Lime-based restoration paints: characterization and evaluation of formulations using a native species from the Amazon flora and PVA-based glue as additives

Tintas à base de cal para restauro: caracterização e avaliação de formulações utilizando uma espécie vegetal amazônica e cola PVA como aditivos

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Abstract

Based on historic documents, two lime-based paint formulations were produced in laboratory in order to evaluate their basic characteristics as restoration materials for historic buildings with lime-based components. The paints were made basically with hydrated lime, clay, water and linseed (Linum usitatissimum L.) oil, and one formulation had PVA (polyvinyl acetate)-based glue as fixative, and the other one, Couma guianensis’ latex. Each paint component was characterized by XRD and FTIR, and color and specular gloss measurements were performed on both paints. A preliminary assessment of the paints was conducted using the Pipe Method, the salt crystallization test, visual analysis for dustiness, and analysis of microbiological growth. The results showed that the laboratory-produced paints are theoretically and technologically compatible with lime-based coatings, however, their superficial performance can be improved to achieve greater durability. This study also brings to light local materials from the Amazon region that have great potential to be used and recognized as raw materials for paints and which could also be investigated for other uses.

Keywords: Limewash. Lime-based paint. Couma guianensis’ latex. PVA-based glue. Conservation and restoration.

Resumo

Com base em referências históricas, foram produzidas em laboratório duas formulações de tinta à base de cal objetivando avaliar suas características para o restauro de edificações com argamassas e pinturas à base de cal. Os materiais utilizados nas tintas foram cal hidratada, argila, água e óleo de linhaça (Linum usitatissimum L.), sendo uma formulação com cola PVA (acetato de polivinila) e outra com látex da sorveira (Couma guianensis) como aditivos fixadores. Cada componente da tinta foi caracterizado por meio de DRX e FTIR, e foram realizadas aferições de colorimetria e brilho. A avaliação das tintas ocorreu por meio das análises de permeabilidade pelo método do cachimbo e análise visual de pulverelência e de colonização microbiológica. Os resultados mostraram que as tintas produzidas são materiais de restauro compatíveis teóricamente e tecnologicamente com revestimentos à base de cal, mas cujo desempenho superficial é passível de melhoramentos, especialmente no sentido do aumento de sua durabilidade. A pesquisa também revela materiais próprios da região amazônica com grande potencialidade, tanto para estudos mais aprofundados, como para seu reconhecimento como matérias-primas de tintas.

Introduction

The evolution of various fields of knowledge has led to the development of different production and application techniques and to changes in the components and characteristics of paints. Lime, a basic component of several historic materials, was widely used in the past, but it gradually disappeared, along with the practical skills of working with it, which leads difficulties in restoration projects (KANAN, 1996).

In addition, restoration work is further hampered by the inadequacy of most commercially available materials, since one of the major issues in the conservation of decaying historic buildings is the maintenance and restoration of mortars, plasters and lime-based coatings. If these structures are not preserved through the use of compatible materials, and if they are exposed to weathering, deterioration will occur more quickly.

Throughout history, traditional paints have suffered many transformations, with lime washes being replaced by modern commercial paints with a completely different composition, derived from very different industrial processes. Hence, modern paints have a totally different physical structure than traditional paints, resulting in materials that are incompatible and do not fulfill many theoretical and technological requirements of restoration.

In conservation and restoration, it has become inadmissible to disregard history and the passage of time. Thus, the acknowledgment of authenticity as an intervention principle points to compatibility issues involving materials and aesthetics. In most cases, these issues can only be resolved, in architecture, by resorting to the original materials and building techniques that are most compatible. This unique materiality and the implications of its transmission to the future have motivated us to study traditional painting practices, not only for aesthetic reasons, but also, and especially, for scientific reasons (AGUIAR, 2013).

The use of materials similar to those used in the past, such as lime-based paints, offers several advantages for restoration projects: the maintenance of the historical and architectural character, harmonious aging, causing less damage, being reversible and having similar physical and chemical properties (KANAN, 1996). That is in addition to those materials’ characteristics of adhesion, power to incorporate sand grains, economy, plasticity and wall consolidation power.

Furthermore, lime-based paints, whose film formation is processed by carbonation, a chemical reaction of hydrated lime and air, with loss of water and formation of calcium carbonate, allow the permeability and porosity needed in porous coatings such as mortars and paints from the 18th- and early 19th century. That permeability and porosity prevents humidity retention and other deterioration factors.

Therefore, studies aimed at developing a restoration paint that resembles traditional lime-based paints in their constitution and organoleptic properties (visual aspect) are an important tool to achieve the durability and compatibility of materials.

The information based on primary sources about Brazilian wall paints from the 17th, 18th and mid 19th centuries refers to a basically mineral material, consisting of lime and clay as pigments (BAENA, 2004; DANIEL, 2004; PAPAYERO et al., 2002). This document legacy includes lime paint formulations using raw materials from the Amazon in the limewashes. The reproduction and evaluation of those washes as restoration paints is a valuable investigative subject for the conservation of historic lime-based constructive systems.

