THE INFLUENCE OF TiO₂ AND N-TiO₂ NANOPOWDERS IN NATURAL LEATHER FINISHING FOR HERITAGE OR MODERN BINDING

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The methods for processing raw hides over time, have been numerous: smoke, fat, fermented milk, egg, volcanic soils, plants (shells, fruits, leaves) and so on. The books binding with leather has its origins in the Orient and are known various types of goatskin and calfskin, tanned with sumac finished marbled (sapphire), in black (Moroccan), by floating and dyeing in various colors (Cordoba leathers). Preoccupations regarding the assurance of optimal characteristics for the binding leathers, respectively the durability of the leathers for the restoration of the patrimony objects or of the modern binding were of the most topicality in the last decades, abroad and also in our country. The paper describes the finishing of vegetable and alum tanned leather samples that have been functionalized with titanium dioxide (TiO₂) or nitrogen-doped titanium dioxide (N-TiO₂) nanopowders, in different concentrations. To simulate soiling in real conditions, four types of soiling agents were applied: tea, coffee, beetroot extract and pen paste. The samples were exposed to irradiation in a photoreactor with various light sources for up to 192 hours. The evaluation of the photocatalytic degradation was performed by the CIELab technique.

Keywords: preserving heritage objects, nanopowders, leather finishing

INTRODUCTION

Leather processing was the first biotechnology developed by mankind, raised to the art level by combining this craft with tradition, skill, talent, beauty and usefulness. In the history of humanity, leather and fur objects have had many fundamental meanings related to the development of society (social distinction, mysticism, aesthetics, defense against enemies) in addition to the basic function, as protection against temperature differences (clothing, footwear, tents, bellows etc., for domestic, common, military use etc.). The first documentary attestation – Sumerians, 2700 BC (Delort, 1993), and on the territory of our country is attested the processing of skins in clay tablet no. 3 from Tartaria, dated 2900 BC, in which animal skins are rendered in the manner of Egyptian ideograms.

Over time, leather processing has gained importance for history, art, but especially for science (Higham, 1999). The methods of processing raw hides were numerous: smoke, fats, fermented milk, egg, volcanic soils, plants (shells, fruits, leaves etc.), urine, excrement or combinations thereof (Bravo, 1964; Deselnicu *et al.*, 1984). This first biotechnology developed by mankind, remained almost unchanged until the end of the nineteenth century, when tanning with Cr salts came into use.

The book binding in leather has its origins in the Orient in the same time with paper, which being fragile had to be protected by a resistant material, such as leather. The most important types of leathers used for book binding were those of goat and calf, tanned with sumac and finished marbled (saphian), in black (marochin), by floating and dyeing in various colors (Cordoba leathers). Information regarding the making of binding leathers up to the 17th century is described in the encyclopedias of *De La Lande* and

Diderot (Thomson, 2000). The leather for book binding had to be smooth, resistant to bending and pressing, thin, vegetable tanned, finished specifically for book covers.

Concerns regarding the identification of optimal characteristics for binding leathers and the elaboration of technical specifications to responsibly ensure the durability of leathers for the restoration of heritage objects have been the most topical in recent decades abroad, but also in our country (Larsen, 1994; Larsen, 1997; Miu *et al.*, 2007; Project CRAFT No BRST-CT98-5535; Project PNCDI-Partnerships PN 91012/2007).

The variety of degradation phenomena that affect works of art, reflects the wide range of materials that have been used by mankind since the beginning. Therefore, both conservatives and scientists are involved in finding effective solutions to counteract aging processes due to the action of light, temperature, relative humidity and microorganisms, chemical degradation and physical erosion or anthropogenic causes such as industrial pollution, vandalism or simple artifact handling.

In the field of preservation, the application of dispersed solid particles is preferable to aqueous solutions or organic solvents for many reasons.

In the last decade, nanostructured materials have been of great interest as catalysts for other applications due to their unique textural and structural characteristics. The most studied materials were metal oxides, such as TiO₂, SnO₂, VO₂ and ZnO.

Nanomaterials are an innovative research direction for the leather industry due to their high potential of replacing potentially toxic volatile organic materials and their ability to develop smart properties. Owing to its many advantages mainly involving most stable and active naturally occurring photocatalyst, TiO₂ is, so far, seen as the best catalytic material for degradation of various soiling agents.

RESULTS AND DISCUSSION

Assortments of natural leather were obtained through ecological tanning processes, with specific characteristics of art and heritage book covers.

Figure 1. Leathers tanned with Al salts (left) and vegetable tanning extracts (right)

The leather samples were then functionalized with titanium dioxide (TiO₂) or nitrogen-doped titanium dioxide (N-TiO₂) nanopowders, in various concentrations.

In order to determine the nanoparticles size and the stability of the dispersions, measurements were performed using the Dynamic Light Scattering (DLS) technique and the Zetasizer Nano ZS equipment.

