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NANOMATERIALS FOR CONSOLIDATION OF MARBLE AND WALL PAINTINGS

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Abstract

This paper presents the study of calcium alkoxides from their synthesis to the final application as $CaCO_3$ precursors for calcareous materials consolidation. These innovative nano-structured molecules have been specifically designed to reach the requirements of compatibility and effectiveness when consolidating cultural heritage carbonaceous substrates such as marble and wall paintings.

The first step was the selection of solvents used to solubilize the alkoxide. Then we selected two types of substrates in order to test its performances: samples of weathered Carrara marble (5x5x1 cm) and wall paintings specimens of frescoes and a secco techniques of green earth, yellow ochre, azurite, lead-tin yellow and cinnabar-white lead mix. Variations of ultrasonic velocity, observations of the coatings by FEG-ESEM and spectrophotocolorimetric measurements were done to evaluate the consolidation effects of the alkoxides and the absence of side-effects such as whitening. The calcium triethylen glycol monoethyl ether ($Ca(TEGmEE)_2$) gave the best results in butanol for wall paintings and it gave good results for consolidation specifications in isopropanol for marble specimens.

This work has been supported by a bilateral project in 2010 by both French and Italian Foreign Affairs Ministries. Further studies will be done on this class of materials within the NANOMATCH project (Nano-systems for the conservation of immoveable and moveable polymaterial Cultural Heritage in a changing environment FTP-ENV-NMP-2011-2183182).

Keywords: wall paintings, marble, consolidation, nanoparticles, ultrasonic velocity, colorimetry, ESEM

1. Introduction

The extensive use of commercial organic polymers over the last 50 years for historical conservation treatments of stone and wall paintings has shown its limits in terms of durability and retreatability. Tailor-made inorganic nano-sized molecules based on calcium alkoxides have been investigated as they are thought to be most likely the most compatible materials with these substrates, as calcite precursors, when facing up to sugaring or powdering issues. A preliminary study was done on calcium alkoxides synthesis (Favaro, Ossola et al. 2008)and on the selection of molecules by the evaluation of their solubility and stability in methanol, ethanol, isopropanol and butanol. Characterization of the compounds was carried out by NMR and FT-IR, their decomposition process by FT-IR and the final crystalline phases (portlandite, vaterite,

calcite) after carbonation of the alkoxides by XRD (Favaro, Tomasin et al. 2008). Then this work started within a Galileo-Egide (Favaro, Detalle 2009), project supported in 2008-2009 by both French and Italian Foreign Affairs Ministries.

2. Mataerials and methods

2.1 Synthesis of the $Ca(TEGmEE)_2$

Calcium granules (1g, 25 mmol) and triethylene glycol monoethyl ether (8.5 mL, 8.7 g, 48.8 mmol) were added to toluene (30 mL). Mixture was refrigerated just above solvent melting point and maintained at this temperature under stirring. NH_3 was bubbled into the mixture at intervals. Reaction took place with gradual consumption of calcium granules and tiny bubbles evolution on calcium surface turning golden yellow (48 h). Mixture was filtered and solvent evaporated under vacuum to give an amber-colored viscous oil which was analyzed and identified as $Ca[O(CH_2CH_2O)_3CH_2CH_3]_2$ (found C 49.69, H 8.77 %; calcd. for $C_{16}H_{34}O_8Ca$: C 48.73, H 8.63; 88% yield).

^{1}H NMR: d_8-toluene, δ ppm: 1.14 (tr, 6H, $OCH_2C\underline{H}_3$), 3.37 (q, 4H, $OC\underline{H}_2CH_3$), 3.49 (t, 4H, $C\underline{H}_2OCH_2CH_3$), 3.60 (sb, 4H, $C\underline{H}_2O$), 3.69 (sb, 4H, $C\underline{H}_2O$), 3.77 (sb, 4H, $C\underline{H}_2CH_2OCa$) 3.81 (sb, 4H, $C\underline{H}_2O$), 4.20 (sb, 4H, $CH_2C\underline{H}_2OCa$).

