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Review of Repellency Treatments

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Abstract

Liquid repellent coatings have become frequently used in many sectors due to their ability to repel a broad range of liquids ranging from high surface tension liquids such as water to low surface tension oils. They are used in the military textile field as the outer layer finish of chemical and biological personal protection equipment such as air permeable coveralls. These finishes can help protect personnel not only from warfare agents, but also from everyday substances such as water, oils, fuel, lubricants, cleaning solvents, and other contaminants. Traditionally, long chain C8 fluorochemical-based finishes were used to achieve this protection; however, due to their potential high toxicity, legislation has been put in place to restrict or ban their usage throughout the world. Alternative coatings have been developed and brought to market. Coatings at all technology readiness levels are summarized and compared in this report. In particular, short chain C6 fluorochemical coatings have come close in performance to traditional coatings without the high environmental risk. Other alternative more benign coatings such as silicone and hydrocarbon based finishes have only shown water repellency properties and no oil repellency to date. Additionally, test methods used to evaluate these coatings, ranging from standard test methods to university laboratory developed tests, are discussed and evaluated.

Resumé

On utilise fréquemment des enduits résistant aux liquides dans de nombreux domaines en raison de leur aptitude à repousser un vaste éventail de liquides, allant de liquides à tension de surface élevée comme l'eau jusqu'aux huiles à faible tension de surface. Ils sont utilisés dans le domaine de textiles militaires et sont appliqués sur la couche extérieure de l'équipement de protection individuelle contre les produits chimiques et biologiques comme des combinaisons perméables à l'air. Ces enduits peuvent aider à protéger le personnel non seulement contre des agents de guerre, mais aussi contre des substances utilisées tous les jours, comme l'eau, l'huile, les lubrifiants, les solvants de nettoyage et autres contaminants. Dans le passé, des enduits à base de substances fluorochimiques en C8 à chaîne longue étaient utilisés pour assurer cette protection. Cependant, en raison de leur toxicité potentiellement élevée, des mesures législatives ont été adoptées pour en restreindre ou en interdire l'usage partout au monde. D'autres enduits ont été mis au point et commercialisés. Des enduits à divers niveaux de maturité technologique sont brièvement décrits et comparés dans ce rapport. Plus précisément, les enduits fluorochimiques en C6 à chaîne courte ont présenté des performances très semblables aux enduits classiques sans poser de risques élevés pour l'environnement. Jusqu'à présent, d'autres enduits moins dommageables comme ceux à base de silicone et d'hydrocarbures ont présenté une résistance à l'eau et non à l'huile. De plus, les méthodes d'essai utilisées pour évaluer ces enduits, soit des méthodes d'essai normalisées ou des essais élaborés par des laboratoires d'université, sont aussi l'objet d'un examen et d'une évaluation.

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1. Introduction

Military personnel, due to the nature of their work could come into contact with a wide array of substances including dirt, oils, gasoline, alcohols, cleaners, chemical and biological (CB) warfare agents, and toxic industrial chemicals, which can potentially be a danger to their health and life [1]. Personal protective equipment (PPE) should therefore be worn to safeguard against any potential hazards. However, selecting the appropriate PPE can be a daunting task. There are thousands of possible toxic substances present in different physical forms and toxic at different dosages. One way to provide protection against liquid hazards is to use protective clothing finished with a liquid repellent outer layer.

Textile liquid repellent finishes do not only benefit military personnel but also civilians. These finishes have been used in the outdoor industry, home products, sportswear, and even the healthcare industry [2]. The most popular liquid repellent textile finishes are based on fluorinated polymers. In particular, fluorochemical (also called fluorocarbon) coatings with long perfluoroalkyl side chains where 8 of the carbon atoms have all the hydrogen atoms replaced by fluorine atoms (C8) have been successful. However, recent studies have shown that these finishes pose an environmental concern [2][3][4]. In particular, their association with perfluoroalkyl carboxylates and sulfonates such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) whose molecular structure can be seen in Figure 1a and b, respectively. These can be emitted into the environment during the chemical manufacturing process, the application of the finish to the garment, the usage of the garment, the re-application of the finish, and the final disposal of the garment [4].

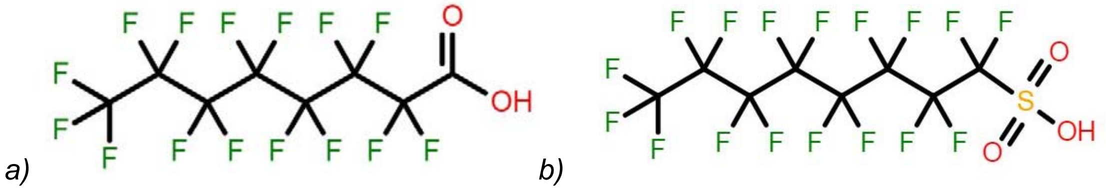

Figure 1: Molecular structure of a) PFOA, and b) PFOS.

PFOA and PFOS do not occur naturally in the environment [3]. Due to the strong and very stable carbon-fluorine bond they do not degrade and are very persistent in the environment. This also leads to their ability to bioaccumulate. High concentrations of these compounds have been reported in wildlife and the environment close to the manufacturing plants, but have also been found in low levels in the environment, in wildlife and in the blood of humans far away from these sites even in the Arctic [3][4]. For example, these chemicals were present in more than 98 percent of 2,094 serum samples collected from the US population between 2003 and 2004 [5]. It is yet not clear of the exact effects these substances have on humans, though they have been found to have toxic effects in laboratory animals such as negatively affecting reproduction and development [3].

