Methodology for the Correct Reproduction of Megalithic Paintings: Substrates and Binders

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Abstract. *Rock art researchers describe the existence of a preparation layer of kaolin (with or without organic binder) on the rock, on which megalithic painting was carried out, using a mixture of pigment and binder. The natural pigments used were mainly hematite, ochre and carbon black. As binders, animal fats, blood, resins, etc. were reported. The uncertainty regarding the composition of these paintings means that there is not a clear procedure for their reproduction in the laboratory as mock-ups. This study shows a methodology based on the assessment of a group of parameters that allow assessing the suitability of a binder (in this case, butter or casein) both in the preparation layer and in the pictorial layer. Covering capacity, drying velocity, binding capacity, grip on the substrate and biological growth were evaluated. It was completed with colour spectrophotometry and scanning electron microscopy. The mixture of butter with pigment applied on a kaolin-based substrate was identified as the most suitable.*

Keywords. Rock art, pigment, ochre, binder, butter, casein, conservation

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1 Introduction

Megalithic paintings are understood to be those expressions created by humans, approximately between the V millennium B.P. and the end of II millennium B.P. They were found on dolmens, shelters, stelae, etc. The main pigments were hematite, goethite, clays and black carbon from the combustion of organic materials such as wood [1-2]. The ochre pigment appeared at least collected in some dolmens studied in Galicia, NW Spain [3]. In the characterized megalithic paintings, blood, urine, egg, vegetable resins, animal fat or casein are usually reported as binders for the pigments [4-6], the latter two being the most common. The use of organic binders has even been reported in the kaolin preparation layer under the paintings of one of the most important dolmens in NW Spain, the Dombate dolmen [4]. Despite the existing hypotheses about the composition of these paints, mainly about the organic binder, no clear and systematic methodology has been found for the laboratory recreation of paint mock-ups. Mock-ups can be exposed to different tests; with them, it will be possible to know their behaviour when are exposed to a polluting gas or to determine the most effective cleaning techniques for this heritage without threatening the integrity of a real work.

This study presents a work methodology to verify the adequacy of the use of organic binder (butter or casein, from animal milk) both in the kaolin preparation layer and in the pictorial layer. Pigment was mixed with butter or casein, either mixed directly or previously dispersed in water.

2 Material and Methods

2.1 Materials

The following materials were purchased: commercial skimmed milk to obtain the casein, commercial clarified butter, kaolin from a quarry in Vimianzo (A Coruña, Spain) with an aggregate size of 50 µm and Ochre Yellow SA pigment with reference PY43.77492 provided by Kremer Pigmente GmbH & Co. .KG. The skimmed milk was mixed with glacial acetic acid to obtain the casein. This was diluted in water (1:3, casein:water by weight) at 30°C. The butter, of industrial origin, was simply heated in a glass to 50ºC. The kaolin was kneaded with deionized water in a 5:2 ratio (kaolin:water by weight). Three types of paste were made (Table 1, check substrate section): kaolin, kaolin mixed with 5% butter (by weight) and kaolin with 5% diluted casein (by weight) and a few drops of NH_3 (2% by weight regarding the diluted casein and added by a Pasteur pipette).

Each paste was applied in Petri dishes (55 mm in diameter) following the methodology described in [4]. Two layers were applied in each dish. Special care was taken in their compaction. To avoid cracks, drying was done by partially covering them. The samples were left for 7 days under laboratory conditions (15±5ºC and 60±10% RH) to identify which of the paste compositions were more suitable as substrates for the application of the paints.

Once suitable substrates were selected, the paint was applied with a brush. As indicated in Table 1 (check paint conditions), 3 types of paint were made: 1) pigment with butter, 2) water dispersed pigments with butter, 3) pigment with diluted casein (1:3, casein:water by weight) with addition of NH3 (Table 1). The application was made with the wet substrate; similar conditions to those that can be found in dolmens and shelters. The samples were evaluated 7 days under laboratory conditions.

Table 1. Substrate and paint compositions.

