SELDEC: Matériaux de protection multispectre auto-décontaminants sous illumination naturelle visible /solaire ou artificielle UV-A

Titanium dioxide functionalized textiles for the photocatalytic destruction of liquid and gaseous chemical warfare agents

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Résumé – Le projet SELDEC propose des nouveaux matériaux pour les tenues de protection pour les intervenants dans les scénarios d'exposition aux agents chimiques et biologiques. En combinant des approches classiques de la tenue filtrante ou adsorbante avec un revêtement photocatalytique à base de nanoparticules de dioxyde de titane (TiO_2), nous voulons améliorer la protection des primo-intervenants en créant un système filtrant ou adsorbant auto-régénérable.

Nous avons dans un premier temps testé différentes techniques de dépôt des nanoparticules de TiO_2 sur le support textile afin de trouver la méthode qui mène au dépôt le plus actif en décontamination photocatalytique (évaluée avec une molécule modèle, le dimethyl methylphosphonate [DMMP]). Les meilleurs échantillons permettent une degradation de plus de 90% de la contamination initiale après 10 min d'illumination solaire. Ces meilleurs échantillons ont été réalisés par une technique innovante de fonctionnalisation de textiles, le LBL (layer-by-layer, en français : couche par couche), et par une technique plus classique de l'industrie textile, l'immersion/foulardage en utilisant un espaceur chimique. Les tests réalisés avec un agent réel (ypérite) au laboratoire DGA Maîtrise NRBC montrent la même tendance, prouvant ainsi la pertinence de la molécule modèle. Nous avons pu démontrer que le dépôt résiste à l'abrasion, au lavage et à l'irradiation solaire en gardant son activité photocatalytique. Des prototypes de tenues ont été confectionnés avec un dépôt simplifié et non-optimisé de TiO_2. Ils ont été testés pour leur confort lors d'essais au porté par des utilisateurs entrainés et familiers des équipements de protection individuelle NRBC, le SDIS 91. A la suite des ces essais, la tenue SELDEC est apparue significativement meilleure qu'une tenue imperméable et qu'une autre tenue filtrante.

Le projet SELDEC a permis de développer et de proposer des prototypes d'une tenue de protection NRBC mieux adaptée aux besoins des primo-intervenants avec une protection améliorée contre les agents chimiques à base d'un revêtement photocatalytique de nanoparticules de TiO_2 actives sous illumination solaire.

Abstract – The SELDEC project offers new materials for protective clothing intended for first responders that are exposed to chemical and biological agents. We aim to improve the protection of these first responders by combining the standard filtering or adsorbing clothes with a photocatalytic top coat composed of titanium dioxide (TiO_2) nanoparticles in order to create a self-regeneration filter system.

In a first step, we have deposited TiO_2 nanoparticles on textile supports by different techniques in order to determine the technique leading to the most photocatalytically active coating (evaluated with a model compound, dimethyl methyl phosphonate [DMMP]). The best performing samples are able to destroy 90% of the initial contamination within 10 min of solar irradiation. These best samples have been synthesized with an innovative deposition method, LbL (layer-by-layer), and by a more conventional method of the textile industry, immersion /padding using a chemical spacer. Real agent tests (using yperite) conducted by the laboratory Maitrise NRBC of the DGA, show the same tendencies, validating thus our choice of the model compound. We have been able to show that the nanoparticle coating resists to abrasion, washing and sun light exposure without losing its photocatalytic activity.

Prototypes of protective clothing have been produced by a simplified and non-optimized coating. They have been tested by trained users towards their comfort. The SELDEC clothing was considered as significantly superior to another filtrating combination and an impermeable combination by the user panel.

1. Introduction

In the scope of the SELDEC projet, we propose new materials for protective clothings intended for first responders to chemical and terroristic threads. We focused on functionalized textiles that are able to self-decontaminate when exposed to light. Titanium dioxide coatings were investigated towards their mechanical resistance and their chemical agent destruction kinetics in UVA and artificial solar illumination. In order to improve the protection of first responders, appropriated clothing must be at their disposal, combining protection adapted to the exposure scenario, ergonomics and longevity. We are studying new materials for protective clothing, self-decontaminating systems that improve the safety of first responders on the field and a new destructive decontamination process based on photocatalysis for chemical and biological agents. The coupling of this photocatalysis process with the existing filtration and adsorption systems leads to a self-regenerating filtration system.

