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Preparation of Cobalt Blue Ceramic Glaze Ink Based on Sol-Gel Method

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Cobalt blue pigment precursor xerogel was prepared by sol-gel method and then calcined to obtain cobalt blue pigment by self-propagating combustion. The effect of process parameters such as pH value, metal ion concentration, dispersant, sol reaction temperature, citric acid dosage and calcination temperature on the crystalline form of cobalt blue pigment was studied. The ultrafine cobalt blue pigment obtained by the above method is used as the inorganic pigment of the blue ink, and the blue ceramic ink is prepared by a dispersion method. The effects of the milling medium size, milling time, dispersion effect of different kinds of dispersants, and solvent addition was studied. Dry gel is processed by self-propagating combustion and then calcined at high temperature. With the calcination temperature increasing, pigment color is more bright. At 1250 ℃, the grain size of the sample is approximately 200 to 500 nm. The sample is tested by a colorimeter, and its b* value is -43.09.

1. Introduction

Sol-gel method refers to such a process that metal alkoxide or inorganic solution constitutes sol-gel by hydrolysis and polycondensation reaction and solidifies, after drying and heat treatment, which generates nano-powder. The preparation method features simple process, reaction at lower temperature, and easy control of the reaction process. The finished nano-powder particles seemed to be uniform and high purity.

Chemlal made from HNO_3, Al_2O_3 and Co $Cl_2{\cdot}6H_2O$ is water-soluble at 50 ℃. The gel prepared in this way is dried at 100 ℃, and then calcined at 400 ~ 800 ℃ to prepare crystals with good crystallinity. The impact of pH on the crystallization and surface properties of cobalt aluminum spinel $CoAl_2O_4$ is also discussed here (Djambazov et al., 1998). Ye Mingquan et al prepared cobalt blue pigment precursor xerogel from $Al(NO_3)_3$, $Co(NO_3)_2$, citric acid and ethylene glycol with sol-gel method (Llusar et al., 2001; Jafari et al., 2014), which had made self-propagating combustion at 255-300 ° C and then calcined at 1000 ° C to get a cobalt blue pigment. Explore the impacts of pH value, metal ion concentration, ethylene glycol, sol reaction temperature, citric acid dosage, etc. on the formation of the gel, the combustion characteristics, the crystal structure of cobalt blue pigment prepared, and of the heat treatment of xerogel and calcination temperature on the cobalt blue pigment crystal form. Studies show that: when pH = 6.5, it is conducive to citric acid ionization, complexation with metal ions, and self-propagating combustion of xerogel. When the concentration of metal ions is 0.01-0.1 mol / L, the higher sol reaction temperature is favor of quick formation of xerogel; Ethylene glycol has no impact on the structure of cobalt blue crystal, but improves the agglomeration of the powders (Pérez-Arantegui et al., 2008; Hadri et al., 2017). The total concentrations of Co^{2+}, Al^{3+} are less than 0.005 mol / L, the intact cobalt aluminum spinel structure can not form; xerogel self-propagating combustion can not precipitate an intact cobalt aluminum spinel structure, but after calcined, it still helps improve the cobalt blue pigment crystal structure and dispersibility. The cobalt blue crystal form gets more complete and sharp in color as the calcination temperature increases (Klevakin et al., 2009).

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2. Experiments

2.1 Test reagents and equipment

Table 1: The chemical materials used in the experiment

Raw material	Purity	Manufacturer
Cobalt nitrate	AR	China pharmaceutical group chemical reagent co. LTD.
Aluminum nitrate	AR	China pharmaceutical group chemical reagent co. LTD.
Ethylene glycol	AR	China pharmaceutical group chemical reagent co. LTD.
Glycerol	AR	China pharmaceutical group chemical reagent co. LTD.
Citric acid	AR	China pharmaceutical group chemical reagent co. LTD.
Ammonia	AR	China pharmaceutical group chemical reagent co. LTD.

Table 2: The apparatuses and equipments used in the experiment

Device	Model	Manufacturer
agitator	-	Gongyi yuhua instrument co. LTD.
Electronic balance	MP-200L	Shanghai hengping science instrument co. LTD.
Constant temperature dryer	101A	Shanghai kang lu instrument equipment co. LTD.
Programmable computer smart muffle furnace	HXK-2	Hongxing machinery instrument manufacturing co. LTD.

The test is conducted with glass rods, beakers, graduated flask, sub-sieve, mortar, medicine spoon, crucible and crucible clamp, pH test paper, filter paper and other common experimental equipment.