Accounts by European naturalist travellers such as Martius and Spix (1819↑ apud FICHÁRIO…, 2001) refer to a particular material used as fixative in lime-based paints named “Sorveira milk” or “sorva”, popular names for the latex from a tree commonly known as Sorveira, couma, or “milk tree”, the Couma guianensis Aubl., from the Apocynaceas family. These trees are found in non-flooded areas of the rainforest and in coastal or estuary regions, occurring mainly in the counties of Belém, Cunani, Almerim and Prainha, in the state of Pará, Brazil. Latex is a thick, viscous white fluid that is insulating, and thus very resistant to weather and humidity. In addition to its function in limewash for walls, it can be used in the industrial production of gums and varnishes (LE COINTE, 1934).

Despite the properties and the abundance of latex, there is a lack of studies about it as a potential additive for paints. Moreover, besides being understudied, latex has fallen out of use. Nowadays, the most commonly used fixative in lime paints is PVA-based glue, cited in the Brazilian literature especially by Kanan (1996) and Uemoto (1991).

It is widely known that the natural wealth of the Amazon and its great potential in terms of locally available raw materials for processing and generating efficient products can be used in

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architecture and other sectors, such as ceramic production (RODRIGUES et al., 2015). Hence, the search for usable regional alternative materials can avoid the need to import products from other states and countries, which makes them more expensive and hampered the restoration of historic buildings.

Hence, the purpose of this study – based primarily on historical references about wall paints from the 18th century - is to reproduce a known lime- and clay-based paint formulation using PVA-based glue, and a variation of it (recently patented by Silva and Sanjad (2016)) with *Couma guianensis*’ latex as fixative, replacing PVA-based glue, and subsequently to characterize their components and conduct a preliminary assessment of the properties and the performance of the materials produced in laboratory to be used as a paint compatible with the lime-based coatings of historical buildings.

**Materials and methods**

The materials used for the production of the paints were: commercial hydrated lime (100g) in powder form, linseed (*Linum usitatissimum L.*) oil (10ml), polyvinyl acetate (PVA) glue (20ml), water (500ml), red clay (10g of pigment) collected from natural deposits located near the city of Belém: in Paracuru, Icoaraci district, state of Pará (PA), Belém County and *Couma guianensis*’ latex (20ml) collected from trees found on Ceasa Highway, 1368-1506 - Curió Utinga, city of Belém - PA (coordinates: 01º 26' 12.69" South, 48º 26' 17.58" West) in a property belonging to the Eastern Amazon unit of the Brazilian Agricultural Research Corporation (EMBRAPA).

The materials were previously characterized by laboratory analysis - X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) - to identify crystalline and amorphous materials. Thereafter, the paints were produced, characterized, and applied on specimens consisting of bases made of ceramic and mortar, and then subjected to a preliminary evaluation concerning their permeability, dustiness, and resistance to salt deterioration and microbiological growth.

The preparation of the specimens on which the paints were applied was as follows: white clay for the ceramic base, and commercial hydrated lime powder, Paracuru red clay and sifted sand for the mortar, according to the 18th century’s technique for traditional lime mortar and paint coatings.

**Sampling**

Approximately 400 ml of latex were collected from *Couma guianensis* trees. The extraction of the material was performed on the tree barks, at approximately 1 m 30 cm from the ground. For the extraction, cuts were carefully made with a rubber-tapping knife in order to minimize injuries to the trees while making the grooves. A plastic container was placed a few centimeters below the cut to collect the latex runoff. The knife was cleaned before its use on new trees to prevent the transmission of fungi and bacteria.

As it is a component of the genetic heritage of the Amazon flora, a Material Transfer Agreement was made to allow the researchers to collect the *Couma guianensis*’ latex. The agreement concerns the transfer of a specimen with genetic heritage component for scientific research without economic potential, according to the relevant requirements from EMBRAPA’s Eastern Amazon unit.

**Specimens**

Eighteen ceramic specimens (Table 1) on which mortar and paint were applied were produced at the Restoration, Conservation and Rehabilitation Laboratory (LACORE) of the Institute of Technology of the Federal University of Pará (UFPA). Two paint formulations were made: one with PVA glue and the other with *Couma guianensis*’ latex, and each paint was applied on half of the specimens.

To make the ceramic bases of the specimens, the white clay was moistened, beaten and manually pressed into 5 cm x 10 cm x 1 cm wooden molds. After molding, the clay was submitted to 24 hours drying in a Q317M-32 microprocessor drying oven, and thereafter, 2 hours at up to 1000°C, plus another 2 hours firing at this temperature in a Jung oven model 10013. The ceramic bases remained in the turned-off oven for a further 24 hours, until the temperature significantly decreased, and then they were removed from the oven.

**Surface preparation**

The ceramic specimens received layers of a laboratory-produced mortar as substrate for the paints. The production and application of the paint substrates followed Kanan’s (1996) recommendations for lime-based mortars. The amounts of lime, clay and sand were measured according to previous results of probable average proportions (in mass) of the mortar components of an 18th century building in Belém, the Pombo Chapel: 1: 0.62: 2.44. The three components were manually blended (beaten) with water, producing a mixture.
Table 1 - Specifications of the laboratory-produced specimens

<table>
<thead>
<tr>
<th>Basic composition of the specimens</th>
<th>Specimens’ name</th>
<th>Permeability by the Pipe Method</th>
<th>Accelerated weathering test of 85% deterioration</th>
<th>Dustless visual analysis</th>
<th>Observations of fungal colonization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic basis + mortar + lime paint with clay pigment, linseed oil and PVA glue</td>
<td>PS-PM1</td>
<td>X</td>
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<td>PS-PM2</td>
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<td>PS-PM3</td>
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<td>PS-SA1</td>
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<td>PS-SA3</td>
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<td>PS-D1</td>
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<td>PS-D2</td>
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<td>PS-D3</td>
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<tr>
<td>Ceramic basis + mortar + lime paint with clay pigment, linseed oil and Couma guianensis’ latex</td>
<td>PG-PM1</td>
<td>X</td>
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<td>Total of specimens</td>
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</table>

The mortar was applied to the ceramic bases of the specimens. The surfaces were previously brushed and wetted, and the first mortar application was made so as to provide maximum impact on the ceramic base. A second layer was applied while this mortar was still a little wet, and then it was manually compressed and leveled with a trowel.

