

European Good Practices in Smart textiles and new ways of production

MANUCOAT-Self-cleaning textiles

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INCDTP is a center of excellence in RDI in the field of textile-clothing, leather-footwear-rubber goods

develops RDI activities having a fundamental and applicative character

small and short series micro production

consultancy & technical assistance services by 2 accredited laboratories

editing & publishing of technical reviews, books, ISI-rated magazine

standardization activity

professional training activities

The research fields of interest for our institute



- **Advanced products and technologies for textiles-clothing and leather-footwear- rubber consumer goods**
- **Functionalities for high performance materials**
- **Increase of flexibility and efficiency in the development of the products and materials through design**
- **Ultralights aircrafts, parachutes, paragliders, autonomous platforms**
- **Invasive and non-invasive medical devices with biomedical and bio-functional characteristics specific to the clinical use in medicine, health**
- **Clean technologies for textile and leather field and environment protection**
- **Conservation and protection of cultural heritage**
- **Support instruments for developing RDI capacity**



Integrated manufacturing process for textiles applications and wood protection

THE OBJECTIVE: to develop new, long life and environmentally stable *photocatalytic textiles* with sensitivity in the solar visible spectrum and *wood* with *durability* to environmental conditions.

THE SPECIFIC OBJECTIVES:

1. *Development of TiO₂ NPs Ag doped/non-doped* with reproducible phase composition and surface properties, with a low cost and scalable hydrothermal technology;
2. *Development of plasma-electrospray innovative complex systems* for the deposition of thin layers of NPs with uniform, homogeneous and well controlled composition;
3. *Development and up scaling of RF sputtering as a innovative technology* for deposit thin photocatalytic NPs layers on textiles and wood at low temperatures, low environmental pollution and low consumption of raw materials.

The research was carried out within the ERA NET MANUNET programme, and involved 4 partners:

- MGM Star Construct, www.mgmstar.ro/
- National R&D Institute for Textiles and Leather-INCDTP, www.certex.ro
- National R&D Institute for Nonferrous and Rare Metals –IMNR, www.imnr.ro
- Innovacio i Recerca Industrial i Sostenible – IRIS, www.iris.cat





SME private company specialized in:

- physical and chemical vacuum deposition
- photolithography technology
- sales, service and upgrade of vacuum equipment
- execution of clean rooms and ozone water treatment systems



R&D and advanced engineering company

Providing solutions to industry:

Process optimization,

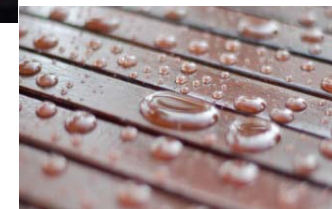
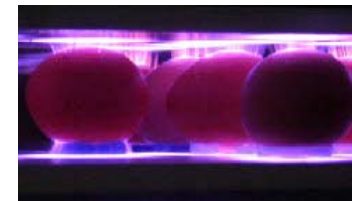
Process control & monitoring,

Process automation,

Development of new technology, products & materials,

Systems control,

Plasma technology.





NATIONAL RESEARCH-DEVELOPMENT INSTITUTE
FOR NON-FERROUS AND RARE METALS – I.M.N.R.



Material:

- Hybrid inorganic-organic nanomaterials
- Doped nanostructured zinc oxide
- Nanostructured iron oxide
- Doped nanostructured titanium oxide
- Doped nanostructured zirconia

Synthesis:

1. Hydrothermal procedure
2. Hydrothermal-electrochemical procedure

Background for the implementation of the GP


- ✓ To eliminate dirt and destroy microorganisms, the textile goods must be washed, meaning a high consumption of energy, water, detergents and a high environmental burden;
- ✓ The hospital-acquired infections are a major financial issue in the European healthcare system;
- ✓ Textile treatment by wet chemical processes are time intensive and with release of large amounts of wastewater and the need of expensive post-treatment of wastewater;
- ✓ Textile treatment by dry processes eliminated altogether these problems.

