PREPARATION OF AN ENVIRONMENTALLY FRIENDLY ULTRAMARINE PIGMENT AND ITS APPLICATION IN THE RESTORATION AND PROTECTION OF COLOR PAINTINGS

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In this paper, an environmentally friendly ultramarine pigment was prepared using coal gangue, waste molecular sieves, corn stalks, Na_2CO_3, and elemental S. Simulation experiments suggested that when the amount of coal gangue, waste molecular sieves, corn stalks, Na_2CO_3, and elemental S was 3.00 g, 1.00 g, 2.00 g, 3.00 g, and 4.00 g, respectively, the prepared product was closest in color to the natural ultramarine and more stable when exposed to temperature and humidity changes and ultraviolet light exposure.

Keywords: Environmentally friendly, ultramarine pigment, painting restoration, coal gangue

1. Introduction

In the long history of Chinese civilization, the art of color painting, with its unique aesthetic value and cultural connotation, has become an important form of expression for ancient architecture, religious murals, court decorations, and folk art [1,2,3]. However, over time, due to factors such as erosion by the natural environment, man-made destruction, and aging of materials, a large number of traditional color paintings have shown phenomena such as fading, peeling, and chalking, urgently requiring scientific and effective restoration and protection measures to intervene [4,5,6]. Traditional ultramarine, with its unique color and stable physical and chemical properties, is widely used in classical painting and decoration. However, high-quality natural lapis lazuli that can be used to make ultramarine pigments is scarce and expensive, and the extraction process has a negative impact on the environment, making it difficult to apply it on a large scale in modern restoration. Although synthetic ultramarine pigments are relatively inexpensive, they may have problems such as heavy metal pollution and poor stability, making it difficult to meet the demands of the restoration of painted cultural relics [7,8]. In this context, the development of environmentally friendly ultramarine pigments is of great significance to the current field of color painting restoration. Environmentally friendly ultramarine pigments need to be safe in

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composition, stable in color, and resistant to aging, highly compatible with the original pigments of painting, and environmentally friendly in the production process. González-Cabrera et al. [9] proposed a multi-sensor hyperspectral method to analyze ultramarine pigments based on the information of four analytical techniques at the elemental and molecular levels. Pizzimenti et al. [10] used thermogravimetric analysis, differential scanning calorimetry, gas chromatography-mass spectrometry (GC-MS), and Py-GC-MS methods to analyze ultramarine pigments in model paintings based on flaxseed oil and safflower oil. Vannoni et al. [11] presented a method for the systematic mass spectrometric investigation of the molecular features of the products of oxidative degradation and cross-linking of oil paint layers upon curing. In this paper, an environmentally friendly ultramarine pigment was prepared using coal gangue, waste molecular sieves, corn stalks, sodium carbonate, and elemental sulfur, followed by simulation experiments.

2. Case study

2.1 Experimental materials

Materials needed included coal gangue, waste molecular sieves, corn stalks, sodium carbonate, elemental sulfur, sodium hydroxide, concentrated sulfuric acid, concentrated nitric acid, concentrated hydrochloric acid, barium chloride, sodium sulfite; anhydrous ethanol. The coal gangue was purchased from Shijiazhuang Yitian Mineral Products Co., LTD. Waste molecular sieves were from Henan Zhonghui Water Purification Materials Co., LTD. Corn stalks were from Zhengyang County Yongjia Prataculture Co. Ltd. The rest of the agents were from Shandong Chicheng Chemical Co., LTD.

2.2 Preparation of ultramarine pigment

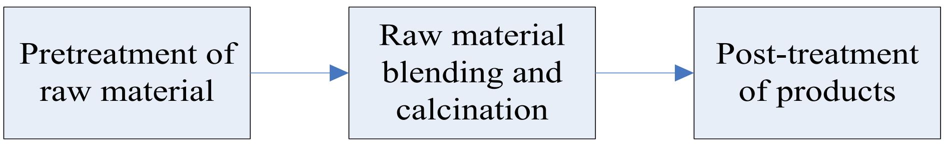

Fig. 1 The process of preparing the pigment

The basic process of preparing the eco-friendly ultramarine pigment is shown in Figure 1. The overall sequence is pretreatment, calcination, and post-treatment. The specific steps are described below.

① Pre-treatment of the raw materials: Coal gangue and corn stalks were washed and dried, then ground, and screened through a 50-mesh sieve. The former was then calcined at 1,000 °C for 3 hours, cooled, and sealed for storage, while the latter was directly sealed for storage. The waste molecular sieves were ultrasonically washed [12,13], dried, sealed, and stored.

② Mixed calcination of the raw materials: Coal gangue, waste molecular sieves, corn stalks, anhydrous sodium carbonate, and elemental sulfur were mixed in a certain proportion. Calcination was then carried out in a muffle furnace [14] for 30 minutes at 400 °C, followed by 120 minutes at 900 °C.

