AG AND AG/TIO$_2$ NANO-DISPERSED SYSTEMS FOR TREATMENT OF LEATHERS WITH STRONG ANTIFUNGAL PROPERTIES

by

CARMEN GAIDAU[a*], AURORA PETICA[b], TEODORA DRAGOMIR[a], HORIA IOVU[c], AND CORINA ANDRONESCU[c]
[a] *Research and Development National Institute for Textile and Leather -*
Leather and Footwear Research Institute Division
93 ION MINULESCU ST., BUCHAREST, 031215, ROMANIA
[b] *INCDIE-ICPE CA – Advanced Research,*
313 SPLAIUL UNIRII, BUCHAREST, 03013, ROMANIA
[c] *Applied Chemistry and Material Science Faculty, "Politehnica" University Bucharest,*
1-7 POLIZU ST., 011061, BUCHAREST, ROMANIA

ABSTRACT

The purpose of our work was to create leathers with enhanced antifungal and antimicrobial properties by treating with efficient and ecological agents. Using a simple and productive electrochemical method, stable and high purity nano-Ag based colloidal solutions containing 35 ppm Ag, with 4 nm diameter and – 44 mV zeta potential and Ag/TiO$_2$ dispersed solutions containing 10g/l TiO$_2$ and 45 ppm Ag, with 19.7 nm diameter and – 36.8 mV zeta potential, were obtained. Solutions obtained in this manner have affinity for wet blue or metal-free leather. Even though both colloidal silver solutions and Ag/TiO$_2$ disperse solutions have a very good antifungal and antibacterial activity, only leather treated with Ag/TiO$_2$, especially wet blue type, exhibits a strong antifungal activity up to 28 days of fungi exposure. Also, wet blue and metal-free leathers treated with colloidal silver solutions and Ag/TiO$_2$ dispersed solutions present inhibitory action against *Pseudomonas aeruginosa* (ATCC 9027) and *Staphylococcus aureus* (ATCC 6538). XPS measurements, relating to composition and chemical state of the Ag on the leather surface, have shown that leather treated with Ag/TiO$_2$ nano-dispersed systems has a greater content of silver Ag^0 than in the case of colloidal silver solutions treatment, Ag being better deposited in the matrix of TiO$_2$ nano-powder, and released gradually as silver ions Ag$^+$. The new products give the perspective of a new range of ecologic products, with applications both in the area of leather articles for medical and everyday use, and in the area of materials for additional treatment of wet blue palletized leathers, etc.

RESUMEN

El objeto de nuestra labor fue el crear cueros con mejores propiedades antimicóticas y antimicrobiales por tratamientos con agentes eficientes pero a la vez ecológicos. Utilizando un sencillo, pero productivo método electroquímico, que produce estables soluciones coloidales basadas en nano-Ag de alta pureza conteniendo 35ppm Ag, de 4 nm de diámetro y -44mV de potencial zeta así cómo también soluciones dispersas de Ag/TiO$_2$ conteniendo 10g/l TiO$_2$ y 45ppm Ag, con 19,7 nm de diámetro y -36.8mV de potencial z, fueron obtenidas. Soluciones obtenidas por estas maneras tienen afinidad hacia wet-blue así como hacia cuero exento de metales. Aunque tanto las soluciones de plata coloidal y las soluciones dispersas de Ag/TiO$_2$, tienen ambas buenas actividades antimicóticas y antibacteriales, pero sólo el cuero tratado con Ag/TiO$_2$, especialmente en el caso del tipo wet-blue, exhiben una fuerte actividad antimicótica por hasta 28 días luego de entrar en contacto con hongos. Tanto el cuero wet-blue cómo el exento de metales, tratados con soluciones de plata coloidal así cómo por dispersiones en solución de Ag/TiO$_2$ presentaron acciones inhibitorias contra *Pseudomonas aeruginosa* (ATCC 9027) y *Staphylococcus aureus* (ATCC 6538). Determinaciones por medio de XPS [Espectroscopía Foto-Electrónica por Rayos X] de la composición química y por estado de oxidación de Ag sobre la superficie del cuero han demostrado qué cueros tratados por el sistema de nano-dispersiones de Ag/TiO$_2$ contiene más plata Ag^0 que por el tratamiento solamente con soluciones de plata coloidal, Ag siendo mejor depositado en la matriz de TiO$_2$ de nano-polvo, y gradualmente liberado cómo iones de plata Ag$^+$. Los nuevos productos dan una visión de una nueva gama de productos ecológicos, con aplicaciones tanto en el sector de artículos de cuero para usos médicos como de uso cotidiano, y en el área de materiales auxiliares como para el tratamiento de cueros wet-blue paletizados, etc.

---

* Corresponding author e-mail: Carmen_gaidau@hotmail.com

Manuscript received June 12, 2010, accepted for publication October 23, 2010

Editor Note - Some of the images, figures and tables in this manuscript were low resolution and may have marginal clarity. It is suggested interested readers contact the author about specific image questions.