2.2 Sample preparation

The cobalt blue pigment sample in this test is prepared by three steps: (1) Preparation of xerogel by sol-gel method: take cobalt nitrate and aluminum nitrate as raw materials, mix them into the solution by 1: 2 molar ratio (Pérez-Arantegui et al., 2009), add citric acid and dispersant by 1: 1 molar ratio (ethylene glycol or glycerol) at 75 °C, magnetically stir them for 2h, and then add ammonium hydroxide, adjust the pH to 6.5, and slowly evaporate by 90 ° C water bath to get a purple transparent sol, stir it again so that the gel is formed. The prepared gel is dried at 110 °C; (2) Xerogel self-propagating combustion: put the xerogel into an oven, and heat it up to 300 °C for 5 h, it self-fumes and generates black loose powder; (3) Calcination to prepare a cobalt blue pigment: put the black loose powder after self-propagating combustion into a muffle furnace at a high temperature, calcine it for 60 min at 900 ~ 1250 ℃, so the cobalt blue pigment is prepared.

3. Test results and discussion

3.1 Impacts of Co^{2+}, Al^{3+} concentrations

In this test, Co^{2+}, Al^3+ are mixed at a molar ratio of 1: 2, but the other conditions remain unchanged. The Co^{2+} varies from 0.01 mol / · L to 0.2 mol / · L. Explore the impact of metal ion concentration on the gel formation duration and cobalt aluminum crystal structure.

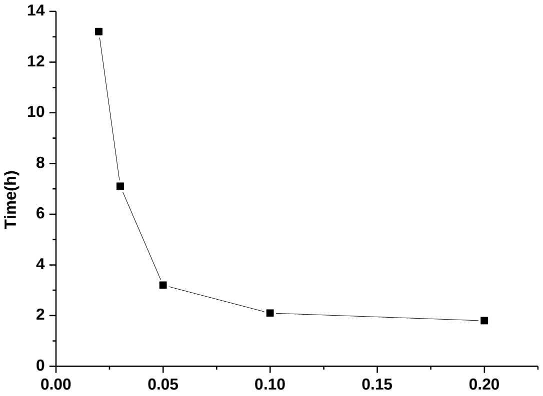

Figure 1: The effect of metal ion concentration on gellation time

It can be seen from Fig. 1 that the gel formation lasts for 13 h when the concentration of Co^{2+} is 0.01 mol / L; while 1.5 h when the Co^{2+}concentration is 0.2 mol / L, which implies that the concentration of Co^{2+} ions has an impact on the formation of gel: the higher the concentration of Co^{2+} ions, the shorter the time required to form the gel. Whereas, the lower the concentration of Co^{2+} ions, the longer it takes to form the gel. The xerogel prepared is calcined at 1150 ° C to form a blue product in any of cases when the Co^{2+} ion concentration is 0.01 mol / L, 0.05 mol / L, 0.10 mol / L and 0.20 mol / L, respectively (Kock and Waal 2010).

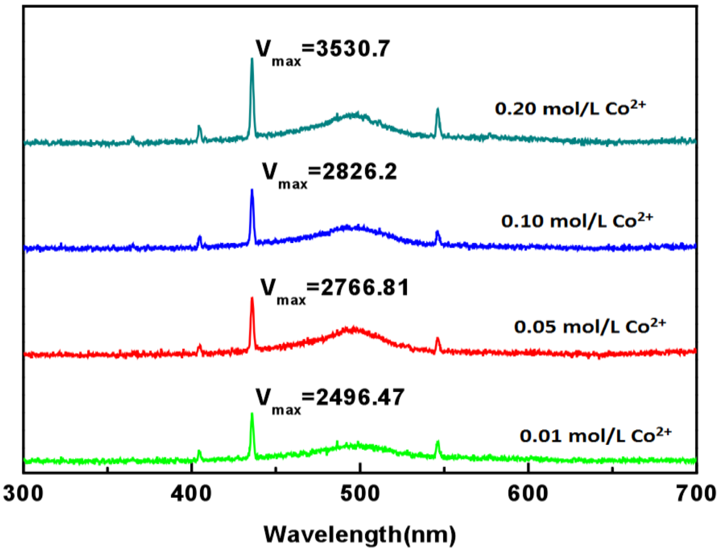

Figure 2: The reflection intensity pattern sunder different metalion concentration

In the Table 3, based on the Lab chromatic value of synthesized pigment as a function of Co^{2+} ion concentration, when the ion concentration increases, the blue chroma *b* of sample gradually goes up. It can be seen from Fig. 2, i.e. the curve of chromatogram of reflection intensity of synthesized pigment as a function of Co^{2+} concentration, that as the Co^{2+} concentration increases, the reflection of the sample at the blue light wave (450 nm) gradually gets more intense, which coincides with the result measured by the colorimeter. This is because when the concentration of metal ion in the solution is too low, it is not easy for it to complex with citric acid, so that the Co^{2+}, Al^{3+} ions to be complexed in the gel process are less, and the self-propagating combustion can not easily occur due to unevenly distributed gel components. This thus makes it impossible to form spinel structure.