^{13}C NMR d_8-toluene, δ ppm: 15.58 ppm ($OCH_2\underline{C}H_3$), 63.49 ($CH_2\underline{C}H_2OCa$), 66.66 ($O\underline{C}H_2CH_3$), 70.52 ($\underline{C}H_2OCH_2CH_3$), 70.70 ($\underline{C}H_2O$), 71.08 ($\underline{C}H_2O$), 76.83 ($\underline{C}H_2CH_2OCa$).

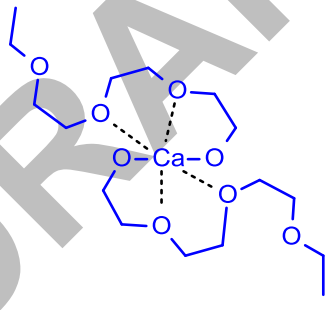

Figure 1. $Ca(TEGmEE)_2$

2.2 Marble specimens

Carrara marble specimens (dimension 5×5×1 cm) were artificially aged by heating in order to get the same compactness than exposed real samples (Delgado Rodrigues, Ferreira Pinto et al. 2007).

2.3 Wall painting specimens

Two kinds of replicate samples have been used: a first one with artificially deteriorated substrates that was meant to test application issues and consolidant effects and another one with classic mechanical properties but with a larger paint palette and techniques (*fresco* and *a secco*, Table 1) on which we carried out evaluation of potential side-effects like pigment and binder alteration from calcium alkoxide and the solvents.

For the first group, we settled mortar proportions (excess of water and lean render) and pigment dilution (saturation in water and lime water) in order to get fragile lime rendering as well as powdering paint layers. These specimens were 15x15x3 cm. The

ground layer was done with one part of lime powder (CAEB Calcia) and 3 parts of washed gravel pit sand (0-4 mm). Then red ochre (ocre rouge RFL, Ôkhra) was applied diluted in water on fresh rendering. After four weeks, a second layer of yellow ochre (ocre oxy-apt jaune, Ôkhra) diluted in lime water was brushed on half of the sample. One of these samples was used for the drilling resistance measurement system (DRMS) investigations after consolidation.

The second set of test models consisted in autoclave cellular concrete (ACC) plates (2.5 cm thick), coated with two layers for frescoes: a ground layer made of slake lime and coarse sand (1:3) and a finishing layer (intonaco) made of lime and fine sand (1:2) tiered up and smoothed. Pigments were diluted in water and applied on fresh plaster.

For the *a secco* techniques a thin layer of intonaco (lime and fine sand 1:2) was applied directly on the ACC, then a whitewash made of chalk (Ôkhra) and skin rabbit glue (Ôkhra, 10%) was brushed. Finally the paint layer of pigment padded out in the organic medium (skin rabbit glue, milk casein, egg yolk and oil) was brushed on the dry plaster.

Pigments used in this study were provided by Kremer Pigmente GmbH with the exception for ochre and earth from Ôkhra.

Pigment	*Binder*	*Technique*
green earth	---	fresco
azurite	animal glue	distemper
lead tin yellow	---	fresco
cinnabar and lead white	animal glue	distemper
yellow ochre	egg yolk	distemper
yellow ochre	animal glue	distemper
yellow ochre	Casein	
yellow ochre	Oil	oil
yellow ochre		fresco

Table 1. Sum-up of the wall painting samples

2.4 Application methodologies

2.4.1 Marble

Marble specimens set horizontally were soaked three times for two hours in alkoxides solutions of isopropanol, with the front side dipped by 2 mm.

2.4.2 Wall paintings

Application issues were related to potential color alteration due to interaction between calcium alkoxide, solvents, pigments and binding media. Then we tested different solvents to get the alkoxide solutions (24 g/l, 0.06M). After a quick screening test, it appeared that isopropanol (I), butanol (B) and an azeotrope (A) of cyclohexane (67%wt) and isopropanol (33%wt) were the most appropriate. The treatment protocol planned the application by brush three times, with 20 min between each one.

The set of powdery samples was treated by brush without any particular precaution. After noting the formation of a white bloom covering the paint layer, we decided to ask a conservator to treat the second set of polychrome replicas. She pre-wetted the surface,

with the same solvent used to solubilize the consolidant, to promote the migration of the solution deep into the layers and then avoid the superficial crystallization of calcite.