Self-cleaning, antibacterial effect and new ways of producing them could considerably reduce this consumption and brings many valuable benefits in a view of end-use properties

Detailed description of the GP

The GP addresses the **new ways of production the self-cleaning** and antibacterial textiles and wood through photocatalytic properties in the visible solar spectrum of TiO_2 and TiO_2 doped with Ag.

Unlike the techniques commonly used, for creating photocatalytic layers, the ***GP brings some new elements:***

- 
- **New method** to extend the absorption domain of photocatalytic compounds in the visible solar spectrum, increasing the photocatalytic yield and photo degradation rate;
 - **New physical deposition methods** of transparent, flexible, smooth nanostructured layers on the surface of textile and wood.

The methods allow the achievement of up to 80% of savings in the chemicals deposited, no generation of polluting residues during the process and high functional performances (e.g. self-cleaning, antibacterial).

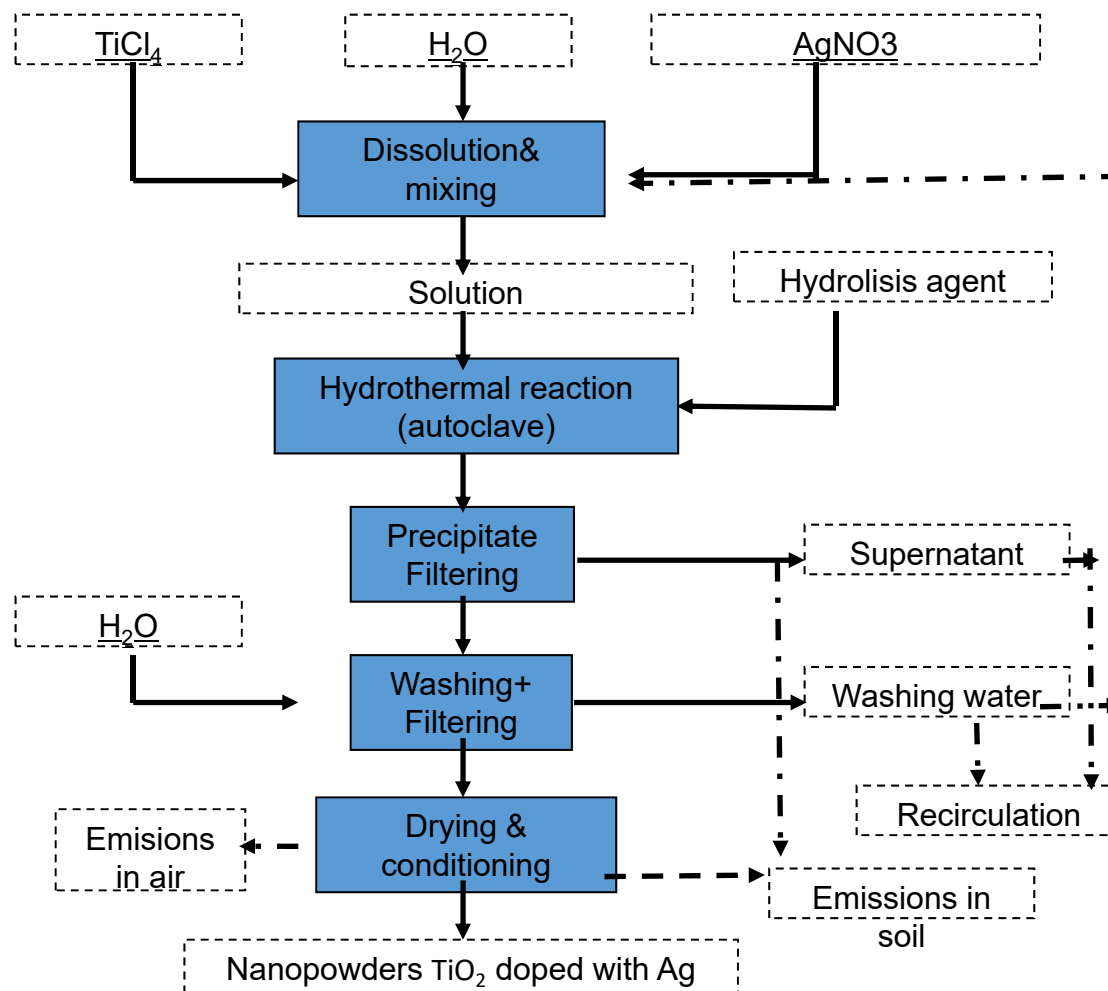
Synthesis of TiO_2 or TiO_2 doped with Ag NPs with absorption in the visible solar spectrum (1)

Why TiO_2 ?