③ Post-treatment of the product: The product from the previous step of calcination was crushed and ground in a mortar, then screened by a 50-mesh sieve, and washed in water at 60 °C. Moreover, the calcined product was washed with a 2% sodium sulfate solution at a solid-liquid ratio of 1:3. Finally, it was washed with deionized water at 60 °C, followed by dry and screening by a 200-mesh sieve.

2.3 Test items

(1) The influence of different additives on ultramarine

Different raw material ratios were used to test the effects of the addition amounts of corn stalks, sodium carbonate, and elemental sulfur on the preparation of ultramarine pigments, as shown in Table 1. Different amounts of corn stalks were used in the A1-A5 samples, different amounts of sodium carbonate were used in the B1-B5 samples, and different amounts of elemental sulfur were used in the C1-C3 samples.

Table 1

Raw material ratios for different samples

Sample number	Coal gangue/g	Waste molecular sieves/g	Corn stalks/g	Sodium carbonate/g	Elemental sulfur/g
A1	3.00	1.00	0.00	3.00	4.00
A2			1.00		
A3			2.00		
A4			3.00		
A5			4.00		
B1	3.00	1.00	2.00	0.00	4.00
B2				1.00	
B3				3.00	
B4				5.00	
B5				7.00	
C1	3.00	1.00	2.00	3.00	0.00
C2					2.00
C3					4.00
C4					6.00
C5					8.00

After preparing the ultramarine pigment according to the steps described earlier and the raw material ratio shown in Table 1, the Lab value of the prepared ultramarine pigment color was tested using a colorimeter, and the Lab value [15] of the natural ultramarine pigment was also determined. The color difference between them was calculated:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}\ , \tag{1}$$

where ΔE is the color difference between the prepared ultramarine and natural ultramarine, and $\Delta L, \Delta a, \Delta b$ are the luminance, red-green axis, and yellow-blue axis difference between the prepared ultramarine and natural ultramarine. When ΔE is smaller than 1, the difference cannot be distinguished by human eyes; if it is between 1 and 2, the difference can be slightly observed by human eyes; if it is larger than 2, human eyes can clearly see the color difference and determine that they are two different colors.

(2) Disease simulation stability test

In order to test the stability of the ultramarine pigment prepared in the restoration of color paintings, this paper used the prepared ultramarine pigment and natural ultramarine pigment to draw paintings and then simulated diseases. Changes in Lab values of the two colors during the simulation process were recorded. The steps for preparing the color painting are below.

① A piece of pine wood with a size of 4 cm × 4 cm × 1 cm, and evenly saw multiple grooves of depth 1mm on the surface of the pine wood.

② The surface of the pine wood was coated with oil paste (a mix ratio of tung oil putty, blood glue, and water: 1:1:20), and let it dry after being fully soaked.

③ After the pine wood was dried, the gap-filling putty, uniform-leveling putty, medium-fine putty, and fine-finish putty were smeared on the surface of the pine wood in sequence. Each layer of putty was compacted, smoothed, and dried.

④ After the fine-finish putty was smeared, flattened, and dried, the surface was smeared with a fine sandpaper and smeared with raw tung oil.

⑤ The bone glue was dissolved and diluted in water, then added with the prepared ultramarine pigment, and stirred. The pigment was evenly smeared on the surface of the pine wood using a brush. The natural ultramarine pigment was treated the same way.

In the temperature and humidity cycling experiment, three samples of natural ultramarine paintings and three samples of prepared ultramarine paintings were taken respectively, and the Lab values of the surface colors of the samples were tested using a colorimeter. The six samples were then placed in a constant temperature and humidity chamber and kept in four environmental states, i..e., high temperature and high humidity, low temperature and high humidity, high temperature and low humidity, and low temperature and low humidity. Sixteen days were taken as one cycle. At the end of each cycle, the average Lab value of the surface color of the samples was measured using a colorimeter. The test lasted for four cycles.

In the ultraviolet aging experiment, three natural samples and three prepared samples were taken, and the Lab value of the surface color of the samples was tested using a colorimeter. Six samples were then placed in a ultraviolet aging chamber for simulated aging. The ultraviolet light intensity was set to 18 W/m^2, and the chamber temperature was 25 °C. Sixteen days were taken as one cycle. The average Lab value of the surface color of the samples was measured using a colorimeter at the end of each cycle. The experiment lasted for four cycles.