2.5 Treatment evaluation

2.5.1 Colorimetric data

The first parameter to assess for the treatment validation was the absence of color modification after application of consolidant. We carried out measurements before treatment and after 8 months by reflectance spectroscopy using a STIL NCS Ruby portable fiber-optics reflectance spectrometer operating in 400-800 nm range. Spectra were acquired at 5 nm intervals at a rate of 0.1 second per data point using a D65 light source at 22°, standard CIE 1931, at 8 cm from the sample surface and with a spot diameter of 7 mm. Total color variation (ΔE) between treated and untreated specimens was determined. Usually $\Delta E<5$ characterizes a slight color change invisible to the naked eye.

2.5.2 FEG-ESEM observations

Morphological examinations were carried out with a FEG-ESEM Fei Quanta 200 high resolution scanning electron microscope. The analytical conditions were: low vacuum, 25 keV accelerating voltage and 10 mm working distance. EDS microanalyses were performed with an Energy Dispersive X-ray Spectrometer EDAX.

2.5.3 Ultrasonic velocity

Ultrasonic investigations were achieved according to European normative RILEM and U.N.I. 9524 with a USG 20 (Geotron Elektronik, Germany) portable device, operated with a point-shaped 46 kHz-vibrator (UPG-T) and receiver (UPE-T) (Favaro, Mendichi et al. 2006).

2.5.4 Drill resistance measurements

Drilling resistance was measured with a SINT Technology cordless minidrill device.

3. Results and discussion

3.1 Marble

To evaluate the effectiveness of consolidation on marble, ultrasonic speed measures were performed on weathered samples before and after treatment. As these values are directly related to the compactness of the stone, they are used to assess the alteration degree of stone samples and also the strengthening improvement by consolidation treatment. The data obtained reveal an increase of the speed of about 28% for marble specimens when treated with a solution of $Ca(TEGmEE)_2$ in isopropanol.

3.2 Wall paintings

Colorimetric measurements were performed on the untreated samples and on treated ones, before consolidant applications and after 8 months. Photographic documentation was carried out and L, a, b coordinates were registered according to the CIEDE2000 (CIE 2001) normative in order to evaluate color alteration due to the

consolidant cure. 3 measurements were performed over each specimen and L, a, b mean values have been considered in the elaboration of data. Isopropanol solutions came out to give general and significant variations for all pigments layers and all techniques except casein with ΔE>5. No major variation was detected for butanol and azeotrope except for all pigments in egg yolk tempera for which we noted that solvent-binder interaction has intensified color saturation. But no whitening was settled with superficial calcite bloom. Data on the color variations for yellow ochre samples are reported in Table 2.

	Untreated			Isopropanol				Azeotrope				Butanol			
Coordinates	L	a	b	L	a	b	**ΔE**	L	a	b	**ΔE**	L	a	b	**ΔE**
Casein	50	43	85	51	43	86	**<5**	51	43	87	**<5**	53	44	90	**<5**
Animal glue	57	37	97	54	39	92	**7**	57	39	97	**<5**	57	38	96	**<5**
Fresco	66	29	110	70	24	115	**8**	70	24	115	**<5**	67	28	112	**<5**
Oil	41	42	70	25	37	43	**24**	39	43	66	**<5**	38	43	64	**<5**
Egg yolk	43	42	73	41	42	69	**7**	47	43	79	**6.5**	48	43	82	**10**

Table 2. Yellow ochre colorimetric values

FEG-ESEM examinations on paint layers pointed out again different behaviors depending on the solvents used. These differences were essentially shown in morphology and distribution of the calcite coating. For instance, the most significant example is related to the treatment of yellow ochre (fig.2) and azurite in animal glue (fig.3) with $Ca(TEGmEE)_2$ in isopropanol that has led to the formation of an irregular coating from 3 to 10 µm with numerous breaks (fig.4). Whereas the same samples treated with the consolidant in butanol show a thinner and homogeneous calcite film of 2-3 µm, without any cracks. The azeotropic solution behaved in the same way than the butanol blend. This may due to the fact that coating deposition and penetration depth are directly linked to the solvent evaporation speed. Calcium alkoxides particles appear to settle more regularly even in depth into the paint layer in high boiling solvent (butanol 117°C) thanks to the slower evaporation, counter to the more volatile ones (isopropanol 82.5°C and azeotrope 68.6°C), where the consolidant is accumulated unevenly on the roughness of the paint surface.