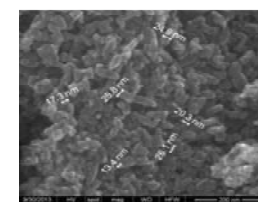
- ✓ High photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price make TiO_2 nanoparticles particularly attractive for manufacturing of different high value-added products;
- ✓ Reasonable safety and stability;
- ✓ TiO_2 doped with Ag NPs are a powerful antimicrobial agent that deactivates several microorganisms.

Synthesis of TiO_2 or TiO_2 doped with Ag NPs with absorption in the visible solar spectrum (2)

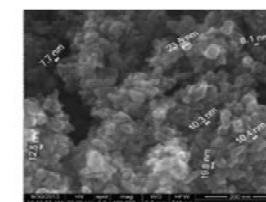
Technological flow-sheet



An innovative hydrothermal technology in aqueous media, at low temperatures ($\leq 200^\circ\text{C}$) and high pressures (> 200 atm.) in one step without any further thermal treatment.



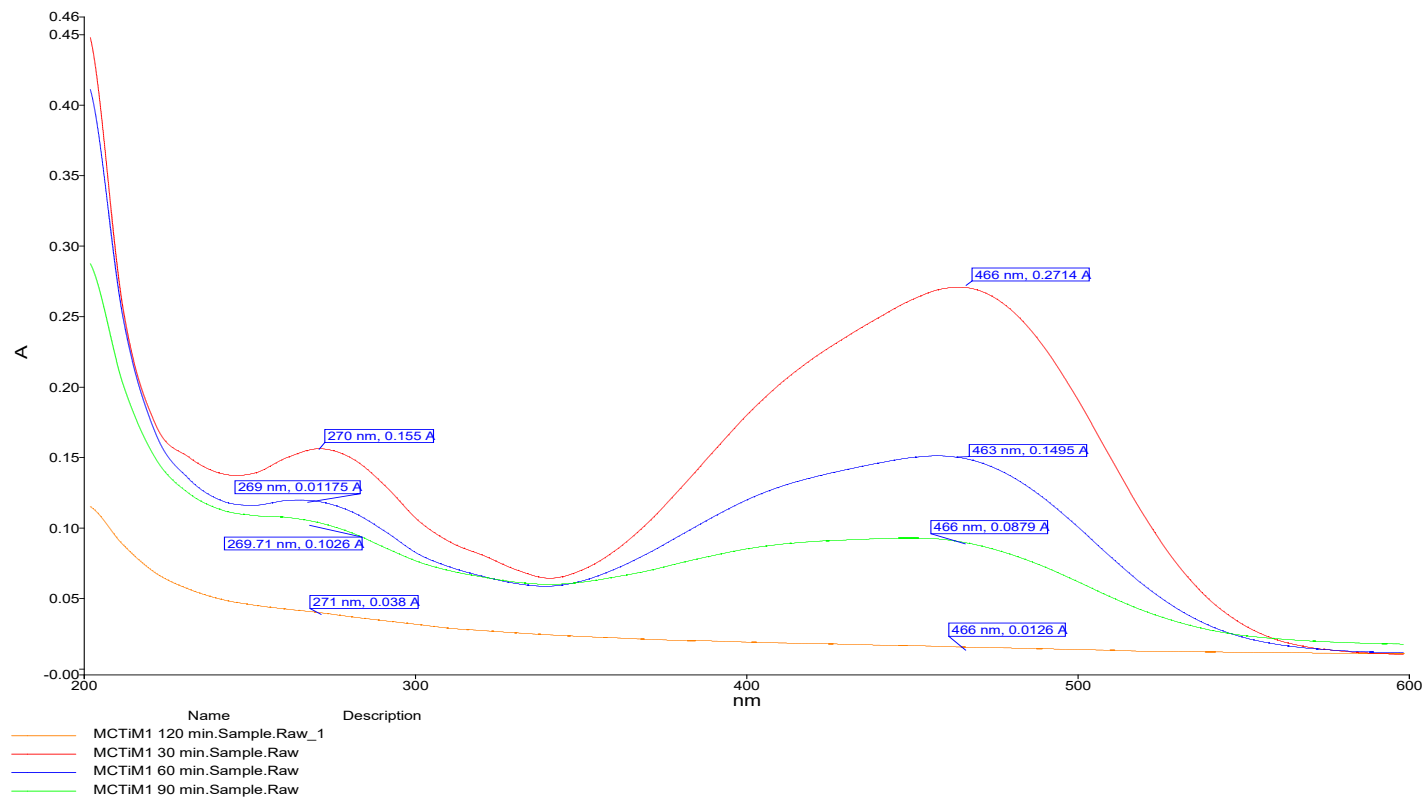
TiO_2 NPs



TiO_2 Ag NPs

- TiO_2 NPs: 98% Anatase
2% Brookite
- TiO_2 /Ag NPs:
93.5% Anatase
6.0% Brookite
0,5% Ag

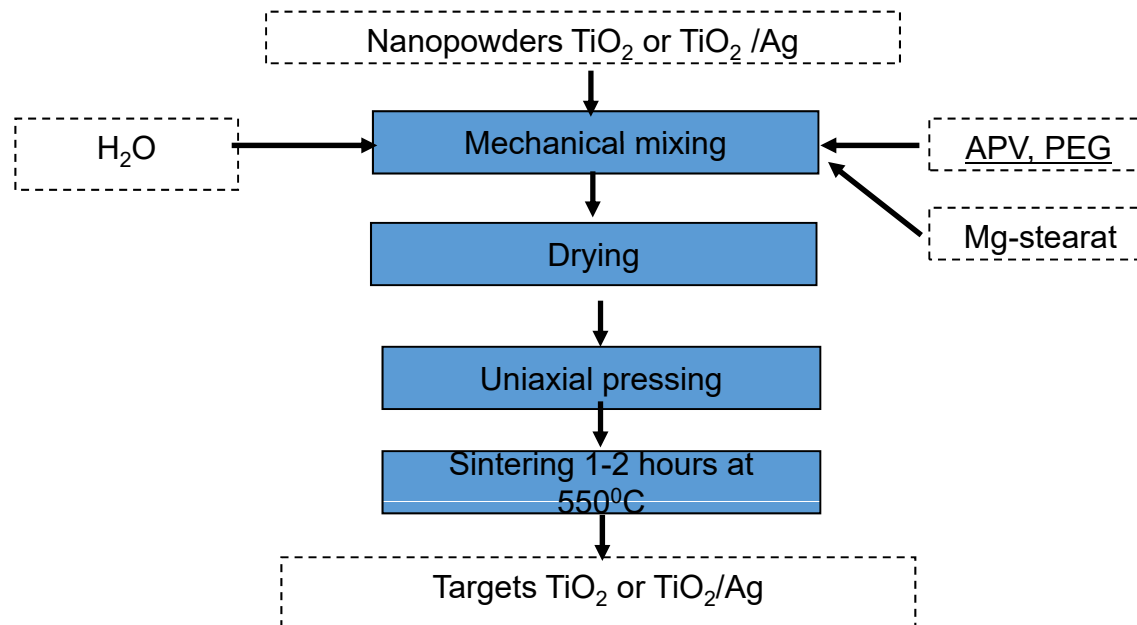
Synthesis of TiO₂ or TiO₂ doped with Ag NPs with absorption in the visible solar spectrum (3)



Absorption spectrum of 0.005 (mg / mL) MO + 0.006g TiO₂ at different degradation times

Deposition of TiO_2 or TiO_2 doped with Ag nanoparticles on the fabric surface by sputtering (1)

➤ Technology flow-sheet: Preparation of targets (cathodes) - Patent claim



The advantages of these targets:

- the thickness of the target is reduced and the heat transfer is faster
- can be used even if they are cracked.

