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Chemical degradation and mineralogical transformations on based lime blue pigment

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***Abstract* – The aim of the study is to explain the process of chemical degradation in short times of the ultramarine blue pigment [$Na_3Ca(AlSi_3O_{12})S$] when used mixed with lime in a highly basic environment for applications on the outside of stone supports or mortars. For the study, mixtures were produced with only lime and commercial ultramarine blue and also with the red pigment based on ferric oxide (hematite). The mixtures were studied and analysed by optical microscopy and Raman to define the transformations of the original crystalline phases into any new secondary phases.**

I. INTRODUCTION

In the restoration of Cultural Heritage today, it is common to use plaster produced using lime as a binder together with inorganic pigments in the restoration of paintings on facades or other surfaces of monuments. Studies on ancient mortars, plasters, and paintings generally focus on the compositional characterization of the raw materials used in their production, including pigments, rather than on long-term degradation [1, 2, 3, 4]. However, only a few scientific studies address the negative aspects of immediate degradation processes, after (or during) preparation, which could be useful as precautions during restoration.

Without considering the alteration processes that lime-based products undergo once installed (dissolution, sulphation), finishing products made with a hydrated lime-based binder can undergo further chemical-mineralogical alterations due to the aggressiveness of the alkaline paint mixing solution.

This study specifically aims to analyse the degradation of the ultramarine blue pigment [$Na_3Ca(AlSi_3O_{12})S$] when used in a mixture with hydrated lime for applications on the external surfaces of stone substrates or mortars. In particular, the research intends to define the chemical interactions and any mineralogical transformations of the ultramarine blue and Venetian red pigments mixed with cyclonate lime putty [$Ca(OH)_2$] without the use of aggregate. The experimental mixtures were analysed using Raman to define the transformations of the original crystalline phases into any new secondary phases or chemical alterations.

II. MATERIALS AND METHODS

A. Experimental mixtures

For the study, following six mixtures were produced (Fig. 1) using for comparison also another pigment (red ferric oxide: hematite) which not shows an evident alteration in alkaline environmental:

1. ultramarine blue pigment + water (named as P-Blu-W);
2. red pigment + water (P_R_W);
3. ultramarine blue pigment + red pigment + water (P_B_R_W) (using the same concentration used on the following blue-red mix);
4. ultramarine blue pigment (50 ml) + *grassello* (300 ml) (P_Blu_G);
5. red pigment (10 ml) + *grassello* (300 ml) (P_R_G);
6. ultramarine blue pigment (50 ml) + red pigment (10 ml) + *grassello* (300 ml) (P_B_R_G).

The three experimental last mixtures (P_Blu_G, P_R_G, P_B_R_G, were placed inside closed containers without CO_2 (Fig. 2) to define any chemical-mineralogical trasformation.

B. Analitycal methods

To define the compositional features of the mixture specimens, optical microscopy in reflected light (OM-RL) was used using an Olympus DSX100 digital microscope.

Infrared micro Raman scattering measurements were carried out in back scattering geometry with the 1064 nm line of an Nd:YAG laser, by a compact spectrometer B&WTEK (Newark, NJ, USA) i-Raman Ex integrated system with a spectral resolution of 8 cm^{-1}.

Spectra were collected with an acquisition time of about 30-60s and power excitation between 20 and 40 mW concentrated in a spot of 0.3 mm^2 on the surface through a Raman Video MicroSampling System (Nikon Eclipse for high-resolution and BAC151B in the other case) equipped with 20X/50X Olympus objectives.

III. COMPOSITION OF BLUE PIGMENTS

The naturally occurring pigment ultramarine blue is one of the oldest and most valuable blue pigments, renowned for its intense, deep colour. It was originally produced by grinding lapis lazuli.

Fig. 1. Experimental mixtures produced at time t_0 placed in contact with the air (so also CO_2).

