt blue pigment was obtained by baking at a certain temperature. Through the single factor test and orthogonal test, the flux formula was optimized and the secret cobalt blue pigment with bright color rendering and good acid resistance was obtained. The results show that the spinel structure is superior to willemite structure in terms of acid resistance and the introduction of the finely ground $CoAl_2O_4$ crystal nucleus can improve the color rendering effect and acid resistance of the spinel cobalt blue material. XRD analysis shows that the main crystal phase of the optimal formula pigment is $CoAl_2O_4$, but there are SiO_2 residues.

1. Introduction

In the ceramic decoration, cobalt blue has always been the main color of ceramic decoration, and it is widely used in daily use, construction and sanitary ceramics. It can also be used as on-glaze, in-glaze and under-glaze pigment, color glaze and body pigment. The majority of the traditional cobalt blue materials are the willemite-structured CoO-ZnOSiO$_2$ system and the spinel-structured CoO-Al_2O_3 system (Jose et al., 2016). Researchers in China began to study the problem of poor acid-resistance of cobalt blue materials from the 1980s (Zhang et al., 2018), but so far no cobalt-blue material with good acid resistance has been found on the market. The cobalt blue material has excellent color rendering effect whether it is used as on-glaze pigment, in-glaze color pigment or under-glaze pigment. Its color is light, bright and stable (Zhang et al., 2018). Most of the traditional cobalt blue materials are of the willemite-structured CoO-ZnO-SiO system. The on-glaze blue pigment on the glaze formulated with the lead flux has a very bright color rendering effect and high color saturation. Most of these pigments are used in domestic on-glaze porcelain lithography and silk screen decals. However, its acid resistance is poor and the amount of lead release is much higher than international standards (Bachar et al., 2018). Therefore, the improvement of the acid resistance and non-toxicity of the cobalt blue pigment has become a problem that needs to be solved urgently in the daily ceramic industry. This paper aims at the problem of poor acid resistance of the existing willemite ceramic pigments and improves the chemical stability of the pigment by adding crystalline phase with strong acid resistance formed by forming ions and coloring ions into the pollution-free ceramic flux. The research first studied the effect of different components of the flux on pigment luster, color rendering and acid resistance through single-factor experiments. Then, the orthogonal test was used to optimize the flux formulation and the on-glaze cobalt blue pigment formula with good effect was obtained. XRD analysis was performed on the optimized formulation samples (Jiang et al., 2018).
At present, the acid resistance of cobalt blue pigments at home and abroad is not ideal. In this study, according to the solid-phase reaction mechanism and by adding crystal nucleus, the pigment with strong acid resistance is developed through the system experiment and improved preparation process of pigments. Also,

the lead-free flux developed by this research group was utilized to develop a lead-free and acid-resistant on-glaze cobalt blue pigments with good color rendering effect (Fischer et al., 2017).

2. Experimental method

2.1 Raw Material of Test Specimen

Experimental materials: Co_2O_3 is the analytically pure; ZnO, MgO and boric acid are all chemically pure, Al_2O_3 and SiO_2 are industrially pure, and the experimental flux is self-made lead-free flux by the research group; the equipment mainly includes muffle furnace, planetary mill, desktop drying oven and electronic analytical balance. All experimental formulations in this study are added with boric acid as the mineralizer with a total mass of 4% of the formulation.

2.2 Comparison between Co_2O_3-ZnO-SiO_2 System and Co_2O_3-Al_2O_3 System

The color rendering and acid resistance of the willemite-structured Co_2O_3-ZnO-SiO_2 system and the spinel-structured Co_2O_3-Al_2O_3 system were compared by experiments. The color rendering and acid resistance of pigments were investigated through the change of the introduction amount of different raw materials and the conclusion was drawn that the Co_2O_3-ZnO-SiO_2 system is superior to Co_2O_3-Al2O whether it was the color of the pigment or the color after baking (Li et al., 2015; but for acid resistance, color fading was found in both systems, but the overall performance of Co2O3-Al2O3 system is better than that of Co_2O_3-ZnO-SiO_2 system. This may be due to the fact that on the one hand, the color resistance of spinel-structured is better than the willemite-structured; on the other hand it may be related to the crystal integrity of the pigment particles. Therefore, the Co_2O_3-Al_2O_3 spinel system was selected for subsequent experiments, and its acid resistance and color rendering ability were improved by modification. The number for the optimal formulation of color rendering and acid resistance of Co_2O_3-ZnO-SiO_2 system and Co_2O_3-Al_2O_3 system was CZS and CA.

