

CHAPTER 3

SYNTHESIS OF ULTRAMARINE BLUE FROM FLY ASH

IN

**Aspects of solid-state chemistry of fly ash and ultramarine
pigments**



3. SYNTHESIS OF ULTRAMARINE BLUE FROM FLY ASH

3.1. Introduction

Ultramarine pigments come in different shades and colours, they are green, blue, greenish blue, reddish blue, violet, pink and red.¹⁻⁸ The sulphur content of these pigments was lower in the violet and red species than in the blue species. In 1828, JB Guimet in France and Christian Gmelin in Germany developed processes for the industrial production of ultramarine products.^{1,9} Several ideal stoichiometries for ultramarine blue were reported: for example $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_x$ (x between 1 and 4),^{4,10} $\text{Na}_{6.9}\text{Al}_{5.6}\text{Si}_{6.4}\text{O}_{24}\text{S}_{4.2}$,¹ $\text{Na}_{6.3}[\text{Al}_{4.79}\text{Si}_{7.21}\text{O}_{24}]\text{S}_{3.74}$ ⁶ and $\text{Na}_{7.5}[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_{4.5}$.⁷ Kaolin was the traditional starting reagent in the synthesis of industrial ultramarine blue (Figure 3-1).^{1,11-16} The ratio of Si to Al in kaolin is 1.16. The samples of fly ash used in this study also had a Si to Al ratio of 1.16 (Table 1-4). This ratio determined the amount of sulphur that could be incorporated into the structure.¹ In ultramarine pigments, sodium ions acted as counter-ions for both aluminium ions and polysulphide species. When fewer aluminium ions were present in the aluminosilicate framework, more sodium ions were free to act as counter-ions for the polysulphide species. More polysulphide molecules could, therefore, be incorporated into the structure. This led to a stronger colour.

Ultramarine was useful in the production of plastics, paints and powder coatings, printing inks, paper and paper coatings, rubber and thermoplastic elastomers, latex products, detergents, cosmetics and soaps, artists' colours, toys and educational equipment, leather finishes, powder markers, roofing granules, synthetic fibres, theatrical paints and blue mattes, cattle salt licks and as a white enhancer.¹ S_3^- , the blue species, and S_2^- , the yellow species,^{2,5,17} were stable in the aluminosilicate framework,^{18, 19} and the quality of the synthesized pigment depended on the quality of the aluminosilicate framework, in other words the framework should be defect-free.²⁰

The present industrial process (Figure 3-1) involved the activation of kaolin, also known as Chinese clay, at approximately 700 °C, after which it was reacted with a source of sodium, sulphur and a reducing agent (Table 3-1).^{1,11,19} Tarling and

others²¹ emphasized that the ratio of the furnace to the sample volume should be close to 1 in order to maintain a concentrated sulphurous environment. Sulphur was lost from the surface of the reagent mix due to over-oxidation. This loss led to a non-pigmentary outer perimeter, 10 to 20 mm thick, which was usually discarded.

3.2. Experimental

3.2.1. Synthesis

The traditional procedure for synthesizing ultramarine blue from kaolin began with clay activation, followed by the blending of raw materials, reductive heating, oxidative heating, and purification and refinement. The lefthand side of Figure 3-1 represents a traditional synthesis.¹ The procedure used for synthesizing ultramarine blue from fly ash differed from the traditional in that there was no clay activation involved – this step was redundant because fly ash was largely amorphous. The intermediate steps (blending of raw materials, reductive heating and oxidative heating) were the same. The last step was also different, but only because the scale of the synthesis differed. An industrial-scale version of the fly ash-based ultramarine blue synthesis would have the same final steps since the same products would be formed.

The process of synthesizing ultramarine blue using fly ash commenced with mixing sulphur (30 %), fly ash (36 %), carbon (4 %) and sodium carbonate (30 %) as starting reagents (Figure 3-1, Table 3-1) in a coffee mill to ensure optimal mixing of the reagents. The fly ash and sodium carbonate were mixed first, then the sulphur was mixed into the combined fly ash and sodium carbonate. Finally, the finely divided activated carbon was added. Because sulphur and carbon were two of the three ingredients of gunpowder, the carbon was added only after the sulphur had been mixed with the largely inert fly ash. The reagent mix was packed into an alumina crucible (height 50 mm, inner diameter 45 mm) with a ceramic tile lid. The crucible was filled to approximately 95 % capacity to minimize the amount of oxygen entrapped in the crucible, in accordance with the observations by Tarling and others.²¹ The filled crucible with its lid was placed into a muffle furnace, preheated to 750 °C. It was found that the synthesis was not successful if the crucible and furnace were allowed to heat simultaneously from room temperature to the desired