3.2 Impacts of dispersants

In the process of sol preparation, the ethylene glycol and glycerin are introduced as dispersants in this test. Two sets of samples are prepared by adding 1 mol ethylene glycol and glycerol respectively when other conditions remain unchanged. As shown in Fig. 3, the xerogels are prepared by adding different alcohol dispersants, then applied with self-propagating combustion at 300 ° C, and calcined at 1150 ° C for 1 h. It can be seen from the figure that the additive alcohol dispersants can improve the agglomeration of the product particles. This is because -COOH in citric acid and -OH in the alcohol form the hydrogen bonds, further esterified at high temperature, which is conducive to the formation of stable sol-gel network (Jonynaite et al., 2012). Since the segregation of the metal salt occurred during the formation of the sol-gel network may lead to uneven gel component, it can be prevented to a certain extent by adding some dispersants in order to ensure the uniformity of gel component and improve product agglomeration. When the dispersant added is the glycerol, the prepared cobalt blue powder particles seems more uniform than that made from additive ethylene glycol. This is because 1 mol ethylene glycol contains 2 mol -OH while 1 mol glycerol contains 3 mol -OH. However, the existence of -OH in alcohol can effectively hinder the close contact between the colloidal particles and reduce the hard agglomeration. In the case of equal molar masses, -OH contained in the glycerin is 1.5 times that in ethylene glycol, which shows that the additive -OH can improve and moderate the agglomeration phenomenon as the amount of -OH increases.

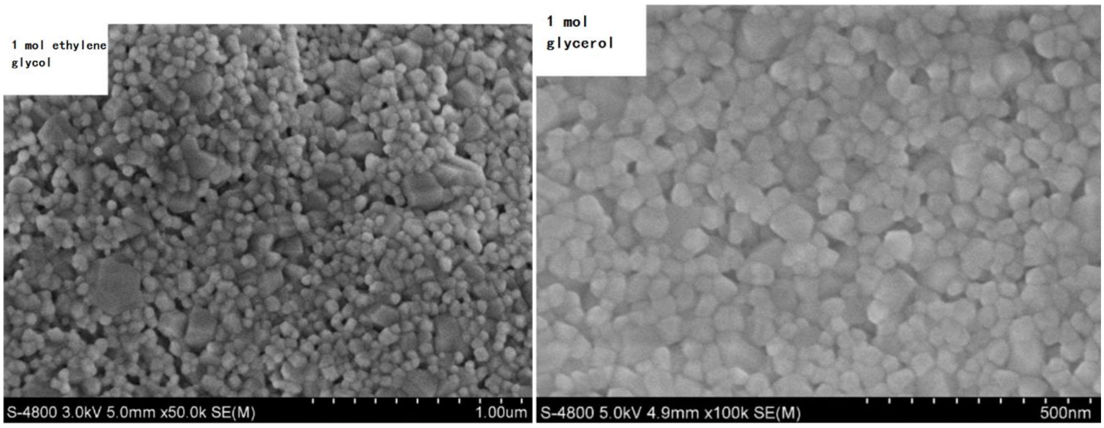

Figure 3: The SEM of the sample

Table 3: The colorimetric result of sample C1 and C2

No.	dispersant	L*	a*	b*
C1	Ethylene glycol	47.15	-16.01	-22.08
C2	Glycerol	46.75	-20.33	-23.52

The Lab chromaticity of samples prepared by adding different alcohol dispersants is shown in the Table 3. It is obvious that: b * in glycerin is greater than that in ethylene glycol, since the particle of cobalt blue powder prepared by using the glycerol as a dispersant is relatively uniform, and its reflective performance is also more consistent, so that its chromatic character is better. The above test analysis shows that: in the preparation process of the gel, the additive glycerol as dispersant is more ideal than ethylene glycol, and increased dosage of additive alcohol can also improve the hard agglomeration phenomenon of powder.

Six types of polymeric dispersants (No. Arodura120, CUR99, PUD-350, CH-3, CH-5 and CH-13) are selected as the study objects to find the best one from them. The impact of the polymer dispersant on the average particle size of the ceramic ink is shown in Fig.4. It is known from Table 3 and Fig. 4 that the average particle size of the ceramic ink containing the polymer dispersant CH-13 is the minimum. As shown in the figure, the *Span* of the ceramic ink containing the polymer dispersant CH-13 is less than that of the ceramic ink of other polymer dispersants. It thus turns out that CH-13, as a polymer dispersant, can effectively prevent agglomeration between particles and has a better effect than other dispersants.