As for today, there is no personal protective equipment available that self-decontaminates under natural or artificial light. We have proposed previously [1-3] to functionalize textiles with titanium dioxide for the decontamination both during use under natural sun light as well as after use by artificial UV-A irradiation using photocatalysis.

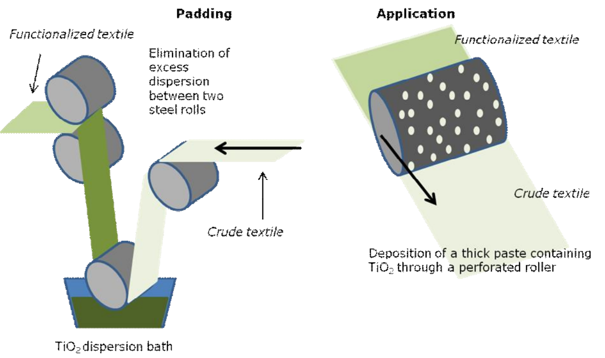
Photocatalysis is a fast, room-temperature process that allows the destruction of organic molecules and biological threads as such bacteria, viruses and spores through the generation of powerful oxidizing species on the surface of the photocatalyst. It has been used for the oxidation of volatile organic compounds (VOC) in air and water [4,5] and, in combination with a textile support, for stain removal [6]. Our laboratory has been the first to use it for the destruction of chemical warfare agents on textiles [3,7].

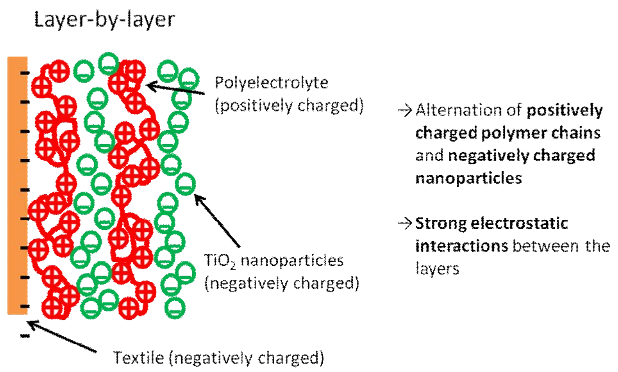
The SELDEC project encloses the whole development chain, form the choice of the catalyst, through the optimization of the catalyst deposition on the textile and the evaluation of the photocatalytic activity of these functionalized textile towards model and real life agents to the fabrication and testing of prototypes.

2. Experimental

In a first step, different deposition techniques were used to deposit TiO_2 nanoparticles onto the textile surfaces. On one hand, the layer-by-layer technique was used, that is innovative for the functionalization of textiles. On the other hand, classic techniques such as padding and enduction were used (see figure 1). Layer-by-layer usually consists of the deposition of alternative layers of oppositely charged polyelectrolytes onto a surface. In our case, we replaced one of the electrolyte by a dispersion of charged TiO_2 nanoparticles (see figure 2). The electrostatic attraction between the alternate layers leads to strong interaction that easily resist to mechanical stress such as abrasion or to washing of the textile in a machine.

A second step was the development of a testing protocol to assess the photocatalytic activity of the functionalized textiles using a model compound. Briefly, droplets of the contaminant were deposited onto small pieces of the functionalized textile and then exposed to artificial UVA





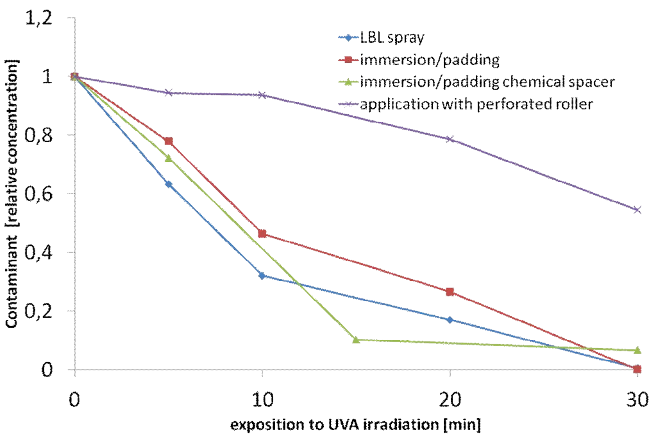
or simulated solar irradiation. After a given period (5, 10, 20 or 30min), the organic residues on the textile were extracted in isopropanol and quantified using mass spectrometer coupled gas chromatography.