2.4 Test results

The colors and color differences from the natural ultramarine pigment obtained by the same preparation process of different ratios of raw materials are shown in Table 2. Samples A1 to A5 in the table were the products under different corn stalk addition amounts. As the corn stalk addition amount increased, the color of the product gradually changed to blue, and the color difference with the natural ultramarine also gradually decreased. But after exceeding a certain amount, the color of the product rapidly changed to black, and the color difference also increased rapidly. Samples B1 to B5 were products under different addition amounts of sodium carbonate. As the amount of sodium carbonate increased, the product changed from grayish-white to blue, the color difference gradually decreased, and when it exceeded a certain amount, the product color gradually deepened to black with variegated colors. Samples C1 to C5 are products under different addition amounts of elemental sulfur. As the amount of elemental sulfur increased, the product gradually changed from white to blue and then became darker, and white particles appeared.

Table 2

Colors of ultramarine pigments at different raw material ratios and color differences with the natural ultramarine pigment

Sample number	Color description	Color difference from the natural ultramarine ΔE
A1	White	4.67 ± 0.56
A2	Light blue	3.38 ± 0.08
A3	Blue	0.17 ± 0.03
A4	Dark blue	1.15 ± 0.16
A5	Black	4.52 ± 0.42
B1	Grayish white	4.63 ± 0.44
B2	Blue and white	3.41 ± 0.61
B3	Blue	0.16 ± 0.03
B4	Dark blue	1.24 ± 0.21
B5	Black with variegated colors	5.92 ± 0.08
C1	White	4.71 ± 0.41
C2	Light blue	2.79 ± 0.34
C3	Blue	0.15 ± 0.02
C4	Dark blue	1.11 ± 0.64
C5	Dark blue mixed with white particles	4.64 ± 0.13

From the comparison of the products composing of raw materials in different ratios mentioned above, it can be seen that when the coal gangue was 3.00 g, the waste molecular sieve was 1.00 g, the corn stalk was 2.00 g, the sodium carbonate was 3.00 g, and the elemental sulfur was 4.00 g, the prepared product was closest in color to the natural one.

The temperature and humidity cycling experiment was used to simulate real temperature and humidity changes in order to test the stability of pigments in color paintings under varying temperature and humidity, as shown in Figure 2 and Table 3. It can be seen from the figure that as the temperature and humidity in the chamber changed over time, the sample colors became increasingly different from the initial surface colors, i.e., the changes in environmental humidity and temperature will change the pigment color on the painting sample surface and become more obvious as time goes on. Under the same duration, the color difference produced by the samples using the prepared ultramarine was smaller than that of the samples using the natural ultramarine, indicating that the prepared ultramarine pigment was more stable than the natural ultramarine pigment in the face of periodic changes in temperature and humidity.

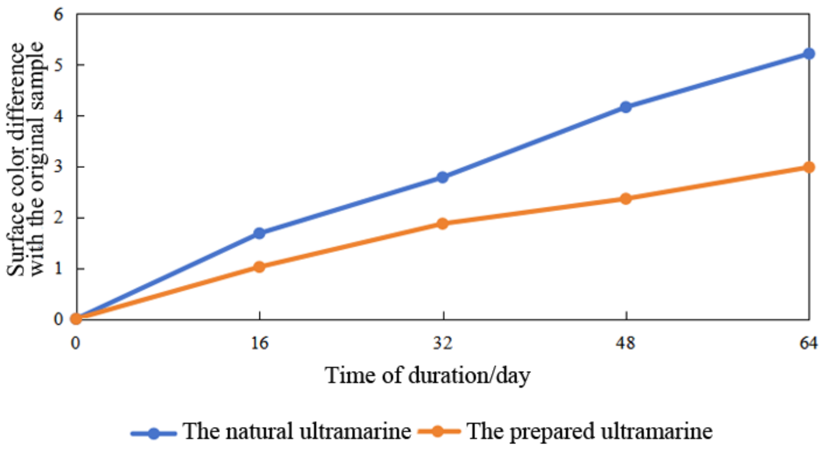

Fig. 2 Results of the temperature and humidity cycling experiment

Table 3

The results of the temperature and humidity cycling experiment

Time of duration/day	The natural ultramarine pigment	The prepared ultramarine pigment
0	0	0
16	1.68 ± 0.56	1.02 ± 0.31*
32	2.78 ± 0.43	1.87 ± 0.25*
48	4.16 ± 0.35	2.36 ± 0.21*
64	5.21 ± 0.46	2.98 ± 0.13*

Note: * indicates that the difference was significant at the level of 5%.

The ultraviolet aging experiment was used to simulate the sun exposure of real paintings to test the stability of pigments in paintings under sun exposure. It can be seen from Figure 3 and Table 4 that the color of the two kinds of samples became more different compared to the initial surface color as the exposure time of ultraviolet light increased, indicating that ultraviolet light in sunlight resulted in changes in the pigment color on the sample surface, and the longer the exposure time, the more the pigment deviated from the original color. Under the same exposure time, the color difference produced by the prepared ultramarine sample was smaller than that of the natural ultramarine sample, indicating that the prepared ultramarine pigment was more stable than the natural ultramarine pigment when exposed to ultraviolet light.

