ALKALINE EARTH ALKOXIDES FOR CONSERVATION TREATMENT OF STONE AND WOOD IN BUILT HERITAGE

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ABSTRACT

Although reduction of pollutants, thanks to a more sustainable industrialization, and conservation treatments have certainly reduced the deterioration of built heritage, recently new threats, such as climate change and ageing of conservation treatments, are threatening the present and future conservation of these historical materials.

On the basis of these premises, the development of innovative surface consolidants specifically designed to meet the requirements of historic building substrates has been addressed in the frame of the EU-project NANOMATCH. In particular, alkaline earth metal alkoxides were synthesized for conservation of stone and wood materials while aluminum alkoxides, synthesized in the EU-project CONSTGLASS, were prototyped for the treatment of deteriorated glasses. Moreover, a selection of biocides has been made according to European standards (Biocidal Product Directive 98/8/EC), to be used in association with the consolidants to mitigate the biological decay of the treated stones.

In the present work, the results obtained for those alkoxides to be used as nano-structured carbonate consolidants for stone and wood will be reported.

Regarding calcium compounds, it has been demonstrated that they are more soluble than the corresponding commercial Ca-bearing consolidants and, after reaction with air, they evolve into calcium carbonate structures. Moreover, it has been observed that the conversion to the different carbonate polymorphs, i.e. calcite and vaterite, depends not only on environmental condition (temperature and RH) but also on the solvent used for their application.

On the other hand, despite the fact that the behavior of magnesium alkoxides and alkyl carbonate could be assumed to be similar to that of calcium compounds, it was demonstrated that, in place of the required magnesium carbonate (magnesite), they evolve into products (magnesium hydrated carbonate and hydroxide) that might be deleterious for the further conservation of stone and wood.

Moreover, a selection of biocides was made according to European standards (Biocidal Product Directive 98/8/EC), to be used in association with the consolidants to mitigate the biological decay of the treated stones, and preliminary results on their behavior will be reported in the present paper.

1. Introduction

The main materials constituting the built heritage (stone, wood and glass) have always been threatened by a great variety of deterioration agents, both natural (water, salts, micro-organism) and anthropic (pollution). Although reduction of pollutants, thanks to a more sustainable industrialization, and conservation treatments have certainly reduced the deterioration of built heritage, recently new issues, such as climate change and ageing of conservation treatments, are threatening the present and future conservation of these historical materials [1].

Currently, several consolidation treatments, namely synthetic polymers, which have been used in the last 50 years, are under reconsideration because of their incomplete removability, their low compatibility with the substrate and poor durability [2].

Inorganic treatments have always been considered more compatible: application of water suspension of slaked limes is a traditional UK treatment for carbonatic stone, whose drawback lies in the extreme low solubility of $Ca(OH)_2$ in water (1.7 g/L at 20°C) which implies many repetitive applications. A new concept in the application of slaked limes was introduced by Baglioni et al. [3] with the use of micro- and nanodispersion of calcium hydroxide in alcohol. The nanodimension allows the penetration of higher quantity of more reactive compound thus ensuring recohesion of deteriorated stone or plaster.

Calcium hydroxide, by atmospheric effect, evolves into $CaCO_3$, which is the main constituent of carbonatic stone. On this carbonation reaction depends also the possible use

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of alkaline earth metal alkoxides, a well-known class of metallorganic compounds [4]. They react easily with water and carbon dioxide leading to the corresponding metal carbonate [5]. The chemical structure of the alkoxides can be opportunely varied by using different starting alcohols, thus allowing a modulation of the physico-chemical properties of the final compounds. In particular, the possibility of obtaining soluble products should guarantee, with respect to nanolimes, a better penetration, even in smaller pores, and a homogeneous distribution with no superficial whitening.

In the frame of the EU-project NANOMATCH, alkaline earth metal alkoxides were synthesized for conservation of stone and wood materials while aluminum alkoxides, synthesized in the EU-project CONSTGLASS, were prototyped for the treatment of deteriorated glass and their performance as conservation alternative treatments were evaluated in the context of European climate change.

Beyond consolidation/protection, another important issue, relevant for both stone and wood materials, is the possible microbiotic attack that strongly affect their conservation [6].