After application of the mortar layers, the ceramic bases were left to dry for 24 hours at room temperature (± 30°C). Thereafter, the mortared surfaces were prepared for painting with the use of sandpaper (grain size 180 mesh) and pre-wetting.

Paint production

The formulation adopted for the paints is an adaptation of the formulation described by Martius and Spix (1819 \(^2\) apud FICHÁRIO…, 2001), Uemoto (1991), Kanan (1996), and Daniel (2004) for traditional lime-based paints, and the use of Couma guianensis’ latex followed Silva and Sanjad’s (2016) patent.

Hydrated lime powder was diluted in water to achieve a fine, creamy consistency, and then mixed with PVA glue (in the case of PVA addition) previously dissolved in water. Thereafter, linseed oil was added and the mixture was filtered with a cloth sieve. In the case of the latex addition, the Couma guianensis’ latex was added to the pre-dispersed clay pigment, and then kneaded together with water. The pigment (or its mixture with latex, according to the formulation) was slowly added to the lime mixture and mixed using a manual beater, diluting it with water until a fine, creamy consistency was achieved.

The pigments were obtained by manual cleaning and sieving to remove excess organic material from the Paracuri red clay, with subsequent decanting, drying and grinding in a Marconi MA 500 / CF model ball mill. Prior to their use in the paints, the pigments were soaked in hot water to ensure complete dispersion, and then mixed using a beater.

Paint application

The paints were applied in three uniform coats, perpendicular to one another, with a soft brush (100 mm). The first - horizontal - coat was a thin layer, without any pigment, intended to impregnate the surface. The two remaining layers, with pigment, were applied perpendicularly, only after sufficient drying.

Characterization of the paints

Colorimetry

In order to evaluate the color and to perform a first spectral pigment discrimination, colorimetric readouts were obtained with a Chroma Meter CR-400 Colorimetry (Tristimulus Colorimeter CR-400, Konica Minolta, NJ) from the Laboratory of Dental Materials at UFPA, and CIE \(L^*a^*b^*\) system.

measurements were performed in five areas of each specimen. The values obtained in the CIE L*a*b* chromatic space were the average of three measurements taken on the surface layer of the painted areas, after soft cleaning with a brush.

**Measurement of the specular gloss**

As well as the color, the specular gloss was measured for the physical characterization of the paints. The measures were taken with a Glossmeter (*Homis Controle e Instrumentação*, HP300) from the Corrosion Laboratory of Eletronorte (*Centrais Elétricas do Norte do Brasil S.A.*). The measures were taken according to the Standard Specular Gloss Test Method (*AMERICAN…*, 2008) based on photoelectric measurements of the incident light reflection geometry at 60° directly on the painted surfaces. In each of the specimens, measurements were made in five areas, with three readings each, and then the average specular gloss value (stated in gloss units) was obtained.

**X-Ray Diffraction (XRD)**

Powder X-ray Diffraction (XRD) analysis, with the powder method, was used to identify the mineralogical phases of the paints’ components. In order to do that, specimens of the clay pigment and the lime used in the paints were grated and ground in an agate mortar, and compacted in a specimen holder for processing in a PANalytical X’Pert PRO MPD (PW3040/60, 0/θ) diffractometer with a ceramic X-ray tube (Cu anode, Kα1=1.540598 Å), Kβ Ni filter, and an X’celerator PSD (Position-Sensitive Detector). The instrumental conditions were as follows: scan range from 5 to 75°, y, tube power of 40 kV and 30 mA, step size of 0.02°, time/step of 60 s, divergence slit of 1/8°, anti scattering slit of 1/4°, mask of 10 mm, and specimen spinning with a rotation time of 1.0 s. The equipment belongs to the Mineral Characterization Laboratory (LCM) of the Institute of Geosciences of UFPA.

**Fourier Transform Infrared Spectroscopy (FTIR)**

A Fourier Transform Infrared Spectroscopy was performed to obtain the chemical characterization of the binders and to identify the organic components. To conduct this analysis, 0.0015 g of each paint formulation (one with PVA glue and the other with latex), and also each of the organic components themselves (linseed oil, PVA glue and *Couma guianensis*’ latex) were powdered with 0.2 g of Potassium bromide (KBr) and compressed as a pellet under a pressure of 1.8 Kbar. FTIR spectra were obtained with a FT-IV absorption spectroscope (FT-IR), Vertex 70, Bruker spectrometer with a spectral range of 400 cm⁻¹ – 4000 cm⁻¹, with measurements taken at every 4 cm⁻¹, at the Laboratory of Applied Mineralogy and Geochemistry (LaMIGA) of the Institute of Geosciences of UFPA.