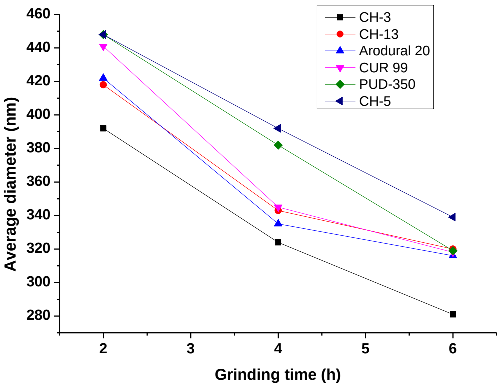

Figure 4: The effect of disperants on the average diameter of ceramic ink

It can be seen from Fig. 4 that the dispersant in ceramic ink is less, but has a significantly great impact on the viscosity of ceramic ink. The viscosity of ceramic ink added with dispersants A and B reached 120 mpa·s at 25 ℃, which differs a lot from the 30mpa·s as required. However, the viscosity of ceramic ink prepared from the other four types of dispersants falls within 50 ~ 70 mpa·s, significantly different from the previous two dispersants. It is likely that the structures or molecular weights of Dispersants A and B are too high, resulting in greater gap between the particles.

3.3 Impact of pH value

Citric acid is a ternary weak acid containing tricarboxylic acid, and by multistage ionization in aqueous solution, it undergoes complexation reaction with metal Co^{2+} and Al^{3+} ions. The pH value of the whole solution system will affect the multistage ionization of citric acid, thus making gel components uneven in the complexation reaction. When the pH of the solution system is less than 4, H + in the solution inhibits the multistage ionization of citric acid. At this time, only part of the metal Co^{2+} and Al^{3+} in the sol system complex with citrate and the other part still exists in the form of nitrate, thus resulting in uneven distribution of gel components; when the pH value falls within 4 ~7, the gel component is mainly citrate; when the pH >7, the solution system is alkaline and the multi-order ionization of citric acid is more complete. However, in the alkali solution, metal Co^{2+}, Al^{3+} ions precipitate with OH- and can not be fully complexed, which also leads to uneven distribution of gel components (Gorodylova, Kosinová et al., 2013). Therefore, the optimum pH value should fall within 6 ~ 7, only in this way can the citric acid have a complex reaction with metal Co^{2+}, Al^{3+} ions to prepare the cobalt blue pigment precursor xerogel.

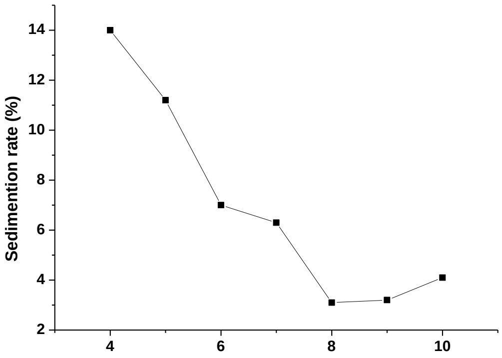

Figure 5: Sedimentation rate of ink under different pH value

The curve of ink stability as a function of pH value is shown in Fig. 5. It is found that the pH value has a great impact on the ink stability, that is, with the increase of pH, the ionization of the dispersant gets more intense. The sedimentation volume percentage of system tends to reduce to the minimum when the pH value reaches 8-9, and the pH value continues to increase, the stability of the ink system is broken, and the sedimentation rate somewhat increases.

4. Conclusion

Prepare cobalt blue pigment precursors by sol - gel method. The reaction time is 13 h when the concentration of Co2+ ions is 0.01 mol/L, and 1.5 h when the concentration of Co2+ ions is 0.2 mol/L, which shows that increasing the concentration of metal ions is beneficial to the rapid form. When the sol reaction temperature is low 65 ℃, the metal ions can not be complexed with citric acid to form a sol. When the temperature rises to 65 ℃, the sol begins to form, and the gel forming time needs to be 13.5 hours at a slower speed. When the temperature rises to 90 ℃, the gel formation time was 3.5 h, we can see that improving the temperature of the sol reaction is conducive to the rapid formation of the gel. From the SEM characterization we can see that the use of dispersant can improve the cobalt blue pigment agglomeration phenomenon. Sample by colorimeter determination shows that the dispersion of glycerol is better than ethylene glycol. XRD characterization shows that two dispersant has no effect on the structure of cobalt-aluminum spinel, and dry gel can not form intact spinel structure after self-propagating combustion.

Acknowledgments

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