In the present work, some of the results obtained for those alkoxides to be used as nano-structured carbonate consolidants for stone and wood will be reported. In particular we will report, as an example, results on one of the chosen compounds: $Ca(OEt)_2$. Moreover, the application of the biocide products, together with the alkoxides, will be described.

2.   Calcium alkoxides

Different synthetic pathways to produce calcium alkoxides were tested and several products obtained. The most effective syntheses were then selected.

Rieke synthesis involves the preliminary formation of a highly reactive activated form of calcium, the so-called "Rieke calcium". This highly reactive species was prepared by reduction of a THF suspension of an anhydrous metal halide with an alkali metal and is highly reactive because of the presence of a high surface area. This can react with the appropriate alcohol.

Alcoholysis reaction of the alkoxide with a second alcohol that easily results in another calcium alkoxide. The calcium ethoxide was chosen as precursor in the formation of other alkoxides due to its easy synthesis, its solubility (too low in the case of methoxide) and reactivity.

Ammonia method. According to literature [7], liquid ammonia can dissolve and activate the metals. Under inert atmosphere, metallic calcium in freshly anhydrous distilled solvent was cooled to -45 to -60°C and gaseous ammonia was bubbled inside. Once the metal had dissolved, a solution of the desired alcohol in the appropriate solvent was added, and the temperature carefully tuned to room temperature. Some difficulties were encountered when working with ethanol because of a strong competition between the coordinating solvent and the alcohol. Few forms of calcium ethoxide have been isolated and identified, some of them are clearly oligomeric (with ^1H and ^{13}C signals really broad). The difficulty in always reproducing the same species is probably due to the impossibility of maintaining a constant temperature during the experiment. This resulted in a final product which often is a suspension rather than a solution.

Direct reaction between alcohol and metallic calcium is, from a synthetic point of view, the easiest way to obtain calcium alkoxides. Under a nitrogen atmosphere, pieces of metallic calcium are vigorously stirred -with or without reflux- in an excess of anhydrous alcohol, with or without the presence of another solvent. First trials were carried out with low boiling alcohols; in the case of calcium methoxide the reaction was run at room temperature (25°C) in neat: 400mg of metallic calcium was stirred for few hours in 50ml of pure anhydrous methanol, without heating. After a period of time (from 15min to 1 hour) the solution became cloudy and after one night the metal totally disappeared, resulting in a solid white powder almost insoluble in the common organic solvents. By this procedure an oligomeric form of calcium methoxide was obtained with a limited solubility only in methanol. Then we examined calcium ethoxide, using a very similar procedure and experimental conditions (400mg of metallic calcium in 50ml of pure anhydrous ethanol) under reflux. The resulting colorless solution, according to NMR and elemental analyses, was recognized as being calcium ethoxide in an oligomeric form. However this reaction is not strictly reproducible and often, working in more concentrated conditions, a suspension is obtained.
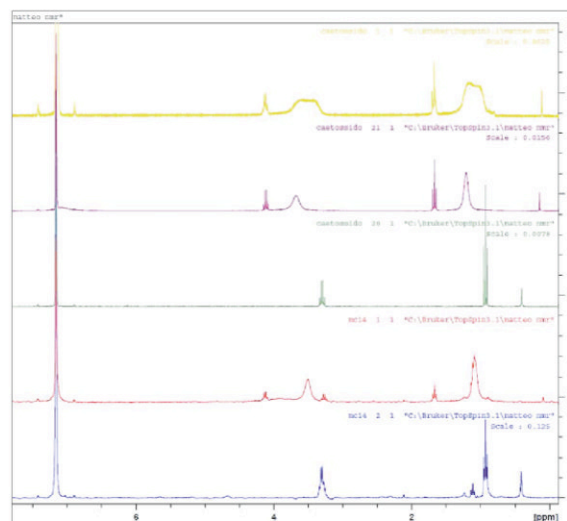

Figure 1 ^1H-NMR of Ca ethoxide.

According to literature [8] at least four different species can be detected: $Ca(OEt)_2$, $Ca(OEt)_2 \cdot 2EtOH$, $Ca(OEt)_2 \cdot 4EtOH$ and $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4 \cdot 14EtOH]$, the so called calcium oxo-ethoxide, the last species being, according to the chemical-physical data, the most interesting because of its high solubility. Following literature procedures, the mixture was refluxed for a few days under a nitrogen atmosphere, until a yellow solution without precipitate was obtained. Even when the solubility of the mixture increased, the pure oxo-derivative ethoxide was never obtained; NMR and elemental analyses showed the occurrence of different similar species (Fig.1).