**Paint evaluation**

Since the laboratory-produced paints were aimed to be used in restoration projects and did not follow the standards for recent commercial and polymer paints, the evaluations of their performance are adaptations of other standard material tests or not based on any standards. The evaluations are a preliminary study about the behavior of these paints.

**Permeability by the Pipe Method**

The Pipe Method was used to evaluate the permeability and water absorption of the coatings. The test procedure is proposed by the *Centre Scientifique et Technique de la Construction* (CENTRE…, 1982) and by the *Réunion Internationale des Laboratoires d’Essais et de Recherches sur les Matériaux et les Constructions* 62 (*GALE*, 1987) as Measurement of Water Absorption Under Low Pressure – Test Method 11.4.

The test was conducted on the painted surfaces of the specimens (three with PVA glue paint and three containing *Couma guianensis*’ latex) at age 6 months. Three pipes from the Laboratory of Experimental Building Materials of the Civil Engineering School of UFPA were used. The pipes are L-shaped glass tubes graded in tenths of millimeters. The pipes were fixed (with the specimens placed vertically) on the paintings with caulk mass. After fixation, the pipes were filled with water up to a volume of 4.00 cm³. Using a timer, readings were made of the decreases in water level for the three pipe gradations in milliliters (ml) until 15 minutes of testing elapsed. The permeability is indicated by the pressure exerted by the water column, and the absorption is verified when the water is in contact with the surface. The individual values of water absorption (ml) and the water absorption rates (ml/min) were obtained and annotated in graph form, and the readings were taken every minute, increasing the accuracy of the graph curve.

In order to compare the permeability results, an 18th century wall painted with lime-based wash in Pombo Chapel was also tested. Due to the influence of seasonal weather changes, since in most rainy periods permeability is reduced, as the walls are...
already soaked (ALMEIDA DIAS; CARASEK, 2003), the test on the wall paint was carried out in July, which is a less rainy period (SANJAD, 2007).

Salt crystallization test
To evaluate the paints’ resistance to salts and to identify the level of deterioration and changes caused by salt attack (crystallization of soluble salts), the specimens were submitted to an accelerated weathering test simulated by immersion in a saturated salt solution and then dried in an oven.

The reagent (salt) used in the analysis was sodium chloride (NaCl), a salt commonly present in 18th century buildings and also in the aerosol, especially in coastal areas.

The method was based on the Portuguese standard 88.26 from the National Civil Engineering Laboratory (LNEC) from January 1971 concerning aggregates, according to adaptations by the Preservation and Restoration Technology Center (NTPR) of the Federal University of Bahia (UFBA).

For the test, the specimens were placed in an oven for 24 hours at 75°C, cooled in a desiccator and then measured for their dry weight. Three specimens with PVA glue paint and three specimens with Couma guianensis’ latex paint were analyzed. Each specimen was put in a 500 ml beaker filled with deionized water saturated with sodium chloride (166 grams) for 24 hours, and then removed to have its wet weight measured. After weighing, the specimens were immediately put in the oven for another 24 hours at 75°C, and then removed for weighing and mass annotation, and so on, until full deterioration of the coating material.

Preliminary evaluation of dustiness
A simple practical test was used to analyze the superficial performance regarding the dustiness of the applied paints: a black cloth was lightly pressed, in circular motions (three movements), on each of the three specimens with each paint formulation.

Analysis of microbiological growth
Given that the literature points to fungi as the microorganism primarily responsible for the microbiological deterioration of painted surfaces (SHIRAKAWA et al., 2002), the susceptibility to microbiological deterioration was evaluated through observations of fungal contaminants’ growth on the specimens after one month of exposure, and an accelerated test of bioreceptivity to fungus species.

Fungal analysis
For the evaluation of microbiological colonization on the painted surfaces, the laboratory-produced paints were applied on 16 RODAC plates (4 cm x 4 cm), which were placed in an 18th century building (Pombo Chapel) in extremely propitious environmental conditions for microorganism proliferation: indoors, moist, with little natural light and no artificial lighting.

The paint containing Couma guianensis’ latex was applied on eight of the RODAC plates, and the paint with PVA glue was applied on the other eight plates. Six of the painted specimens (three with each type of paint) were placed next to the plates inside the chapel.

Four plates (two painted with the latex paint and two with the PVA glue paint) were placed inside the building, but they remained sealed to avoid contact with atmospheric environmental agents. These were control specimens for comparative purposes.

The specimens remained in place for thirty days. Before the start of the experiment and at the end, the paint on the RODAC plates and the paint on the specimens were analyzed using a Nikon Japan Y-IDT optical microscope with 400 x magnification (with this value converted by a 2.5 factor). The corresponding photographic documentation was obtained with a digital Nikon camera mounted on the microscope, and the Nis-Elements F software from the Biological Sciences Institute of UFPA was used to observe the microorganisms.

Accelerated test
To evaluate the bioreceptivity of the laboratory-produced paints, an accelerated experiment was conducted by inoculating spores of fungi on the painted surfaces. The experiment took place at the Mycology Laboratory (LAMIC) of the Biological Sciences Institute of UFPA.