Introduction

The use of antimicrobial agents has greatly contributed to material conservation and improvements in health quality of life. Such antimicrobial agents have been introduced for decades to treat and prevent mould, yeasts and bacteria development but, unfortunately, their excessive use has been accompanied by an increasing prevalence of micro-organisms that have acquired resistance to one or more of these, so-called 'antimicrobial resistance'. A brief inventory of the existing biocides with restricted use,[1,2] shows that some antimicrobial agents are extremely irritant, harmful and toxic for environment and human health, and there is much interest in finding ways to formulate new types of safe and ecological biocides materials[3,4] with strong activity, a broad spectrum of action, oligodynamic activity and which do not create resistant germs as antibiotics do. Such problems and needs have led to the resurgence in the use of Ag-based antiseptics that may be linked to a broad-spectrum activity and far lower propensity to induce microbial resistance than antibiotics.[5] In fact, it is well known that Ag ions and Ag-based compounds, including silver nanoparticles and metal oxides powders (TiO_2), are highly toxic to microorganisms, such as virus, fungus and bacterium, showing strong biocidal effects.[6,7] It is a well known fact that as the nanoparticles size becomes smaller, the surface area increases and consequently the microbial activity is improved.[8,9] Thanks to the new chemically or electrochemically synthesized methods, it is possible to obtain great quantities of nanomaterial with well-shaped surface and structural properties.[10]

Silver ions have long been known to possess strong inhibitory and bactericidal effects, as well as a broad spectrum of antibacterial activities,[11] and therefore, silver has been commercially used to take advantage of its antibacterial properties.[12,13] Silver nanoparticles have been also used in clothing industry to limit bacterial growth.[14] Immobilized Ag was widely used in antibacterial plastics, coatings and functional fibers. However, the silver particles on bulk matrixes have weak washing resistance and can induce the fast release level of silver ion and a short lived antimicrobial effect.[15] If silver is immobilized on porous hosts, the release time of silver ions can be delayed for a long time, and so silver-supported materials are of great potential for antibacterial and antifungal applications.[16] It was reported that the washing resistance of Ag could be improved by immobilizing Ag in the pores of substrates thus gaining a long-term antimicrobial activity.[17] Because of its excellent structure, properties such as high surface areas and continuous pore structure, mesoporous TiO_2 is an excellent support material of silver nanoparticles. Furthermore, because fungal growth is a common problem in the leather industry and because of the restriction of legislation, many fungicides such as the phenolic or heterocyclic compounds that are often used in the tanning industry[18] are susceptible to become unacceptable, it is extremely important to find new compounds that have no toxicity and are capable of exhibiting a prolonged antifungal effect. Functionalization of different products, including leather and medical furskins, by using nanomaterials, represents a new challenging research field with large promising perspectives.[19-21] In our paper we have improved the treatment with nanosilver colloidal solutions[22] by developing disperse systems of silver nanoparticles deposited on TiO_2 nanoparticles to create leathers with enhanced antifungal and antimicrobial properties.

Experimental

Chemicals and materials

- deionized water with conductivity < 1 μS, resistivity of 18 μΩ.cm and pH = 5– 7;
- poly [1-vinyl- *2*-pyrrolidone], $(C_6H_9NO)_n$ (PVP10) with M=10,000 from Sigma– Aldrich;
- sodium-lauryl sulfate (SLS), from Sigma – Aldrich;
- sodium polyacrylate (Na-PAA) from Sigma – Aldrich;
- TiO_2 with 99.5% purity, with size particle of max. 20 nm, from Metall Rare Earth ltd.; specific surface of 115 m^2/g and pore size:130 Å;
- leathers originating from raw sheepskins processed for lining shoes with usual technologies based on chromium and without chromium (metal-free).[23]

Methods

Synthesis of CSS and Ag/TiO_2 nano-dispersed systems

The synthesis of Ag nano-dispersed system was performed by so-called "sacrificial anode method," involving a constant current pulse generator, with stirring and alternating polarity, electrodes of 99.999 Ag with sizes of 155/27 mm. To prepare stable nano-dispersed system in the form of CSS (colloidal silver solution) with a higher content of nano Ag, a mix of stabilizer and co-stabilizer agents have been used,[24] respectively PVP10 and SLS.

The Ag/TiO_2 nano-dispersed system was synthesized by electrochemically covering TiO_2 nanoparticles with silver nanoparticles. Electrosynthesis process time was 4-6 h. Typically, 5g TiO_2 was dispersed in 1L of deionized water and then Na-PAA and PVP10, in a molar ratio of 1:10 against TiO_2 were added.[25]

Analyses of CSS and Ag/TiO_2 nano-dispersed systems

Silver concentration was determined by quantitative analysis and UV-Vis absorbance spectra recording by a JASCO V 500 spectrophotometer and by atomic absorption spectroscopy-AAS (Analitik Jena spectrometer). A calibration curve using standard colloidal silver nanoparticles in the range of our measurements was recorded. The nanoparticles sizes and Zeta potential were measured by DLS (Dynamic Light Scattering) technique using Brookhaven 90 Plus equipment. The silver nanoparticles morphology and dispersability were evidenced by transmission electron microscopy (TEM) measurements, using an electronic microscope Philips CM 100. The specimens for TEM investigations were prepared through deposition on 400 mesh grids with formvar film. To evaluate the antifungal effect, the antibiogram method was used, with a fungi mix from the following species: *Aspergillus, Penicillium, Trichoderma* containing different micotoxines (e.g. aflatoxins). The fungistatic properties are expressed by the presence and magnitude of inhibition area for mould growth around a filter paper with 30 mm diameter, padded with tested solutions. To evaluate the antimicrobial efficiency, the minimal inhibitory concentration (MIC) was determined on: *Staphylococcus aureus* (ATCC), *Pseudomonas aeruginosa* (ATTC), *Escherichia coli* (ATCC). According to the scheme of Ericcson and Sherris,[26] the agar dilution technique was used.