3.   Deposition of $Ca(OEt)^2$

Saturated solutions of $Ca(OEt)_2$ in different solvents, prepared under a dry atmosphere, were deposited on a

flat golden surface. The solvents Tetrahydrofuran (THF), 2-Methyltetrahydrofuran (MeTHF), 1,3-Dioxolane (1-3 DO), propan-2-ol (*i*-PrOH), Dimethyl carbonate (DMC), Tetrahydrofurfuryl alcohol (THFOH), N,N'-Dimethylpropylurea (DMPU) were selected according to their physical-chemical and toxicological properties. A summary of the obtained results is reported in Table 1. The kinetic of carbonation was followed by micro FT-IR measurements. A Nicolet microscope connected to a Nicolet 560 FT-IR system, equipped with a MCT (Mercury Cadmium Telluride) detector, was used. Investigated microareas were about 50x50 mm^2 of size. IR spectra were recorded in reflectance mode in the 4000-650 cm^{-1} range (esolution of 4 cm^{-1}).

After few minutes Ca(OEt)$_2$ in THF, Me-THF and alcohols converted to ACC (amorphous calcium carbonate) while some hours are needed for the conversion from DMPU solution. Furthermore, from an initial step of amorphous carbonate, it then evolves into a more structured carbonate structure. The conversion of alkoxides from volatile solvents clearly shows the formation of calcium carbonate as vaterite and from low volatility solvents, such as DMPU, as calcite (even if, obviously, after a longer time). It was also observed that vaterite partially turned to calcite with time, i.e. after 7 days from i-PrOH and EtOH solutions from calcium ethoxide.

	THF	Me THF	1,3-DO	iPrOH	EtOH	DMC	DMPU
Vapor pressure (20°C) [mmHg]	143	102	93	43	43	24 (21°C)	0.49 (57°C)
ACC	1'	2'	1'	1'	1'	15'	
vaterite	3'	5'	3'	2'	2'	30'	
portlandite	3'	5'	3'				
calcite				7 days	7 days		7days

Table 1 Carbonation time of Ca(OEt)$_2$ from its solution in different solvents.

These first results clearly show that the higher the vapor pressure of the employed solvent, the faster the carbonation due to a fast evaporation rate. Moreover, with high volatile solvents the carbonation leads to a kinetically favored vaterite phase, while low volatile solvents allow a better organization of the calcium carbonate structure, resulting in the thermodynamically favored calcite phase.

High resolution morphological observations were collected by Fei Quanta 200 FEG-ESEM using an accelerating voltage of 25 keV in low vacuum mode. The carbonate coating showed that they are mainly composed of spheroidal aggregates and flat platelets. Spheroids are even composed of spherical particles: this morphology is in agreement with that of natural and artificial particles of vaterite.
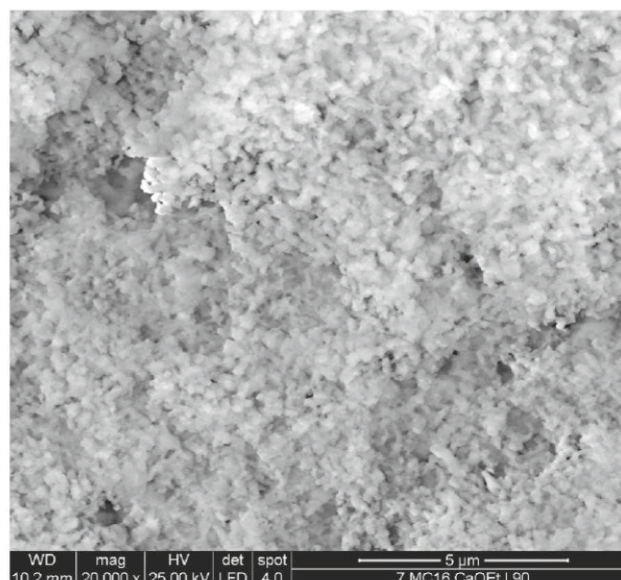

Figure 2 SEM microimages collected from coatings of Ca(OEt)^2.