The targets are stuck with an electro-conductive paste on a copper plate



TiO_2 Target

Deposition of TiO_2 or TiO_2 doped with Ag NPs on the fabric surface by sputtering way (2)

- A vacuum equipment VU-2A were ***up-scaled to pilot*** with sputtering module consist of: TORUS 2" HV circular sputtering source; a Glow Discharge system; R301 MKII radio frequency power supply; a mass flow controllers for the introduction of working gases; a carousel for fixing textiles or wood.



Versatile equipment for sputtering treatment of textiles and wood

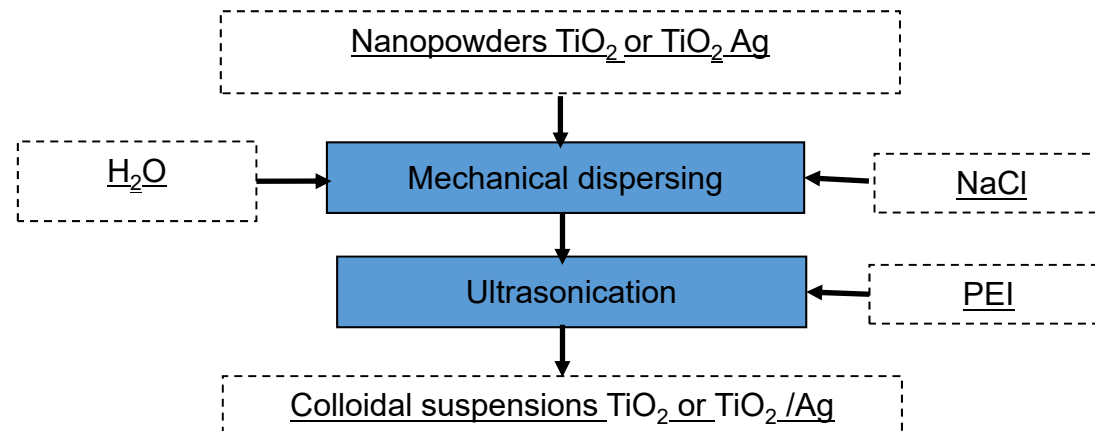


Pilot vacuum chamber with sputtering source, carousel, and glow discharge cathode

- ✓ Textile surfaces was been cleaned and activated using plasma a Glow Discharge technique, in vacuum and Ar atmosphere;
- ✓ RF Sputtering deposition at controlled parameters (working vacuum, RF power, carousel rotation speed, gas mixture Ar/O_2 flow).

Deposition of TiO_2 or TiO_2 doped with Ag NPs on the fabric surface by electrospray way (1)

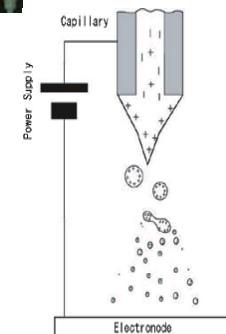
➤ Technology flow-sheet: colloidal suspensions