Treatment of leathers with CSS and Ag/TiO$_2$ nano-dispersed systems

The two kinds of leathers, chromium tanned (wet blue) and metal-free (crust) were washed for 30 minutes, with distillated water in a "Wacker" drum. The treatment applied for interaction with CSS and Ag/TiO$_2$ nano-dispersed systems was by 1 hour immersion, at 30°C, followed by free drying. Every experiment was repeated and tested in duplicate. The influence of Ag/TiO$_2$ on color of treated leathers was tested by dyeing in comparison with control samples in deep and light colors and assessment of differences by using spectrophotometery method (Datacolor Instrument with color management software interface). In this regard we used the color difference expressed as DE* which refers to overall or composite color difference between the sample and the control.

Analyses of leathers treated with CSS and Ag/TiO$_2$ nano-dispersed systems

The silver content was analyzed by atomic absorption spectroscopy-AAS, the silver concentration, chemical state and binding energy on the leather surface were evidenced by X–ray photoelectron spectroscopy (XPS) with a K-Alpha Thermo Scientific device (monochromatized Al K$_\alpha$ X-ray source (1486.6 eV), 2×10^{-9} mbar pressure, compensation of surface charge with an Ar flood gun, pass energy of 200 eV). To evidence fungitoxic properties, the antibiogram method was used and standard methods[27] for leather materials. These methods are applied by using following fungi: *Penicillium glaucum*, *Aspergillus niger* and *Trichoderma viride*. Besides these, two other fungi, with biodegradation potential for leather, were inoculated, namely: *Scopulariopsis brevicaulis* and *Paecilomyces variotii*. Antibacterial properties of leather functionalized with CSS and Ag/TiO$_2$ nano-dispersed systems were evaluated by antibacterial activity tests.[28]

Results And Discussion

Characteristics of CSS and Ag/TiO$_2$ nano-dispersed systems

Ag and Ag/TiO$_2$ dispersed systems can be obtained as colloidal solution (CS), slurry or powder. To obtain reproducible CSS and Ag/TiO$_2$ solution, an efficient and ecological electrochemical process was used, by which disperse Ag and Ag/TiO$_2$ pure solutions were obtained with different antifungal and antibacterial activity. Firstly, a colloidal silver solution (CSS) with 35 ppm Ag concentration with a maximum wavelength at λ = 426 nm, obtained in the presence of a mix of two stabilizing agents (PVP10 and SLS) was electro-synthesized.

From grain size distribution diagram (Fig.1) and TEM image (Figure 2) it can be seen that 99.82% of particles number is up to 4.03 nm, silver particles shows spherical and uniform shape without agglomeration tendency. The Zeta potential distribution is a monomodal one; -44.05 mV value indicates a very stable CSS.

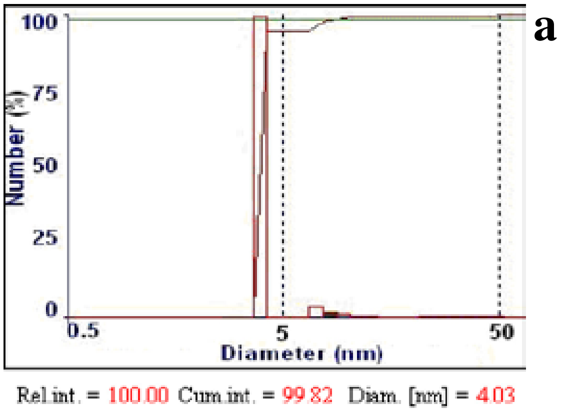

Figure 1: Silver grain size distribution of 35 ppm CSS

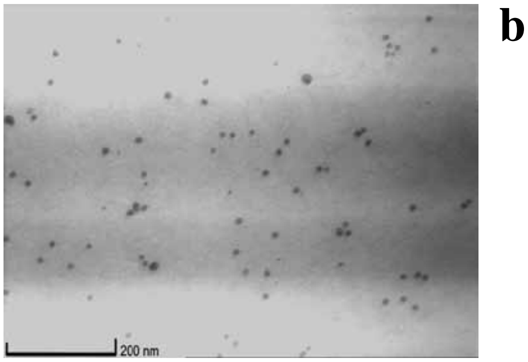

Figure 2: TEM micrography of 35 ppm CSS

To increase antimicrobial activity of Ag, nanoTiO_2 was added, which ensures both a synergistic effect beside TiO_2 and a matrix for silver nanoparticles deposition. With this in view a Ag/TiO_2 dispersed solution was electrochemically synthesized with the following main characteristics: cream-colored, 45 ppm Ag content, absorbance in UV-Vis spectra at $\lambda = 525$ nm, grain size of 19.7 nm (Fig.3), mainly spherical shape of nanoparticles with slight tendency to agglomeration (Fig.4) and a good stability (-36.84 mV for Zeta potential) .