X-Ray Diffraction (XRD) measurements were carried out by using a Philips PW 3020 powder diffractometer with a Bragg-Brentano θ-2θ geometry. The radiation used was the Cu Kα (λ = 1.05456 Å) operating at 40 kV and 30 mA. All the patterns were collected in the 10°-65° 2θ range and the phase identification was performed with the support of the standard patterns reported in 2002 ICDD databases.

Ca(OEt)$_2$, in suitable quantity, was dissolved in THF solvent (8 g/L Ca equivalent). The resulting solution was spread on two pre-cleaned glass slides (washed with soap and rinsed with distilled water) which were then placed for 14 days in two glass crystallizers maintained at 25 °C, in atmosphere but at different relative humidity (RH) of 50% and 90%, respectively, in order to establish the effect of the relative humidity on the Ca(OEt)$_2$ decomposition. The RHs of 50 and 90% were maintained by an over-saturated calcium chloride (CaCl$_2$) and potassium nitrate (KNO$_3$) solutions, respectively, and the RH anf Temperature values were monitored by a Hygrometer (Oregon Scientific).

White coatings were produced on the surface of the glass substrates as a result of the Ca(OEt)$_2$ reaction with air and then were structurally investigated by XRD.

The XRD patterns obtained are reported in Fig. 3 Both the deposits were polycrystalline without preferential orientation, as evidenced by the analysis of the relative intensities of XRD reflections. However, amorphous phases cannot be excluded. Both patterns clearly show the co-presence of vaterite (*ICDD: 01-072-0506*) and calcite (*ICDD: 01-072-1651*) as carbonatic phases. This suggests that, in these experimental conditions, the different RHs employed seem not to preferentially influence the formation of the calcite phase rather than the vaterite phase.
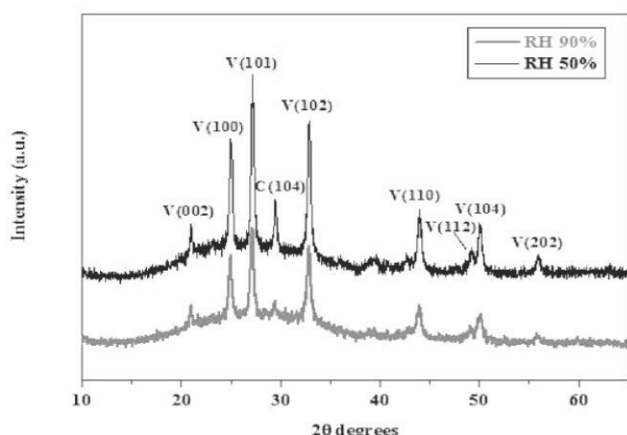
Figure 3 XRD patterns of the coatings obtained from a solution of Ca(OEt)$_2$ in THF solvent maintained at different relative humidity (50% and 90%) for 14 days (with C = calcite, V = vaterite).

IR spectra on the coatings obtained in different humidity conditions, confirmed the results of XRD measurements, showing no differences between the two samples maintained at different RH (Figure 4). Moreover, only the vaterite form is detected by IR measurements.
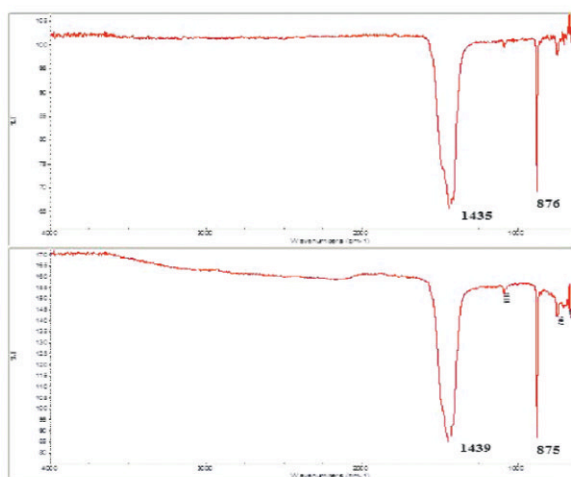

Figure 4 IR spectra collected after carbonation completion of Ca(OH)2 suspension at 50 (upper spectrum) and 90 % RH (lower spectrum).

