



# PROJECT DELIVERABLE REPORT

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## TEX-SHIELD

Environmentally friendly and Durable Oil and Water Repellency Finish on Technical Textiles

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### D5.3 Life cycle analysis and techno-economic assessment

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# 1 Introduction

Water, oil and soil repellence are desirable characteristics for fabrics in many market segments and the textile industry has developed a variety of finishes which impart such properties.

Perfluorinated polymers (fluoropolymers) are known for their excellent water, oil and soil (wet or dry dirt) repellent properties and are the basis of the dominant technology used to apply a functional finish on textiles, particularly for waterproof clothing. Perfluorinated polymers are based on perfluorocarbons (PFCs) which have eight carbon atoms – frequently referred to as C8 chemistry. These perfluorocarbon units are side chains along an acrylic or urethane polymer backbone.

However, C8 based polymers have significant health and environmental concerns because they are possible carcinogens, stable in the environment and bioaccumulative. The level of concern is such that perfluorinated chemistry is now subject to legislation and is no longer manufactured in Europe or the US.

Replacement of C8 chemistry is therefore topical, and for the textile industry critical. The aim of the TEX-SHIELD project is to examine candidate approaches to the replacement of C8 chemistry.

In Work Packages 1-4, three coating routes were developed:

1. Fluorinated C6 based polymer coating – developed by UCG, products with C6 chemistry are of lower health risk, and are more rapidly degraded in the environment than polymers based on the C8 PFCs. This product is the closest to commercialisation.
2. Polysiloxane – developed by INSA-LYON, this product has a shorter PFC chain and lower fluorine content than C8 PFC polymers, but is at an earlier development stage than the UCG product.
3. Fluorine-free nano-silica – developed by TWI, this product will degrade the quickest, but has the lowest technology readiness level.

In Work Package 5, the aim was to develop a coating route to pilot scale production, and to evaluate the health, safety and environmental risks in more detail. The upscaling activity for the pilot scale production will be demonstrated in D5.1, and the risk assessment for health, safety and environment will be given in D5.2. In this deliverable, we give the results of the life cycle analysis and techno-economic assessment.

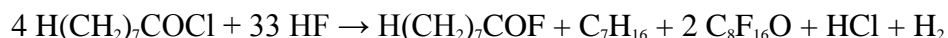
## 2 Objectives

- Evaluate the environmental impacts of producing each of the three coatings, including energy and water usage.
- Determine the techno-economic benefit of the non-fluorinated silicone coating, and establish whether it is commercially viable.

## 3 Background

### 3.1 C8 process route

C8 (Perfluorooctanoic acid) is mainly produced by electrochemical fluorination of octanoyl chloride with hydrofluoric acid:



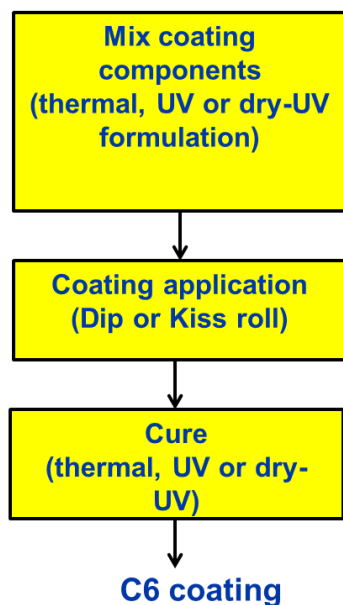
This reaction produces multiple by-products and is only 15% efficient.

Octanoyl chloride is produced from the reaction of octanoic acid with thionyl chloride. Octanoic acid can be produced from palm oil, in which it occurs as a minor component. Thionyl chloride is prepared from sulfur dioxide and chlorine. HF is made commercially from sodium fluoride and sulfuric acid.

C8 is known for its long term stability and carcinogenic properties and the global warming characteristics have received less attention. For the purposes of this analysis, C8 is assumed to be analogous to PTFE, which has an environmental impact of 7.5kg CO<sub>2</sub> per kg.<sup>1</sup>

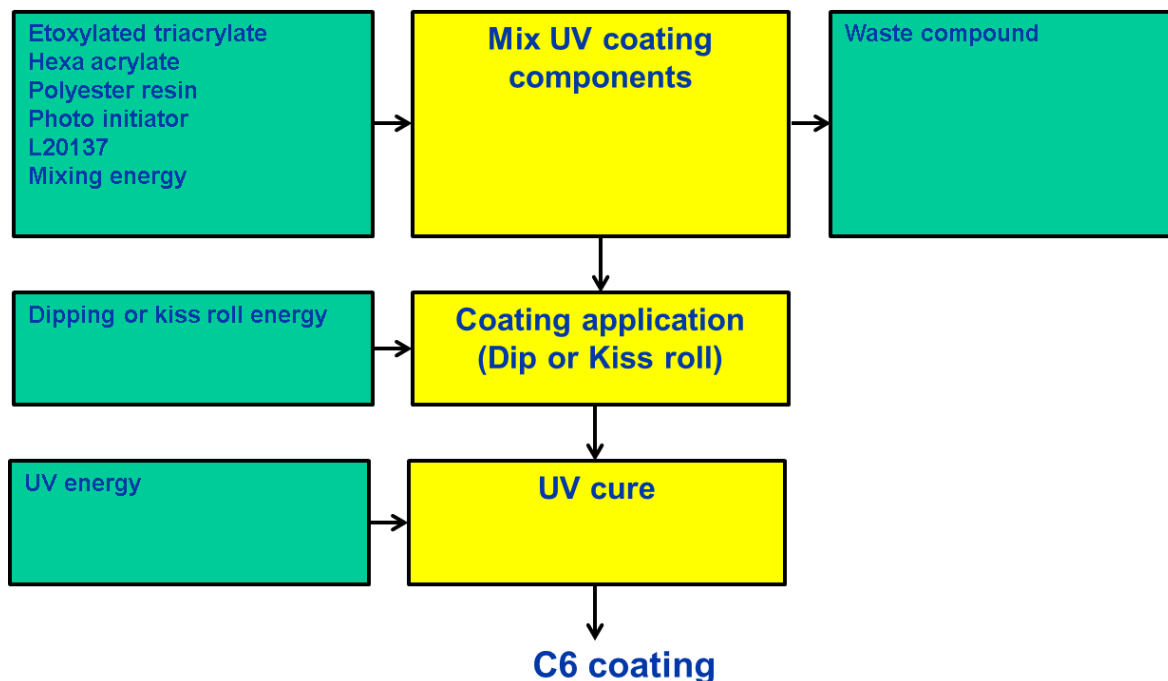
### 3.2 C6 process route

UCG has developed a range of coatings for the project, requiring either thermal cure, UV cure, or a drying process followed by a UV cure (Figure 1). Each system has a different formulation, but all can be coated either by dip or kiss rolling. For the purposes of this analysis, only the UV cure system was considered, using a dip rolling method of applying the coating.



