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Case study

The effect of lead additives on ancient Chinese Purple pigment synthesis

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ABSTRACT

The effect of three kinds of lead additives on Chinese Purple synthesis was studied in this research. The barium source of the Chinese Purple was barium carbonate ($BaCO_3$), and three common lead additives in the ancient samples, lead oxide (PbO), lead sulfide (PbS) and lead carbonate ($PbCO_3$), were used in this study. The microstructures of the three additives were observed by SEM, and the thermal analyses of three formulation powders were conducted by TG. After the reaction, compositions and chrominance of the pigments were measured by XRD and colorimeter, respectively. It is shown that $PbCO_3$ could decrease the synthesis reaction temperature effectively, thus the pigment synthesis reaction could occur under the low temperature (720 °C–900 °C), and a brighter, purer Chinese Purple pigment could be obtained.

1. Research aim

Chinese Purple (Han Purple), a barium copper silicate, was the first anthropogenic purple pigment in ancient China. For its synthesis lead compounds were needed, and the function and introduction of these lead components were the most interesting part of the research concerning this pigment. But current studies were mainly focusing on the composition analysis and PbO was the major object of the lead additive research. However, with the booming of Chinese Alchemy (*Liandanshu*) in 3rd–2nd B.C., alchemists had been very skillful in obtaining lead compounds such as PbO, PbS and $PbCO_3$. In order to study the effect of lead additives on Chinese Purple synthesis, for the first time three lead compounds (PbO, PbS or $PbCO_3$) are used as additives to conduct simulated experiments with $BaCO_3$.

2. Introduction

Chinese Purple ($BaCuSi_2O_6$) was a kind of alkaline earth copper silicate with quite similar molecular structure to Egyptian blue ($CaCuSi_4O_{10}$). According to X-ray diffraction JCPDS database, there were four species of barium copper silicates: $BaCuSi_4O_{10}$ (Chinese Blue), $BaCuSi_2O_6$ (Chinese Purple), $BaCu_2Si_2O_7$ (Chinese Dark Blue) and $Ba_2CuSi_2O_7$. In ancient times, Chinese Purple ($BaCuSi_2O_6$), Chinese Blue ($BaCuSi_4O_{10}$) and Egyptian blue ($CaCuSi_4O_{10}$) were used as pigments and faience chromogenic substances, which could be described as a resonance of ancient Chinese and Western civilizations [1–4].

As early as the Warring States Period (475–221 B.C.), Chinese Purple was used in beads and colored paintings. It underwent booming development in the Qin and Western Han dynasties (221 B.C.–8 A.D), and then faded from history after the Eastern Han Dynasty. Its unique lead-barium constituent in the samples was quite similar to the basic composition of typical ancient Chinese lead-barium glass [5]. Lead additives were the unique parts in the lead-barium glass system and had two functions: on the one hand they served as the catalyst to accelerate barium minerals decomposition at lower temperatures, and on the other hand acted as the fluxes [6].

As to how the lead component was introduced into the system, different researchers hold different views. Zhao proposed that the lead additive was mainly introduced by calcining the galena (PbS) [5]. However, Li and Zhang found that the ancient Taoist and Alchemist research achievements in lead compounds might be the sources of lead, which made it possible to add $PbCO_3$, PbO and others into the synthesis formulation [7,8]. As a proof, $PbCO_3$ [8,9] and PbS [8] were often detected in some Chinese Purple samples.

In addition to the lead source discussion, Berke and Corbiere also worked on the purple pigment synthesis and came up with the PbO catalytic principle during the decomposition of $BaSO_4$. Both $BaCO_3$ and $BaSO_4$ could be the barium source in the Chinese Purple synthesis reaction. $BaSO_4$ was a very stable compound with a high decomposition temperature up to 1470 °C. However, in Berke's

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Table 1
Formulations of Chinese Purple with different types of lead additives.

Component No.	$BaCO_3$ (g)	SiO_2 (g)	$Cu_2(OH)_2CO_3$ (g)	Lead additives (10 wt.% PbO) (g)
F1#	5.03	3.06	2.84	PbO: 1
F2#	5.03	3.06	2.84	PbS: 1.1
F3#	5.03	3.06	2.84	$PbCO_3$: 1.2

$BaCO_3$: barium carbonate; PbO: lead oxide; PbS: lead sulfide; $PbCO_3$: lead carbonate.

work, with the accelerating help of lead oxide, decomposition reaction of $BaSO_4$ could take place and produce BaO at about 1000 °C [10]. Nevertheless, the effect of the different lead additives (PbO, PbS and $PbCO_3$) on $BaCO_3$ used for the Chinese Purple synthesis was not involved.

In this project, based on the previous studies, three kinds of lead additives, PbO, PbS and $PbCO_3$, were selected as the research object using solid phase method to study the effect on $BaCO_3$-Chinese Purple synthesis, optimize the formulation and lay a solid foundation for the simulation experiment of Chinese Purple products.