4. Magnesium alkoxides

Great interest has been devoted to magnesium alkoxides as precursors for the preparation of complex oxides or solid oxide solutions, in particular the synthesis of nanoscale magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)$_2$ particles via the magnesium alkoxide Mg(OR)$_2$ route. Generally, an alkoxide is hydrolyzed in an alcohol solvent to yield the hydroxide, which is followed by isolation and thermal dehydration [9]. Pure magnesium oxide are commercially produced by hydrolysis of Mg(OCH$_3$)$_2$ or Mg(OC$_5$H$_{11}$)$_2$ with the following thermal treatment or through the use of solutions obtained dissolving magnesium in methoxyethanol [4]. Since the main target of our research was to obtain suitable deposits of Mg(CO$_3$)$_2$, a preliminary study of deposition and subsequent carbonation of soluble commercial products was performed.

The following is an example of the characterization of the coating obtained by the deposition of a solution of Mg(OCH$_3$)$_2$ in MeOH (ca. 10 wt.%) on a glass slide and analysed by XRD after 20 days of air exposure. The XRD pattern of the sample reveals very large reflections, indicating a low crystallinity and difficult to assign (Figure 5). The most probable phase seems to be brucite [hexagonal Mg(OH)$_2$]. The presence of hydromagnesite [Mg$_3$(CO$_3$)$_4$(OH)$_2$•4H$_2$O], Mg oxide/periclasio (MgO) and magnesite (MgCO$_3$) can be excluded.

The 10 wt. % solution was then diluted with MeOH (1:2) and the XRD spectrum of its deposit gave even larger peaks, which were extremely difficult to assign.

IR measurements performed on the same coatings confirmed the presence of hydrated magnesium carbonate and low ordered carbonate structure (broadening of the bands around 1420 cm-1), that might explain the amorphous phases identified in the XRD patterns.
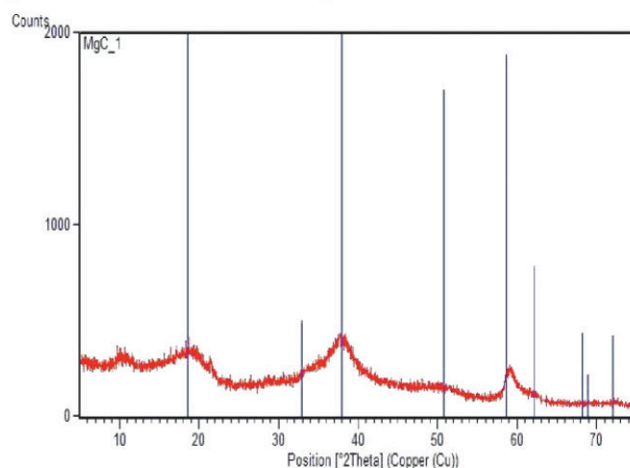

Figure 5 XRD pattern collected from the magnesium carbonate formed after deposition of a solution of Mg(OCH$_3$)$_2$ in MeOH (ca. 10 wt.%).

XRD and IR results of analysed magnesium compounds evidenced that they gave rise to coatings with a very low degree of cristallinity. Furthermore, the identified phases revealed the formation of magnesium carbonate into the required phase magnesite did not occur, while these magnesium compounds preferably convert to different hydrated structure of magnesium carbonate and also magnesium hydroxide. Hydrated magnesium carbonates are reactive towards water and, if applied on stone substrates, could be a possible source of efflorescence of soluble magnesium salts rather than evolve to stable magnesium carbonate. On the other hand magnesium hydroxide, i.e. brucite, is rather insoluble and, once formed, it will rarely convert to magnesite.

For this reason, magnesium compounds were abandoned as precursors for magnesium carbonate formation.

5. Biocides selection and test

5.1 General criteria for the selection of biocides

Initially, the project proposed to add inorganic colloidal metals or biomolecules to the metal-alkoxides solution with the aim of obtaining a carbonate matrix with immobilized

biocide additives.

The question arises about the relevance of mixing the biocide with the calcium alkoxide consolidant prior to their application on the substrate or whether to apply the two products separately.

If the two products are mixed, the resulting solution then becomes a new biocide formulation which may require a new evaluation procedure to be approved for use in the European Union. Such procedure cannot be carried out within the framework of Nanomatch since the project's main focus is to develop innovative consolidants, with biocide properties if doped with appropriate biocide molecules, not new biocide molecules.

In addition, many commercial biocides are formulated in aqueous solution, while the calcium alkoxide consolidants cannot be in contact with water.