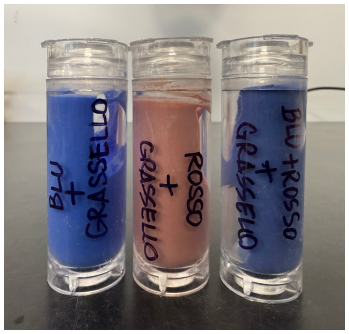

Fig. 2. Experimental mixtures produced at time t_0 placed inside closed containers (without CO_2).

Lapis lazuli is composed of a combination of various minerals from the sodalite group, the principal one being lazurite, a complex silicate with the generic formula $(Na_2,Ca)_2$ $[(Cl,NaS_3,NaSO_4)Al]$ $Al_2(SiO_4)_3$ or $Na_3Ca(Al_3Si_3O_{12})S$. Calcite (secondary mineral) and pyrite are also associated with it. Accessory minerals (not always present) include: sodalite, another blue mineral similar to lazurite; hauyne, a member of the feldspathoid group, similar in colour to lazurite but lighter; nosean, a feldspathoid similar to sodalite, greyish or bluish in colour; diopside, a pyroxene that can occur in small quantities, especially in some varieties of lapis lazuli; and scapolite, found in certain deposits, which can influence the rock's structure.

Depending on the different mineral compositions, lapis lazuli can exhibit colour variations from a deep, opaque ultramarine blue to green-blue, purplish, or grey. It is often found uneven, dotted with spots and even golden flecks due to the bright pyrite.

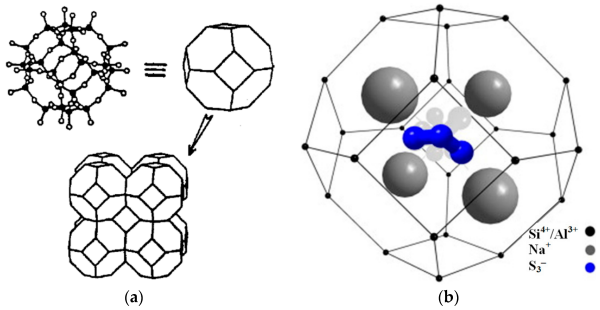

Fig. 3. (a) sodalite structure composed of β-cages and packing type [5]; (b) blue chromophore S_3^- anions encapsulated in β-cages and surrounded by Na^+ cations [6].

Synthetic ultramarine is an artificial pigment that reproduces the intense blue colour of natural lapis lazuli, but with a controlled composition and a much lower cost. In 1828, French chemist Jean-Baptiste Guimet discovered a way to produce ultramarine synthetically, making it accessible to artists. The pigment was called "Guimet bleu" for a time. It was one of the first synthetic pigments to be mass-produced in the 19th century. The active component of synthetic ultramarine is a feldspathoid of the sodalite group, called synthetic lazurite with the approximate chemical formula: $Na_7Al_6Si_6O_{24}S_3$ which has a cubic sodalite structure (Fig. 3), with tri-sulphide ions (S_3^-) embedded in the channels of the crystal structure that are responsible for the intense blue colour [7]. Tri-sulphide ions (S_3^-) is a radical anion with an unpaired electron, composed of three sulphur atoms bonded in a straight line or at a slight angle.

The synthetic pigment is produced in furnaces at controlled temperatures, between 700–800°C, in a reducing environment by mixing the following basic components: silica, to provide the backbone of the structure; alumina for part of the sodalite structure; soda (Na_2CO_3 or Na_2SO_4), a source of sodium; sulphur for the S_3^- anions responsible for the colour; calcium carbonate, sometimes used as a flux or reaction medium; charcoal or pitch as reducing agents necessary for the formation of the S_3^- ions. The mixture is ground and forms a dry or granular paste, and then it is heated in closed furnaces, leading to the formation of a sodalite/lazurite-like structure. The reduced sulphur forms S_3^- anions, which are trapped in the crystalline structure, giving it the

typical intense and homogeneous blue colour. S_3^- absorbs light in the orange region of the visible spectrum (wavelengths of approximately 590–620 nm), and consequently, due to selective subtraction, our eye perceives complementary light, namely blue.