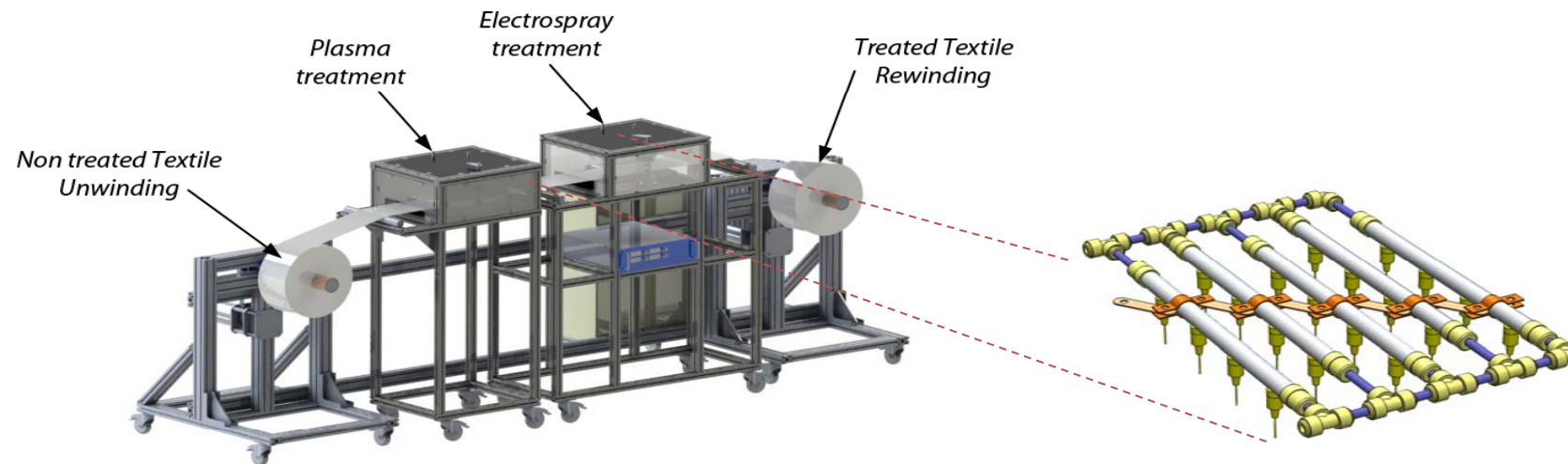
➤ Electro spray deposition of nanostructured film

Textile surfaces was been cleaned and activated using the atmospheric Dielectric Barrier Discharge Plasma

Electrospray deposition using needles polarized at a voltage of several kV while the surface to be coated is grounded or is polarized to a negative voltage value.



Deposition of TiO_2 or TiO_2 doped with Ag NPs on the fabric surface by electrospray way (2)



Pilot electrospray equipment

Results achieved (1)

❖ Self- cleaning textiles

The ***photocatalytic effect*** was determined according to ISO 105 B02 by measuring the degree of discoloration of the stain with Hunterlab equipment, after exposure at visible light in the Xenotest.

The **color difference** is noted from 1 to 5. A low value of the note indicates a good photocatalytic effect.

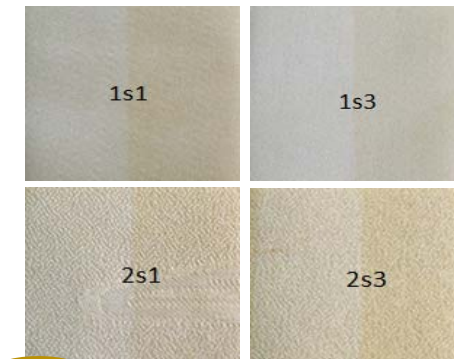
The substances for staining were Methyl orange and Methylene Blue with a concentration of 100 mg / l.

Results achieved (2)

❖ Self-cleaning textiles

Textiles treated with NPs by sputtering

Samples/treatment	After 9 h Xenotest Note	After 14 h Xenotest Note	2 washing cycles	
			After 9 h Xenotest Note	After 14 h Xenotest Note
1s1:Satin PES 100%/TiO ₂	2.5	1.5		
2s1:Crepe PES 100%/TiO ₂	3.0	2.5		
3s1:Cotton 100%/TiO ₂	3.5	2.0		
1s3: Satin PES 100%/TiO ₂ Ag1%	2.5	1.5	2.5	2.0
2s3: Crepe PES 100%/TiO ₂ Ag1%	2.5	2.5	2.5	2.5
3s3: Cotton100%/TiO ₂ Ag1%	4.0	2.0	2.5	3.5



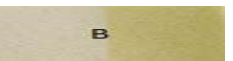




After 9 h Xenotest

The self cleaning properties of the samples treated by sputtering are **good** and increase after a long exposure at light.