temperature. The carbon monoxide atmosphere reduced the elemental sulphur (S_8) at 750 °C. The time allowed for the reduction step was between 24 and 36 hours. After the reduction step, which yielded a green product, the crucible was opened to the air atmosphere of the muffle furnace, without any effort to establish a sulphur dioxide atmosphere, at 300 - 400 °C. The ultramarine green was now allowed to oxidize over a 48-hour period to form the desired ultramarine blue. The ultramarine product was milled in a coffee grinder and in an agate mortar. The fine powdery pigment was washed with boiling water to remove excess Na_2SO_4 . X-ray diffraction analysis revealed the importance of washing (Figure 3-2). The water-filtered product was then dried at 100 °C.

3.2.2. Kinetic Experiment

The oxidation of ultramarine green to ultramarine blue was followed by reacting 2 g portions of ultramarine green at 1 000 °C in a 5 % Au/Pt crucible in a muffle furnace for 10, 30, 60 and 90 minutes. The reacted samples were allowed to cool and later studied by Raman spectroscopy.

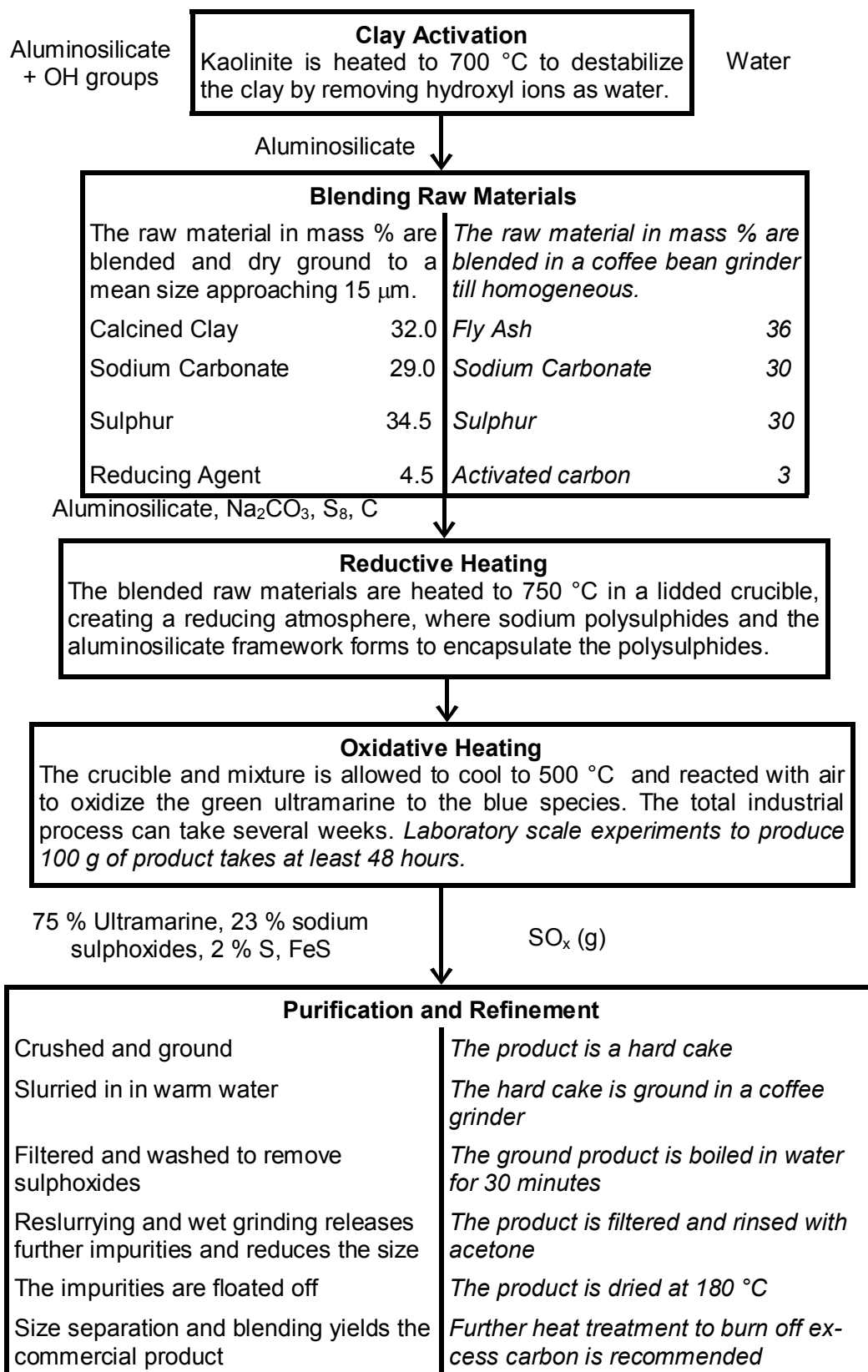


Figure 3-1: Flow diagram of the production of ultramarine blue; the left-hand side represents the industrial process, described by Cork,¹ and the right-hand side represents the reported process