SUSBTRATE		
Kaolin	***Kaolin+butter***	***Kaolin+diluted casein+ NH_3***
Kaolin: 300 g H_2O: 120 g	Kaolin: 300 g H_2O: 120 g Butter: 21 g	Kaolin: 300 g H_2O: 120 g 21 g casein:water (1:3 wt.) + 1.68 g NH_3
PAINT CONDITIONS		
Ochre +butter	***Ochre+water+butter***	***Ochre+diluted casein+NH_3***
Pigment: 1 g Melted butter: 2 mL (50ºC)	Pigment: 1 g Water: 1 mL Melted butter: 2 mL (50ºC)	Pigment: 1 g 4.28 g casein:water (1:3 wt.)+ 0.15 g NH_3

2.2 Methods

2.2.1 Characterization of the pigment

The mineralogical composition of the Ochre Yellow SA pigment was determined using X-ray diffraction (XRD) by means of a SIEMENS D5000.

2.2.2 Characterization of the substrate and the painting

After 7 days of drying, under naked eye, the substrates were evaluated considering the appearance of fractures and biological growth. The substrates without fractures and biological colonization were used to apply the paints.

During the paint application, the covering capacity and drying velocity were considered.

Once paint mock-ups were dried, a stereomicroscope (SMZ 1000, Nikon) was used to study their superficial appearance, to determine binding capacity, grip on the substrate and biological growth.

Then, the colour of the surface was characterized using CIELAB and CIELCH colour spaces [7] using a Minolta CM-700d spectrophotometer. In the CIELAB space, L* (lightness), a* and b* (colour coordinates) were measured. L* is the lightness, a* indicates the colour position between red and green and b* indicates the colour between yellow and blue. The chroma or saturation (C*ab) was also measured. Five measurements were made at random points on each sample to provide statistically consistent results, with each measurement being the average of three. The measurements were made in the Specular Component Excluded (SCE) mode, for a spot diameter of 3 mm, using D65 as the illuminant and an observer angle of 10 ∘ .

The microtexture and elemental composition of the paint mock-ups were studied by scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDS) using a FEI QUANTA 200 in both Secondary Electron (SE) and Back Scattered Electron (BSE) modes.

3 Results and Discussion

3.1 Selection of the substrate conditions

Cracks were not generated in any of the substrates. The same could happen in shelters, caves or dolmens where the high RH% remains constant. In the substrate where casein was added, rapid biological colonization was detected. The substrates executed just with kaolin and kaolin with butter were evaluated as adequate.

3.2 Pigment characterization

Ochre Yellow SA pigment was composed of goethite (FeOOH) and calcite ($CaCO_3$).

3.3 Painting mock-ups characterization

During the application of the paint on the substrate, it was detected that the paint with the best covering capacity was the mixture of water dispersed pigments with butter regardless of the substrate (just kaolin or kaolin with butter). The paint mock-ups drying faster were those made with diluted casein regardless of the substrate.
After drying, the highest binding capacity was identified in the painting with pigment and butter on kaolin-based substrate. The addition of water to the pigment before mixing with the butter decreased the binding capacity markedly on both substrates. Moreover, the application of pigment with butter on kaolin with butter-based substrate also reduced the binding capacity. The casein mock-ups, despite paint layer lifted, had a good binding capacity. The painting with pigment (without water) mixed with butter showed a high grip on the substrate in both substrates. Adding water to the pigment before mixing with butter slightly decreased adhesion. Biological colonization was not detected after 7 days of drying.

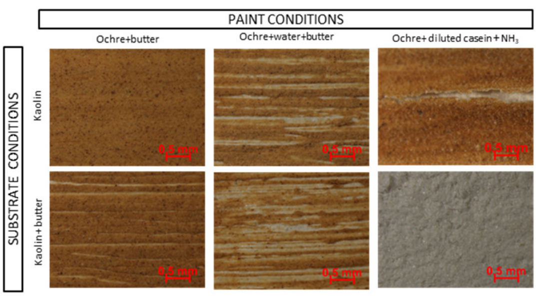

Figure 1. Micrographs of the paint mock-ups

Based on this qualitative evaluation, an evaluation methodology (Table 1) is proposed in which these parameters are evaluated on a scale from 1 (low) to 5 (excellent) with the objective of determining which procedure for the elaboration of megalithic art mock-ups is the most appropriate. Considering the highest score, the condition with the best evaluation was the application of pigment mixed with butter on a kaolin-based substate (without binder).