**Figure 1** An overview of the C6 coating routes developed.

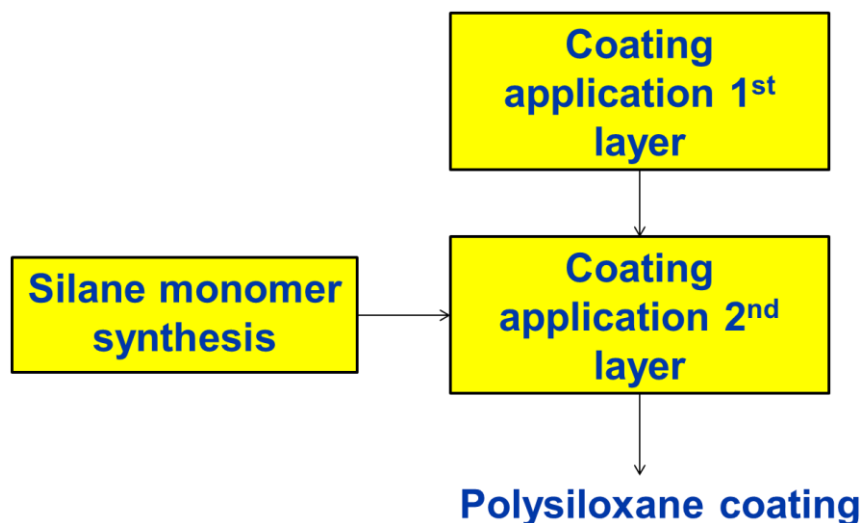
Figure 2 shows a breakdown of the UV curing steps, with the basic coating components, and energy and material inputs and outputs. The main coating components by mass are the ethoxylated triacrylate and the Hexa functional acrylate. The main electricity input is at the UV curing stage.



**Figure 2** Breakdown of the main processing steps, materials and energy flows to produce an ethoxylated C6 coating using the UV cure method.

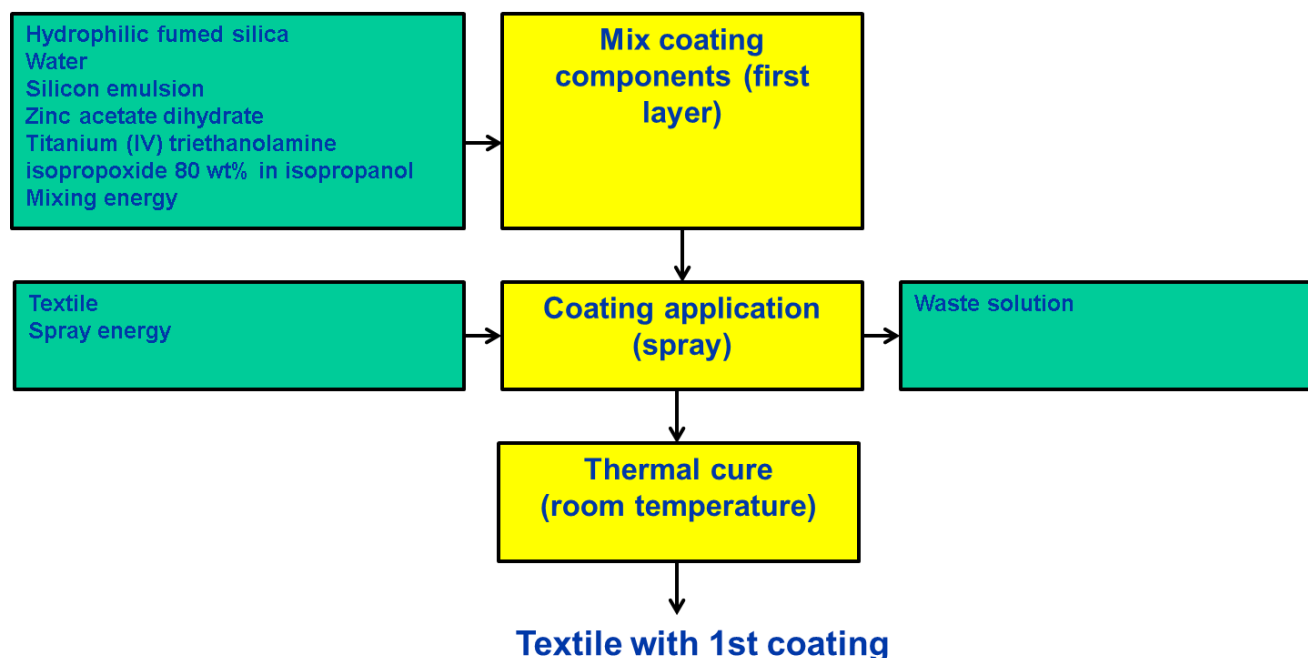
### 3.3 Polysiloxane

The polysiloxane route is a two layer coating process (Figure 3). The first coating provides a link to the textile, and a preliminary repellancy. The second coating provides an improved repellancy using chemical and surface roughness characteristics.



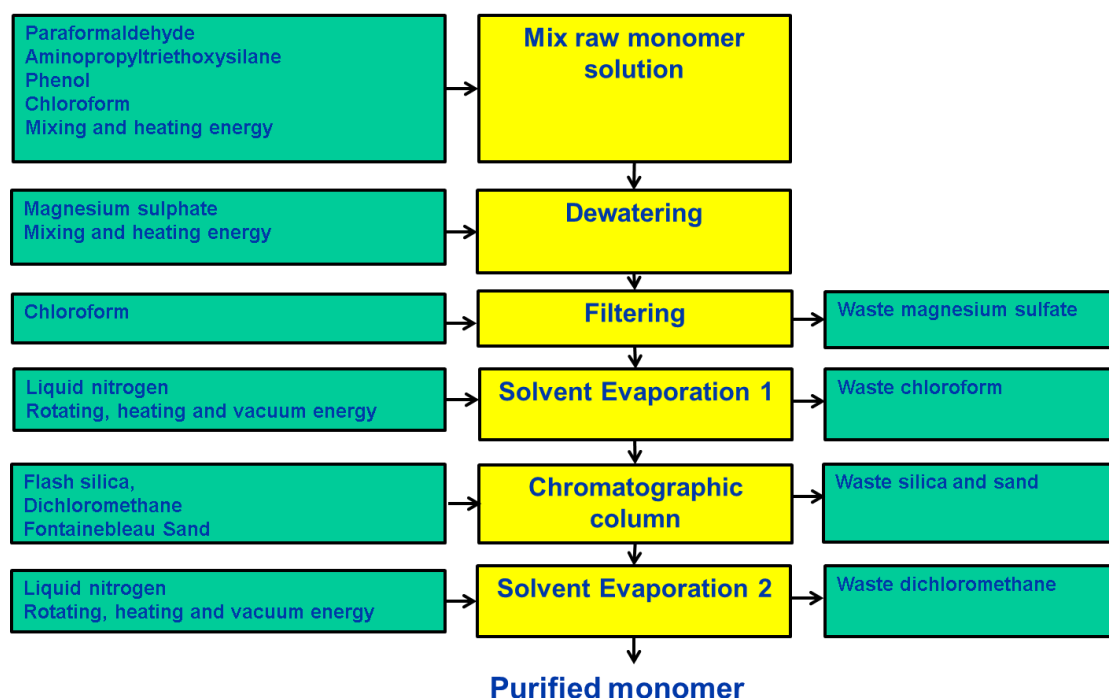
**Figure 3** Overview of the fluorinated silicone route.