Table 3-1: Raw mix compositions for ultramarine production^a

	Current work	ref 11	ref 11	ref 11	ref 12	ref 13	ref 14,15
Kaolin					37	31	34
Dried china clay		30	43				
Calcined china clay				34			
Diatomite		7	11	5			5
Fly ash	36						
Sodium sulphite						24	
Soda ash	30	28	41	31	37		31
Caustic soda			0.4				
Reducing agent (e.g. resin)						4	
Charcoal	4				4		
Rosin		4	5	2			2
Sulphur	30	31		28	22	41	28

a. Numbers indicate parts per mass and have been normalised to add up to 100

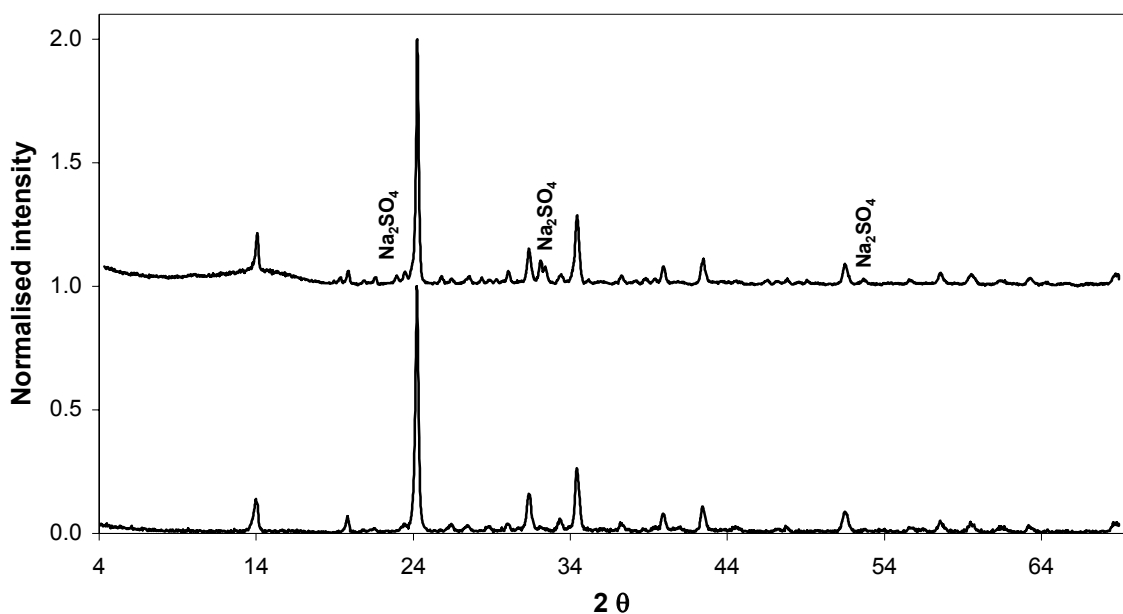


Figure 3-2: X-ray diffraction patterns of washed (bottom) and unwashed (top) ultramarine products identified as ultramarine blue, ultramarine red and Lazurite, and Na_2SO_4

3.3. Results and Discussion

X-ray fluorescence analysis indicated that, as far as the toxic trace elements were concerned, Lethabo fly ash was not significantly less environmentally friendly than kaolin (Table 1-4). The fly ash used contained more iron than kaolin. Iron in the aluminosilicate was known to be detrimental to the successful production of ultramarine,^{22,23} and this should be taken into account when the process is applied on a larger scale.