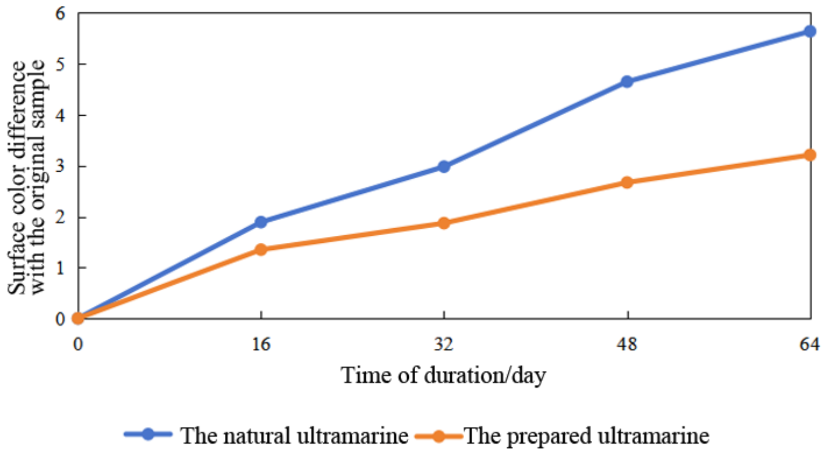

Fig. 3 Results of the ultraviolet aging experiment

Table 4

Results of the ultraviolet aging experiment

Time of duration/day	The natural ultramarine pigment	The prepared ultramarine pigment
0	0	0
16	1.89 ± 0.67	1.35 ± 0.26*
32	2.98 ± 0.68	1.87 ± 0.21*
48	4.65 ± 0.59	2.67 ± 0.18*
64	5.64 ± 0.45	3.21 ± 0.17*

Note: * indicates that the difference was significant at the level of 5%.

3. Discussion

As an important art form of human civilization, color paintings are widely used in murals, scroll paintings, architectural decorations, religious art, and cultural relics, carrying rich historical, cultural, and aesthetic values. Ultramarine pigment is a blue pigment with a long history, bright color, and excellent stability. Traditional ultramarine pigment is derived from lapis lazuli and obtained through complex grinding, rinsing, and purification processes. However, natural lapis lazuli resources are scarce, and excessive mining will damage the environment. With the increasing global emphasis on the concepts of environmental protection and sustainable conservation of cultural heritage, developing a new type of ultramarine pigment that is environmentally friendly, low in energy consumption, high in purity, and suitable for cultural relic restoration has become an urgent need in the fields of materials science and cultural relic protection. In this paper, waste materials such as coal gangue, waste molecular sieves, and corn stalks were used to prepare an ultramarine pigment. Then, simulation experiments tested the effects of different addition amounts of corn stalks, sodium carbonate, and elemental sulfur on the color of the ultramarine. The stability of the prepared ultramarine pigment in color paintings was tested through disease simulation experiments. As described above, the ultramarine pigment prepared from waste materials was nearly the same in color as the natural ultramarine pigment and showed higher stability in disease simulation experiments.

The innovation of this paper lies in the preparation of ultramarine pigment using waste materials such as coal gangue, waste molecular sieves, and corn straws, making full use of waste resources. The limitations of this paper are as follows. When testing the stability of the prepared pigment, the set cycle duration was not long enough, and more extreme environments, such as acid rain, were not set up. In addition, when designing the environmentally friendly pigment to replace the natural ultramarine pigment, this paper only considered the environmental friendliness of the raw materials. This study is a small-scale verification of the method of preparing ultramarine pigment from the above waste raw materials in the laboratory and did not fully consider the energy consumption and waste gas treatment during the preparation process. Therefore, the future research direction is to further verify the stability of the prepared pigment, and at the same time explore the energy consumption and waste gas treatment during the large-scale production of ultramarine pigment using the above-mentioned waste raw materials.

4. Conclusions

In this paper, an environmentally friendly ultramarine pigment was prepared. The effects of different corn stalks, sodium carbonate, and elemental sulfur addition amounts on the ultramarine color were tested in subsequent simulation experiments, and the stability of the prepared ultramarine pigment in painting was tested using a disease simulation experiment and compared with the natural ultramarine pigment. When coal gangue was 3.00 g, waste molecular sieves were 1.00 g, corn stalks was 2.00 g, sodium carbonate was 3.00 g, and elemental sulfur was 4.00 g, the prepared product was closest in color to the natural ultramarine pigment. The ultramarine pigment prepared was more stable than the natural ultramarine pigment in the face of periodic changes in temperature and humidity. The ultramarine prepared was more stable than the natural ultramarine when exposed to ultraviolet light.

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