Figure 4 shows a breakdown of the main processing steps, materials and energy flows of the first layer coating process. The coating is applied using a spraying process, and then thermally cured.

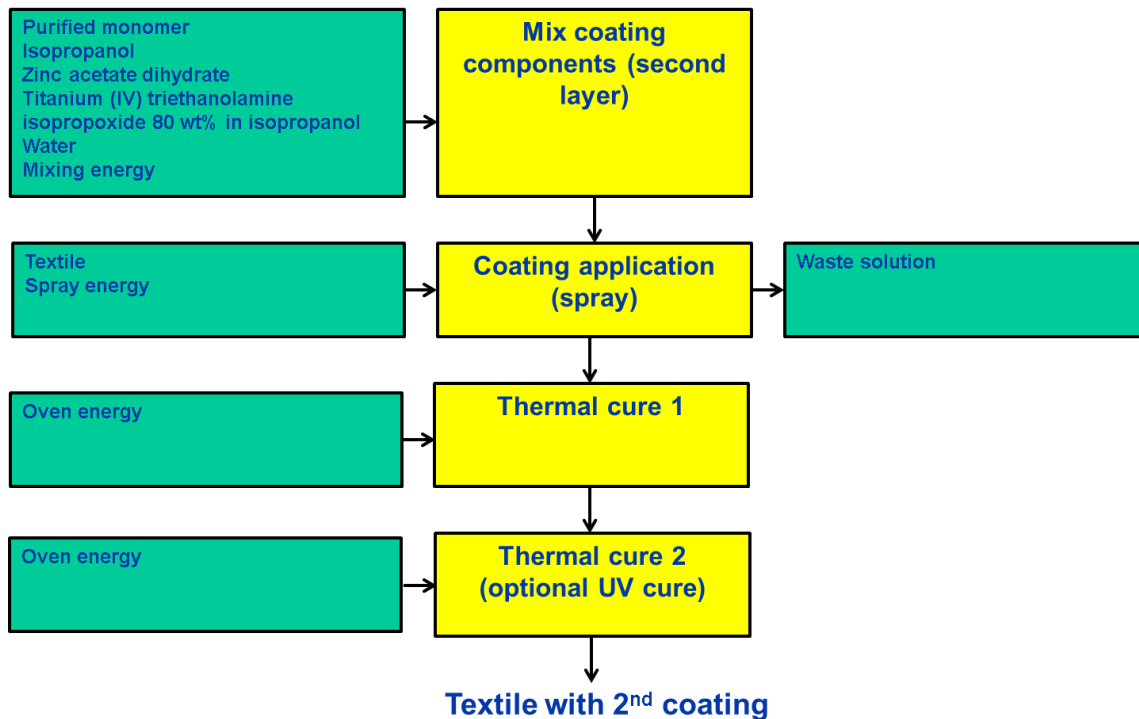


**Figure 4** Breakdown of the main processing steps, materials and energy flows for the first layer of the coating using the polysiloxane emulsion coating.

Figure 5 shows a breakdown of the main processing steps, materials and energy flows for the synthesis of the INSA Lyon monomer, and Figure 6 shows how this monomer is then incorporated into the second coating.



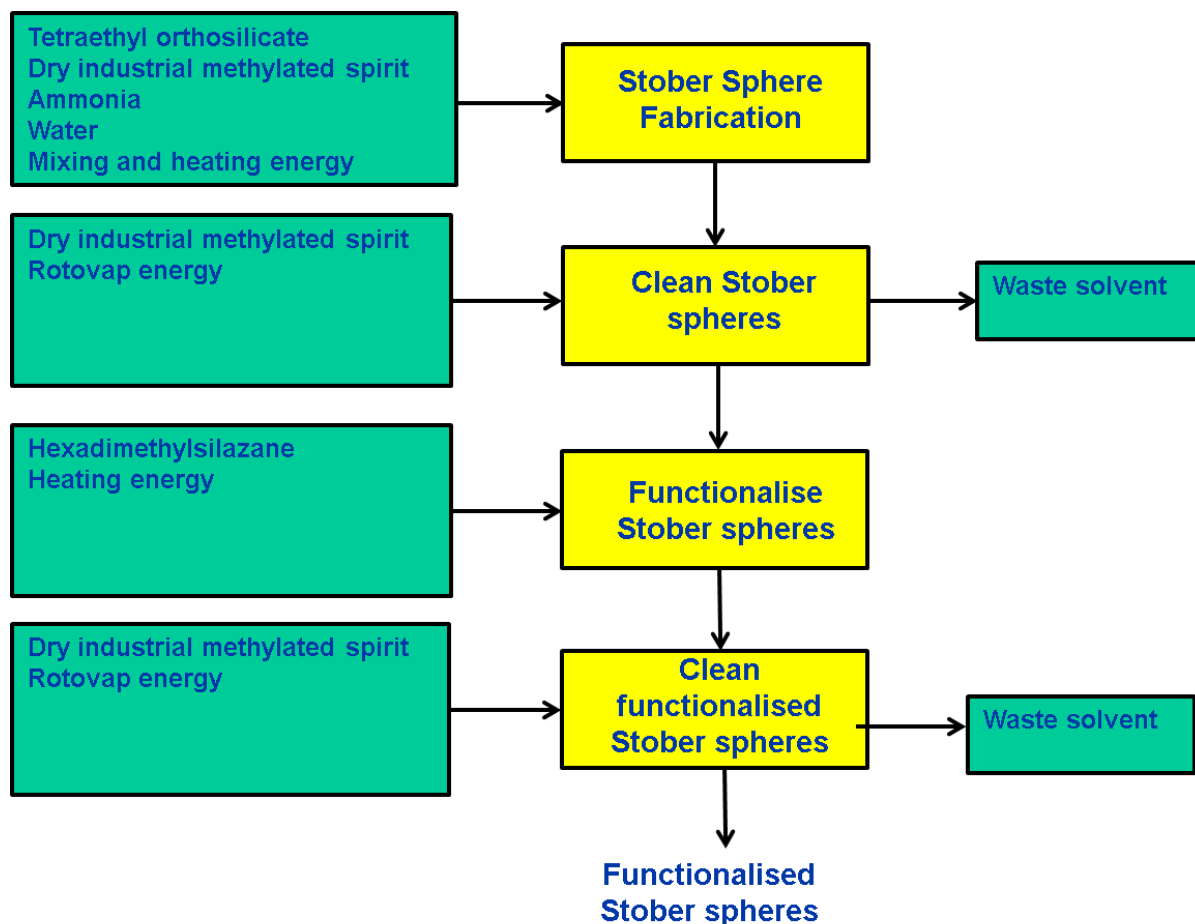
**Figure 5** Breakdown of the main processing steps, materials and energy flows for the synthesis of the purified monomer (polysiloxane coating).