The reaction was repeated several times, with an 80 % success rate. When water vapour was allowed to come into contact with the reagents, the synthesis was unsuccessful. As described above, the heating method also played an important role. Changes in the composition, viscosity and heat capacity of the sulphur melt and vapour^{16,24,25} were probably responsible for the increased reactivity of the fly ash during the formation of the ultramarine pigments. The fact that these pigments formed only when the reactant mixture was added to a preheated furnace could be ascribed to the nature of sulphur.^{16,24,25} The ultramarine blue laboratory synthesis resulted in an agglomerated pigment cake. The caking coincided with an increase in the volume of the reagents, which sometimes caused the ceramic tile lid to become cemented to the crucible. At other times, the ceramic tile lid broke and the reduction process was not completed. The agglomerated pigment cake had a distinctive layered appearance (Figure 3-3) and the top part of the cake was grey due to the loss of dopant caused by excessive firing time. The agglomeration necessitated grinding, which influenced the colour strength.

The X-ray diffraction patterns of the products (Figure 3-2) compare well with the X-ray diffraction patterns²⁶ of ultramarine blue and ultramarine red, as well as lazurite, the naturally-occurring archetype. Sodium sulphate was also present in the unwashed samples, as can be seen from the X-ray diffraction patterns (Figure 3-2). The X-ray diffraction patterns for different ultramarine species were similar.¹⁹

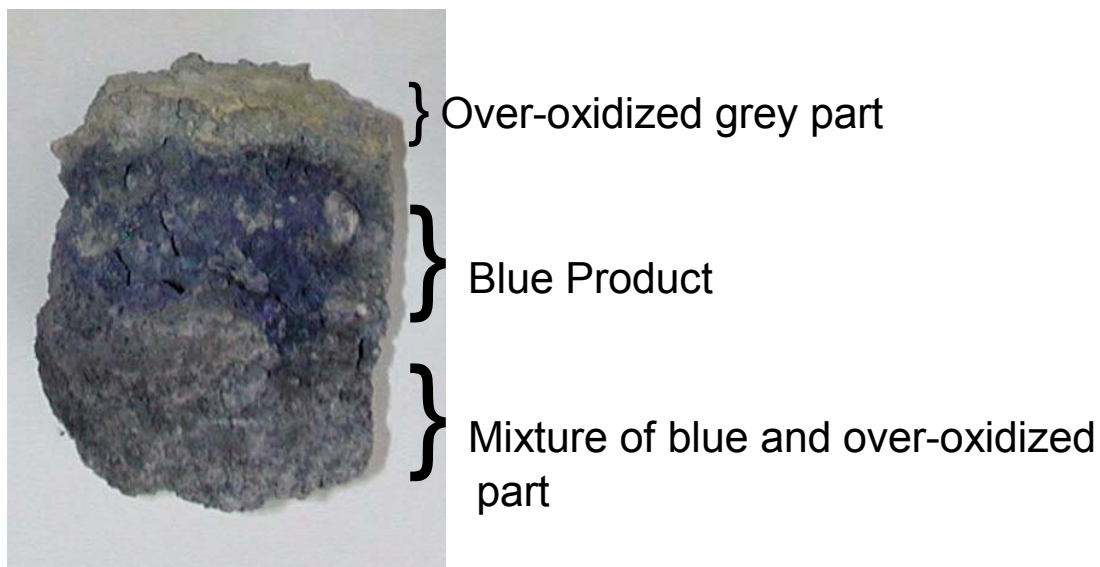


Figure 3-3: Agglomerated layered pigment cake formed during the synthesis of ultramarine blue, using fly ash as a starting reagent

The infrared spectra showed the aluminosilicate framework of this pigment, but the bands related to the chromophore species were obscured (Figure 3-4). Clark and

Cobbold² obtained the infrared spectrum of ultramarine blue in a Nujol mull and observed a strong band at 582 cm^{-1} , assigned to ν_3 of S_3^- , and a weak band at 547 cm^{-1} , assigned to ν_1 .² These bands were visible in the infrared spectrum of ultramarine blue reported by Afremow and Vandenberg,²⁷ but only the 582 cm^{-1} band was visible in the current infrared spectra (Figure 3-4), which accorded with the literature.^{4,28} The spectrum, however, was undoubtedly that of ultramarine blue, which confirmed the identity of the product.