Spectrophotometry allowed us to determine that the mock-up with the water dispersed pigment with butter on a kaolin and butter-based substrate showed the greatest L* and its C^*_{ab} was closer to that of the original pigment (Fig. 2). Samples with casein, regardless of the substrate, showed lower L* and higher C^*_{ab} than those of the original pigment. Mock-ups with pigment mixed with butter regardless of the substrate showed similar L* and C^*_{ab}; these samples showed similar L* and higher C^*_{ab} than the original pigment. The condition identified as the most adequate to obtain megalithic paintings following our methodology (i.e., pigment with butter on a kaolin-based substrate) showed a similar L* to that of the pigment but a slight increase in C^*_{ab}.

Table 2. Methodology to determine the adequacy of the procedure for simulating megalithic paintings. Evaluation from 1 (low) to the 5 (excellent)

SUSBTRATE	**PIGMENT CONDITIONS**	Covering capacity	Drying velocity	Binding capacity	Grip on the substrate	Growth of micro-organisms	**TOTAL**
KAOLIN	Butter	3	3	5	5	5	21
	Water+butter	4	3	2	4	5	18
	Casein + NH_3	3	4	4	2	5	19
KAOLIN+ BUTTER	Butter	3	3	3	5	5	19
	Water+butter	4	3	2	4	5	18
	Casein + NH_3	2	4	4	1	5	17

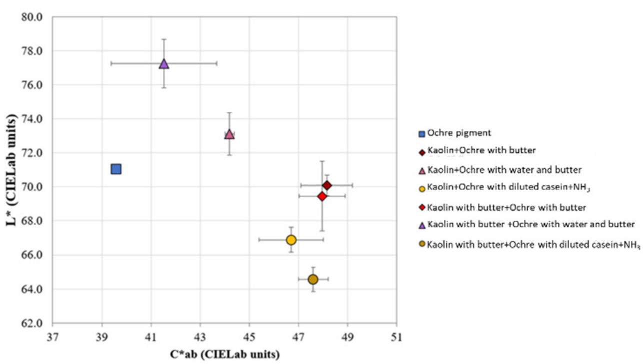

Figure 2. Mean values and error bars for L* and C^*_{ab} parameters registered in the different mock-ups.

Using SEM, it was detected that mock-ups with pigment and butter showed a greater agglutination than the samples with diluted casein (Fig. 3a and b respectively). In the casein-mock-ups (Fig. 3b) longitudinal cracks were observed crossing the pictorial layer.

4 Conclusion

A methodology based on the quantitative evaluation of the covering capacity, drying velocity, binding capacity, grip on substrate and biological growth in megalithic paint mock-ups allowed us to identify the suitability of the procedure to recreate them. In this case study, the best condition was achieved with the pigment mixed with butter on a substrate just with kaolin. However, it is necessary to consider the effect caused by the binder on the resulting colour, since both butter and casein change the original colour of the pigment.

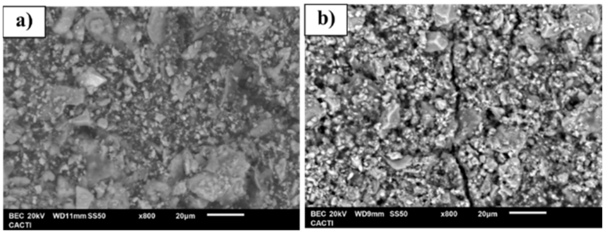

Figure 3. SEM micrographs of some of the mock-ups. a) ochre with butter on a kaolin-based substrate. b) ochre with diluted casein+NH_3 on a kaolin with butter-based substrate.

Acknowledgements

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