3. Experiments

3.1. The composition and microstructure research of lead additives

In this experiment, PbO and $PbCO_3$ were analytical reagents bought from Tianjin Fuchen Chemical Reagent Factory and PbS was laboratory-made according to the reaction equation below:

$$Pb(CH_3COO)_2\,(aq) + Na_2S\,(aq) = PbS \downarrow + 2NaCH_3COO\,(aq) \quad (1)$$

After fully ground in the agate mortar, the PbS was analysed by the RigakuD/max2200 XRD and then with the rest of two kinds of lead additives. The microstructure observation was conducted by using SUPRA - 55 SEM of ZEISS company.

3.2. Chinese Purple synthetic experiment

The $BaCO_3$-Chinese Purple basic formulation was prepared from analytical grade $Cu_2\,(OH)\,_2CO_3$, $BaCO_3$ and SiO_2 (Tianjin Fuchen Chemical Reagent Factory) according to the stoichiometry 1:2:4 [10]. After adding 10 wt.% (calculated with content of lead oxide) PbO, PbS and $PbCO_3$, F1#, F2# and F3# formulations (Table 1) were obtained and the powders were used to study the thermal process of reactions with the STA409PC thermal analyzer for thermal analysis. The scanning range was 30–1200 °C and the heating rate was 10 °C/min. Then, the TG and DTG curves were obtained.

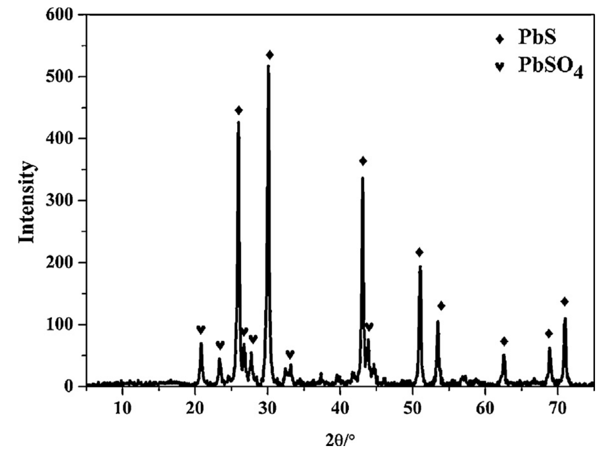


Fig. 1. The X-ray diffraction spectrum and analysis of homemade lead sulfide.

Finely grounded F1#, F2# and F3# were then put into clay crucibles, burned at 900 °C for 12 h in a muffle furnace. Finally, the products 1#–3# were obtained. The product powders were used for the colorimetric analysis conducted by JZ-300 universal colorimetric scanner (Kingwell company), the measured L, *a, *b data were processed with Adobe PhotoshopCS5 software to get the color swatches. In addition, the chemical compositions of the products were conducted by XRD test. The synthesis reaction equation of Chinese Purple was as below:

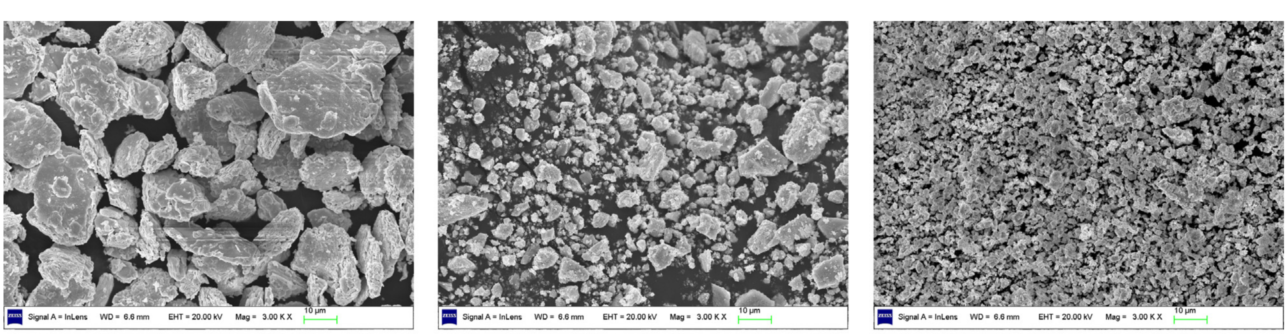
$$Cu_2(OH)_2CO_3 + 2BaCO_3 + 4SiO_2 \rightarrow 2BaCuSi_2O_6 + H_2O + 2CO_2 + O_2 \quad (2)$$

4. Results and discussion

4.1. The compositions and microstructures of lead additives

The composition analysis of homemade PbS product was shown on Fig. 1. By XRD spectrum, homemade product mainly includes PbS and a little $PbSO_4$ without any reactant. This suggests that the homemade PbS can be used for the next experiment.

As shown from the SEM photographs on Fig. 2, the particle size of PbO is about 10–20 μm and the grain size is uniform; the particle size of PbS is in a 5–30 μm range with an uneven distribution due to the $PbSO_4$ impurities while $PbCO_3$ has a minimum particle size of those lead compounds, which is only about 2 μm, and the particle size distribution is very uniform.



(a) (b) (c)

Fig. 2. The microstructures of three kinds of lead additives used in experiment: a: lead oxide (3k X); b: lead sulfide (3k X); c: lead carbonate (3k X).

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