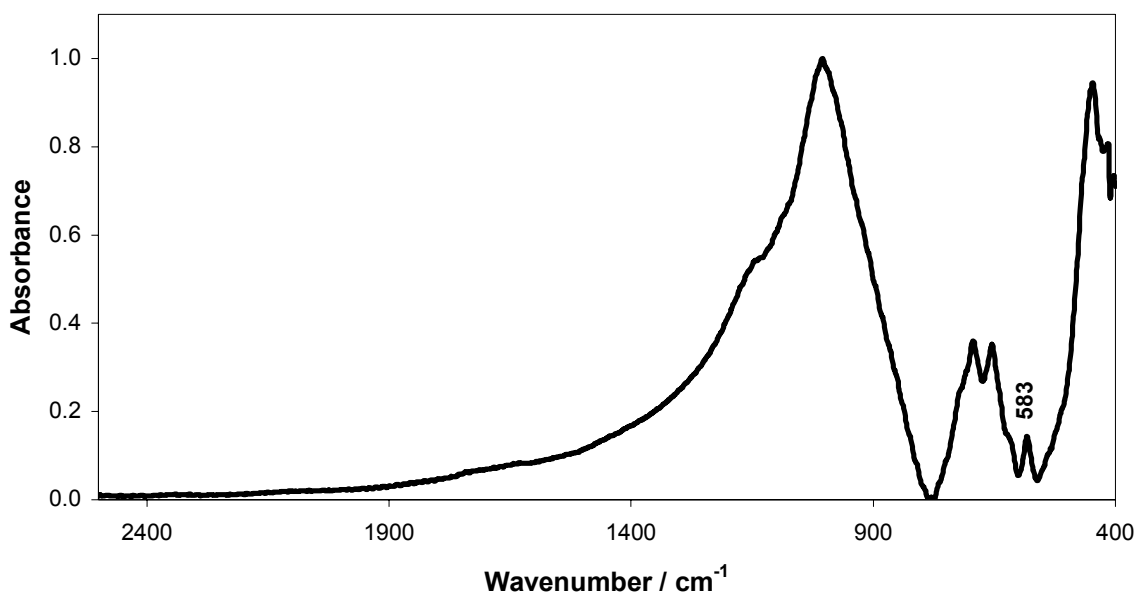


Figure 3-4: Infrared spectrum of the ultramarine blue product obtained from this process between $2\ 500\text{ cm}^{-1}$ and 400 cm^{-1} ; the band at 583 cm^{-1} was assigned to ν_3 of S_3^- .

The observed Raman spectra of the prepared ultramarine blue and industrial product were compared (Figure 3-5). It was found that the spectra of the prepared product corresponded to those presented in the literature.^{4,5,16} The assignments of the observed bands were known from the literature (Table 3-2).^{4,16,29}