The best performing textiles with the fastest decontamination kinetics were subjected to aging tests (abrasion, washing in a machine and prolonged solar irradiation) and then tested for their photocatalytic activity again. In parallel, their decontamination capacity was tested with the real life agent yperite.

Prototypes were produced using an un-optimized deposition technique and subjected to sensorial testing with a group of fire fighters. They were able to assess the comfort of the clothing during dressing and undressing as well as under effort.

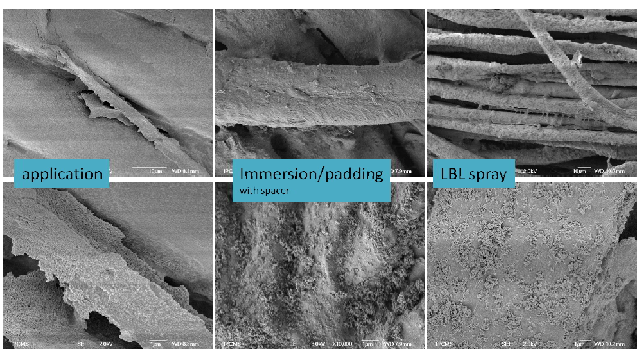
3. Results

The deposition of titanium dioxide nanoparticles onto cotton/polyester textiles leads to coatings composed of agglomerated particles that spread over the entire fiber. In the case of polyamide textiles, the particles agglomerate and are located preferentially in the fiber interstices, showing insufficient adhesion of the particles on the fiber surface. When using a pretreatment with chemical spacers (succinic acid), the coating is more homogenous and spreads over the fiber surface. Except for the application



method, the coated textiles almost retain their initial color with light fading. Fabrics treated through application appear considerably whitened after deposition. Application coatings also change the surface feel of the textile, rendering them stiff and rough.

The best decontamination kinetics were obtained with textiles produced by Layer-by-layer deposition or the immersion/padding approach (see figure 3). In both cases, the adhesion of the coating can be improved using chemical spacers or a mild basic hydrolysis prior to deposition. Deposition with application leads to thick coatings that peel of the textile fiber (see figure 4 for



scanning electron micrographs) and are low in activity. This observation is in good agreement with the changed macroscopic aspect of these fabrics.

After aging, the textiles retain their initial photocatalytic activity towards the simulant. Neither washing nor abrasion nor irradiation with solar light alters the photocatalytic activity of the textiles, proving that the coatings are stable under physical wear. We can therefore conclude that the textiles can be used several times.

Using yperite instead of a simulant for the test of the photocatalytic activity, we observe the same tendencies as for the simulant. On the one hand this shows that the choice of the simulant was pertinent, on the other hand the kinetics with the real agent are much slower. In the future we will have to extend the time of exposition to the irradiation.

Sensorial tests showed improved comfort of the SELDEC clothing compared to two already commercialized models, a long-term protection based on cotton/polyester with filtrating membrane and an impermeable combination. The design and confection of the protection are therefore suitable for the use by first responders.

4. Conclusion

During the SELDEC project we have managed to develop functionalized textiles that are able to degrade both simulants and real life agents deposited on their surface under UVA or simulated solar irradiation. These textiles can be transformed into protective clothing for first responders with improved comfort during dressing, undressing and wearing.

Due to the positive outcome of the SELDEC project, the consortium has been enlarged and is now engaged in the bi-national French-German SAFECOAT project which focuses on the fabrication of new catalyst for photocatalytic destruction of chemical warfare agents, the deposition of these catalysts onto textiles and the scale-up of the deposition as well as on the application of protective clothing in civilian areas (ANR-11-SECU-0003).

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