SEVENTH FRAMEWORK PROGRAMME

Research for SME Associations

Proposal full title: **Environmental friendly** and **Durable Oil and water repellence finish on Technical Textiles**
Proposal acronym: **TEX-SHIELD**
Type of funding scheme: **R**esearch for the benefit of **S**ME **A**ssociations.

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List of participants:

Participant no./ Type of participant	Participant name	Participant Short name	Country
1/SME-AG (Co-ord)	NORTH WEST TEXTILES NETWORK	NWTEX	UK
2/SME-AG	ASSOCIATION UP-TEX	Up-Tex	France
3/SME-AG	UNITEX	Unitex	Belgium
4/SME-AG	ASSOCIATION TECHTERA	Techtera	France
5/OTHER	PANAZ LIMITED	PAN	UK
6/OTHER	EVA COMMERCE LTD	EVA	Bulgaria
7/OTHER	DECCA	DECCA	Belgium
8/OTHER	SAMPAS NANOTEKNOLOJI ARAS. GEL. Paz. Tic. Ltd. Sti.	SNano	Turkey
9/OTHER	CTF 2000 n.v	CTF	Belgium
10/RTDP	TWI Limited	TWI	UK
11/RTDP	UNIVERSITY COLLEGE OF GHENT	UCG	Belgium
12/RTDP	INSTITUT NATIONAL DES SCIENCES APPLIQUEES DE LYON	INSA-LYON	France

Context and Objectives

In the current market, the well-known brands of textiles are usually protected with a fluorocarbon based treatment to provide high durability and a stain repellent finish. The most common treatments are based on impregnation of perfluorocarbons (PFCs) into the fabrics, due to their good water repellence properties. Unfortunately, the best performing PFCs, known as C8 (due to the 8 carbon atoms in their backbone chain), also raise significant health and environmental concerns, by being very stable in the environment (bio-accumulative). Research has indicated that they are possible carcinogens and, consequently, eight carbon PFCs (PFC-C8) are currently subject to high regulatory pressure.

Various alternatives have been considered. Shorter chain materials such as those based on C6 chemistry are more rapidly degraded in the environment, but in the longer term any PFC material may have potential issues with sustainability and ecological performance. Additionally, neither the shorter chain PFCs nor the current silicone- based alternatives have been developed to a point where they deliver the necessary performance to meet the industry's durability and repellence standards. Consequently, we, the Textile industrial community, need an alternative to PFC-C8 to be developed, which is durable and equally performs. To emend the solution will require both chemical and process expertise beyond that available in our community and, consequently, we are seeking funding to employ experts in the field to develop a solution.

The main purpose of the TEX-SHIELD project is to address this by:

- Eliminating problems with C8 PFCs' by-products associated with textile treatments.
- Providing a cost-effective alternative treatment which allows textiles to be provided with durable anti- soiling/anti-staining characteristics.
- Reducing the total fluorine content in the treatment by means of new sol-gel derived additives in the form of nanoparticles or inorganic-organic hybrid networks.
- Demonstrating performance on a representative scale, with regards to key technical parameters including soil resistance, abrasion resistance, cleaning cycle resistance.
- Creating additional advantageous functions such as anti-static and anti-microbial characteristics to improve stability against mechanical, chemical impacts. Developing flexible and versatile solutions for a broad range of textile supports different in structure (woven, knitted) and basic fibres (natural, synthetic or mixtures).
- Developing a solution with a low ecological footprint, based on REACH-proof chemicals and taking in to account safety and health issues.
- Providing a full Life Cycle Analysis (including washability cycle) and assessment of techno-economic benefits, via benchmarking against current products.
- Providing the necessary technological transfer and training via SME associations to ensure awareness and take up throughout the EC.

Health issues addressed by TEX-SHIELD

The current fluoropolymer-based stain repellent treatments are known to pose significant health concerns. PFCs are either produced by electrofluorination or teleromerisation, manufacturing processes which give out unintended by- products of perfluorooctane sulphonates (PFOS) and perfluorooctanoic acid (PFOA respectively). PFOA has the molecular formula C8F1502H while PFOS is C8HF17O3S.

During service life, the PFC treatment is gradually leached from the fabric, and decomposes to PFOA and PFOS. Both PFOA and PFOS are very stable in the environment and, hence, are a significant ecological threat, as the levels reached in higher organisms (including people) can become significant.

Consequently, the U.S. Environmental Protection Agency (EPA) and some of the biggest fluoropolymer

manufacturers have cooperated in studies and have collected and shared their findings. The following results have been highlighted from this research about PFOA and PFOS:

They are very stable in the environment, so they do not readily degrade. Once they enter the human body they are eliminated very slowly. This means that they remain in the body for relatively long periods of time: the half-life in humans is about 4.5 years. They cause adverse effects in laboratory animals that have been given high doses over a long period of time.