Consequently, it was decided that the biocide and the consolidant products would be applied separately and that the biocides chosen should already be approved for use in the EU, or at least registered to be evaluated for approval.

The active substances of the commercial biocides chosen should, ideally, already be approved for use in the EU, that is, should be included in Annex I or IA of the European Biocidal Product Directive 98/8/EC. However, the approval process is still on-going and few biocides are already on these lists, in particular, there is still no active substance approved as a Masonry Preservative (Product Type 10). It was therefore decided to choose the commercial biocides among those already approved for use in the EU or at least already included in the list of active substances to be examined under the review program (Annex II of Commission Regulation 1451/2007).

5.2   Biocides for stone

Another important criteria used for the choice of the biocide is its harmlessness for cultural heritage materials, in particular the most sensitive, such as wall paintings. The biocide should not induce any surface color change or chemical modification of the cultural heritage materials. It was therefore decided to use biocides that have already been thoroughly tested on heritage materials and that have a proven record of harmlessness.

For stone, only biocides containing quaternary ammonium compounds as active substances are both well-known commercial products with a proven safe use for cultural heritage applications and on the list submitted for approval of Biocidal Product Directive 98/8/EC. Consequently, the biocides chosen for stone treatment in combination with the calcium alkoxide consolidant are quaternary ammonium biocides. Such molecules work as a biocide by deteriorating the cell membranes of all micro-organisms and therefore they can be used to prevent the growth of both algae and fungi.

Finally, the choice of biocides to apply also depends on the kind of micro-organisms whose growth needs to be prevented. It was decided to focus on algae for stone substrates and on fungi for stone-like substrates, a choice which reflects the micro-organisms most commonly found

on such substrates on site. Consequently, for both stone and stone-like substrates, two commercial biocides were chosen for testing, both containing a quaternary ammonium compound as an active substance:

- Biotin T (CTS, Paris) which contains didecyldimethyl-ammonium chloride (large spectrum biocide efficient against all types of micro-organisms) and 2-octyl-4-iso-thiazolin-3-one (fungicide).
- Proxymousse (Société PCD Peintures, Caudry, France) which contains benzododecinium chloride (large spectrum biocide).

5.3   Biocides for wood

To obtain a surface consolidation with a combined biocide treatment against xylophagous organisms, the compatibility of suitable biocide molecules with the alkoxide has been investigated. The fungicide tebuconazole was found compatible and a commercial wood preservative based on this biocide should be considered for further use in the ongoing project.

5.3.1   Criteria type of biocide

The potential wood objects to treat with the Nanomatch consolidant is indoor wood objects of historical or artistic value. It is not meant for consolidation of construction timber. It is therefore interesting to treat wood degraded by rotting fungi, that else should be cut away and replaced with new sound wood. The project has focused on consolidation after fungal degradation as the loss of hemicellulose and cellulose makes the wood fragile and the degradation products causes acidification that catalyses further cellulose hydrolysis and brake down [10]. Wood could also be attacked by boring insects, but this type of degradation was not studied. The life cycle of common wood deteriorating insects (around a year) is not compatible with the project timeframe. Furthermore differences between laboratory samples deteriorated by insects show a large variety. This makes comparing treatments with each other more difficult. In the contrary fungi degraded wood samples can be made in a matter of months and are more reproducible. Therefore only fungicides were included in the study.

A second criterion was that the fungicide to be chosen should ideally be already approved for use in the European Union i.e. to be included in Annex I or IA of the Biocidal Product Directive 98/8/EC (BPD) for wood preservation (Product Type 8).

5.3.2   Selection of fungicide molecules

Four different biocides were initially considered of which two were finally left out. One is Antimic (alkylalkoxysilane quarternary ammonium salt developed by project partner Nanotego, but it is only approved for use in Turkey and submitted for approval in the US. The other biocide is Cu-HDO (Bis-(N-cyclohexyldiazeniumdioxy) –copper) which has a blue-violet colour and therefore could be a potential source of problems on cultural heritage materials. The two fungicides which were selected for screening of compatibility with alkoxide treatment were: Quaternary ammoniums and Tebuconazole (Table 2).