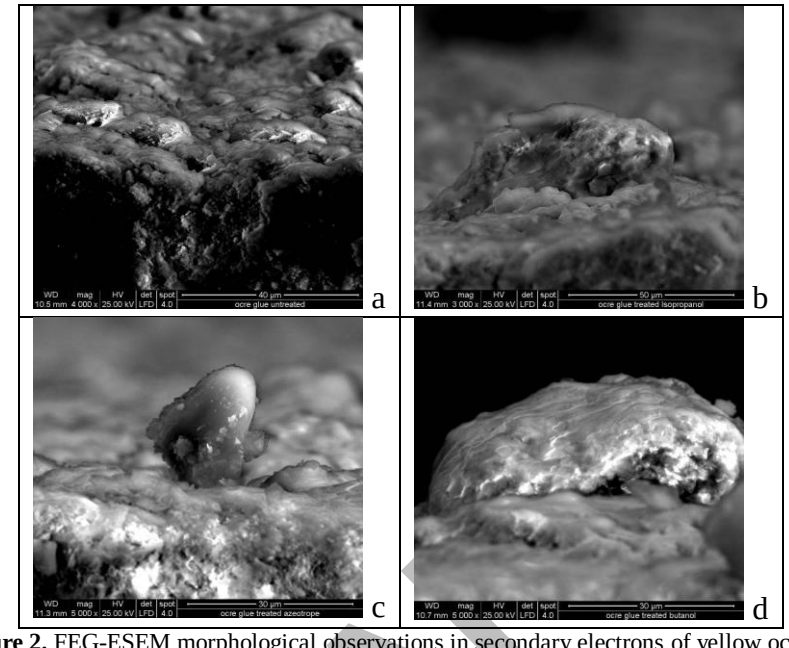

Figure 2. FEG-ESEM morphological observations in secondary electrons of yellow ochre in animal glue distemper before treatment (a: 4000x), after treatment in isopropanol (b: 3000x), azeotropic solution (c: 5000x), butanol (d: 5000x).

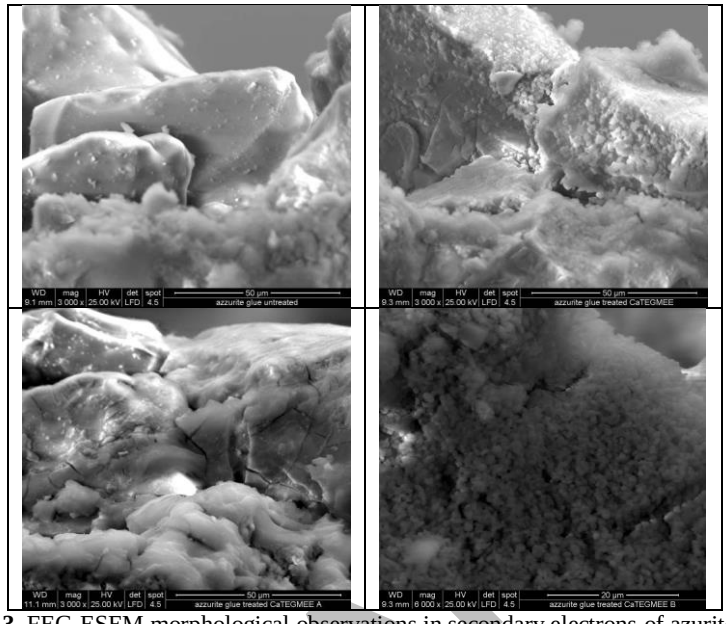

Figure 3. FEG-ESEM morphological observations in secondary electrons of azurite in animal glue distemper before treatment (a: 3000x), after treatment in isopropanol (b: 3000x), azeotropic solution (c: 3000x), butanol (d: 6000x).