EPA classifies PFOA as carcinogenic in animals and some developmental toxicity studies in rats resulted also in death1. In terms of regulation in Europe, the Environment Agency Wales in the UK assessed the risks to health and the environment from PFOS2. PFOS shown to cause death in both rats and monkeys at doses of 6 and 4.5 mg/Kg per day respectively in repeat dose 90 days toxicity studies. Health concerns coming from the use of PFOS and PFOA chemicals have found significant interest also among different countries of the European Union such as Denmark, Germany, Spain and Italy.

To date, significant adverse effects have not been found in the general human population. However, perfluorooctane sulphonates have been recognised to be bio-persistent, bio-accumulative and toxic, which has led to restrictions being adopted in the market in regards to the use of PFOS in the UK. Studies have been carried out in order to assess the health hazards of the workers within the eight major fluoropolymer manufacturers (eg 3M, Dupoint, Arkema). High levels of fluorochemicals like PFOA appear to be a risk factor for cancers of the male reproductive system. Furthermore, medical studies recorded significant increases in the thyroid-stimulating hormone (TSH) with consequent altered thyroid response in workers with higher PFOA blood levels. Studies have also shown that PFOA alters reproductive hormones in the male, causing increased levels of oestrogen and abnormal testosterone regulation. PFOA has also long been known to damage the immune system and in the most recent study scientists learned that exposures to PFOA early in life are more harmful than in adulthood. In summary, toxicological studies have demonstrated a range of adverse health effects due to PFOS and PFOA, these effects include hepatotoxicity, developmental toxicity, immunotoxicity, hormonal effects and carcinogenicity.

3. Approach to market

The SME Associations within this project wish to ensure that the solution to the problem described above is made available for exploitation to their members. The approaches identified by the RTDs in delivering the necessary performance attributes (foreground), will be owned exclusively by the SME Associations. This will be used to ensure that, following the project, the approach will be licensed to their interested members for exploitation. Neither the RTD nor the SME partners in the project will receive any property rights from this project. To emend the problem we are likely to require the manufacture of a nanomaterial solution, derived by a sol-gel approach, this will fall outside the expertise of the members of SME associations in the field of textiles. It is, therefore, anticipated that IP rights will be used by the SME associations to establish a supply infrastructure that makes available the active multifunctional materials that can then be accessed by the SME end-users.

As SME Associations (NWTEX, Up-Tex, UNITEX, Techtera), we will direct the research activities, validate the results of the project by field trials at the demonstrators and disseminate the final project results to our members. The SME textile printing/dyeing participants in this project will provide the technical requirements and contribute to the research and demonstration activities. They will benefit from the results through advanced knowledge of the available solutions and consequent early implementation. SNano is an SME in the field of nanomaterials, who will ensure the manufacturability of the solution and benefit by exploiting the knowledge gained in advanced sol-gel systems. The delivery of the necessary high durability stain-repellent performance to match that currently available on the market requires overcoming a number of technical challenges. The first significant challenge is the identification and

development of a suitable molecular structure which incorporates both low surface energy properties (hydrophobic/oleophobic) and suitable binding groups to facilitate chemical bonding to the fibre surface to promote durability. Whilst it is desirable that the former property should be achieved without the use of fluorination, it is expected that a significant reduction in fluorine content both by amount of fluorinated agent and by the fluorine content of the agent will provide an expedient intermediate route to the ultimate elimination of fluorine. Alternatives to be explored will be hydrocarbon chains that contain a small number of carbon atoms in their backbone such as C2 and C4. The low surface energy aspect can therefore be provided by short chain PFCs or hydrocarbons that are long or short chain. The actual performance will be dictated in detail by the selection. Binding these low energy groups to the textile can be achieved by the use of suitable cross-linking agents that are widely known. These include amine, epoxy and isocyanate groups.

The second challenge for the development of the treatment will be to incorporate these cross-linking groups with the low energy groups to form a nanoscale building block prior to application on the textile. The development of such building blocks is the central aim of sol-gel technology, which chemically manipulates functional silanes to produce the required nanostructure.

The third challenge to be faced is the impregnation/deposition technique, in order to produce a suitable layer on the surface of the fabric without excessive loading which could alter the 'feel' of the material, with regard to weight or stiffness. It is also desirable to use the minimum loading possible for cost and environmental reasons. It is expected that a spray, print or immersion process will be required, with varying parameters of loading, dispersion and curing in order to optimise against the above properties. The development of the above materials and corresponding deposition process requires detailed characterisation and analysis based on in-depth understanding in the field. This is a significant technical challenge, since these materials are structurally complex. One particular advantage of the PFC-C8 treatments over its current alternatives is that they result in a very thin film covering each filament and fibre in the textile. This thin film has little effect on the stiffness or feel of the textile, but a significant impact on the functional characteristics.

Even though the SME Associations and the SME members of this consortium are experts in the field of fabrics, we lack the R&D expertise to overcome the technical barriers. Our survey of expertise available has convinced us that there is no single Research provider with a sufficiently broad range of technological knowledge of both chemical formulation and textile finishing. Consequently, we have recruited 3 RTD performers with the necessary skills to deliver this project: TWI, Insa-Lyon and the University College of Ghent.