**Figure 6** Breakdown of the main processing steps, materials and energy flows for the second layer of the coating (polysiloxane coating).

### 3.4 Fluorine-free nano-silica

Figure 7 shows a breakdown of the main processing steps, materials and energy flows for the fluorine-free nano-silica. At the time of writing, the process for applying the coating and curing the coating had not been finalised. As an initial approximation, it can be assumed that it would go through dipping and curing steps as per the UCG coating (Figure 2).



**Figure 7** Breakdown of the main processing steps, materials and energy flows for the non-fluorinated functionalised silica particles route.

## 4 Approach

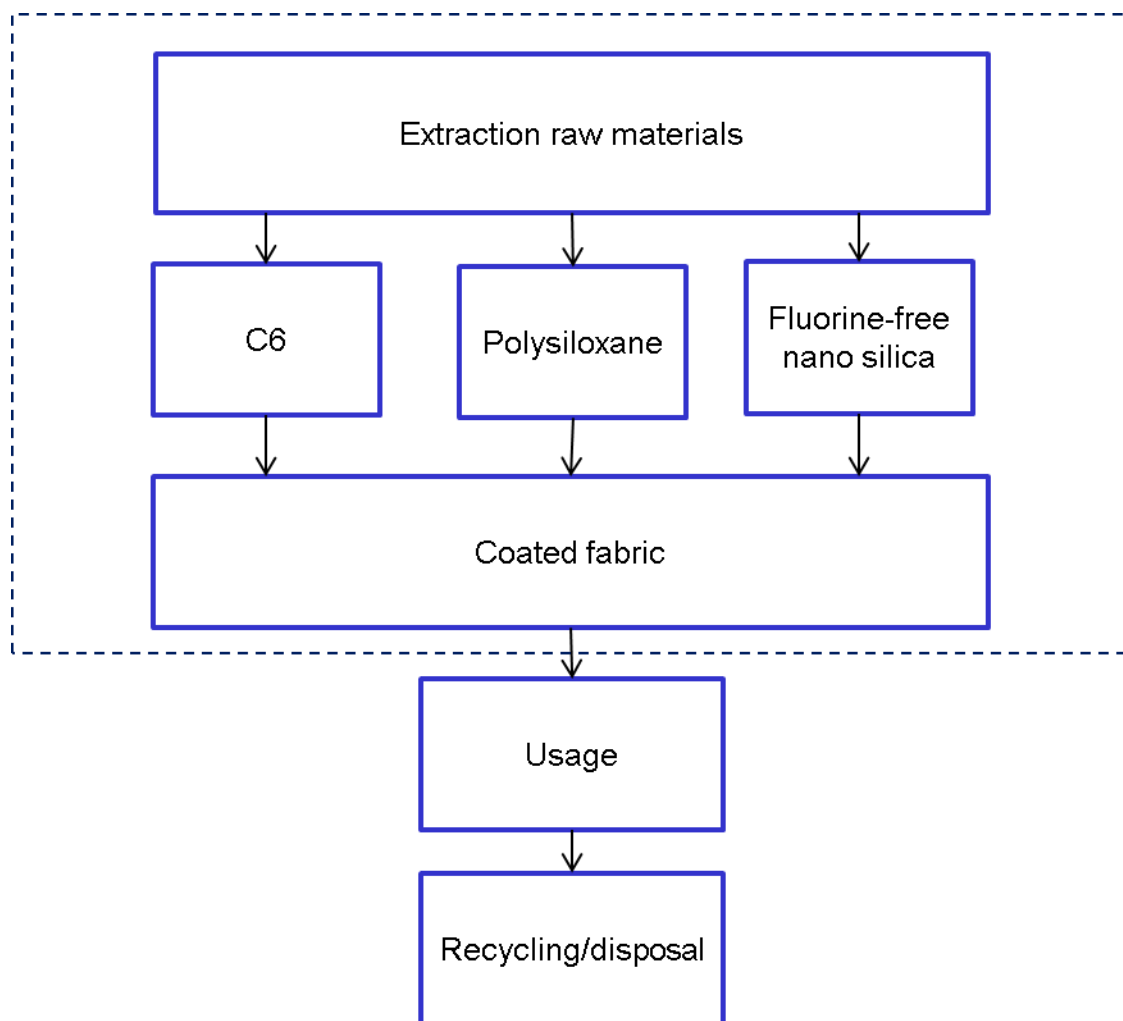
### 4.1 Goal of the study

The goal of the study was to evaluate the environmental impacts of the three TEX-SHIELD coatings and compare them to the C8 coating solution. The relative costs and technical benefits of the coatings were considered in parallel, to give both an environmental and technoeconomic evaluation.

### 4.2 Scope

Figure 8 shows the scope of the TEX-SHIELD LCA. The coatings were evaluated from the point of extraction of raw materials, through coatings production, usage and recycling. The main focus was on the coatings production, where primary laboratory data was available.





**Figure 8** Scope of the TEX-SHIELD LCA.

### 4.3 Model and assumptions

Quantities of materials and energy for coating production were based on laboratory scale data, determined by the research partner leading the development of the coating. Whilst this is primary data, it is likely to represent the worst case in environmental impact. Where a chemical was purchased, the GaBi database was used as the first source, and then if unavailable, a literature review was carried out.

#### 4.3.1 Data analysis

Analysis was carried out using GaBi software, with a software database containing literature sources between 2010 and 2012. Environmental impact was assessed in terms of GWP for 100 years and given in units of kg of carbon dioxide equivalents (kgCO<sub>2</sub>e).

#### 4.3.2 C6 coating

Table 1 shows a list of chemicals and assumptions used. The L20137 is a fluorinated polymer, and was approximated to PTFE for this analysis, with a carbon contribution of 7.5kg CO<sub>2</sub> per kg<sup>1</sup>. Unfortunately it was not possible to obtain suitable data to model the photoinitiator within the timescales of this project. However the amount of it is very small, so it is unlikely that it would have a large impact.

Electricity values were all based on laboratory data, and particularly for the UV system it was felt that there could have been optimisation on a commercial scale.

**Table 1** Chemicals and associated assumptions for the C6 coating

Item	Assumption
Ethoxylated triacrylate	Approximated to PMMA, used GaBi dataset.
Hexa acrylate	Approximated to PMMA, used GaBi dataset.
Polyester resin	Used GaBi dataset.
Photo initiator irg 500	Data unavailable.
L20137	Approximated to PTFE.
Electricity	All electricity values based on laboratory equipment. Used GaBi dataset EU-27 electricity grid mix.