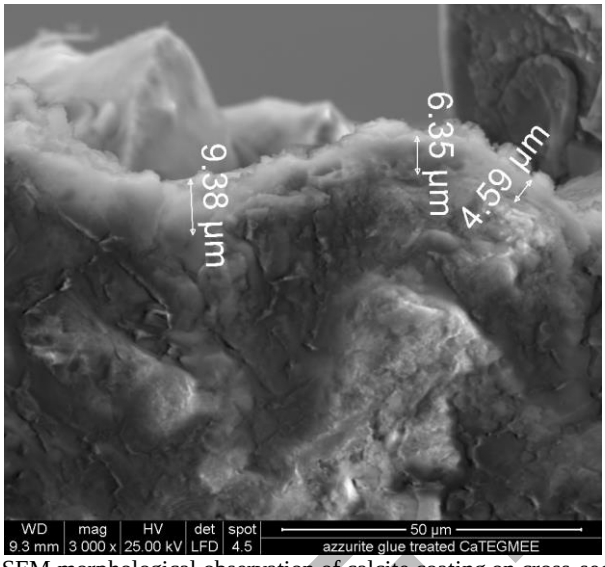

Figure 4. FEG-ESEM morphological observation of calcite coating on cross-section of azurite in glue distemper treated with $Ca(TEGmEE)_2$ in isopropanol (x3000).

Unfortunately, ultrasonic velocity differences measured on painted samples before and after treatment were between -0.2 and + 7 which are included in the 10% of experimental error. Neither drilling resistance measurements gave fruitful data to evaluate the strengthening due to the treatment.

4. Conclusions

The calcium triethylen glycol monoethyl ether ($Ca(TEGmEE)_2$), used as calcite precursor in porous materials was selected for its high solubility in polar protic solvents and the relative good workability and penetration when brushed on powdery surfaces.
The results of ultrasonic velocities measurements on weathered marble indicate an increasing of compactness revealing a cohesion enhancement thanks to calcite crystallization.

As far as wall paintings are concerned, this work highlighted the paramount role of solvents choice and applications modalities. The chromatic variations induced by the product application range within acceptable limits when butanol is used to prepare the solution while the most significant alteration is observed for isopropanol solution, whatever pigments or binding media are. Regarding coating morphology, it appears that butanol calcium alkoxide solution promotes the formation of a more regular film. In an attempt to adopt stone classical consolidation evaluation system (DRMS, ultrasonic velocity) for wall paintings purposes, we have seen that most of techniques are not suitable to rate thin layers strengthening.

This particular point and further studies will be elaborated under the framework of the NANOMATCH project (Nano-systems for the conservation of immoveable and moveable polymaterial Cultural Heritage in a changing environment FTP-ENV-NMP-2011-2183182) which deals with stone, wall paintings, stained glass and wood

consolidation. New calcium alkoxides molecules will also be tested along with biocide combinations.

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References

CIE 2001. Improvement to industrial colour-difference evaluation. C. Publication. Vienna, Central Bureau of the CIE.

Delgado Rodrigues, J., A. P. Ferreira Pinto, et al. 2007. Preparation of aged samples for testing stone treatments. Il consolidamento degli apparati architettonici e decorativi: conoscenze, orientamenti, esperienze: atti del convegno di studi, Bressanone, 10-13 luglio 2007. G. Biscontin and G. Driussi. Marghera Venezia, Italy, Arcadia Ricerche**:** 597-605.

Favaro, M., Detalle V. 2010. Progetto Galileo 2008/2009: Materiali innovativi per il consolidamento della pietra calcarea e dei dipinti murali/Nouveaux matériaux consolidants pour pierre calcaire et peintures murales.

Favaro, M., Mendichi R., Ossola F., Russo U., Simon S., Tomasin P., Vigato P.A., 2006. "Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering." Polymer Degradation and Stability **91**(12): 3083-3096.

Favaro, M., F. Ossola, P. Tomasin, P.A. Vigato, G. Rossetto, N. El Habra, M. Casarin, 2008. A novel approach to compatible and durable consolidation of limestone. 11th International Congress on Deterioration and Conservation of Stone: 15-20 September 2008, Torun, Poland: proceedings. J. W. Lukaszewicz and P. Niemcewicz, Torun, Poland, Wydawnictwo Naukowe Uniwersytetu Mikolaja Kopernika**:** 865-872.

Favaro, M., Tomasin P., Ossola F., Vigato P.A., 2008. "A novel approach to consolidation of historical limestone: the calcium alkoxides." Applied Organometallic Chemistry **22**(12): 698-704.