Textiles treated with NPs by electrospray

Sample	Types solution/ concentration mg/ml	Fabrics Speed / plasma time (m/min/s)	After 9 h Xenotest Note	After 14 h Xenotest Note
A Crepe PES 100%	TiO ₂ Ag 1%	1/21	1.5	1.0
B Crepe PES 100%	TiO ₂ Ag 1%	3/7	1.5	2.0
C Crepe PES 100%	TiO ₂ Ag 1%	5/4.2	2.0	1.5
D Crepe PES 100%	TiO ₂ Ag 1%	8/2.6	2.0	1.5

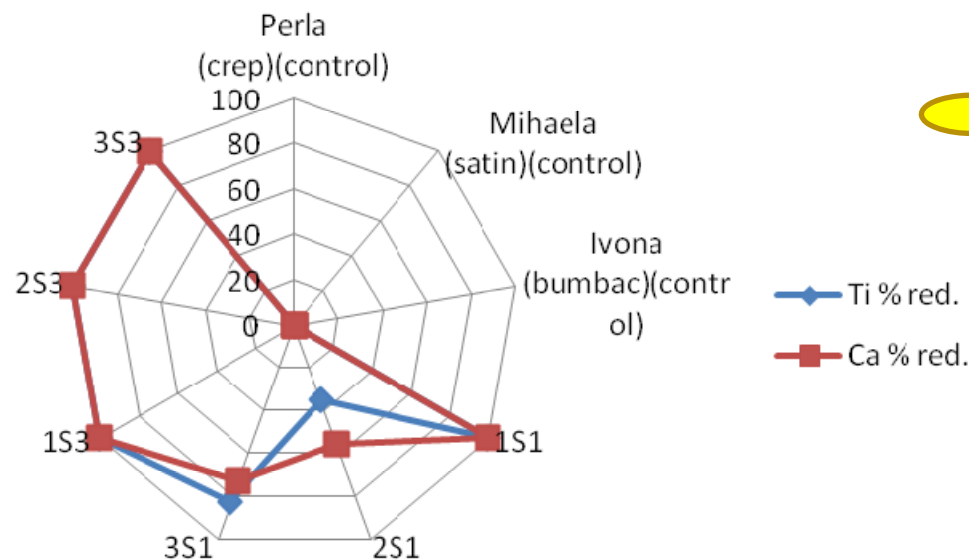
				
Control	A	B	C	D

All samples treated by electrospray present a **very good** self cleaning properties.

Results achieved (3)

❖ Antibacterial activity: Textiles treated with NPs by sputtering

Antifungal activity: ISO 20743:2013: Textiles. Determination of antibacterial activity of textile products; *quantitative method*



All samples treated with TiO_2 / 1% Ag present **excellent antifungal and antibacterial activity**

Antibacterial activity: SR EN ISO 20645:2005-Textile fabrics. Determination of antibacterial activity; *qualitative method*

Sample	Treatment	Growth	Assessment Escherichia coli ATCC 8739	Assessment Staphylococcus aureus ATCC 6538
1s3: Satin PES 100%	TiO_2 Ag 1%	None	Satisfactory effect	Satisfactory effect
3s3: Cotton100%	TiO_2 Ag 1%	None	Satisfactory effect	Satisfactory effect

Results achieved (4)

❖ Antibacterial activity: Textile fabrics treated with NPs by electrospray

SR EN ISO 20645:2005-Textile fabrics. Determination of antibacterial activity; Agar diffusion plate test- *qualitative method*

Sample	Types solution/ concentration mg/ml	Fabrics Speed/ plasma time m/min/s	Growth	Assessment Candida albicans	Assessment Staphylococcus aureus
A Crepe PES 100%	TiO ₂ Ag 1%/10	1/21	None	Satisfactory effect	Satisfactory effect
B Crepe PES 100%	TiO ₂ Ag 1%/10	3/7	None	Satisfactory effect	Satisfactory effect
C Crepe PES 100%	TiO ₂ Ag 1%/10	5/4.2	None	Satisfactory effect	Satisfactory effect
D Crepe PES 100%	TiO ₂ Ag 1%/10	8/2.6	None	Satisfactory effect	Satisfactory effect



All samples treated with solutions of TiO₂Ag by plasma - electrospray deposition at 20 mm electrospray conditions Gap, showed **very good antifungal and antibacterial activity**