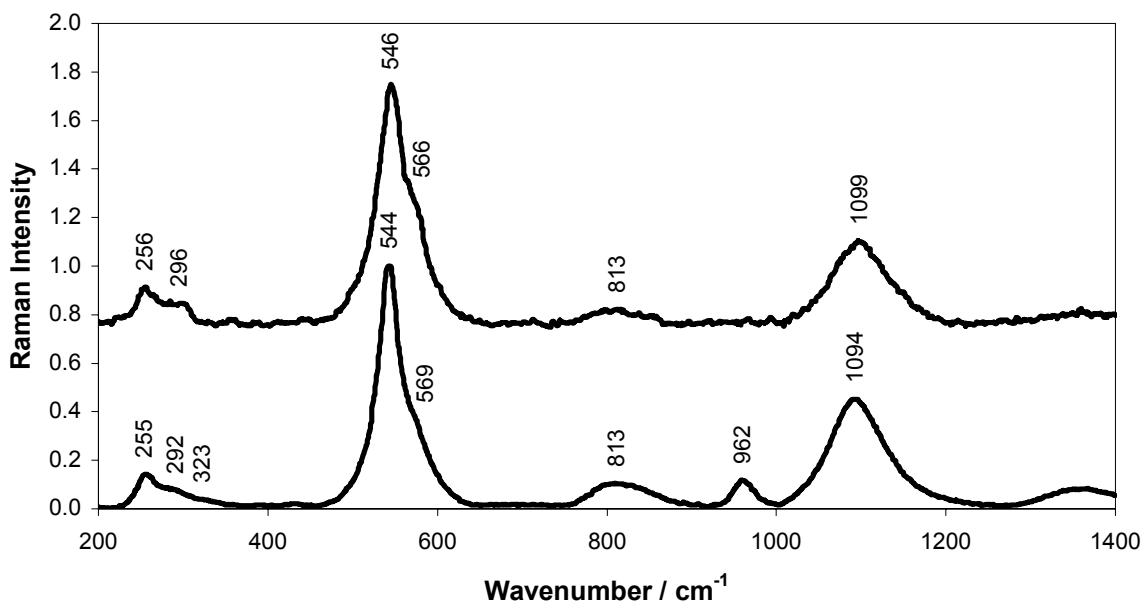


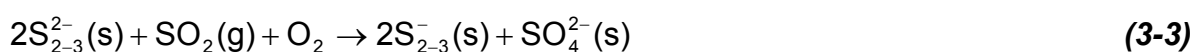
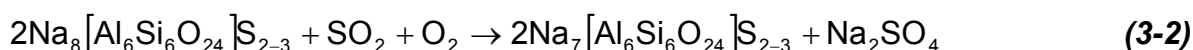
Figure 3-5: Raman spectra of the ultramarine species obtained (bottom) and an industrial ultramarine blue sample (top)

Table 3-2: Assignments of Raman bands for ultramarine products^a

Lazurite	Ultramarine Red	Industrial Ultramarine Blue	Ultramarine Blue	Assignment ^b
258w b ^c	216w b	255w b	257w b	-
Obs ^e		293sh	287sh	S ₃ ⁻ Bending ^d
			323sh	-
548st s	461w b	545st s	543st s	S ₃ ⁻ Symmetric stretch
Obs ^e		568sh	573sh	S ₂ ⁻
822w b	626w b	813w b	804w b	-
	994st s		967w b	Si-O
1096m b		1097m b	1092m b	S ₃ ⁻ Overtone

- The following notation is used to describe the intensity and general shape of the peaks: w – weak, m – medium, st – strong, b – broad, sh – shoulder, s – sharp
- From references 4 and 29
- The description given differs from those in the cited reference, so as to have the same notation as the rest of the data
- In accordance with the plausible assignment by Chivers and Drummond¹⁷
- The corresponding bands were observable, but were not assigned in reference 29

Ultramarine blue was synthesized in two steps (Equation 3-1): a reduction step, followed by an oxidation step. However, the nature of these steps was disputed. Some authors endorsed Equation 3-1,^{2,5,17,30} whereas others promote the questionable existence of divalent species as in Equation 3-2^{11,32,31} and Equation 3-3.^{1,32}



Beardsley and Whiting¹¹ described the production of ultramarine blue and mentioned that oxygen was originally used as oxidizing agent; these authors introduced the use of SO₂ in the synthesis of ultramarine blue. For the current synthesis any sulphur dioxide formed during the oxidation of ultramarine green was vented from the furnace, as evidenced by the smell. The evolved SO₂ should be treated in an environmentally friendly way. Nevertheless a blue oxidation product was observed. Oxygen was probably responsible for the oxidation process, without the help of external SO₂. Gorshtein's mechanism^{32,31} was based on the slow participation of oxygen in the transformation from the green to the blue species. The present evidence suggested that it was possible that external SO₂ did not play a role in the reaction.

Gorshtein^{32,31} (Equation 3-2 and 3-3) successfully explained the formation of Na₂SO₄ and the role of SO₂, noted by Tarling and others,²¹ and Gobeltz and others.¹⁸ However, this explanation was premised on the basis of the questionable identification of both S₃²⁻ and S₂²⁻ as the species responsible for the yellow chromophore, and of both S₃⁻ and S₂⁻ for the blue chromophore. These assignments were questionable in the light of the evidence that S₃⁻ was responsible for the blue colour, and S₂⁻ for the yellow colour.^{2,5,17} No spectroscopic evidence of the divalent species was recorded in the literature, nor in the current observed spectra. Molecular modelling results, however, support this hypothesis (Chapter 5). Weller and others,³³

who synthesized ultramarine from thiocyanate sodalites, concluded that a colourless polysulphide sodalite was the initial product at high temperatures. They maintained that this initial product underwent a secondary in-cage reaction, producing the coloured polysulphide radical anions *in situ* when heated in SO₂ at about 500 °C. The presence of a doubly charged species might be supported by the formation of a noselite-like (nosean) phase, which implied that divalent anions are present, with only half the cages occupied.³³ The high ratio of sulphur atoms to unpaired electrons in the ultramarine green species found by Hofmann and others⁶ supported the possibility of the existence of divalent non-radical sulphide species in the green ultramarine pigments. The validity of these results is, however, questionable.³⁴