For the selection of the microorganisms, the sedimentation technique was used to collect fungi from the air. This method consisted in exposing Petri plates containing Sabouraud agar with chloramphenicol for 15 minutes in the internal environment of the Pombo Chapel. After growth, a filamentous fungus colony with rapid development and sporulation was selected. The colony was isolated in Sabouraud agar, and the identification was based on the macroscopic features, the preparation of glass slides for the examination of the microstructural characteristics in an Olympus BX41 optical microscope, as well as on a comparative study using the parameters from classical taxonomy as in the literature (LACAZ et al., 1998).

In view of its growth rate, the selected species was
identified as *Penicillium sp.*, characterized by the production of conidia (asexual spores) produced in branched conidiophores. This fungus is commonly found in the air and has been reported in the literature (SILVA, 2009; SHIRAKAWA et al., 2002; SAAD, 2002; GUGLIELMINETTI et al., 1994; SORLINI et al., 1982) as one of the contaminants of painted walls.

For the assay, a spore suspension was prepared in 10 ml of saline solution with 0.1% Tween 80. The conidia of *Penicillium* were obtained from a colony by scraping the surface of a 7-day-old culture with a sterile needle, and then suspended in 10 ml sterile saline solution. After homogenizing in a Phoenix AP56 solutions mixer, an aliquot of the suspension was taken for counting the spores. A Neubauer chamber was used to estimate the number of spores (conidia)/ ml in the suspension. The counting of conidia was conducted under an Olympus BX41 optical microscope with 250 x magnification.

To ensure conditions of sterility, the procedure was performed in a vertical laminar flow hood, where 1 ml of the suspension containing 3.5 x 10^6 conidia/ ml was seeded in a 90 mm diameter Petri plate on which 20 ml of Sabouraud agar with chloramphenicol were poured (pour plate method). The paints were applied in two coats on previously sterilized 24 x 24 mm glass coverslips, 0.13 - 0.16 mm thick. After the culture medium solidified, it was deposited on the painted coverslips by gentle pressure.

The tests were conducted in triplicates, with a total number of seven plates, three with the application of paint with *Couma guianensis*’ latex, three with paint containing PVA glue, and one plate without any application of paint on the coverslip, to be used as control specimen. The plates were incubated at ambient temperature (± 30°C), with daily observations and photographic records taken with a Canon Ultrasonic EOS20D digital camera with a 100 mm lens from the Laboratory of Dentistry Materials of UFPA. The results were evaluated by visual observation of the fungal growth.

### Results and discussion

The specular gloss average measures are similar in the paint with *Couma guianensis*’ latex and the one with PVA glue (Table 2). The values are around 1gu (gloss unit), classifying the coatings as matte. The low values occur due to the accentuated roughness of the surfaces, as they are manually- produced paintings. Besides roughness, other factors like pore structure, the color formulation of the coating and the role played by particles in the matting of paints undergo shrinkage during drying and curing. It has been shown that increased roughness (amplitude) increases the spread of the reflected light, thus increasing diffuse scattering and reducing gloss (JÄRNSTRÖM et al., 2008; FLETCHER, 2002).

The XRD pattern of the sample of commercial hydrated lime used in the two paint formulations highlights an abundance of portlandite (Ca(OH)_2) and, in smaller amounts, calcite (CaCO_3) (Figure 1). The formation of calcite is probably due to the carbonation of portlandite in contact with atmosphere CO_2 during the preparation of the specimens.

A mineralogical analysis of the clay pigment showed quartz (SiO_2) and kaolinite (Al_2Si_2O_5(OH)_4) as dominant minerals, followed by muscovite and montmorillonite (Figure 2). The great intensity of the quartz peaks compared with the clay minerals’ peaks in the diffratogram is attributed to the manual process of collecting and producing the pigment, which can lead to the presence of grains of sand.

While these clay minerals produce hues of color similar to those of traditional lime-based paints with yellow ochre earth pigments, they also give the property of expansivity to the paints. Due to this property, large amounts of pigment can decrease the paint’s resistance and lead to pathologies such as cracking and excessive dustiness.

Pigment volume is also an important paint parameter, determining gloss and permeability. In addition, its relation with the susceptibility of the paint film to the growth of biofilm influences biodeterioration. A lower pigment volume increases waterproofing, leading to lower biodeterioration, but it also reduces permeability to water vapor, increasing the time of wetness after rain (GAYLARDE et al., 2011).
The chemical compositions of the PVA glue, the Couma guianensis’ latex, the linseed oil and of both paint formulations were determined by FTIR analysis. Table 3 shows the approximate assignments of the identified spectra bands. The main bands of hydroxyl (OH) are the widest ones, measuring between 3697 cm\(^{-1}\) and 3426 cm\(^{-1}\); fatty acids (CH\(_2\)) from around 2928 cm\(^{-1}\), 2854 cm\(^{-1}\), 1465 cm\(^{-1}\) up to 1427 cm\(^{-1}\) and 1097 cm\(^{-1}\); carbonyl, such as esters (lipids) (C=O) around 1735 cm\(^{-1}\); carbonates (CO\(_3^{2-}\)) at 875 cm\(^{-1}\) and Si-O at 694 cm\(^{-1}\) and 796 cm\(^{-1}\) (Figure 3). Some infrared measured bands are similar to those of the common paint binders such as oil, proteins, carbonates and carbohydrates identified in the literature (KUCKOVA et al., 2005).