### 4.3.3 Polysiloxane coating

Table 2 shows a list of materials and assumptions used for the polysiloxane coating.

Siloxanes and silanes are produced originally from silicon, following by various chemical processing steps to produce the desired chemical structure. Brandt et al, have analysed the production of poly dimethyl silane (PDMS or silicon oil) and show the precursor steps to include the manufacture of methyl siloxanes and methyl chlorosilanes.<sup>2</sup> Silicone oil has been used in this analysis as an estimate for silicone and methyl silane. Although not illustrated specifically by Brandt et al's analysis, methyl silane would be produced at the early synthesis stages, and so the estimate would be conservative.

Aminopropyltriethoxysilane would be produced by a different route, although it would share silicon as the primary raw material. For this analysis it has been approximated to silicone oil (1 part) + ethanol (3 parts) + ethylamine (1 part).

Hydrophillic silica, flash silica was approximated to sand and Fontainebleau sand were all approximated to silica sand, which is available in the GaBi database.

Zinc acetate dihydrate was approximated to 50% zinc and 50% acetic acid by weight.

Titanium (IV) triethanolamine isopropoxide 80wt% in isopropanol was approximated to isopropanol (3 parts), ethylamine (3 parts), and TiO<sub>2</sub> (1 parts). Propanol and ethylamine were available from the GaBi database, but TiO<sub>2</sub> was approximated to the literature value of 9 kgCO<sub>2</sub>e/kg.<sup>3</sup>

Chloroform and dichloromethane cooling water are considered from a laboratory perspective, where no recycling was possible.

**Table 2** Chemicals and associated assumptions made for the polysiloxane

Item	Assumption
Silicone emulsion	Approximated to silicone oil, 6.31kgCO <sub>2</sub> e/kg, based on estimation of Brandt et al (2012).
Water	Approximated to desalinated, deionised water, using GaBi dataset.
Zinc acetate dihydrate	Approximated to 50% zinc, 50% acetic acid by weight. Used GaBi datasets.
Titanium (IV) triethanolamine isopropoxide 80wt% in isopropanol	Approximated to isopropanol (3 parts), ethylamine (3 parts), and TiO <sub>2</sub> (1 part). GaBi datasets were used for propanol and ethylamine, and TiO <sub>2</sub> was approximated to 9 kgCO <sub>2</sub> e/kg using Middlemas et al, 2015.
Hydrophilic fumed silica	Approximated to silica sand, used GaBi dataset.
Paraformaldehyde	Approximated to formaldehyde, used GaBi dataset
Aminopropyltriethoxysilane	Approximated to silicone oil (1 part) + ethanol (3 parts) + ethylamine (1 part). GaBi datasets used for ethanol and ethylamine.
Phenol	Used GaBi dataset.
Chloroform	Approximated to dichloromethane, used GaBi dataset.
Cooling tap water	Assumed that a cooling bath was used, and no water was wasted.
Magnesium sulphate	Used GaBi dataset.
Liquid nitrogen	Used GaBi dataset.
Flash silica	Approximated to silica sand, used GaBi.
Dichloromethane	Considered at the laboratory scale.
Fontainebleau sand	Approximated to silica sand, used GaBi dataset.
Electricity	All electricity values based on laboratory equipment. Used GaBi dataset EU-27 electricity grid mix.

#### 4.3.4 Fluorine-free nano-silica

Table 3 shows a list of materials, energies and assumptions for the fluorine-free nano-silica. Tetraethyl orthosilicate and hexamethyldisilazane were approximated to silicone oil, using data from Brandt et al.<sup>2</sup> Electricities were based on laboratory scale ovens filled to maximum capacity.

**Table 3** Chemicals and associated assumptions for the fluorine-free nano-silica approach

Item	Assumption
Tetraethyl orthosilicate	Approximated to silicone oil, 6.31kgCO <sub>2</sub> e/kg, based on estimation Brandt et al (2012).
Hexamethyldisilazane	Approximated to silicone oil, 6.31kgCO <sub>2</sub> e/kg, based on estimation Brandt et al (2012).
Industrial methylated spirit	Approximated to ethanol, used GaBi dataset.
Electricity for the oven	Electricity based on laboratory oven, filled to maximum capacity. Used GaBi dataset EU-27 electricity grid mix.
Electricity for rotovap	Electricity based on laboratory rotovap. Used GaBi dataset EU-27 electricity grid mix.

### 4.3.5 GaBi datasets

Table 4 lists the GaBi datasets used in the analysis, a description of the content and the date of update. European averages were used where available, and region specific data in the rest.

**Table 4** Gabi data sets used in the analysis

Dataset	Description	Date
Silica sand	Mining and refining of silica sand. Based on German data.	2012
Zinc re-distilled zinc	Production of zinc including ore mining and beneficiation, two-stage roasting, leaching, electrolysis and re-melting. Based on German data.	2012
Isopropanol	Production of isopropanol by esterification of sulphate acid with propene and hydrogenation of the formed sulphate esters with water. Based on German data.	2012
Ethylamine	Production of ethyl amine from ethanol and ammonia. Based on German data.	2012
Acetic acid	Production of acetic acid from methanol. Based on German data.	2012
De-salinated, deionised water	Production of deionised water using ion exchange. Data represents an average for Europe.	2012
Ethanol	Production of ethanol via hydration of ethylene. Based on German data.	2012
Liquid nitrogen	Production of liquid nitrogen via cryogenic air separation. Based on German data.	2012
Dichloromethane	Production of dichloromethane via chlorination of methyl chloride. Based on German data.	2012
Magnesium sulphate	By product of potassium chloride production. Based on German data.	2012
Formaldehyde	Production of formaldehyde via the dehydrogenation of methanol. Data represents an average for Europe.	2012
Phenol	Production of Phenol from Cumene. Data represents an average for Europe.	2012
Polymethylmethacrylate (PMMA)	Production of PMMA through bulk polymerisation. Based on German data.	2012
Polyester resin	Production of polyester resin. Based on German data.	2012
EU-27 Electricity grid mix	Average electricity supply mix for Europe.	2012

## 5 Results

### 5.1 Data and inventory

Table 5 shows the masses and energies for each component for the C6 coating.

**Table 5** Masses and energies for each component of the C6 coating

		Per kg coating components		Per m <sup>2</sup> textile coated	
Processing step	Item	Amount	Unit	Amount	Unit
<b>Mixing of components</b>	Electricity magnetic stirrer	12.9	MJ/kg	0.8	MJ/m <sup>2</sup>
	Ethoxylated triacrylate	1.1	kg/kg	0.1	kg/m <sup>2</sup>
	Hexa acrylate	0.2	kg/kg	9.75E-03	kg/m <sup>2</sup>
	Polyester resin	0.1	kg/kg	3.25E-03	kg/m <sup>2</sup>
	Photo initiator irg 500	0.1	kg/kg	3.33E-03	kg/m <sup>2</sup>
	L20137	0.03	kg/kg	1.67E-03	kg/m <sup>2</sup>
<b>Dipping (Foulard)</b>	Textile			1	m <sup>2</sup>
	Electricity pneumatic pick-up			2.00E-02	MJ/m <sup>2</sup>
<b>UV cure</b>	Electricity for UV lamp			100	MJ/m <sup>2</sup>
	Electricity motor			1.85E-02	MJ/m <sup>2</sup>

Tables 6-8 show the masses and energies for each component for polysiloxane coating. Note that compressed air was used to spray coat the second coating (Table 8) and an energy value could not be estimated within the timescales of the project.