Gobeltz-Hautecoeur and others³⁴ suggested that the intermediate sulphur species was S²⁻. S²⁻ would not be observable by infrared spectroscopy, nor by electron paramagnetic resonance spectroscopy. Therefore, S²⁻ was favoured above S₃²⁻ and S₂²⁻ to be the intermediate species. Köhler and others³⁵ were able to synthesize ultramarine yellow from the thiocyanide derivative of sodalite. They confirmed that the yellow chromophore is S₂⁻ and that the oxidation of ultramarine yellow leads to the formation of ultramarine green, with the simultaneous formation of S₃⁻. The evidence supports the formation of S₃⁻ from S₂⁻ rather than from S₃²⁻.

For the kinetic study the band at 545 cm⁻¹ and the shoulder at 580 cm⁻¹ in the Raman spectra of the heated ultramarine green were fitted with Gaussian-Lorentzian peaks and the intensity ratio of these two fitted peaks was used to estimate the relative concentrations of the S₃⁻ species and the S₂⁻ species (Table 3-2). Because the concentrations of the individual species were not known³⁴ no direct kinetic study could be done on the reactions with the current data. The pseudo-kinetic analysis did, however, lead to a mathematical description of the generally observed trend that the ratio of S₃⁻ to S₂⁻ increased as the green ultramarine species changed to the blue species.^{2,5,18,30} A plot of Equation 3-4 indicated that the transformation from S₂⁻ to S₃⁻ was pseudo-second order relative to the ratio of the concentration of the S₂⁻ species and the concentration of the S₃⁻ species (Appendix B1, Figure 3-6), with a rate constant, k, of 0.060 ± 0.002 min⁻¹. The second-order kinetics might indicate that two S₂⁻ molecules were needed to react with each other for S₃⁻ to form.

$$\frac{1}{R} - \frac{1}{R_0} = kt \quad (3-4)$$

where R is the ratio of the peaks in question and R_0 is the ratio of the peaks at time 0.³⁶

