Organic Binders in Archaeological Wall Paintings

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Binding media are complex materials, employed to allow pigment grains to adhere to each other and to the surface of the support, through the formation of a coherent and homogeneous film. The function of the binder consists, therefore, in keeping the pigment particles firmly together and at the same time adhering them in the form of a coherent thin film to the surface of the support. The binder must obviously be in the fluid state, in order to form with the pigments a stable, homogeneous, stretchy, and viscous dough.

For the realization of wall paintings and, in later times, for their preservation, different materials with functions of binders, adhesives, paints, protective and consolidating were and are still necessary. There is a very large class of products which can have both constitutive functions but also a function of conservation and restoration.

Keywords: wall paintings ; organic binder ; characterization ; non-invasive techniques ; micro-invasive techniques ; GC-MS

1. Introduction

Wall painting realized using binders is the oldest form of parietal painting and precedes the birth of the fresco by about 20000 years. The first testimonies of parietal paintings made with organic binder date back, in fact, to the Upper Paleolithic: between 40000 and 10000 years ahead of Christ. These are cave paintings found in different geographical sites: in Africa, Europe and Asia. They were made using egg binders, blood, blood serum, urine, animal fat, animal marrow and milk. Throughout history the use of organic binders on the wall had a widespread diffusion, at all times, often combined with fresco in a mixed technique [1].

The investigation of the wall paintings in the tomb of Nefertari, the wife of Rameses II, recognized a gum Arabic, without rhamnose which could have come from a local acacia species still growing in the Luxor region. Later, vegetable tempera painting was replaced by animal tempera, characterized mainly by the presence of proteins [2].

Another example of the use of organic binders on the wall are the African cave paintings in Algeria and Libya, dating back to the early Bronze Age. It is dry painting with the use of milk and casein as binders (probably since they were peoples of sheep breeders), application carried out not with hands, but with brush prodrome tools [1].

To understand the pictorial technique, a valuable help is provided by the scientific approach of the diagnostics of pictorial works, which allows the identification of the organic binder. In some cases, chemical-physical analyses, performed on wall paintings, revealed the presence of organic material used as binder for the application of pigments on the surface of dried plaster, as reported by different studies, some of which are chosen to be described in this entry.

2. The Binders in the Wall Paintings

Binding media are complex materials, employed to allow pigment grains to adhere to each other and to the surface of the support, through the formation of a coherent and homogeneous film.

The function of the binder consists, therefore, in keeping the pigment particles firmly together and at the same time adhering them in the form of a coherent thin film to the surface of the support. The binder must obviously be in the fluid state, in order to form with the pigments a stable, homogeneous, stretchy, and viscous dough.

The proteinaceous materials most used in the artistic field as pictorial binders in tempera technique, as well as protective, adhesive and consolidating, are obtained from the following materials:

egg, which can be used either whole, or separately yolk (red) or egg white (white);

animal glues, extracted from scraps of animal skins and other cartilage parts (skin glue), mammalian bones (bone glue) and various parts of fish (fish glue);

milk and casein.

The most widely used polysaccharidic materials in the artistic field refer to sugary substances deriving from vegetable gum exudates, honey, steeds and starches contained in cereal seeds, tubers and other parts of green plants. The types of vegetal gums most used historically were: arabic gum, tragacanth gum and gum from fruit plants.

Different factors can affect the choice of the binder to use in wall paintings, i.e., the presence of pigments, which can be more or less stable in specific conditions, the exposure of the work and the knowledge in the time. Moreover, the information about the type of materials present in wall paintings and the knowledge of their chemical-physical properties results very important for the conservators in case of restoration interventions.

3. Techniques and Procedures to Characterize the Organic Binders in Wall Paintings

The characterization of organic materials in the wall paintings and their chemical-physical properties is fundamental for the knowledge of ancient paint techniques and for development of suitable conservation procedures.

Firstly, non-invasive techniques, which require the use of portables instruments for a general analysis in situ without sampling, can give information about the distribution of organic materials on the wall painting especially in the surface. Non-invasive methods represent a speed procedure to obtain general information about the composition of paintings.

Very often to complete the study it is necessary to obtain specific information about chemical composition, the presence of degradation products or information about the stratigraphic distribution of organic binding media in the wall paintings. For this reason, after a general investigation performed by non-invasive methods, the taking of samples is necessary, in order to carry out a detailed characterization of analytes.

For this reason, when we decide to arrive at an in-depth characterization of the organic binder, it is necessary to resort to laboratory investigation techniques on pictorial material, thus having to provide for a sampling of material from wall painting.

A relevant limit in the study of organic materials in wall paintings is represented by the low quantity of these, compared to inorganic materials (mortar and pigments).

Finally, the presence of materials used in past conservative interventions, i.e., fixatives based on egg, can alter the original composition of the paintings, and makes the identification of original organic materials more difficult.

4. Exploring Research Results

Scientific investigations carried out in recent decades on a number of wall paintings have revealed some important information about the techniques and the use of different materials, in relation to the geographical sites where the works of art are located.

Rosi et al. have proposed a study with the aim is to develop a method for the not-invasive and in situ identification of organic binders in wall paintings by fiber optic fiber optic reflectance infrared spectroscopy [3]. As part of the OMWP project, wall painting replicas of known composition from the collection of the Tintori Center in Prato have been employed to classify and interpret reflectance mid-FTIR spectra [4].

One of the very first articles on the characterization of binding medium, conducted on samples taken from the wall painting, was carried out by De Silva [5]. In this work it has been proposed the use of thin layer chromatography for a preliminary recognition of unknown compounds, using standard reference substances.

Interesting papers present overviews of the literature highlights that the analytical approach for use in GC-MS analysis of organic media in painting samples is strongly dependent on the specific problematic posed by conservators and art historians. The complex mixtures of molecular species present in organic materials, the requests to be answered, and consequently the analytes to be examined for, determine the choice of analytical approach, especially concerning sample pretreatment [6][7].

A study looked at an extensive series of standard compounds, reference pure materials, and reference paint materials prepared at Opificio delle Pietre Dure in Florence (Italian Ministry of the Cultural Heritage) Italy, simulating ancient painting techniques, using GC-MS to determine amino acids and fatty acids and submitting the results obtained to statistical analysis [8] [9].

A proteomic approach, spectrometry using liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used to study the degradation of proteins present in the wall paintings of the Monumental Cemetery in Pisa, Italy. The authors noted that the deamidation of some amino acids present in the proteinaceous binder causes a process of deterioration in works of art, including wall paintings [10].

Always linked to the decay of the organic binder in ancient wall paintings, a recent article addressed the problem of blurring of the paint layer. Based on the experimental results obtained, the authors believe the decay of the organic binder can cause the blurring of wall paintings while keeping the pigment unchanged. Studies have been conducted on simulated wall paintings and on a fragment of the blurred ancient tomb mural painting Zang Huailiang Tomb, AD 730, Tang Dynasty, Sanyuan, Shaanxi, Chin [11].

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