Results achieved (5)

Wood treated with NPs by sputtering

Tested characteristics	OAK WOOD	
	Treated by sputtering with TiO ₂	Treated by sputtering with TiO ₂ Ag1%
Effectiveness of antiseptization of wood against mold fungus (STAS 8022-91)	Very good	Very good
Efficacy of protection against blueberries (SR 13154:1993)	Very good	Very good
Protective efficacy against lignicium basidiomycete mushrooms (rotting fungi) (SR EN 113:2003)*	1,81% (Sufficient)*	0,82% (Sufficient)*
Efficacy threshold against the species Reticulitermes (European termites) (SR 117:2013)	No attack	No attack

*Limit ≤ 3%



Success factors of GP

- ✓ The pilot lines based on a one step deposition process by sputtering in order to produce self-cleaning, antibacterial textiles and wood with durability increase;
- ✓ Development of functional textiles (self -cleaning and antimicrobial) by new method;
- ✓ Development of a process environmentally friendly and with economic efficiency;
- ✓ Open-up new market for durable art wood objects.

Difficulties encountered and lessons learnt from the practice

- One of the major difficulties was the deposition by sputtering on the textiles with large width, because of the size of target (cathode);
- At the assessment of self-cleaning properties because there are no standards by which their effectiveness can be gauged, compared and contrasted;
- The assessement of photocatalytic effect of photo catalysis is not easily assessed visually, and the photo catalysts property cannot be evaluated with a single method.



The durability of the GP results and impacts

Compared to other methods for producing self-cleaning and antimicrobial fabrics the **new ways of coating by deposition of thin films of TiO₂ NPs** has the potential to be competitive on both economic and environmental terms.

Environmentally friendly technique because of :

- the low energy consumption and the fact that it is a dry technique, which means that there is no waste disposal problem and disposal cost;
- qualitative and full controllable process: all parameters are controlled by the unit and quality control possible by print-out and data-logging;
- operator friendly technique: no chemical products, gases, etc.;
- no substrate damage or bulk property changes;
- different processes can run in the same unit;
- no limit to substrate geometries: small and large, simple or complex, parts or textiles are possible.



Good Practice value added at regional and transregional (EU) levels

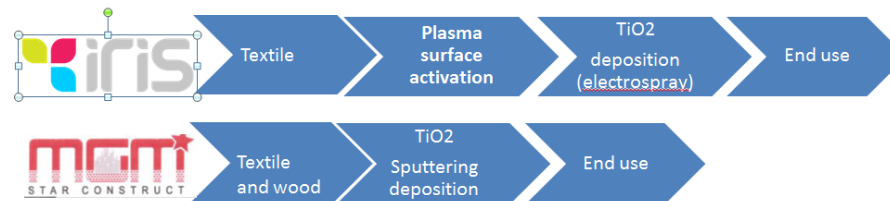
- New ways of production and methodologies of self-cleaning, antimicrobial and durable wood;
- The new ways of production and their implementation could have an important and durable impact on economy and employment if the products are commercialized;
- Contributes directly to the quality of the European citizen by reducing number of laundering and of potential infections;
- Reduced costs related to the cleaning of textiles, treatment of infectious diseases acquired during hospitalization and maintenance of art wood objects.

This GP could be spread not only in our geographical area, but also at an international level, transferring the knowledge to European textile sector as a possible way to raise awareness in friend environmental production and products.

Conditions and requirements of GPs transferability

Conditions for transferring the GP to other regions/countries should consider several issues:

- ✓ Existing and new companies will need to invest in the new production ways of the self-cleaning, antibacterial textiles and durable wood; to invest in the new equipment for deposition of TiO₂ NPs;
- ✓ Training education and know-how transfer by specialists and experts;
- ✓ Know-how and industrial property of the technology developed in the MANUCOAT project to be taken in account.



2 technical ways of producing self-cleaning and antibacterial textiles

MANUCOAT-Self-cleaning textiles

GP Contact



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European Union
European Regional
Development Fund

Thank you!

Chemnitz, 20th June 2017



Project smedia