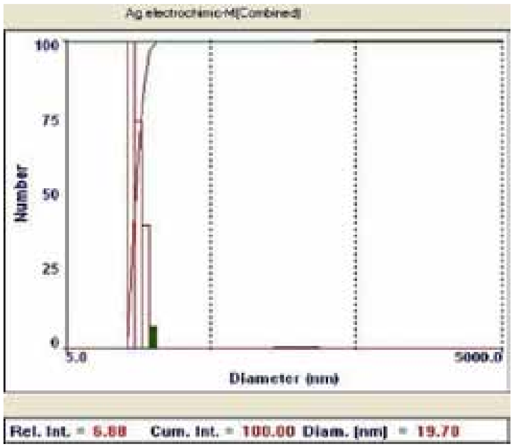

Figure 3: Silver grain size distribution of 45 ppm Ag/TiO_2 dispersed solution

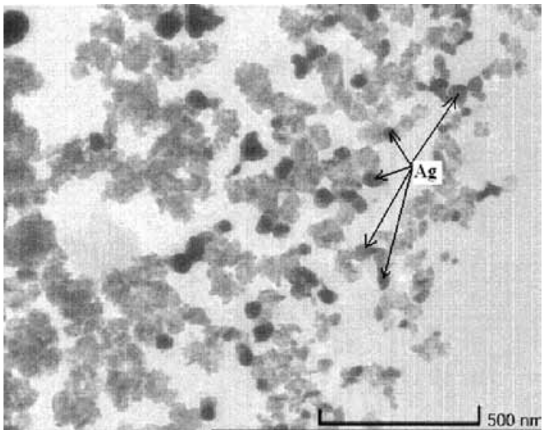

Figure 4: TEM micrography of 45 ppm Ag/TiO_2 dispersed solution

Antifungal characteristics of Ag and Ag/TiO_2 nano-dispersed systems and treated leathers

Besides the well known silver nanoparticles which have a remarkable comeback as a potential antimicrobial agent, TiO_2antimicrobial activity has been also reported.[29] Lifen and co-workers assert that this behavior is due to the oxidative species formation. Photocatalytic oxidation on surfaces coated with titanium dioxide might offer a possible alternative for disinfection of surfaces in order to reduce the numbers of fungi and bacteria and to prevent their transmission. In the presence of water and oxygen, highly reactive OH-radicals are generated by TiO_2 and mild ultraviolet A (UVA) which are able to destroy bacteria, and may therefore be effective in reducing bacterial contamination.[30] On the other hand, silver nanoparticles enable the activation of visible light excitation of TiO_2. Recently, it was shown that Ag doped TiO_2 highly improved photo catalytic inactivation of bacteria.[31] It is generally believed that Ag nanoparticles enhance the photoactivity of TiO_2 by lowering the recombination rate of its photo-excited charge carriers and/or providing more surface area for adsorption.[30] Visible light absorption by surface plasmon resonance of Ag nanoparticles is also thought to induce electron transfer to TiO_2 resulting in charge separation and thus activation by visible light.[31] Therefore, Ag/TiO_2 nanocomposites show great promise as efficient and visible light response photocatalytic materials in the future. Ag/TiO_2 nanoparticles have a much stronger antifungal/antibacterial activity in comparison with single Ag or TiO_2 in the presence or in the absence of light. Comparative studies have shown synergistic effect of Ag and TiO_2 nanoparticles that enhance their own germicidal activity.[29]

Kühn and co-workers suggest that, by light and scanning electron microscopic examinations, the germ destruction achieved takes place through direct damage to cell walls caused by OH-radicals.[30] On the other hand, the nucleophilic Ag nanoparticles adhere to the electrophilic bioactive sites of bacterial cell membrane and continuously supply the Ag^+ ions which bond the -S-H groups of bacterial cell enzymes.[33]

In the case of fungus, according to literature,[29] their destruction is slower than in the case of bacteria because of their chemical stability. Our experimental results have shown a good antifungal resistance in the case of colloidal silver solutions and a very good biocidal activity for electrochemically obtained Ag/TiO_2 solutions. In the case of leather treated with solutions mentioned above, only leather treated with Ag/TiO_2 solution has a very good antifungal resistance, even after 28 days of moulds exposure, while CSS have presented a much poorer antifungal activity compared with silver electrochemically deposited on TiO_2, proving the synergistic activity of the Ag nanoparticles. An investigation conducted on a mix of 35 ppm CSS with 10g/l of nanoTiO_2 powder, shows a good antifungal property for solution, but a poorer one in the case of treated leathers, which confirm that only silver deposited in the matrix of TiO_2 is efficient, in agreement with XPS data, presented later.