**Table 6** The masses and energies for each component on Coating Layer 1 for the polysiloxane coating

		Per kg coating components		Per m <sup>2</sup> textile coated	
Processing step	Item	Amount	Unit	Amount	Unit
<b>Mix silicone emulsion</b>	Silicone emulsion	0.04	kg/kg	8.21E-03	kg/m <sup>2</sup>
	Water	0.36	kg/kg	7.38E-02	kg/m <sup>2</sup>
	Electricity to mix silicone emulsion	0.06	MJ/kg	1.23E-02	MJ/m <sup>2</sup>
<b>Mix zinc acetate dihydrate and titanium triethanolamine</b>	Zinc acetate dihydrate	0.0775	kg/kg	1.59E-02	kg/m <sup>2</sup>
	Titanium (IV) triethanolamine isopropoxide 80wt% in isopropanol	0.1325	kg/kg	2.72E-02	kg/m <sup>2</sup>
	Water	0.2125	kg/kg	4.36E-02	kg/m <sup>2</sup>
	Electricity to mix zinc/titanium solution	0.3	MJ/kg	6.15E-02	MJ/m <sup>2</sup>
<b>Mix coating components</b>	Hydrophilic fumed silica	0.00975	kg/kg	2.00E-03	kg/m <sup>2</sup>
	Water	0.4	kg/kg	8.21E-02	kg/m <sup>2</sup>
	Electricity ultrasound probe	0.225	MJ/kg	4.62E-02	MJ/m <sup>2</sup>
	Dilute silicon emulsion	0.4	kg/kg	8.21E-02	kg/m <sup>2</sup>
	Zinc/titanium solution	0.0045	kg/kg	9.23E-04	kg/m <sup>2</sup>
<b>Coating application 1st layer</b>	Mixed coating components	1.03925	kg/kg	2.13E-01	kg/m <sup>2</sup>
	Electricity for spraying	0.25	MJ/kg	5.13E-02	MJ/m <sup>2</sup>
		0.835	MJ/kg	1.71E-01	MJ/m <sup>2</sup>

**Table 7** The masses and energies for each component in the synthesis of the monomer, for the polysiloxane coating

Processing step	Item	Per kg of monomer produced		Per m <sup>2</sup> fabric	
		Amount	Unit	Amount	Unit
<b>Mix raw monomer solution</b>	Electricity for mixing	40	MJ/kg	4.12E-02	MJ/m <sup>2</sup>
	Electricity for heating	4000	MJ/kg	4	MJ/m <sup>2</sup>
	Paraformaldehyde	0.37	kg/kg	3.78E-04	kg/m <sup>2</sup>
	Aminopropyltriethoxysilane	1.23	kg/kg	1.27E-03	kg/m <sup>2</sup>
	Phenol	0.57	kg/kg	5.89E-04	kg/m <sup>2</sup>
	Chloroform	7.45	kg/kg	7.67E-03	kg/m <sup>2</sup>
<b>De-watering</b>	Electricity for mixing	1	MJ/kg	1.03E-03	MJ/m <sup>2</sup>
	Raw monomer solution	9.62	kg/kg	9.91E-03	kg/m <sup>2</sup>
	Magnesium sulphate	0.23	kg/kg	2.40E-04	kg/m <sup>2</sup>
<b>Filtering</b>	De-watered solution	9.63	kg/kg	9.92E-03	kg/m <sup>2</sup>
	Chloroform	20.69	kg/kg	2.13E-02	kg/m <sup>2</sup>
<b>Solvent Evaporation 1</b>	Filtered solution	30.09	kg/kg	3.10E-02	kg/m <sup>2</sup>
	Liquid nitrogen	112.22	kg/kg	1.16E-01	kg/m <sup>2</sup>
	Electricity for rotating	80	MJ/kg	8.24E-02	MJ/m <sup>2</sup>
	Electricity for heating	1320	MJ/kg	1	MJ/m <sup>2</sup>
	Electricity for vacuum	160	MJ/kg	1.65E-01	MJ/m <sup>2</sup>
<b>Chromatographic column</b>	Evaporated product	1.95	kg/kg	2.01E-03	kg/m <sup>2</sup>
	Flash silica	97.22	kg/kg	1.00E-01	kg/m <sup>2</sup>
	Dichloromethane	3694.44	kg/kg	4	kg/m <sup>2</sup>
	Fontainebleau sand	8.33	kg/kg	8.58E-03	kg/m <sup>2</sup>
<b>Solvent Evaporation 2</b>	Chrom. product	3696.39	kg/kg	4	kg/m <sup>2</sup>
	Liquid nitrogen	112.22	kg/kg	1.16E-01	kg/m <sup>2</sup>
	Electricity for rotating	480	MJ/kg	4.94E-01	MJ/m <sup>2</sup>
	Electricity heating energy	7920	MJ/kg	8	MJ/m <sup>2</sup>
	Electricity for vacuum	960	MJ/kg	1	MJ/m <sup>2</sup>
	Total energy	14961	MJ/kg	15	MJ/m <sup>2</sup>

