Journal of Cultural Heritage xxx (2017) xxx–xxx

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EM|consulte
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Original article

Calcium alkoxides as alternative consolidants for wall paintings: Evaluation of their performance in laboratory and on site, on model and original samples, in comparison to conventional products

Elsa Bourguignon [a], Patrizia Tomasin [b,*], Vincent Detalle [a], Jean-Marc Vallet [c], Martin Labouré [d], Iulian Olteanu [e], Monica Favaro [b], Matteo Andrea Chiurato [b,f], Adriana Bernardi [g], Francesca Becherini [g]

[a] LRMH, 77420 Champs-sur-Marne, France
[b] CNR-ICMATE (previously CNR-IENI), Padova, Italy
[c] CICRP, 13003 Marseille, France
[d] Prestim Groupe, 67560 Rosheim, France
[e] SC DUCT SRL, Bucuresti, Romania
[f] Department of Life Science and Biotechnology (SVeB), University of Ferrara, Ferrara, Italy
[g] CNR-ISAC, Padova, Italy

ARTICLE INFO

Article history:
Received 3 February 2017
Accepted 25 July 2017
Available online xxx

Keywords:
Calcium alkoxides
Wall paintings
Consolidation treatment
Consolidants' performance evaluation
Cultural heritage conservation
Impact testing device

ABSTRACT

In the field of cultural heritage conservation, wall paintings treatment is a particularly complex issue, which requires a suitable choice of materials. In this paper, two innovative calcium alkoxides, calcium tetrahydrofurfuryl oxide [$Ca(OTHF)_2$] and calcium ethoxide [$Ca(OEt)_2$], are proposed as new products for the consolidation of wall paintings. They were developed during the NANOMATCH European project and their efficacy, compatibility with the substrate and durability were evaluated in comparison with commercial products on both model and real samples. Model samples were exposed in four different sites around Europe to investigate the treatments' behaviour under different climatic conditions. The main research results are reported here: alkoxides showed to be a good option for wall paintings' consolidation especially in presence of certain binders and pigments. Finally, an impact testing device was used for the first time for the evaluation of the consolidants' efficacy and thus proposed as a reliable methodology for their performance assessment.

1. Introduction and research aim

Wall paintings are one of the most ancient forms of art. Wall paintings decorate architectural surfaces, and unlike other types of paintings, they cannot be isolated from the architectural structure they adorn and its environment [1,2]. A wall painting is a multi-layered system applied to an architectural support. A common European historic wall painting is often composed of three layers: a coarse mortar ground layer (*arriccio*), applied to the support, then a fine mortar finishing layer (*intonaco*) onto which is applied the painting layer. Several painting techniques exist; in the *fresco* (*affresco*) technique, the pigments, dispersed in (lime) water, are applied on a fresh and still damp lime mortar (*intonaco*). Pigments can also be applied on a dry and set *intonaco* (*a secco* technique): in that case they require to be mixed with an organic binder, such as yolk/egg, casein/milk, glue, natural gums, oils, etc.

The conservation of wall paintings is thus a complex issue due to their layered nature and their position as an integral part of an architectural structure. Many factors can play a role in their deterioration: lack of stability of the architectural structure itself, water, salts, light, and so forth. Multiple agents of deterioration often act in synergy, however the presence of water is often the key deterioration factor as it enables the migration of salts and determines the location of their re-crystallization, it acts as solution for polluting acids, it is a requirement for frost damage. Moreover, most biological attack and some chemical reactions (especially in pigments) do not take place in the absence of water [1]. Various deterioration

* Corresponding author.
E-mail address: patrizia.tomasin@cnr.it (P. Tomasin).

http://dx.doi.org/10.1016/j.culher.2017.07.008
1296-2074/

Please cite this article in press as: E. Bourguignon, et al., Calcium alkoxides as alternative consolidants for wall paintings: Evaluation of their performance in laboratory and on site, on model and original samples, in comparison to conventional products, Journal of Cultural Heritage (2017), http://dx.doi.org/10.1016/j.culher.2017.07.008

mechanisms can act on the different wall painting layers leading to a number of alteration phenomena: cracks, lack of adhesion and losses in the support, loss of cohesion of each layer (powdering), peeling, detachment and, eventually, complete loss of the paint layer. Conservation intervention on a wall painting often includes the application of a treatment. Defective past treatments have led to additional conservation problems, a choice of the most suitable and appropriate treatment is thus a priority.

Many inorganic and organic products have been used in conservation as wall paintings' fixative or consolidant. In the second half of the 20th century, natural organic products have been extensively replaced by synthetic polymers, which were initially favourably welcomed because of their good adhesion properties, low cost, their supposed reversibility and aesthetic compatibility [3]. A wide range of synthetic resins has been applied [4] (e.g. polyvinylacetates, polyvinylalcohols, acrylates), but after decades of extensive use they have shown their limitations and drawbacks, particularly after aging: incompatibility with the porous support of the paint layer [5,6], changes in physical, chemical and optical properties of the synthetic resins over time (crosslinking, chain scission, colour change [7]...), loss of adhesive/consolidant properties, limited removability/retreatability and even an unexpected lack of resistance to microbiological attack [8]. Over time, these products not only lost their functionality as consolidant, but often their presence itself became a source of deterioration of the wall painting.