Antifungal activity of the Ag/TiO_2 dispersed solution has 0 rating mark and an inhibition area for mould growth around the filter paper padded with this solution up to 20 mm, after 14 days of exposure. Leathers treated with the colloidal silver solution (CSS) exhibit very good fungitoxic action after 7 days of exposure in the case of chromium-tanned variants – rating mark 0.1 and a good one in the case of metal-free leathers –

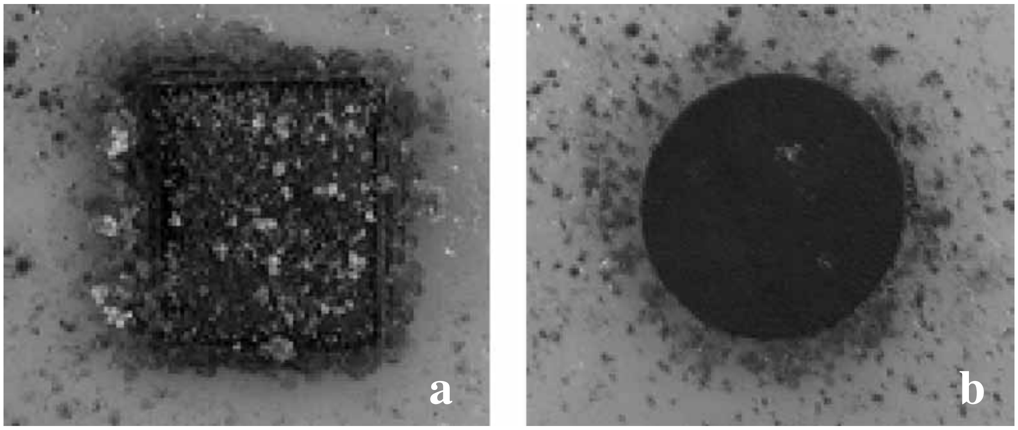

Figure 5: a) Wet blue untreated leather and b) wet blue leather treated with Ag/TiO_2 dispersed solution after 28 days of exposure to mold colony

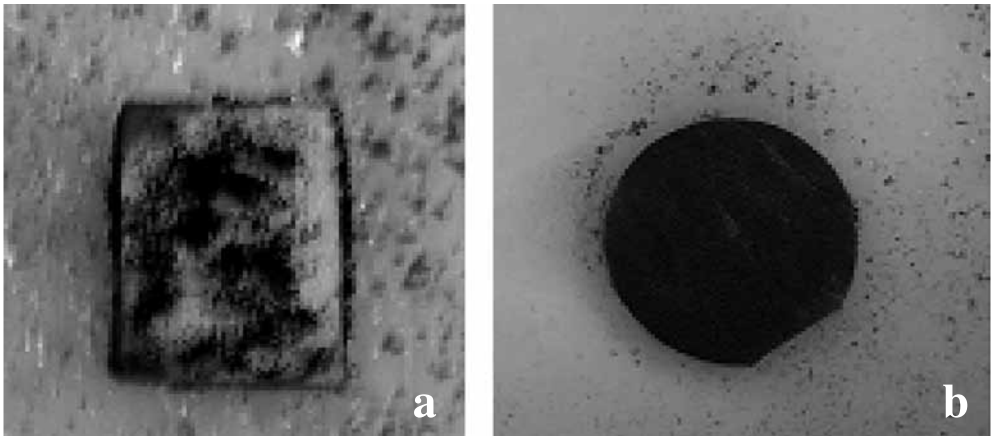

Figure 6: a) Metal-free untreated leather and b) metal-free leather treated with Ag/TiO_2 dispersed solution, after 28 days of exposure to mold colony

rating mark 1. Control samples are of rating marks 2 and 4 respectively. Analysis regarding the estimation of fungicide activity of sheep lining leathers treated with disperse suspension of Ag/TiO_2 indicates very good fungitoxic properties, expressed by rating mark 0 and an opaque inhibition area up to 25 mm, aspects maintained for up to 28 days of exposure in the case of chromium-tanned leathers (Fig.5).

Metal-free lining leather exhibits good fungitoxic properties, graded by 1 rating mark, even after incubation, but does not exhibit an inhibition area (Fig. 6).

Bacterial resistance of Ag solutions and Ag/TiO_2 nano-dispersed systems and of leathers treated with these solutions

For the tested 35 ppm CSS, minimal concentration with inhibitory effect (MIC) is 17.5 ppm for *Staphylococcus aureus* and 8.75-4.37 ppm for *Pseudomonas aeruginosa*, which means that bacteriostatic effect is achieved at a dilution of 1/2 from the initial CSS concentration, in the case of *S. aureus* and 1/4-1/8 for *P. aeruginosa*. In the case of Ag/TiO_2 disperse solution; MIC is 10.44 ppm for *S. aureus* (ATCC 6538) and 6.71 ppm for *P. aeruginosa* (ATCC 9027), values slightly higher than in the case of CSS. The high resistance of *S. aureus* compared to the other strains is connected to its morphological characteristics. It has a thick peptidoglycan membrane and as a result, it is very resistant to destroying factors. The results are in agreement with literature.[32] Testing resistance to the action of bacteria was performed by calculating the percentage of reduction of bacteria.[28] In the case of leather samples treated with CCS an inhibitory action is recorded on *Pseudomonas aeruginosa* (ATCC 9027), and those treated with Ag/TiO_2 solution have shown resistance to *Staphylococcus aureus* (ATCC 6538), for both types of treated leathers.