2.3 Modification of Co_2O_3-Al_2O_3 System

The formulation of Co_2O_3-Al_2O_3 system with relatively good acid resistance was determined and then the SiO_2 and MgO were introduced to improve its color rendering ability and acid resistance. The amount of alumina oxide and silicon dioxide remained unvarying, and the effect of the content of Co_2O_3 and MgO on the color rendering ability and acid resistance was investigated. The specific experimental arrangement is shown in Table 1.

Table 1: Experimental arrangement for Co2O3-MgO-Al2O3-SiO2 system

Index	CO2O3	MgO	AL2O3	SiO2
1-1	2	18	33	47
1-2	4	16	33	47
1-3	6	14	33	47
1-4	8	12	33	47
1-5	10	10	33	47
1-6	12	8	33	47
1-7	14	6	33	47
1-8	16	4	33	47
1-9	18	2	33	47

2.4 Introduction of CoAl2O4 Crystal Nucleus

The pigment sample with the best effect of the Co2O3-Al2O3 system CA was taken and the wet grinding of the sample was conducted with in a planetary mill with a zirconia ball of diameter 5 mm until it completely passed through the 400 mesh. After drying, it was added as a nucleus to formula 1 to 5in the Co_2O_3-MgO-Al_2O_3-SiO_2 system, which had the optimal effect(Ashkenazi et al., 2017). The volume of addition ranged from 2% to 13%, 1% every time. A total of 12 formulations were numbered 2-1 to 2-12.

$$X = \left(a_1, a_2, ..., a_n\right) \quad (1)$$

2.5 Experimental Process

(1) Pigment preparation process
The pigment was compounded, mixed, roasted, ground to passing through the 250 mesh screen. The baking system of pigments was: heating rate 6°C/min, synthesis temperature 1250°C, heat preservation 120min,

natural cooling, atmosphere being oxidizing atmosphere (Polić et al., 2015).

$$C_j \in \{C_1, C_2, ..., C_n\} \quad (2)$$

(2) Baking process
The ratio of fixed pigment and flux is 1:3; the baking temperature is 800°C; the heating rate is 10°C/min; and heat preservation time is 10 minutes. The specific process flow is shown in Figure 1.

$$T = T_{ij} \quad (3)$$

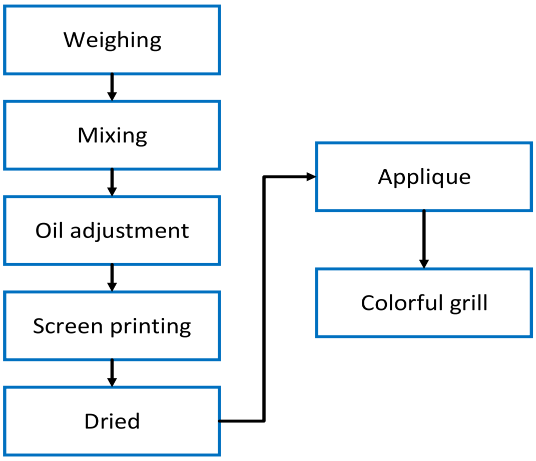

Figure 1: Color baking process flow chart

2.6 Characterization Test

According to the QB/T2455.2-99 standard, the sample was soaked in 4% acetic acid at 22±2°C for 24 hours. The corrosion of the flower surface was observed by visual observation and the acid resistance of the pigment was described. The German Brock D8Advance X-ray powder diffractometer was used to identify the crystal phase composition. CuKα radiation, target voltage 40kV, electric current 40mA, λ=0.15418nm, graphite monochromator filter, scanning range 2θ=10° to 70°, scan rate 0.02 (°)/s. The chromatic value of the sample was measured using the WSO-3A colorimeter from Beijing Kangguang Instrument Co., Ltd. (Betancur-Granados et al., 2017); the spectral reflectance of the sample was measured with a Lamda850 UV-Vis spectrophotometer of PerkinElmer Co., Ltd., whose wavelength range was 400- 780nm.