**Table 8** The masses and energies for each component in Coating Layer 2 for the polysiloxane coating

		Per kg Coating Layer 2		Per m <sup>2</sup> textile coated	
Processing step	Item	Amount	Unit	Amount	Unit
<b>Mix zinc acetate dihydrate and titanium triethanolamine</b>	Zinc acetate dihydrate	0.10	kg/kg	1.59E-02	kg/m <sup>2</sup>
	Titanium (IV) triethanolamine isopropoxide 80wt% in isopropanol	0.17	kg/kg	2.72E-02	kg/m <sup>2</sup>
	Water	0.27	kg/kg	4.36E-02	kg/m <sup>2</sup>
	Electricity to mix zinc/titanium solution	0.38	MJ	6.15E-02	MJ/m <sup>2</sup>
<b>Mix coating components (second layer)</b>	Purified monomer	0.01	kg/kg	1.03E-03	kg/m <sup>2</sup>
	Isopropanol	0.49	kg/kg	8.06E-02	kg/m <sup>2</sup>
	Zinc/titanium solution	0.01	kg/kg	9.23E-04	kg/m <sup>2</sup>
	Electricity to mix coating components (second layer)	0.04	MJ/kg	6.15E-03	MJ/m <sup>2</sup>
<b>Spray coating</b>	Mixed coating components (second layer)	1.03	kg/kg	1.68E-01	kg/m <sup>2</sup>
	Electricity 3 (Compressed air)	0.00	MJ/kg	0.00E+00	MJ/m <sup>2</sup>
	Textile coated with first layer	6.1	m <sup>2</sup> /kg	1.00E+00	kg/m <sup>2</sup>
	Water for cleaning	31.3	kg/kg	5.13E+00	kg/m <sup>2</sup>
	Isopropanol for cleaning	12.3	kg/kg	2.02E+00	kg/m <sup>2</sup>
<b>Thermal cure 1</b>	Textile coated with second layer	6.1	m <sup>2</sup> /kg	1.00E+00	m <sup>2</sup> /m <sup>2</sup>
	Electricity for curing step 1	4725	MJ/kg	775	MJ/m <sup>2</sup>
<b>Thermal cure 2</b>	Fabric cured from step 1	6.1	m <sup>2</sup> /kg	1.00E+00	kg/m <sup>2</sup>
	Electricity for curing step 2	1575	MJ/kg	258	MJ/m <sup>2</sup>
	Used to coat 0.195 m <sup>2</sup> of textile	6300.41	MJ/kg	1.03E+03	MJ/m <sup>2</sup>



Table 9 lists the masses and energies for each component in the fluorine-free nano-silica coating.

**Table 9** The masses and energies for each component in the fluorine-free nano-silica coating

		Per kg of HMDS-TSS4 solution produced		Per m <sup>2</sup> of TWI textile	
Processing step	Item	Amount	Unit	Amount	Unit
<b>Stober sphere fabrication</b>	Electricity for oven	1.3	MJ/kg	1.35E-02	MJ/m <sup>2</sup>
	TEOS	0.1	kg/kg	1.22E-03	kg/m <sup>2</sup>
	Dry industrial methylated spirit	0.7	kg/kg	7.25E-03	kg/m <sup>2</sup>
	25% ammonia	0.0174	kg/kg	1.74E-04	kg/m <sup>2</sup>
	Distilled water	0.02	kg/kg	2.17E-04	kg/m <sup>2</sup>
<b>Clean stober spheres 1</b>	Electricity for Rotovap	0.664	MJ/kg	6.64E-03	MJ/m <sup>2</sup>
	TSS4 solution	0.886	kg/kg	8.86E-03	kg/m <sup>2</sup>
	Dry industrial methylated spirit	1.063	kg/kg	1.06E-02	kg/m <sup>2</sup>
<b>Functionalise stober spheres</b>	Electricity for oven	2.746	MJ/kg	2.75E-02	MJ/m <sup>2</sup>
	Cleaned TSS4 solution	0.886	kg/kg	8.86E-03	kg/m <sup>2</sup>
	Hexamethyldisilazane (HMDS)	0.114	kg/kg	1.14E-03	kg/m <sup>2</sup>
<b>Clean stober spheres 2</b>	Electricity for Rotovap energy	0.8	MJ/kg	7.50E-03	MJ/m <sup>2</sup>
	HMDS-TSS4 solution	1.0	kg/kg	1.00E-02	kg/m <sup>2</sup>
	Dry IMS	1.2	kg/kg	1.20E-02	kg/m <sup>2</sup>

## 5.2 Environmental impact

Table 10 shows a breakdown of the total environmental impact for each coating in units of CO<sub>2</sub>e per m<sup>2</sup>. The environmental impact of the fluorine-free nano-silica coating is 0.17 kgCO<sub>2</sub>/m<sup>2</sup> based on the coating components only. However if the C6 and polysiloxane processes are broken down (Tables 10A and B), the curing stage is seen to have the largest environmental impact. Hence this stage should be evaluated if the coating processes were going to be compared.

**Table 10** Comparable breakdown of then environmental impacts of the C6 and polysiloxane materials

Stage	kgCO <sub>2</sub> e/m <sup>2</sup>
C6	14
Polysiloxane	150

**Table 10A** Breakdown of the environmental impacts of curing the second coating for the UCG coating

Stage	kgCO <sub>2</sub> e/m <sup>2</sup>
UV cure	13.2

**Table 10B** Breakdown of the environmental impacts of curing the second coating for the polysiloxane coating.

Stage	kgCO <sub>2</sub> e/m <sup>2</sup>
Curing Layer 1	102
Curing Layer 2	34

The environmental impact of the TEX-SHIELD coatings are largely governed by the curing process. It is often possible to reduce the environmental impact of thermal treatments during scale up to the manufacturing stage. For instance, by packing more effectively in a furnace, increasing insulation, or by using a high energy efficient oven.

Alternative methods of curing can also be used to reduce the environmental impact. For instance whilst a typical thermal cure might be 5 minutes at 150°C, UV initiated systems can be developed that enable cure in under a minute offering the ability to increase material throughput. Additionally, traditional UV light sources (such as used in this project) use mercury bulbs to provide the UV radiation. The trend within the radiation cure industry is to move to the far more energy efficient LED light sources. These can be tuned to specific emission wavelengths and reduce the amount of energy required to achieve cure initiation. For instance a typical mercury system would give a broad spectral output that would have a total energy output in the order of 2-3 kW/m<sup>2</sup>. An LED, tuned to emit at the precise wavelength required to cause initiation could have energy outputs as low as 1.5 mW/m<sup>2</sup>.

The CO<sub>2</sub> values reported for the experimental systems are 14 kg CO<sub>2</sub> / m<sup>2</sup> for the C6 and 150 kg CO<sub>2</sub> / m<sup>2</sup> for the polysiloxane, which are mainly a result of the laboratory scale curing systems and processes employed. Although not for a textile application, Tianjin and RMIT Universities determined that a ptfe coating, over an area of 140m<sup>2</sup>, would contribute 473 kg CO<sub>2</sub> in a commercial process.<sup>4</sup> This is equivalent to 3.37 kg CO<sub>2</sub> / m<sup>2</sup>. Whilst this is a slightly less than the C6 PFC and much less than the polysiloxane values quoted above, these experimental materials have been prepared using small scale laboratory instrumentation that will not have the same level of efficiency as those used on the industrial scale. Consequently, it is recommended that the values for the experimental systems should be reassessed when they are prepared and run at the pilot scale and again at the production scale.

### 5.3 Usage

Textiles in applications such as personal protection, sportswear and furniture, for example, use the properties of fluorocarbons to provide water and stain repellency required of such demanding applications. The fluorocarbons traditionally used are based on an eight-carbon chain and are often referred to as PFOS or PFOA (perfluorooctane sulfonic acid or perfluorooctanoic acid). As previously discussed, such materials are harmful and accumulate in the environment and are subsequently being phased out of use through Environmental Protection Agency restrictions on usage rules. All of the TEX-SHIELD coatings developed offer reductions in the fluorine content compared to C8 perfluorocarbons.