AAS and XPS analyses of silver in treated leathers

In order to elucidate the way in which silver nanoparticles are distributed and maintained in 0 valence state (specific to nanostructure), as a result of the interaction with variously processed leather, and of the correlation with microbiological resistance, Ag content and valence state on the surface of

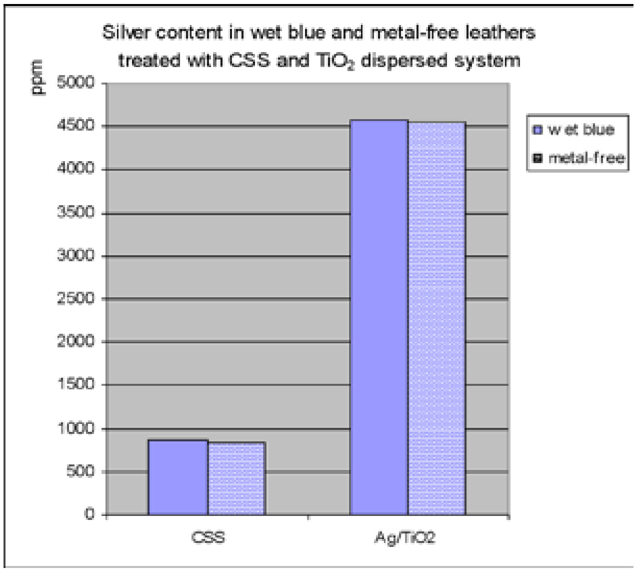

Figure 7: Silver content in wet blue and metal-free leathers treated with CSS and Ag/TiO_2 dispered system

TABLE I

XPS elemental quantification of Ag concentration on the leather surface treated with CSS and dispersed Ag/TiO_2

Leather	Treatment	Ag concentration At%
wet blue	CSS	0.18
metal free	CSS	0.11
wet blue	Ag/TiO_2	0.31
metal-free	Ag/TiO_2	0.49

treated leathers were analyzed. Ag content in the two types of leathers, determined by AAS is comparable for each type (wet blue and metal-free leathers) and much higher in the case of treatment with disperse systems of Ag/TiO_2 (Fig. 7).

XPS is a highly sensitive technique for surface analysis, which can effectively be used to investigate the composition and chemical state of the surface, and in this case it is important to evidence valence state of Ag. As it is known, silver exists in three different states:[35] the AgO state with binding energy of 367.0 eV; the Ag_2O state with binding energy of 367.7 eV and Ag^0 state with binding energy of 368.2 eV. It can be noticed that silver is present (Table I) in larger quantity on the surface of leathers (0.31-0.49% At) and exhibits a greater binding energy (368-374.06 eV) (Fig. 8) in the case of leather treatment with disperse systems of Ag/TiO_2, compared to leathers treated with CSS (367.44-373.59 eV) (Fig. 9), which is correlated with a higher fungal resistance of these leathers, compared to those treated with CSS.

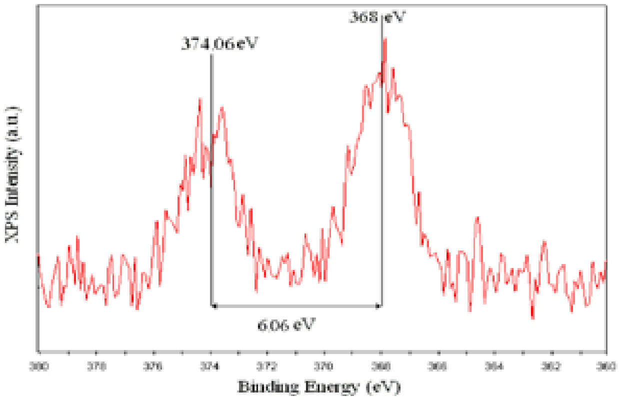

Figure 8: The Ag3d XPS spectra on the wet blue leather surface, treated with Ag/TiO_2

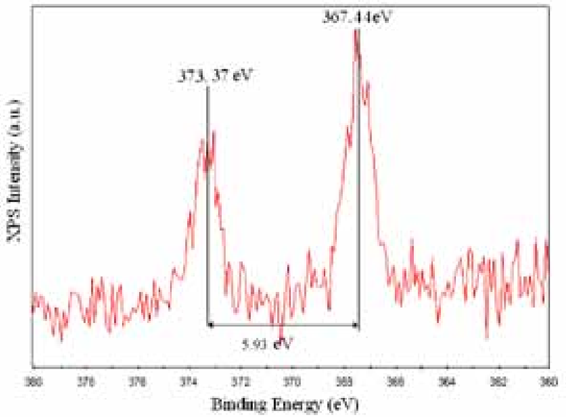

Figure 9: The Ag3d XPS spectra on the wet blue leather surface, treated with CSS

Moreover, from the high resolution spectra, it can be seen that the slitting of the 3d doublet of Ag is 6.06 eV in the case of wet blue leathers treated with Ag/TiO_2 (Fig.8), indicating the formation of a zero valence silver particle.[36] Ag^0 is preserved in a greater proportion in the case of wet blue leathers treated with Ag/TiO_2, probably due to the higher availability of Ag^0 deposited on TiO_2 for complexing by means of aminic groups, active in the case of chromium-tanned leathers. Comparing the binding energies in the case of wet blue and metal-free supports, treated with CSS and Ag/TiO_2 dispersed system, it is clear that Ag mainly exists in the Ag^0 state in the case of leathers treated with Ag/TiO_2, in other words, Ag is successfully loaded on the surface of TiO_2 in Ag^0 state, capable of long term release of Ag^+ with their bactericidal activity.