3. Results and discussions

3.1 Modification of Co2O3-Al2O3 System

Table 2: Results of Co_2O_3-MgO-Al_2O_3-SiO_2 system

Index	Appearance shape	Color color	Colorful roasting	Acid resistance
1-1	Dispersion difference, Agglomeration	Light blue	Light blue	No obvious fading
1-2	Dispersion difference, Agglomeration	Light blue	Light blue	No obvious fading
1-3	Better dispersion, Slightly agglomerate	Light blue	Light blue	No obvious fading
1-4	Better dispersion, Slightly agglomerate	Light blue	Light blue	No obvious fading
1-5	Good dispersion, fluffy	blue	blue	No obvious fading
1-6	Good dispersion, fluffy	Bright blue	blue	No obvious fading
1-7	Good dispersion, fluffy	Bright blue	blue	No obvious fading
1-8	Good dispersion, fluffy	Bright blue	blue	No obvious fading
1-9	Good dispersion, fluffy	Dark blue	blue	No obvious fading

The modified experimental results for the Co_2O_3-Al_2O_3 system are shown in Table 2. It can be seen from Table 2 that the acid resistance and color rendering of the pigment obtained with the introduction of MgO and SiO_2 based on the Co_2O_3-Al_2O_3 system are improved significantly. According to the acid resistance test standard, that is, soaking in 4% acetic acid at 22±2°C for 24 hours. There is no obvious fading, which meets the acid resistance requirements of ceramic on-glaze pigments, but the color saturation after baking is not satisfactory (Veronesi et al., 2017). Therefore, considering the color rendering, acid resistance and cost, the formula CA with finely ground baking pigments was introduced as crystal nucleus based on formula 1-5 in subsequent experiments to improve the crystal integrity with a view to further improve the color rendering effect and acid resistance.

3.2 Experimental results of after Introducing $CoAl_2O_4$ Crystal Nucleus

Table 3 shows the experimental results after the introduction of $CoAl_2O_4$ crystal nucleus. It can be seen from Table 3 that with the increase in the amount of crystal nucleus, the color rendering of the synthesized pigment is from light to dark. The dispersion is good and the particles are loose and easy to crush (Grazenaite et al., 2016). The color rendering of formula 2-5 is the optimal. The porcelain plate after baking is soaked in 4% acetic acid at 22±2°C for 24 hours and the results show that there is no significant fading in the pigment and there is slight fading in others.

$$\frac{\max C_i + \min C_i}{2} \quad (4)$$

Table 3: Addition of CoAl2O4 as nucleating agent

Index	Appearance shape	Color color	Colorful roasting	Acid resistance
2-1	Good dispersion, fluffy	Light blue	Light blue	Slightly faded
2-2	Good dispersion, fluffy	Light blue	Light blue	Slightly faded
2-3	Good dispersion, fluffy	Light blue	Light blue	Slightly faded
2-4	Good dispersion, fluffy	Light blue	Light blue	Slightly faded
2-5	Good dispersion, fluffy	Bright blue	blue	Slightly faded
2-6	Good dispersion, fluffy	Bright blue	blue	Slightly faded
2-7	Good dispersion, fluffy	Bright blue	blue	No obvious fading
2-8	Good dispersion, fluffy	Bright blue	blue	No obvious fading
2-9	Good dispersion, fluffy	Dark blue	blue	No obvious fading
2-10	Good dispersion, fluffy	Dark blue	Dark blue	Slightly faded
2-11	Good dispersion, fluffy	Dark blue	Dark blue	Slightly faded
2-12	Good dispersion, fluffy	Dark blue	Dark blue	Slightly faded

3.3 Color Rendering Analysis

Table 4 shows the chroma test results of the pigment sample CA, CZS, and 2-5.

