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Antifungal treatment of paper with calcium propionate and parabens: Short-term and long-term effects

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ABSTRACT

A deacidifying/antifungal mixture composed of calcium propionate, methylparaben and propylparaben was tested against *Aspergillus niger*, *Cladosporium cladosporioides*, *Chaetomium globosum*, *Penicillium chrysogenum* and *Penicillium corylophilum*. The preventive treatment of paper samples resulted in a complete fungal growth inhibition on 4 of the 5 tested species. The antifungal properties of the formulation remained unaffected for a minimum period of one year. The disinfecting treatment with the mixture led to a total elimination of all tested fungal species. The effects of the tested formulation on paper were evaluated in terms of pH, colourimetry, folding endurance, FTIR and XRD, using moist heat artificial ageing. Aside from plain paper, paper previously colonized by *A. niger* was tested to evaluate the potential of the formulation in preventing deterioration caused by fungal metabolites. In plain paper, an effective deacidification and long-term prevention of mechanical resistance loss were achieved, although a slight paper discoloration occurred. On previously colonized by fungi, the treatment effectively prevented the deterioration caused by fungal metabolites.

1. Introduction

Paper documents and works of art are very susceptible to fungal development due to their organic composition and hygroscopicity. To prevent and stop fungal deterioration of paper based materials several toxic methods have been used throughout history (Sequeira et al., 2012), but more recently a growing concern about environmental and health issues has led the research to find new antifungal alternatives with lower toxicity (Afsharpour et al., 2011a, 2011b; Havermans, 2011; Rakotonirainy and Lavedrine, 2005). In that sense, in 2009 Neves et al. (2009) tested the use of a multipurpose deacidifying/antifungal mixture composed of calcium propionate (Fig. 1 a), methylparaben (Fig. 1 b) and propylparaben (Fig. 1 c) to treat fungal biodeterioration of paper.

Calcium propionate is one of the most used antimicrobial preservatives in the fermented foods industry, especially in bread, since it does not inhibit yeast growth. In aqueous solution, calcium propionate dissociates in propionic acid (the active antifungal ingredient) and calcium ions. Propionic acid acts by interfering with the electrochemical gradients in the cell membrane, disrupting the transport processes, and inhibiting the uptake of substrate molecules, such as phosphate and amino acids (O'Connell and Dollimore, 2000). The calcium salt is more commonly used than propionic acid itself since it is readily soluble and easier to handle (Hutkins, 2006). Calcium propionate has also been used as a deacidifying agent for paper collections (Bicchieri et al., 2012; Botti et al., 2011; Iannuccelli and Sotgiu, 2010; Zappalà, 1990). Calcium propionate is considered by the United States Environmental Protection Office to have no teratogenic activity (ability to cause birth defects) or reproductive toxicity (US-EPA, 1991). Even when administered in large doses, propionic acid is excreted in the urine and there is no risk of accumulation in the human body (Paulus, 2004, p. 291).

Parabens are esters of *p*-hydroxybenzoic acid and are among the most common antimicrobial agents in pharmacy and cosmetics' industries, due to their low toxicity, pH range of activity, good stability and minimum secondary effects (Nguyen et al., 2005;

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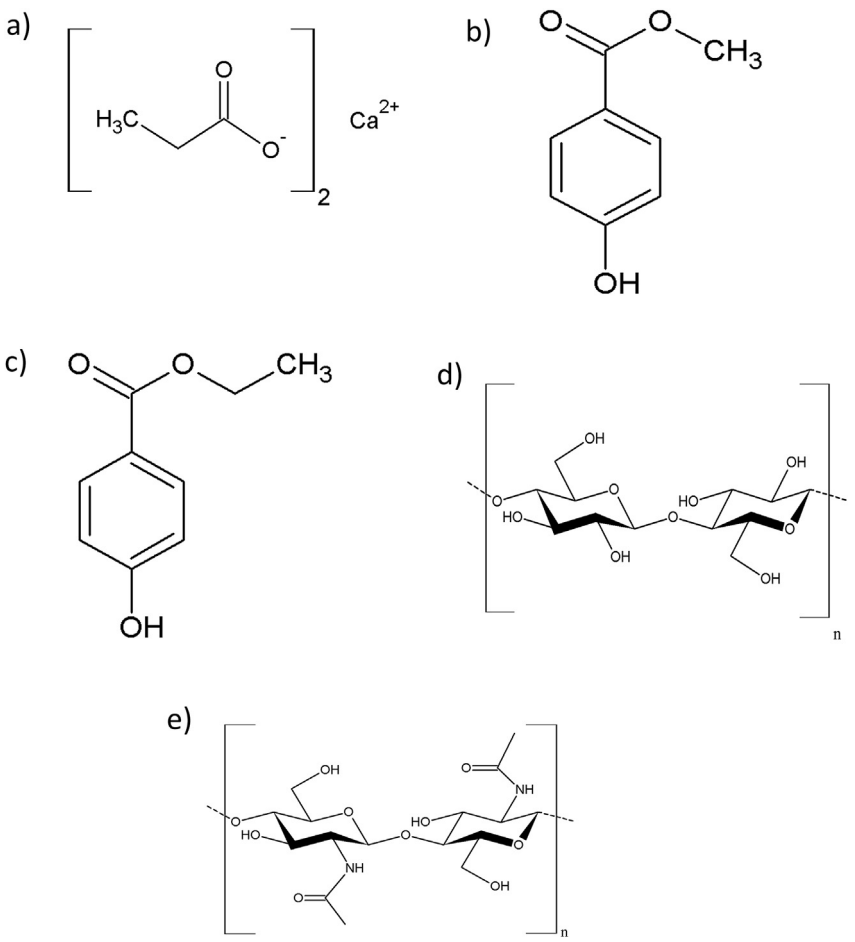