Technological and economical consideration on Ag/TiO_2 nano-dispersed systems application in leather industry

Nanomaterials for the leather industry are in an early stage of development in terms of both synthesis[20-22,25] and application.[19] Industrial application of these materials implies an additional research effort in the direction of finding inexpensive methods of synthesis and use in processing of a wide range of leathers. Without exhausting possibilities of innovation in application of nanomaterials, our paper focused on proving the transfer potential of bactericidal properties of new nanomaterials on leather supports tanned with chromium salts or without metals in order to create assortments with properties of protection upon wearing and added value, destined for a target group of users with sensitive health problems (medical leathers and furskins, ecological leathers).

The study of the influence of nano-disperse systems based on Ag/TiO_2 on leather dyeing has shown that total color modification (**DE***) is low in the case of dark colors (**DE*** =3.6 for wet blue leathers and **DE***= 4.9 for metal-free leathers) and slightly higher in the case of light colors (**DE*** =6.4 for wet blue leathers and **DE***= 17.5 for metal-free leathers), comparable with those generated by dyeing various types of leather assortments with the same dyeing agent.[23] In terms of the cost of creating nanomaterials based on Ag/TiO_2 , the paper brings a novelty in the field of research, as the electrochemical synthesis we have approached, compared to chemical synthesis (the most frequently used) ensures not only much lower costs (estimated 5 times lower), but also products with higher purity, without reaction precursors, placing their application at present at the cost level of natural products (such as those in the category of essential oils from plants) and justifying their application for medical and ecologic leathers, for which the cost is not the main issue.

CONCLUSIONS

Using an efficient and simple electrochemical method, stable and high purity nano-Ag based colloidal solutions containing 35 ppm Ag, with 4 nm diameter and - 44 mV zeta potential and Ag/TiO_2 dispersed solutions containing 10g/l TiO_2 and 45 ppm Ag, with 19.7 nm diameter and – 36.8 mV zeta potential, were obtained. Solutions obtained in this manner have affinity for wet blue or metal-free leathers. Even though both CSS and Ag/TiO_2 have a very good antifungal and antibacterial activity, in the case of leather treated with these, the situation is completely different. Leather treated with CSS has an antifungal activity up to 7 days, very good in the case of wet blue (rating mark 0.1) and good enough for metal-free leather (rating mark 1) compared with control sample, which has rating mark 2 for wet blue leather and 4 for metal-free leather respectively. Leather treated with Ag/TiO_2 solutions has a very strong antifungal activity up to 28 days of fungi exposure, rated by 0 mark and an inhibition zone up to 25 mm in the case of wet blue leather and rated by 1 mark, without inhibition zone for metal-free leather, respectively. In both cases, control samples are almost completely covered with fungi after 28 days.

Wet blue and metal-free leathers, treated with disperse systems of nano-Ag and nano-Ag/TiO_2 have exhibited inhibitory activity for *Pseudomonas aeruginosa* (ATCC 9027) or *Staphylococcus aureus* (ATCC 6538) bacteria. Electrochemical deposition of silver nanoparticles on TiO_2 nanoparticles provides the best fungicide effects, attributed to both the capacity of preserving the valence specific to the metal state of silver and the greater affinity for chromium-tanned or metal-free leather. Analysis regarding concentration and valence state of Ag on the leather surface by XPS has permitted the identification of a greater concentration of Ag^0 in the case of leathers treated with disperse systems of nano-Ag/TiO_2 compared to those treated with nano-Ag, correlated with improved biocide properties. Deposition of silver nanoparticles on porous nanoparticles provides a better interaction with variously tanned leather, preserves the atomic state of Ag, which is reactive due to silver plasmon, and potentiates synergic biocidal effects.

The new products give the perspective of a new range of ecologic products, with applications both in the area of leather articles for medical and everyday use, and in the area of materials for additional treatment of wet blue palletized leathers etc.

ACKNOWLEDGMENT

The work was supported under the projects PN 71-146/2007 and 199/2008 financed by CNMP and ANCS.

REFERENCES

1. *DIRECTIVE 98/8/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 February 1998 concerning the placing of biocidal products on the market,* Official Journal of the European Communities 24.4.98 EN L 123/1
2. FIFRA-Federal Insecticide, Fungicide and Rodenticide Act
3. Stockman G., Didato D.T., Rangarajan R.; Alternative solutions for fungal protection of packaged wet blue, *JALCA* **101**, 461-466, 2006
4. Dalton, D.L.; New Generation Fungicide for the Leather Industry, Ist International Leather Engineers Symposium on Leather Industry-Environment and Progressive Technologies, Izmir, Turkey, 29th April-1st May 2009
5. Jones SA, Bowler PG, Walker M, Parsons D. Controlling wound bioburden with a novel silver-containing Hydrofiber dressing. Wound Repair Regen **12**,3,288- 94, 2004
6. Sondi I, Salopek-Sondi B. Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for gram-negative bacteria. *J Colloid Interface* **275**,177–82, 2007
7. Song HY, Ko KK, Oh LH, Lee BT. Fabrication of silver nanoparticles and their antimicrobial mechanisms. *Eur Cells Mater* **11**,58, 2006.