**Evaluation of the paints**

The evaluation of the paints as to their permeability by the Pipe Method (Figure 4) revealed that both
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Table 3 - Approximate assignments of the FTIR measured bands of PVA glue, *Couma guianensis'* latex, linseed oil and the produced paints (Continues...)

<table>
<thead>
<tr>
<th>Bands (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>PVA glue</th>
<th><em>Couma guianensis'</em> latex</th>
<th>Linseed oil</th>
<th>Paint with <em>Couma guianensis'</em> latex</th>
<th>Paint with PVA glue</th>
<th>Approximate assignment</th>
<th>References</th>
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<tbody>
<tr>
<td>3694</td>
<td>3697</td>
<td>3696</td>
<td>-OH stretching</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
<td></td>
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<tr>
<td>3643</td>
<td>3644</td>
<td>v mode of H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
<td></td>
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<tr>
<td>3621</td>
<td>3622</td>
<td>v mode of H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
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<tr>
<td>3451</td>
<td>-OH stretching</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>3386</td>
<td>3393</td>
<td>3398</td>
<td>-OH stretching</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
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<td>2924</td>
<td>2928</td>
<td>2926</td>
<td>2928</td>
<td>-OH stretching</td>
<td>ROleri et al., 2015; ŠERIFAKI et al., 2009; EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
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<tr>
<td>2919</td>
<td>v sym.--CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>ROleri et al., 2015; ŠERIFAKI et al., 2009</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2851</td>
<td>2856</td>
<td>2854</td>
<td>v sym.--CH&lt;sub&gt;2&lt;/sub&gt;- fatty acids</td>
<td>ROleri et al., 2015; ŠERIFAKI et al., 2009</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1739</td>
<td>1735</td>
<td>1744</td>
<td>1739</td>
<td>v R(=--(C=O)--O--R&lt;sub&gt;2&lt;/sub&gt; combination band; esters (lipids)</td>
<td>ROleri et al., 2015; ŠERIFAKI et al., 2009; EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
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<tr>
<td>1645</td>
<td>v C-C</td>
<td>EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
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<tr>
<td>1465</td>
<td>v CH&lt;sub&gt;2&lt;/sub&gt;; v C--OH</td>
<td>EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1456</td>
<td>v CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1435</td>
<td>1427</td>
<td>1427</td>
<td>δ CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1378</td>
<td>v asyn.--CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>GOPI, RAMANATHAN &amp; SUNDARARAJAN, 2015; ROleri et al., 2015</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1240</td>
<td>1245</td>
<td>1168</td>
<td>δ O-H</td>
<td>PARO et al., 2013; EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1146</td>
<td>v C-C</td>
<td>carotenoid</td>
<td>EDWARDS, FARKHELL &amp; DAFNTER, 1996</td>
<td></td>
<td></td>
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</table>

Paints are porous. They presented considerable water absorption, albeit not high enough to absorb the 4 ml in 15 minutes. Although laboratory-produced paints showed similar curves in the absorption per minute graph, the paint with PVA glue was more permeable, absorbing 3.3 ml by the end of the test. The final absorption of the paint with *Couma guianensis'* latex, at around 2.9 ml, was closer to that of the 18th century lime-based paint from Pombo Chapel. Hence, these paints, especially the paint with latex, are porous and have great water absorption capacity, similarly to the traditional lime-based washes used in historic buildings (GONÇALVES; PEL; RODRIGUES, 2009). Regardless of similar permeability results, water absorption can vary depending on the paint’s age and lime carbonation. Moreover, the mortar-plus-paint system should be considered. The microstructure of alteration of lime-based coatings with the hydration and carbonation of calcium hydroxide leads to a decrease in porosity and, consequently, a reduction in permeability and water absorption (GALE, 1987).

The time of the accelerated weathering deterioration test by salt was 10 days until complete deterioration of the paints. During the ten cycles of 24 hours, the specimens increased in volume due to the absorption of the salt dissolved in water; after the start of salt crystallization, the specimens began to lose weight, but subsequently increased in volume again (Table 4).
Table 3 - Approximate assignments of the FTIR measured bands of PVA glue, *Couma guianensis*’ latex, linseed oil and the produced paints (continuation)

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1097</td>
<td>τ -CH₂-</td>
<td>ROLERE et al., 2015</td>
</tr>
<tr>
<td>1076</td>
<td>ν C-C-C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>1026</td>
<td>ν C-O-H</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>985</td>
<td>τ C=C</td>
<td>ROLERE et al., 2015</td>
</tr>
<tr>
<td>946</td>
<td>ρ -CH₂-; δ C-O-C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>902</td>
<td>ω -CH₃- =C-H out of plane bending</td>
<td>ROLERE et al., 2015</td>
</tr>
<tr>
<td>882</td>
<td>ν asym. C-O-C</td>
<td>ROLERE et al., 2015; ŞERIFAKI et al., 2009; MADEJOVA &amp; KOMADEL, 2001</td>
</tr>
<tr>
<td>875</td>
<td>ν carbonate CO₃²⁻</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
</tr>
<tr>
<td>828</td>
<td>δ C=C-H</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>806</td>
<td>δ C=C-H</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>779</td>
<td>CH₃ rocking</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>796</td>
<td>Si-O stretching of quartz and silica</td>
<td>MADEJOVA &amp; KOMADEL, 2001</td>
</tr>
<tr>
<td>719</td>
<td>ν C-C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>663</td>
<td>ν C-O-C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>536</td>
<td>ν C-O-C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
<tr>
<td>468</td>
<td>δ C=C=C</td>
<td>EDWARDS, FARWELL &amp; DAFFNER, 1996</td>
</tr>
</tbody>
</table>
Figure 3 - FTIR spectra of the paints with Couma guianensis' latex and with PVA glue