5.3.3 Biocide screening test

The compatibility of the Nanomatch alkoxide and the two selected fungicide molecules was assessed on treated small wood samples in a resistance test to brown rot (*Coniophora puteana*) following the "plate-agar rapid test" methodology based on the European standard EN113, [11] (Table 3). This screening method is performed with smaller (3x30x10 mm) than the standard size sapwood (*Pinus sylvestris*) samples to have results already after 8 weeks in contact with fungi, before determining the weight loss. A desired protection of the wood is deemed if a treatment reduces the weight loss to below 3% and that the untreated control samples have a weight loss over 20%

The biocides used were tebuconazole (CAS: 107534-96-3) provided by Lanxess and Bardap 26: N,N-Didecyl-N-methylpoly(oxyethyl) ammonium propionate (CAS No.: 94667-33-1) provided by Lonza.

Table 2. Properties of the initially considered biocides.

Suggested biocide	function	BPD listed Annex I (PT8)	comments
Covalent silicate	Anti-microbial		In use mainly for textiles
Quat. ammoniums: BAC, DDAC	Fungicide/ algaecide stone/wood	Yes	Commercial most used products
Cu-HDO	Fungicide/ algaecide stone/wood	Yes	Preferable to organic biocides. Blue-greenish colour
Tebucona-zole	Fungicide stone/wood	Yes	Active at low concentration. No colour

Table 3: Screening results of EN113 testing after 8 weeks contact with *Coniophora puteana* brown rot fungi. *Pinus sylvestris* sap wood previously impregnated with biocide solutions or in combination with a final superficial alkoxide treatment (2.5% alkoxide in THF/2-propanol 1:3, 5min soaking). a.i.: active ingredient: tebuconazole or Bardap 26 (quaternary ammonium).

Sample treatments	Retention a.i. in wood (kg/m3)	Weight loss (%)	Weight loss Corrected (%)	Control WL (%)
Tebuconazole	0.211	1.8	1.3	19.4
Tebuconazole + Alkoxide	0.212	2.0	1.5	24.0
Bardap 26	2.10	0.8	0.0	21.1
Bardap 26 + Alkoxide	1.96	12.8	12.8	22.2
Alkoxide	-	20.1	19.5	23.2

The treatments consisted in full cell vacuum impregnation of the two biocides to an effective known retention value that protects against wood-rot. Tebuconazole was dissolved in acetone and Bardap 26 in water. After fully drying the samples in a climatic chamber (62% RH and 20°C), the second superficial treatment of Ca-alkoxide was performed by 5 minutes of soaking in a 2.5% solution in dry tetrahydrofurane / 2-propanol (1:3). Applying the consolidant first might hinder penetration of the fungicide because the surface is densified (that is the aim), therefore the consolidant was applied after the biocide. A final incubation time of one week in climatic chamber was allowed before initiating the biological testing with fungi. This to allow for full evaporation of solvents and reduction of the surface alkalinisation.

6. Conclusions

Many synthetic pathways were tested for the preparation of different alkoxides. The best products were then selected on the basis of solubility criteria, safety and health effects, cost, etc. The coatings obtained from the deposition of different solutions of Ca(OEt)$_2$ (reported as an example) show the relation of the carbonation process with volatility of the solvents: low volatile solvents allow the formation of thermodynamically favored calcite. In the experimental conditions used, non influence of humidity on the calcite/ vaterite ratio was detected. As far as magnesium compounds are concerned, the deposition of commercially available products shows the formation of magnesium hydrated carbonate and hydroxide that might be deleterious for the further conservation of the stone and wood. For this reason they were discarded.

The conclusions of the screening assay were that the two biocides tested at their expected effective retention values in wood, protected the wood and gave a weight loss of under 3%. When combining the biocide impregnated wood samples with a second superficial treatment with Ca-alkoxide solution, an important result was that the efficacy was badly effected by the Bardap 26 treatment, and the weight loss increased to 12.8%, see Table 2. Possible reasons could be the known adverse effect of hard Ca-containing water on quarternary ammonium compounds or the high pH of the pure alkoxide that could catalyse cleavage of the ammonium compound (Hoffman elimination). The result of combining the tebuconazole treatment with the alkoxide treatment did not reduce the efficacy of this biocide and the commercial biocide product to select for further work could contain tebuconazole. Finally, the effect of the treatment with only Ca-alkoxide did not give any notable effect in reducing the weight loss and protecting the wood against the brown-rot.

7. Acknowledgements

8. References

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111