Table 4: Results of colorimetric analysis

Index	L	a	b
CA	47.68	5.81	-23.97
CZS	46.48	7.09	-30.56
2-5	46.94	6.34	-40.63

From Table 4, It can be seen that the difference between the L value and the a value of each pigment sample is not significant, but the difference of -b value (blue) is significant. The -b value of 2-5 is the highest, which means that the color is the bluest. Figure 2 is the spectral reflectance curve of the optimal formula 2-5 sample. It can be seen from Figure 2 that sample 2-5 has significant reflection of blue light at 430-480 nm and also there is a small reflection peak for cyan light at 480-500 nm; there is a significant absorption peak at 550-650 nm, indicating that it mainly absorbs yellow light, together with a small amount of yellow-green and orange light. The displayed color is mainly blue, with a slight purple and cyan tone. The reflection peak of the sample at the blue light wavelength of 450 nm is narrow, which indicates that the color saturation of the sample is relatively high.

$$\overline{X} = \frac{\sum_m x_m}{m} \quad (5)$$

3.4 XRD Analysis

The XRD analysis is performed on CZS, CA and 2-5 pigment samples and the results are shown in Figure 2 and Figure 3.

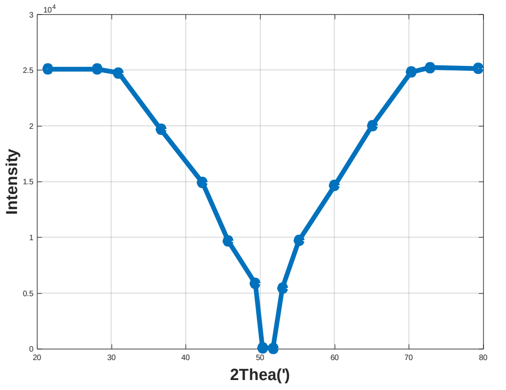

Figure 2: XRD patterns of sample CZS with using (Co, Zn)2SiO4

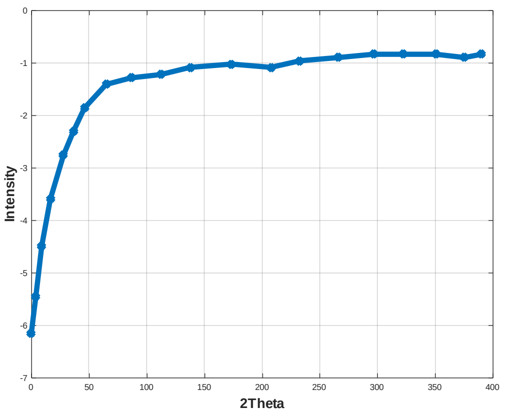

Figure 3: XRD patterns of sample CA with using the CoAl2O4

The crystal phase of CZS pigment is willemite (Co,Zn)2SiO4 and the crystal phase of CA pigment is spinel CoAl2O4. The crystal phase of pigment 2-5 with the optimal color reddening and acid resistance is CoAl2O4 and SiO2. Due to the introduction of the CoAl2O4 crystal nucleus, the pigment particles grew continuously with CoAl2O4 as the crystal nucleus within the same temperature preservation time, resulting in the formation of CoAl2O4 spinel. This indicates that the solid solubility of Co2+ is relatively high and is less susceptible to corrosion by H+. In addition, the SiO2 in pigment 2-5 does not participate in the reaction to form a new phase. On the one hand, the acid resistance of SiO2 itself is stronger, which improves the acid resistance of the pigment. On the other hand, SiO2 may promote the formation and growth of spinel phase during the solid phase reaction process and the mechanism needs further study.

$$\frac{\left(\max C_i - \min C_i\right) \cdot Threshold}{100} + \min C_i \qquad (6)$$

4. Conclusions

In this study, the synthesis technology of cobalt blue pigment by the solid phase method is studied by adding crystal nucleus and the on-glaze cobalt blue pigment with bright color rendering, high color saturation and good acid resistance was developed. Its b value is -40.63, and there is a significant reflection of blue light at 430-480 nm. Studies have shown that the acid resistance of the CoAl2O4 spinel structure is better than that of the traditional willemite structure. On the basis of Co_2O_3-MgO-Al_2O_3-SiO_2 system, 6% finely ground $CoAl_2O_4$ nucleation agent is introduced to improve the color rendering effect and acid resistance of the spinel cobalt blue pigment. The results of XRD analysis show that the crystalline phase of the optimal formula pigment is $CoAl_2O_4$, but there are SiO_2 residues.

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