8. Cho, K.-H., Park, J.-E., Osaka, T., Park, S.-G.; The study of antimicrobial activity and preservative effects of nanosilver ingredient. *Electrochimica Acta* **51**, 5, 956-960, 2005.
9. Rai, M., Yadav, A., Gade, A.; Silver nanoparticles as a new generation of antimicrobials. *Biotechnol Adv* **27**, 1, 76-83, 2009.
10. *www.nanocentral.eu*: Nano Perspective//March 2009.
11. Feng, Q.L., J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, J.Q. Kim, *Journal Biomedical Material Research* **52**, 662, 2000
12. Gaonkar T.A.,, L.A. Sampath, S.M. Modak, *Infection Control and Hospital Epidemiology* **24**, 506, 2003
13. Percival S.L., P.G. Bowler, D. Russell, *Journal of Hospital Infection* **60**, 1, 2005.
14. Vigneshwaran N, Kathe AA, Varadarajan PV, Nachane RP, Balasubramanya RH. Functional finishing of cotton fabrics using silver nanoparticles. *J Nanosci Nanotechnol* **7**, 1893-7, 2007
15. Wang Y.L., Y.Z. Wan, X.H. Dong, G.X. Cheng, H.M. Tao, T.Y. Wen, *Carbon* **36**, 1567,1998
16. Dong D. W., Y.S. Yang, B.Z. Jiang, *Materials Chemistry Physics* **96**, 90, 2006
17. S. Zhang, R. Fu, D. Wu, W. Xu, Q. Ye, Z. Chen, Preparation and characterization of antibacterial silver-dispersed activated carbon aerogels, *Carbon* **42**, 3209, 2004
18. Adminis U., Huynh C., Money C.A.; The need for improved fungicides for wet-blue, *JSLTC* **86**, 3, 118-121, 2002
19. Bitlisi B.O., Yumurtas A.;Self cleaning leathers-the effect of nano TiO_2, *JSLTC* **92**, Sep-Oct, 183-186,2008;
20. Chen Y., Zhang X., Fan H., Shi B., Nano-TiO_2 in-situ hybrid polyurethane with enhanced permeability for PU leather manufacture, *JALCA* **104**, 210-216, 2009
21. Zhou N., Chen W., Li S., Gu H., Lin Y., Jia L., Preparation and characterization of collagen-TiO2 nanocomposite improved with glutaraldehyde, *JSLTC* **90**, 197- 200, 2006
22. Gaidau C., Petica A., Trandafir V., Ciobanu C., Martinescu T.; Nanosilver Application for Collagen Based Materials Treatment, The XXX th International Congress IULTCS Beijing 11-15 October, 2009
23. Metal-free TFL commercial technologies, www.tfl.com
24. A. Petica, S. Gavriliu, M. Lungu, N. Buruntea, C. Panzaru, “Colloidal Silver Solutions with Antimicrobial Properties”, in “*Materials Science and Engineering B*” **152**, 22-27, 2008
25. L. Anicai, A. Petica, S. Gavriliu, Patent demand: “*Electrochemical procedure of obtaining ecologic disperse nanostructured systems with photocatalytic and antimicrobial activity*” OSIM file: A00961 from 23.11.2009, BOPI no.5 of 2010
26. Ericcsson H.M., J.C. Sherris, Acta Pathol. Microbiol. Scand. Suppl. 217B (64) (1971).
27. SR CEI60068-2-10/2006; Pr. PI – 14, 2007; ASTM D: 4576-86, 1996
28. Document no. FTTS-FA-002 Test method of specified requirements of antibacterial textiles for medical use, 2000
29. L. Lifen, J. Barford, Y.K. Lun, Non-UV germicidal activity of fresh and Ag/TiO_2, *J. of environmental sciences*, 21(5), 2009
30. Kühn K.P., I. F. Chaberny, K. Massholder, M. Stickler, V. W. Benz, H-G Sonntag and L. Erdinger, *Chemosphere* **53**, 1, 71-77, 2003
31. Seery M.K., R. George, P. Floris, S.C. Pillai, *J. Photochem. Photobiol. A* **189**, 258, 2007.
32. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, *J. Photochem. Photobiol. A* **163**, 37, 2004
33. Elechiquerra J.L., J.L. Burt, J.R. Morones, A. Camacho-Bragado, X. Gao, H.H. Lara, M.J. Yacaman, *J. Nanobiotechnol.* **3**, 6, 1–10, 2005
34. Gill S.R., D. E. Fouts, G. L. Archer, E. F. Mongodin & all., J. Bacteriol. **187**, (7), 2426-38, 2005
35. Wang.H., Niu J., Long X., He Y.; Sonophotocatalytic degradation of methyl orange by nano-sized Ag/TiO_2 particles in aqueous solutions. *Ultrasonic Sonochemistry* **15**, 386-392, 2008
36. Moulder J.F., Stickle W.F., Sobol P.E., Bomben K.D. (Eds.), Hand Book of X-ray Photoelectron Spectroscopy, Perkin–Elmer Corporation Physical Electronics Division, 1992.