IV. RESULTS

A. Compositional characterization of pigment samples

From the Raman measurements carried out on the blue pigment (Fig. 4), it is possible to state that it is a synthetic lazurite, as main component, whose characteristic peak is found at 548 cm^{-1} with a shoulder around 580 cm^{-1}. The same pigment also shows the presence of pyrite (peak at 363 cm^{-1}), probable resulting from residual by-products of the synthesis process. The red pigment (Fig. 5), on the other hand, exhibits the characteristic peaks of hematite at 225, 290, 411, 496, and 611 cm^{-1}. In addition, the spectrum reveals the presence of calcium sulphate, identified by the peaks at 1006 and 1136 cm^{-1}.

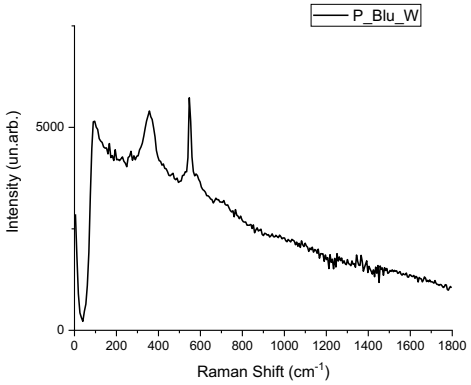

Fig. 4. Raman spectra of sample P_Blu_W realized with the blue pigment and water (then evaporated).

A. Blu pigment degradation on alkaline conditions

To test the degradation process of the blue pigment in an alkaline environment, two different tests were carried out on different mixtures (i.e., blue pigment, red pigment, blue + pigments) in the presence of hydrated lime (*grassello*) with curing (1) in the air in the presence of oxygen and CO_2, and with curing (2) in an isolated environment container in the absence of oxygen and CO_2.
The blue pigmented sample (labeled P_Blu_G) with *grassello* is characterized (Fig. 6) by the presence of lazurite (548 cm^{-1}), calcite (1087 and 276 cm^{-1}), due to the carbonation of hydrated lime, portlandite (hydrated lime not carbonated) identified by a luminescence band with a maximum at 780 cm^{-1} and pyrite (363 cm^{-1}).
In the P_Red_G pigmented sample with *grassello* (Fig. 7), the luminescence band associated with portlandite, centered at 780 cm^{-1}, is also observed, along with the characteristic calcite peaks at 1087 and 276 cm^{-1}. In this spectrum, the presence of hematite can also be confirmed, although it is not very prominent, by the peak at 411 cm^{-1}.

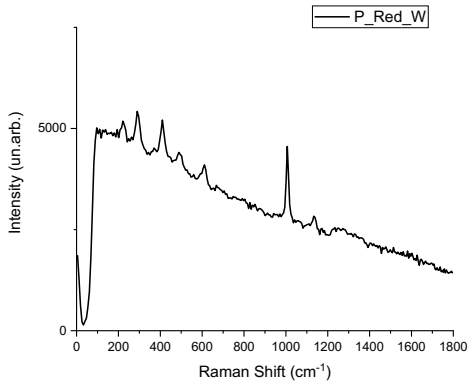

Fig. 5. Raman spectra of sample P_Red_W realized with the red pigment and water (then evaporated).

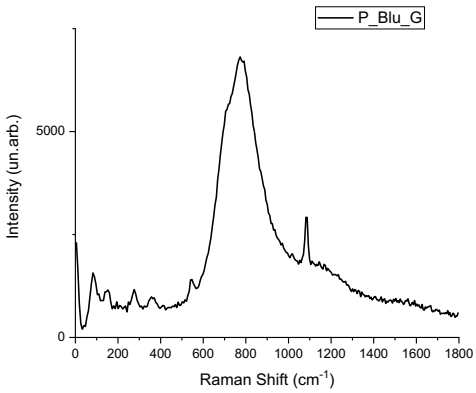

Fig. 6. Raman spectra of sample P_Blu_G realized with the blue pigment and grassello.