Traditional inorganic treatments (lime water, barium treatment...) are generally much more physically and chemically compatible with wall paintings but often provide inadequate consolidation effect due to their low solubility in water and very limited penetration, and therefore require repeated applications to achieve any effect (e.g. lime water). A common inorganic treatment is the Ferroni–Dini method based on $Ba(OH)_2$, a satisfying treatment only in a limited number of cases [2,9]. In the last 20 years, new consolidation solutions for lime-based wall paintings based on nanotechnology (nanolimes) have been proposed [2,5,10].

Recent research has proved the consolidation action of a new family of inorganic compounds, calcium alkoxides on stone and stone-like materials [11,12]. Calcium alkoxides (or alcoholates), which are basically produced reacting metallic calcium with an alcohol, react with the atmosphere and, by hydrolysis and carbonation, form $CaCO_3$. When dissolved in organic solvents and applied on a deteriorated carbonate substrate, they are able to fill the microcracks and re-consolidate the structure. Their properties (tailored use of solvents and carbonation [13]) seemed promising for their use in wall paintings. Nevertheless, alkaline earth alkoxides with monodentate ligands are characterized by low solubility and low volatility, due to their tendency to oligomerise, which minimize their utilization also in other fields of application [14]. During the project this has been overcome by the scaling up of the alkoxides, which brought to the production of nanosuspensions with a very high concentration of Ca^{2+} [15].

The NANOMATCH European project (FP7-ENV-NMP.2011.3.2.1-1 Grant Agreement No. 283182), which results regarding wall paintings are presented in this article, aimed at evaluating more thoroughly the performance of these new products as consolidants in terms of compatibility, efficacy and durability for indoor and outdoor applications. The first systematic evaluation in laboratory of their performance is reported here and they are compared to commercial products on different substrates: powdered pigments with or without the addition of salts and wall painting mock-ups. Then, the durability of the treatments is evaluated after outdoor exposure in four different sites in Europe. Finally, trials on original wall paintings and some further practical demonstrations are described to give a broader overview of the potentiality of calcium alkoxides as new consolidants for wall paintings.

2. Experimental

The performance as consolidants of the new calcium alkoxides for painted substrates was evaluated in two different ways. Preliminary experiments were first carried out on powdered pigments mixed with one of the new NANOMATCH consolidants, with or without the addition of one of two salts commonly found in historic buildings, halite (NaCl) and thenardite (Na_2SO_4). The second set of experiments used man-made model substrates that replicate historic wall paintings on lime mortar support. The pigments were applied with different painting techniques, which may influence the effect of a consolidant on a painted substrate: *fresco*, with egg binder or with oil binder. The NANOMATCH consolidants were compared with two commercially available consolidants.

2.1. Material

2.1.1. Consolidants

2.1.1.1. NANOMATCH products. $Ca(OTHF)_2$, a whitish crystalline solid, and $Ca(OEt)_2$, a nanosuspension in THF/EtOH, were produced at a kilo-scale by ABCR, Spain, with a modification of the ammonia method already described in the literature [11,15].

Nanosuspensions were tested to assess their particle dimension, by transmission electron microscopy (TEM) and/or dynamic light scattering (DLS) analysis (see Supplementary material S1 for details): fresh $Ca(OTHF)_2$, in ethanol/ligroin showed a dispersion centered around 50 nm, with all particle dimensions between 20 e 120 nm (DLS and TEM gave similar results), while $Ca(OEt)_2$ in THF/EtOH, presents particles distribution between 70 e 700 nm and centered around 250 nm according to DLS and between 10 and 77 nm centered at 33 nm (TEM). $Ca(OEt)_2$ in THF/EtOH shows a greater stability, in fact after 2 years from the production the dimensions changed very little (94% of particles have dimensions between 164 nm e 452 nm centered at 290 nm). On the other side, in later applications $Ca(OTHF)_2$ showed an increase of particle dimensions with formation of clusters visible to the naked eye: however this problem (probably deriving from the presence of residues not eliminated at the small industrial purification level) was partially reduced with the sonication of the suspensions. The exact calcium content of the suspension was determined by ICP-OES (see Supplementary material S1). Carbonation process and crystal habit of deposits of calcium alkoxides were studied by microFT-IR and by XRD [13].

Optimal application procedures (solvent, concentration) were selected after different trials. The two NANOMATCH consolidants were used as:

- $Ca(OTHF)_2$ dissolved in 1:1 ethanol:ligroin at 20 g/L of Ca;
- $Ca(OEt)_2$ diluted in ethanol at 20 g/L of Ca.

Ethanol was purchased from Grupp (Souffelweyersheim, France), ligroin 100/140° from CTS (Paris, France).

2.1.1.2. Commercial consolidant products. The two commercial products were selected for comparison:

- Primal™ E 330 S, distributed by CTS (Paris, France), an acrylic emulsion in water, applied pure as recommended by the manufacturer (Dow chemicals, Midland, United States);
- CaLoSiL® E50 (calcium hydroxide nanoparticles), manufactured by IBZ-Salzchemie (Freiberg, Germany) applied diluted in ethanol to obtain the same concentration of Ca (20 g/L) than that of the calcium alkoxides.

All consolidant solutions (NANOMATCH and commercial) were applied one time by brush on the samples.

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