Figure 4 - Variation of the paints' water absorption per minute by the Pipe Method

Table 4 - Weight measurements of 10 cycles (days) of salt crystallization test

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>DRY WEIGHT</th>
<th>1st cycle (wt)</th>
<th>2nd cycle (dry)</th>
<th>3rd cycle (wt)</th>
<th>4th cycle (dry)</th>
<th>5th cycle (wt)</th>
<th>6th cycle (dry)</th>
<th>7th cycle (wt)</th>
<th>8th cycle (dry)</th>
<th>9th cycle (wt)</th>
<th>10th cycle (dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-SA1</td>
<td>121.38</td>
<td>145.77</td>
<td>135.98</td>
<td>146.81</td>
<td>138.82</td>
<td>142.49</td>
<td>136.48</td>
<td>139.55</td>
<td>134.18</td>
<td>138.28</td>
<td>133.97</td>
</tr>
<tr>
<td>PS-SA2</td>
<td>129.31</td>
<td>155.00</td>
<td>143.30</td>
<td>157.15</td>
<td>148.00</td>
<td>155.33</td>
<td>146.65</td>
<td>152.48</td>
<td>145.20</td>
<td>151.45</td>
<td>144.15</td>
</tr>
<tr>
<td>PS-SA3</td>
<td>141.37</td>
<td>167.53</td>
<td>156.93</td>
<td>168.81</td>
<td>160.13</td>
<td>166.95</td>
<td>159.04</td>
<td>165.37</td>
<td>158.00</td>
<td>159.37</td>
<td>153.44</td>
</tr>
<tr>
<td>PG-SA1</td>
<td>114.19</td>
<td>135.31</td>
<td>125.33</td>
<td>137.39</td>
<td>129.91</td>
<td>133.14</td>
<td>129.41</td>
<td>134.54</td>
<td>129.94</td>
<td>133.98</td>
<td>130.43</td>
</tr>
<tr>
<td>PG-SA2</td>
<td>119.92</td>
<td>143.65</td>
<td>130.78</td>
<td>145.35</td>
<td>135.03</td>
<td>144.21</td>
<td>134.28</td>
<td>143.80</td>
<td>134.05</td>
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<tr>
<td>PG-SA3</td>
<td>120.70</td>
<td>143.25</td>
<td>132.48</td>
<td>145.44</td>
<td>136.06</td>
<td>143.30</td>
<td>135.82</td>
<td>142.93</td>
<td>136.43</td>
<td>142.80</td>
<td>137.44</td>
</tr>
</tbody>
</table>
The process of weight gain and loss occurred initially by salt absorption by the porous materials of the specimens. When the pores were totally filled by the crystallized salt, the materials started to break. As well as causing the expulsion of material from the specimen, this process leads to further expansion of the pores, making more space to absorb a new amount of salt. With the total occupation of the specimen’s pores, a new disruption phase occurs, with the consequent loss of mass and a further increase in porosity, and so on until the total rupture of the material.

This process and the formation of salt crusts and subeflorescences are explained by Lopez-Acevedo (1997) (LOPEZ-ACEVEDO et al., 1997). The saline solution moves towards the surface of the specimens, thus becoming supersaturated, but without reaching the surface itself at first. Then, the salt crystals produce the cementation of the superficial particles of the specimens, with the appearance of a thin, indurated crust. Later, the crust loses its support and starts peeling off as the salts start to crystallize underneath. The outer crusts wrinkle and warp. When the crystals formed at this stage are highly anisotropic in their morphology, the crusts are detached by their growth and eventually peel off. After this peeling, the surface of the specimen is ready for the formation of another crust, as the process is repeated.

The two paints had different result patterns. The detachment of the paints began in the third cycle (Figure 5). The surfaces painted with Couma guianensis’ latex were the first to show signs of detachment of the paint layers. In the surfaces painted with PVA glue, the rupture of the material occurred with the first detachment of small pieces of paint from the mortar in the 4th cycle, however, in the 10th cycle, they showed complete peeling of the pictorial layer, similarly to a film. On the other hand, at the end of the 10th cycle, part of the latex paint was still adhered to the mortar.

Hence, the researchers observed that the incorporation of Couma guianensis’ latex in the paint formulation helped improve the fixation of the paint on the substrate, while the glue provided a more cohesive material more similar to a film, and extended the time period before the beginning of the rupture. That, however, does not mean that the paint with PVA glue is more resistant, since when the rupture does takes place, it leads to complete detachment of the surface.

The presence of inorganic salts is one of the main causes of deterioration in works of art with a porous nature, particularly wall paintings (KOTULANOVA et al., 2009). In this case, the high porosity of the paints, as also shown by the Pipe test results, provides more passive absorption of salt. This can be observed in the swelling of the pictorial layer, and the materials’ mass gain. Soluble salt crystallization inside porous materials generates crystallization and/or hydration pressures likely to exceed the elastic limit of the material, causing its failure.