In the mix sample (Fig. 8) with blue (50 ml), red (10 ml) pigments and *grassello* (300 ml) put in an isolated environment container in the absence of oxygen and CO_2, we can see very well the portlandite, but we don't clearly see the presence of the two pigments. Obviously we cannot see the calcite due to the absence of $Ca(OH)_2$ carbonation. The characteristic spectra of the two pigments are not clearly visible in Fig. 8. In particular, the phases of the original blue colour (lazurite), attributable to a sodalite structure, has undergone partial structural destruction due to the aggressive action of the alkaline environment (with a pH of 12,5), with the separation of the tri-sulphur ion chromophore (S_3^-) from the β-cage. Therefore, it spontaneously decomposes, transforming into more stable sulphur species in the absence of oxygen (S^{2-} ions, sometimes also elemental sulphur S^0), typical in highly alkaline environments. The phases of red pigment are not clearly visible (Fig. 8), due to the low concentration of this pigment in the solution

(10 ml) with respect to the blue pigment (50 ml).

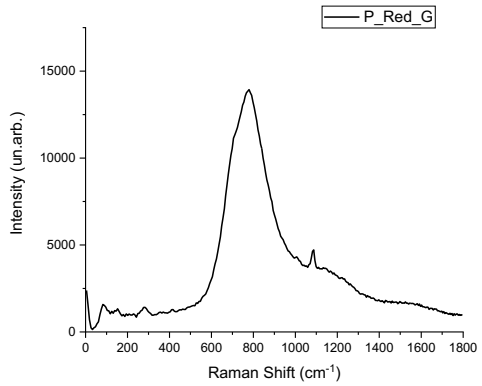

Fig. 7. Raman spectra of sample P_Red_G realized with the red pigment and grassello.

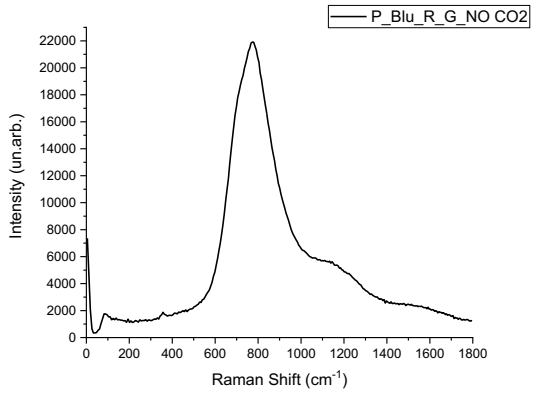

Fig. 8. Raman spectra of P_Blu_R_G realized with the blue (50 ml), red (10 ml) pigments and grassello (300 ml) in isolated environment in absence of oxygen and CO_2.

In Fig. 9 we can observe the three prepared mixtures (P_Blu_G, P_Red_G, P_Blu_R_G, respectively) inside the closed containers in absence of oxygen and CO_2, in which the mixes P_Blu_G and P_Blu_R_G show a fairly evident discoloration after 1 week of curing, while the mix made with the red pigment and the lime does not show any discoloration, demonstrating good resistance even in the presence of a strongly alkaline environment.

V. CONCLUSIONS

The results indicate that when the mixtures are not immediately put into use a contact with air a series of reactions occur that gradually lead to a discoloration of the original shades of ultramarine blue towards light shades, especially when the product is stored inside closed containers in the complete absence of CO_2. When Venetian red is used in combination, the final shades following degradation of the mixture produced take on the colours of the unaltered subordinate pigment, i.e. towards pinkish, although with lower intensity than the colour of lime – red pigment mixture (without blue). The changes of ultramarine blue pigment from blue to whitish (or pink if used with red pigment) in the absence (or slow) carbonation in a strongly basic environment (with pH about 12,5) induced by lime putty $Ca(OH)_2$ are due to a combination of chemical factors involving the chromophores (S_3^- ions) with their leaching from the lazurite crystal-structural β-cage.

Fig. 9. Experimental mixtures at time t_1 (1 curing week) inside closed containers (without oxygen and CO_2).

VI. REFERENCES

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