Figure 2. Size distribution (left) and Zeta potential (right) for simple TiO₂ nanoparticles

Figure 3. Size distribution (left) and Zeta potential (right) for N-doped TiO₂ nanoparticles

TiO₂ nanoparticles have sizes of approximately 25 nm, those doped with N of 30 nm and the Zeta potential is -45 mV for simple nanoparticles and -47 mV for doped ones, which suggests a high stability of the samples.

To simulate dirt in real conditions, 4 types of soiling agents were applied onto leather surfaces: tea (t), coffee (c) and beetroot extract (b), which were applied to the skin in the form of drops (0.01 mL) and pen paste (p), applied as a hatch.

Depending on the type of applied treatment, the samples were exposed to irradiation in a photoreactor (Labtech) with different light sources, as follows: TiO₂-treated leathers were exposed to UV light provided by Osram L BL UVA 8W / 78 G5 lamps and the leathers treated with N-TiO₂, due to the known efficiency of this photocatalyst in these conditions, were exposed to visible light, using Osram L 8W / 756 Cool Daylight lamps.

The leather samples were exposed for 192 hours, performing 4 measurements, initial, after 48, 96 hours and at the end.

In the Tables below are presented the results, before and after irradiation.

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Table 1. Photographic images of leather samples treated with N-TiO₂ and exposed to Vis irradiation

Sample	Before exposure				After exposure			
	t	c	p	b	t	c	p	b
Alum Untreated
Alum 3% N-TiO ₂
Alum 6% N-TiO ₂
Quebracho Untreated
Quebracho 3% N-TiO ₂
Quebracho 6% N-TiO ₂
Chestnut Untreated
Chestnut 3% N-TiO ₂
Chestnut 6% N-TiO ₂

Vis lighting irradiation for 192 hours determine the photodegradation of all 4 types of soiling agents from the surface of functionalized leathers, as can be seen in Table 1.

Table 2. Photographic images of leather samples treated with TiO₂ and exposed to UV irradiation

Sample	Before exposure				After exposure			
	t	c	p	b	t	c	p	b
Alum Untreated
Alum 3% TiO ₂
Alum 6% TiO ₂

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It can be observed that after 192 hours of UV irradiation, all 4 types of contaminants have undergone color changes, which suggests the efficiency of photocatalysts.

The evaluation of the photocatalytic degradation of the dyes was performed by the CIELab technique with a Datacolor Check II spectrophotometer, following the color change by recording the parameters L * (brightness), a * (red-green), b * (yellow-blue), C * (chrome) and h * (hue angle). To demonstrate dyes degradation, the parameter L was selected, which measures the brightness of a color from completely opaque (0) to completely transparent (100), which best highlights the color variation.

From both photographic images and CIELab analysis, can be observed the efficiency of the N-TiO₂ photocatalysts, following the irradiation with Vis light. The best results were obtained as follows:

- in the case of tea stains, for the leather sample tanned with Quebracho and functionalized with 3% N-TiO₂ nanoparticles, where the L parameter varies from 68 to 74, which suggests the degradation of the dye;
- for coffee stains, for leather samples tanned with Alum and functionalized with 3%N-TiO₂ nanoparticles; L parameter varies from 78 to 94;
- the pen stain was mostly discolored in the case of the Alum tanned leather sample and functionalized with 3% N-TiO₂ nanoparticles; the L parameter varies from 51 to 80;
- for beet extract stain, for the leather sample tanned with Alum and functionalized with 6% N-TiO₂ nanoparticles, the L parameter varies from 84 to 87.

Simple TiO₂ nanoparticles have also been shown to be effective in the case of UV irradiation, an aspect that results from both photographic images and CIELab analysis.

For each type of soiling agent, the best results were obtained as follows:

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- in the case of tea stains, for the leather tanned with Alum and functionalized with 3% TiO₂ nanoparticles, the L parameter varies from 88 to 94;
- for coffee stains, in the case of the leather tanned with Alum and functionalized with 9% TiO₂ nanoparticles, where the parameter L varies from 80 to 92;
- pen stain was discolored mostly in the case of Alum tanned leather sample and functionalized with 9% TiO₂ nanoparticles; L parameter varies from 48 to 67;
- for beet extract stain, in the case of the sample tanned with Chestnut and functionalized with 6% TiO₂ nanoparticles, where the parameter L varies from 41 to 43.

CONCLUSIONS

New doped nanoparticles with improved photocatalytic properties for heritage leather treatment were developed. TiO₂ dispersions characterized by dynamic light scattering technique indicate that these are very stable and well dispersed.

The experimental results evidenced the photocatalytic activity of the new synthesized TiO₂ nanoparticles, both in UV and visible light. The photocatalytic properties were confirmed by colorimetric measurements for the spots applied to the treated leather surface exposed to UV and visible light irradiation.

The obtained results suggest that TiO₂ nanoparticles are a good candidate for the treatment of leathers for art and heritage book covers.

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