Fig. 1. Chemical structures of calcium propionate (a); methylparaben (b); propylparaben (c); cellulose (d) and chitin (e).

Zhang et al., 2005). The use of parabens as antifungal agents for cultural heritage objects was published for the first time in 1990, on a study about alternatives to thymol on fumigation chambers (Gustafson et al., 1990). At low concentrations, parabens selectively inhibit the proton motive force across the microbial cell membrane, and at high concentrations they affect the membrane permeability, causing leakage of intracellular constituents (Russell, 2003). Several studies have proven parabens to be practically non-toxic, non-carcinogenic, non-genotoxic and non-teratogenic (SCCP, 2005). Currently, it is of general agreement that parabens have a weak estrogenic activity, and this activity appears to increase with increasing chain length (SCCS, 2011). However this activity is thousands to millions of times weaker than the activity of natural hormones (Routledge et al., 1998; SCCS, 2011), and as such, it is considered biologically implausible that parabens increase the risk of any oestrogen-mediated endpoint, including effects on the male reproductive tract or breast cancer (Golden et al., 2005).

In the study by Neves et al. (2009) a total inhibition of fungal development (by parabens) on the two tested species and an effective deacidification effect (by calcium propionate) were obtained. This formulation showed therefore encouraging results as a multi-purpose solution for the treatment of paper documents suffering from acidity and fungal colonization. Nevertheless, before application on cultural heritage materials, conservation treatments have to be thoroughly tested to assess if they can cause any damage on the treated materials in the short and long term. Besides, the antifungal effectiveness should be more thoroughly studied. To this end, in the present work the formulation containing parabens and calcium propionate was tested against four fungal species commonly isolated from paper collections: *Aspergillus niger*; *Chaetomium globosum*; *Cladosporium cladosporioides*; *Penicillium chrysogenum* (Bergadi et al., 2014; Mesquita et al., 2009; Zielińska-Jankiewicz et al., 2008); and also *Penicillium corylophilum*, for comparison with the study by Neves et al. (2009). Moreover, the durability of the formulation's antifungal activity was evaluated along time. The effects of the tested formulation on paper samples in the short and long-term were assessed through colorimetry, pH, folding endurance, infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses, before and after moist heat artificial ageing. Colourimetry, allowed for an evaluation of aesthetic alterations caused by the antifungal treatments, which could also indicate chemical modifications. pH measurements were used to evaluate the deacidifying capacity of calcium propionate and also any acidification or excessive alkalinisation caused by the treatment, which could cause acid hydrolysis or alkaline deterioration, respectively. Folding endurance is the most sensitive mechanical property for the detection of changes induced by artificial ageing on paper, and is highly correlated with the percentage of the hydrolysed glycosidic bonds on cellulose (Zervos and Moropoulou, 2006). FTIR and XRD analyses allowed to have an insight into the molecular alterations on cellulose, or degradation of the applied antifungal and deacidifying compounds. Artificial ageing tests cannot perfectly mimic slow natural degradation processes (Bansa, 2002), but are considered indispensable to evaluate relative long-term stabilities of paper and conservation treatments (Bégin and Kaminska, 2002). Besides plain paper, previously colonized paper was also tested to