The coatings developed have been designed to comply with existing processes used within the textile industry. They are waterborne materials that can be applied using many of the standard application processes and, with the exception of the UV cure systems, be cured using existing thermal processes and profiles.

The C6 and polysiloxane materials would be applied at typical coating levels. The nano-silica option, has the potential to have a lower cured mass per unit area of the textile since the individual particles would be chemically bound to the surface of the textile fibres rather than surrounded by an additional matrix. If the nanoparticles became dislodged this could present safety concerns. This is considered and discussed in Deliverable 5.2.

### 5.4 Recycling

In the UK 13% of textiles are recycled, 13% are incinerated and 74% go to landfill.<sup>5</sup> Textiles are typically recycled in one of a two ways. Some are cut and reused as rags or are reused in developing countries. Synthetic thermoplastic fabrics may be reprocessed through melting of the materials with other waste of the same polymer type. Products containing mixtures or dissimilar materials that are to be reprocessed in this way need to be separated first. This may be achieved by solvent processing for example. It is also possible to recover fibres for reprocessing into yarn.

In the case of the TEX-SHIELD coated fabric, two recycling scenarios may be envisaged. One in which the whole fabric is reprocessed in solvents to separate all the useful polymers. These could be reused as if in virgin form. The second in which the fabric is shredded and reformed into a less valuable product which does not require (and also does not suffer if provided with) the hydrophobic properties.

### 5.5 Techno-economic evaluation

Of the coatings described the C6 chemistry approach closely mimics the chemistry of the C8 perfluorocarbons, but without the associated environmental hazards. Since the chemistry is similar the material can be handled and processed in the same way. Subsequently, it is expected that such materials can be implemented into existing production processes with minimal changes to process or equipment.

The polysiloxane could also be used in the same application and curing processes as the incumbent C8 materials. However, due to the low surface tension of such polysiloxanes it may be that some small process changes would be required to enable the coating to be applied by e.g. kiss roll. The rollers on such a coater would have to be rubber coated, as opposed to steel, to enable consistent coating of the product to the textile surface. This material would be suitable for textile applications where water repellency is of concern but oil repellency is not.

Within the textile industry curing of coatings is mainly by a thermal process. The use of UV to achieve cure is not wide spread. This means that implementation of a UV cure systems requires an investment in the cure equipment. Although LED UV cure offers the potential for lower energy consumption and faster throughput, the required capital investment prohibits the uptake of such materials unless the technological

benefits offer a significant advantage. It is believed that the UV cure systems will have niche applications, with thermal cure being the most common.

Whilst repellency has been demonstrated, the nano-silica approach is still at a low technology readiness level and requires continued development before it could be considered for implementation into the textile market.

## 6 Conclusions

The coatings that have been developed and evaluated through this programme were intended to replace the incumbent materials but designed in such a way that the environment would be more tolerant toward them. To achieve this three approaches were followed:

- 1 Fluorocarbons with carbon chains smaller than eight.
- 2 A polysiloxane loaded with silica nanoparticles.
- 3 A completely fluorine-free nano-silica functionalised to provide repellency whilst binding to textile fibre surfaces.

Of these, Approach 1 can be considered as being closest to market as it was exploring the use of commercially available materials, such as C6 PFC. However as was established during this project that these shorter chained PFCs do not give comparable performance to the C8 PFCs. This implies that either the applications will have to accept a reduction in properties or the coatings will have to be boosted in some manner. This approach does offer a reduction in the perfluorocarbon content on a sheet of fabric and reduces the environmental impact. The approach of a direct replacement of C8 by C6 perfluorocarbons also would fit with existing processes currently used in the textile industry. This means that energy and waste expenditure would be similar to current systems but with a reduction in the environmental impact caused by the C8 fluorocarbons.

The second approach again uses commercially available materials although the specific materials are not currently used within the textile industry. These were siloxane monomers and silica nanoparticles that when combined were able to be applied and cured onto textile. These materials are fluorine-free and therefore fundamentally more environmentally friendly than the incumbent products. They were found to provide water repellency, which for some applications would be suitable for use in the textile industry.

However, the repellency to oil (oleophobicity) was not as good as the incumbent C8 perfluorocarbons. During the course of the project, attempts were made to improve the oil repellency, but that required the development of a novel post treatment that required a high temperature process and was also fluorine based, although they were smaller than the C8 fluorocarbons. It should also be stated that despite the post treatment, the level of oleophobicity was not still not comparable to the C8 PFC materials and so would require further development work before commercial trials were possible.

Using surface energy and contact angle measurements on model materials, the third approach demonstrated that by using functionalised nano-silica it should be possible to obtain a coating that had superhydrophobic and oleophobic properties without any fluorine. content This approach is still at the lower technology readiness levels and requires further product development before it could be considered for market evaluation.

The information gathered and subsequent calculations undertaken in this report show that the environmental impact of the materials in development will reduce the fluorine content of fabrics with several approaches completely removing fluorine from the systems. With the exception of the UV cure process, all of the approaches discussed have been designed to fit with existing practices within the textile industry. The environmental impact of processing of these materials is mainly governed by the curing processes rather than the components or manufacture of the coatings themselves. The curing process can be improved in a

number of ways, for instance by increasing packing efficiency as material is pushed through the ovens, or improving the efficiency of the oven, reducing cure times and temperatures, but these are outside the scope of this project, although the cure time is in some ways begun to be addressed with the UV cure system.

## 7 References

1. Chaouki Ghenai (2012). Sustainable Engineering and Eco Design, Sustainable Development - Energy, Engineering and Technologies - Manufacturing and Environment, Prof. Chaouki Ghenai (Ed.), ISBN: 978-953-51-0165-9, InTech, Available from: <http://www.intechopen.com/books/sustainable-development-energyengineering-and-technologies-manufacturing-and-environment/sustainable-engineering-and-eco-design>.
2. Bernd Brandt, Evelin Kletzer, Harald Pilz, Dariya Hadzhiyska and Peter Seizov (2012) "Silicone-chemistry carbon balance: An assessment of Greenhouse Gas Emissions and Reductions" Available online: [http://reports.wacker.com/2012/sr/servicepages/downloads/files/sil\\_exec-summary\\_en.pdf](http://reports.wacker.com/2012/sr/servicepages/downloads/files/sil_exec-summary_en.pdf).
3. Middlemas, S., et al. (2014) LCA comparison of emerging and traditional TiO<sub>2</sub> manufacturing processes, Journal of Cleaner Production, <http://dx.doi.org/10.1016/j.jclepro.2014.11.019>.
4. Thermolon.co.kr:  
[http://w.thermolon.co.kr/html\\_e/image/mn01/ComparisonofThermolonvsPTFE\\_06October2010.pdf](http://w.thermolon.co.kr/html_e/image/mn01/ComparisonofThermolonvsPTFE_06October2010.pdf)
5. Institute of Manufacturing, Uni of Cambridge, 'Well Dressed', ISBN 1-902546-52-0, 2006.