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Original article

Influence of metal cations on leather degradation

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ABSTRACT

In the presence of ions of transition metals, mainly iron and copper, there occurs a heavy damage in historical leathers: loss of firmness, fragility and even powdering. Ions of transition metals are contained in pigments used for leather dying or they come from chemicals used for leather marbling or from direct contact of leather with metal clips etc. After accelerated ageing of samples the influence of transition metal cations was evaluated by determination of changes in mechanical properties, pH values and shrinkage temperatures. Structural changes in leather were examined by means of scanning electron microscope, SDS-PAGE electrophoresis and spectroscopy of electron paramagnetic resonance. In leather samples a semiquinone radical has been detected, which initiates their oxidation. Transition metal cations catalyse this oxidation process thus increasing the damage extent when compared to leathers not containing these ions.

1. Research aims

Many significant historical items of cultural heritage or their parts involve leathers. In the presence of transition metal ions, mostly iron and copper, there occurs a serious damage as illustrated in Fig. 1. Macroscopic signs of the damage are loss of firmness, fragility and powdering of collagen fibres [1–5]. The mechanism of the damaging process, knowledge of which would lead to the proposal of effective preservative means, has not been explained yet.

The aim of this study was to experimentaly evaluate the influence of iron and copper cations on degradation of leather samples. The results were evaluated on the basis of changes in chemical, mechanical and hydrothermal properties of the studied samples after exposure to accelerated ageing conditions.

2. Introduction

Ions of transition metals present in leathers are either a part of pigments that were used for their dying or they come from marbling of leathers or from water or other substances used in the tanning production or they may come from the direct contact of leathers with metals in the final stage of their processing (nails, decorative clips) [2–6].

The chemical basis of leather mainly consists of the protein called collagen. Under real conditions i.e. in the oxygen atmosphere and at laboratory temperature this collagen protein is damaged due to oxidation and acidic hydrolysis. Long-term storage conditions of leather objects such as relative humidity of environment, temperature, light, pH values of packaging material or presence of pollutants may support those reactions. Under conditions of long-term natural exposure to environmental conditions those mechanisms often cooperate and support each other, changes of the collagen structure and chemical composition being their result. Tannins in leathers are also a subject to hydrolysis and oxidation. Their decomposition products may then initiate hydrolytic and oxidative damage of collagen [1,2,7–9].

Negative influence of transition metal cations on leather may manifest in [4]:

- their oxidation where they act as catalysts;
- reactions with tannins which lead to detanning of leathers;
- crystallisation pressure occurring due to recrystallisation of some salts, which loosens the collagen network.

Generally, oxidation of organic material polymers takes place via the radical mechanism. In the first stage of this reaction, during

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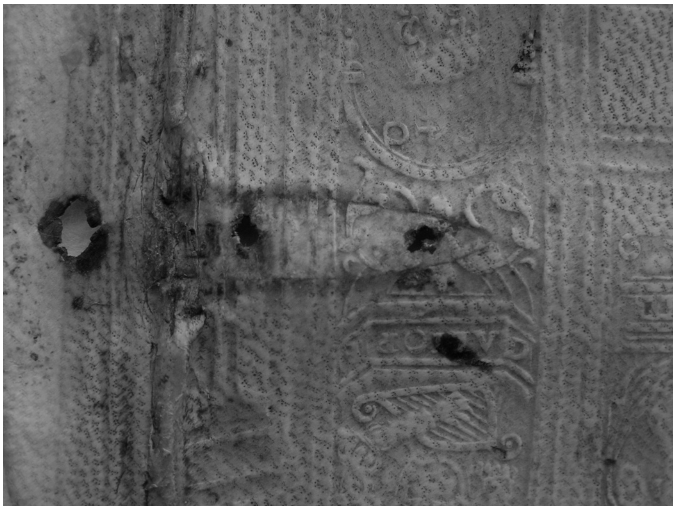

Fig. 1. Example of binding leather damaged by the contact with book fittings.

the so called initiation, radicals R• arise from polymers due to dissociation of carbon–carbon and carbon–hydrogen bonds. However, the velocity constant of the initiating reactions is extremely low for saturated polymers in darkness and at common temperatures (up to 100 °C). The created radical then reacts with oxygen giving rise to peroxide radical which enters other reactions afterwards. The catalytic effect of transition metals Me during oxidation of polymers can be explained by accelerated decomposition of polymer hydroperoxides ROOH as obvious in Eqs. (1) and (2). The rise of a hydroperoxidic (HOO•) and an organic radical (R•) is the result of decomposition of hydroperoxides (2). However, peroxide radicals may also occur in the structure of the materials due to UV radiation affecting free water stored in the supramolecular structure of collagen as well as some kind of tannins or unsaturated oils used for leather surface treatment [4,10].