Figure 5 - Specimens after the third cycle of accelerated weathering deterioration test by salt, showing their first detachments
Due to their high porosity, these paints are quickly deteriorated by salt when compared with other materials such as façade tiles, whose material rupture time was three months and one week, as reported by Sanjad (2002). However, despite the negative aspects concerning the porosity of these coatings in view of saline deterioration, the high permeability of lime- and clay-based paints is a positive aspect when compared with new polymers and less permeable paints. The modern paints usually applied to historic wall surfaces further reduce the evaporation rate and, hence, the damaged surface area progressively increases (GONÇALVES; PEL; RODRIGUES, 2009).

Visual comparison of the superficial performance in terms of the dustiness of the paints (Figure 6) clearly showed that the specimens painted with the formulations containing Couma guianensis’ latex allowed more particulate matter to deposit on the surface of the black cloth, demonstrating how easily it detaches from the substrate through simple pressure. In turn, the test showed that the paint with PVA glue had more adhesion and cohesion, which are better qualities, since paint dustiness should be low in order to ensure good superficial performance (D’ALMEIDA, 2008).

Concerning the preliminary evaluation of microbiological growth on the paints’ surface, optical microscopy images (Figure 7) showed the presence of fungal structures in both paints after thirty days of exposure in an indoor environment. Although the microscopy images suggest fungal growth, the macroscopic appearance of the specimens does not show any signs of these colonizers and much less of aesthetic alterations like coloring and discoloration, or other problems such as blistering, peeling and cracking that might result from fungal growth (GAYLARDE et al., 2011; SHIRAKAWA et al., 2011) in this short time of exposure (30 days). It is important to evaluate the long-time effects of biodeterioration, not only in terms of visual alterations, but also chemical modifications, by SEM analysis, for example, and to proceed with the identification of the species on the analyzed surfaces. The environmental conditions of humidity and temperature must also be monitored to complete the picture of biodeterioration.

In contrast to the evaluation of the specimens, the visual macroscopic analysis in ten days of accelerated test indicated some resistance of the two paint formulations to Penicillium sp. (Figure 8).

The bioresistance to Penicillium sp. obviously does not cover the whole spectrum of microorganisms that could grow on the painted surfaces, as shown in the microscopy images. Although they did not show bioreceptivity to Penicillium sp., other fungal species might occur on the painted surfaces. Quantitative and qualitative analysis of microorganism propagules should be carried out in order to document and isolate a wide variety of microorganisms that thrive on the paints, and further accelerated tests should be conducted.

Conclusions

The two laboratory-produced lime- and clay-based paints are visually similar, characterized as matte yellow ochre. Their mineralogy includes calcite, quartz, kaolinite, muscovite and montmorillonite, and their organic components are fatty acids and esters.
Figure 7 - Optical microscopy (100X magnification) images showing fungal presence in the paints with PVA glue: conidia and conidiophore (A); spore (B); and in the paints with Couma guianensis latex: spore conglomerates (C); dark septate hyphae (D)

Figure 8 - Painted surfaces after 5, 10 and 15 days of accelerated test with Penicillium sp.
The conclusions after the evaluation of the paints were:

(a) the two paint formulations resulted in permeable and porous coatings, wherein the paint with PVA glue showed higher water absorption and the paint with Couma guianensis latex had results that were more similar to 18th century lime-based paints. Further studies on the paints’ permeability using the Pipe Method should be conducted, especially comparing the results at various ages of lime curing and carbonation;

(b) several stages were observed in the weathering of these materials: the rise of the saline solution through the material, intumescence, evaporation of water and consequent salt crystallization. All of them with gain and loss of weight and the deterioration of materials. These aspects bear an important relationship with high porosity, which is a specific characteristic of lime-based building materials such as mortar and paints. Hence, both paints presented short-term resistance to saline weathering in accelerated tests with NaCl. The paint with Couma guianensis latex showed better substrate fixation capacity, while salt attacked the paint with PVA glue. The paint containing PVA glue formed a film that delayed the beginning of material detachment, but when it occurred, the whole paint layer peeled off;

(c) PVA glue provided a more cohesive material and better results in terms of dustiness, but both paints presented poor superficial performance properties; and

(d) at a preliminary assessment, the paints did not show significant macroscopic surface alterations, but a first fungal colonization front occurs already at 30 days of paint exposure. In addition, the paints showed to be resistant to Penicillium sp. in a 10-day accelerated test. Studies to identify microbiological contaminants of paints and the bioreceptivity of these materials to other fungal species should be carried out.

An aspect to be considered is that paints with plastic additives (natural or industrialized) generally have the disadvantage of greatly reducing the permeability of mineral paints. However, Couma guianensis’ latex has shown to be more permeable than PVA glue. Permeability is a good quality for lime-based coatings, especially for monuments from the colonial period. Therefore, it is assumed that this type of additive could have a more limited type of application and should be considered primarily for the painting of constructions built around the second half of the 19th century, or for coatings from the colonial period submitted to specific weathering.

Hence, this study plays a fundamental role in the pursuit of adequate and compatible materials for the conservation and restoration of architectural heritage, providing information about local materials and their performance as paint components.

References


Lime-based restoration paints: characterization and evaluation of formulations using a native species from the Amazon flora and PVA-based glue as additives


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