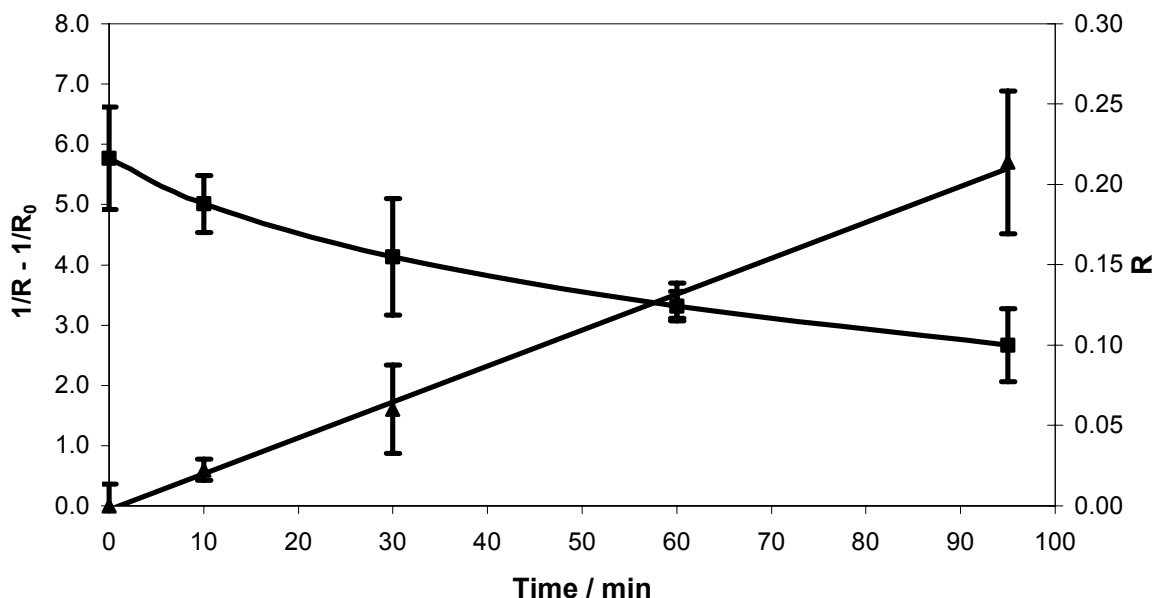


Figure 3-6: Plot of the ratio, R , between the concentration of the $S_2^{\cdot-}$ species and the concentration of the $S_3^{\cdot-}$ species, against time (right axis, ■); plot of the second-order rate law for the conversion of $S_2^{\cdot-}$ to $S_3^{\cdot-}$ (left axis, ▲)

The synthesized blue pigment was dark blue. A drawdown test (Figure 3-7) indicated that the pigment contained some black contaminants. These contaminants were not visible in the pigment because of the dark colour of the ultramarine blue pigment. The black contaminants were made visible by the drawdown test, because the black contaminants and the ultramarine blue had different colour strengths. The drawdown test further indicated that the current ultramarine blue product was of weaker colour strength than the industrial pigment. The prepared pigments were also tested within plastic samples (Figure 3-8).

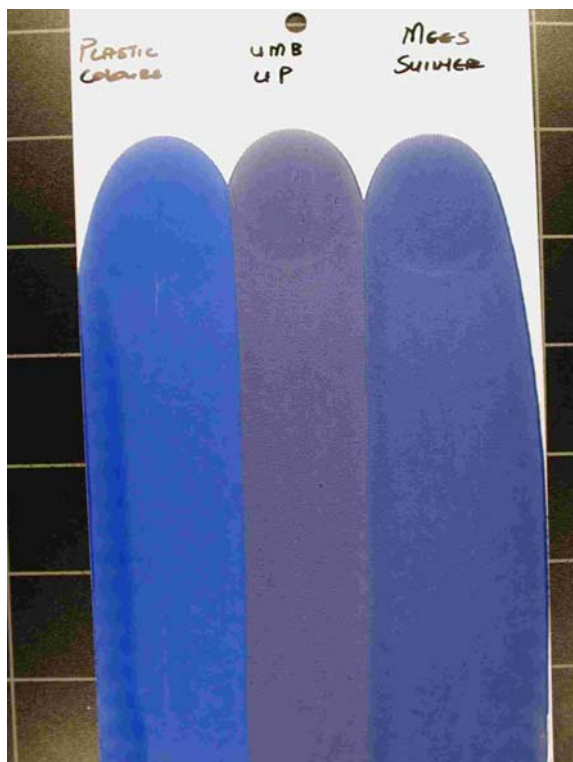


Figure 3-7: Drawdowns of two sets of ultramarine products from this research and a commercial standard



Figure 3-8: Plastic samples prepared with ultramarine products from this research and a commercial standard as pigments

According to Cork,¹ the mean particle size of a commercial product ranged from 0.7 to 5.0 μm . This was considerably smaller than the particle size of the current ultramarine product. The weaker colour strength of the product could be due to its larger particle size and the related higher crystallinity. This higher crystallinity was demonstrated by the higher Raman intensities of the current product compared with those of the commercial pigment. A further improvement in the product quality could possibly be obtained by discarding the white or grey over-oxidized parts before milling. The use of fly ash as starting reagent for the synthesis of ultramarine blue would be beneficial to the environment because less fly ash would end up as landfill. Since only one size fraction of fly ash was used to synthesize the ultramarine blue product, other size fractions need to be tested and evaluated. The non-magnetic fraction of fly ash could also be tested (for a further discussion on future possibilities see Chapter 7).

3.4. Conclusions

The traditional starting reagent for the synthesis of ultramarine blue, namely kaolin, had to be heated before the synthesis to weaken the structure of the kaolin. Two batches of fine fly ash were successfully used to synthesize ultramarine blue. Infrared, Raman and X-ray diffraction results confirmed the formation of the product. Fly ash had the advantage over kaolin of being amorphous. The results further showed that the transition from the green ultramarine species to the blue species coincided with an increase in the ratio of the amount of S_3^- species relative to the amount of S_2^- species.

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