$$\mathrm{ROOH} + \mathrm{Me}^{n+} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{Me}^{(n+1)+} + \mathrm{OH}^{-} \quad (1)$$

$$\mathrm{ROOH} + \mathrm{Me}^{(n+1)+} \rightarrow \mathrm{ROO}^{\bullet} + \mathrm{Me}^{n+} + \mathrm{H}^{+} \quad (2)$$

A direct reaction with oxygen (3) is another mechanism of transition metal effects. This reaction may come into action in the stage that proceeds the creation of hydroperoxides. Some ions, e.g. of iron, create a complex with oxygen which in the next stage reacts with polymers giving rise to free radicals: hydroperoxidic (HOO•) and polymer radical (R•), as described by the reaction (4) [4,10].

$$\mathrm{Me}^{n+} + \mathrm{O}_2 \leftrightarrow \mathrm{Me}^{(n+1)+} + \mathrm{O}_2^{\bullet} \quad (3)$$

$$\mathrm{Me}^{(n+1)+} + \mathrm{O}_2 + \mathrm{RH} \rightarrow [\mathrm{Me}^{(n+1)+}\mathrm{O}_2] + \mathrm{RH} \rightarrow \mathrm{Me}^{n+} + \mathrm{HOO}^{\bullet} + \mathrm{R}^{\bullet} \quad (4)$$

Besides the quality and ripeness of leathers mainly the type of applied tanning influences their stability. Leathers not containing tanning material (pseudotanned) or tanned minerally are well resistant against ageing and that is why they often show no signs of damage [1,7,11]. However, the largest group of historical leathers are treated with tannins and their stability is thus dependent on the type of the selected tannin. On the basis of tannin chemical structure the tannins may be divided into two groups – hydrolysable and condensed. Hydrolysable (or pyrogallic) tannins are formed by derivatives of gallic acid (see e.g. Fig. 2). Among the most common hydrolysable tannins there belong oak bark, oak wood, myrobalan, tara and sumac. Condensed tannins (or catecholic tannins) consist of derivatives of the flavonoid aromatic structure (e.g. Fig. 3). Among the most common tannins in this group there belong pine barch, tambur, gambier, mimosa and quebracho [1,11–14]. Larsen [8] states that leathers tanned with hydrolysable tannins are generally more resistant against oxidation than leathers treated with condensed tannins. He also states that leathers treated with condensed tannins have a greater tendency to absorb acidic pollutants from the atmosphere which increases the hydrolytic damage of leathers.

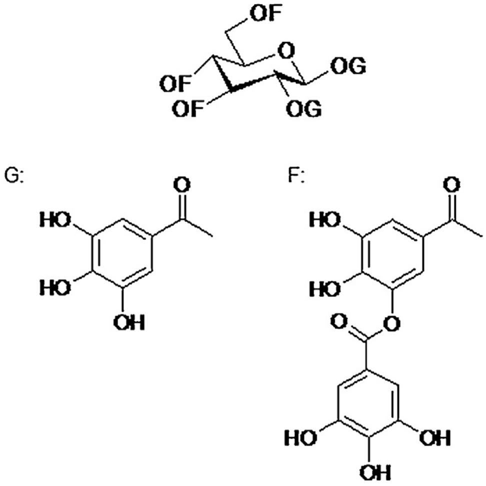

Fig. 2. Structure of heptan-octa-galloyl-β-D-glucose (hydrolysable tannin contained in extract of sumac leaves). [8,13].

3. Experimental

Influence of transition metal cations was observed on leathers treated with hydrolysable tannins and a mixture of condensed and hydrolysable tannins, which are listed in Table 1. Due to great anisotropy of leather mechanical properties only the area of the 300 mm width from the animal dorsal line was used for preparation of samples. Samples of 100 × 100 mm were drafted from the leather centre, which was determined as the intersection point of the dorsal line and diagonals leading through animal limbs. Based on the studies of historical formulas [15–17] there were selected ions of copper and iron in the form of $\mathrm{FeSO_4}$ and $\mathrm{CuSO_4}$.

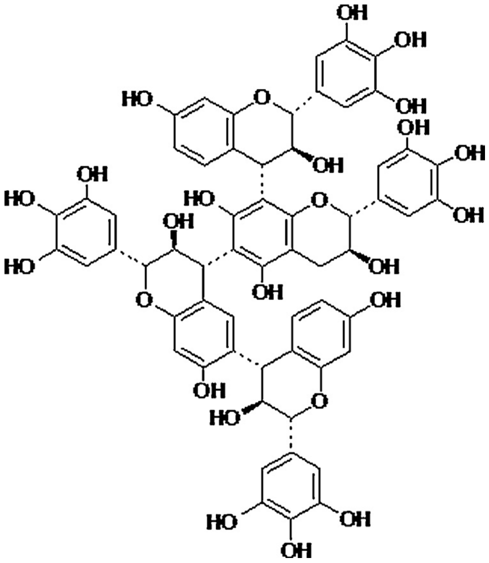

Fig. 3. Tetraflavonoid structure (i.e. condensed tannins contained in extract of mimosa leaves). [8].

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