New legislation and policies throughout the world have highly restricted the use of these chemicals, PFOA and PFOS; this, in turn, has affected the production and availability of liquid repellent textiles finished with C8 based fluorochemicals. These new policies include regulations added to the Canadian Environmental Protection Act to list these substances as toxic [6], the United States Environmental Protection Agency (US) 2010/2015 PFOA stewardship program [3], and the European Union Registration, Evaluation, Authorisation and Restriction of Chemicals 2017/1000 regulation [7]. The US 2010/2015 PFOA stewardship program led to the elimination of PFOA from both emissions and products for eight major leading companies in the perfluoroalkyl industry, Arkema, Asahi, BASF Corporation, Clariant, Daikin, 3M/Dyneon, DuPont, and Solvay Solexis [3]. Thus, the manufacture and import of PFOA has been phased out in the US due to this Stewardship program, but existing stocks of PFOA can still be used. In the case of PFOS, it was not reported as manufactured or imported into the US as part of the 2012 and 2006 Chemical Data Reporting. Tougher legislation is also expected in the future. Eventually, these types of repellent coatings will become very hard to procure or will no longer be available.

C8 based fluorochemical fabric finishes have been very successful due to their excellent properties. They have very high and broad repellency towards water and oil [2]. Liquid droplets tend to bead up and easily fall off the fabric. Alternative, environmentally friendly, highly liquid repellent coatings are needed to replace these finishes. Recent laboratory studies and commercial products have been focused on using similar fluorochemical coatings as replacements. These coatings are made of shorter chain fluorinated chemicals such as C6 where only 6 carbon atoms have all the hydrogen atoms replaced by fluorine atoms. These are considered to be a more environmentally friendly alternative. They are less toxic and less bio-accumulative in wildlife and humans. Nonetheless, these are still very persistent chemicals. Thus, fluorine-free options such as silicone elastomers are also being explored. Silicones are considered to pose a low hazard to humans and the environment. In general, all these alternatives are not performing as well as the C8-based fluorochemical products in providing broad spectrum liquid protection.

1.1 Aim

The aim of this project is to establish an approach for investigating alternative liquid repellent textile coatings as replacements for historical C8-based fluorochemical repellent treatments. In particular, the aim is to provide recommendations on establishing the suitability of liquid repellent treatments for application to air permeable CB protective suits/uniforms for the Canadian Armed Forces (CAF).

1.2 Scope of work

The scope of this work is to review, compile, and summarize existing alternative liquid repellency fabric treatments at all technology readiness levels from commercially available coatings, to proof-of-concept laboratory experiments, as well as review the methods used to assess textile properties, from in-house experimental assessments, to industrial standard tests. An evaluation, based on publicly available information, of the suitability of these alternative textile finishes to replace C8-based fluorochemical treatments is also performed. Recommendations on approaches to the procurement and application of liquid repellency finishes to CB protective suits/uniforms in the short-, medium- and long-term are explored. In addition, recommendations on test methods are also presented.

2. Background

Surfaces can exhibit various degrees of liquid repellency ranging from complete wetting, when a liquid completely spreads on the surface and can penetrate into an absorbent material, to complete non-wetting, where a liquid does not spread at all on the surface and does not penetrate into an absorbent material. For example, textiles are porous materials typically with no liquid repellency. Liquid such as water or oil completely wet the surface and penetrate into them. At another end of the spectrum are superhydrophobic materials such as lotus leaves which have a very high repellency towards water [8]. On lotus leaf surfaces, water droplets contract to form a spherical shape and at slight angles on inclination these droplets roll off the leaf. If there is any contamination on the leaf such as dirt, the rolling water droplet would be able to pick it up and remove it from the surface. This self-cleaning property of certain types of superhydrophobic liquid repellent surfaces is in fact also known as the “lotus effect”. The ultimate goal is a superomniphobic surface, highly repellent to both water and oils. A number of wetting theories have been developed to try to explain and define a surface’s degree of liquid repellency. These theories can be used to both understand and design repellent materials. Thus, it is possible to modify the degree of liquid repellency of surfaces to achieve the desired performance goals.

2.1 Surface wetting theories

The ability of a material to be wetted by, or repel, a liquid can be determined from the contact angle (CA). The CA is the angle between the solid-liquid and liquid-gas interfaces of a liquid droplet placed on a surface measured through the liquid droplet as shown in Figure 2. According to Young’s theory, surfaces with water CAs lower than 90° are considered hydrophilic, while surfaces with water CAs greater than 90° are considered hydrophobic [9]. However, this theory assumes that the surface is completely smooth and chemically homogeneous, which is not the case for most surfaces. Further theories were developed by Wenzel [10] and Cassie and Baxter [11] to explain wetting behaviour on a rough surface. In the Wenzel state, a liquid droplet makes full contact with the rough surface as can be seen in Figure 3a. In this state, the contact area of the droplet with the surface is larger. Also, since the droplet makes full contact with the surface, strong adhesive forces must exist between the solid and the liquid. The liquid droplet will not be able to easily move and roll off the surface. In the Cassie-Baxter case, a liquid droplet sits on top of the rough surface and only makes an intermittent contact with the rough surface, as can be seen in Figure 3b. In this latter case, air pockets get trapped underneath the droplet. The droplet is not pinned in place by the rough features and is able to move, leading to a facile removal of the liquid from the surface. Under certain circumstances, such as in the presence of applied pressure, it is possible to transit from the Cassie-Baxter state to the Wenzel state, usually due to the loss of the air pockets. The same theories apply to water and oil liquid droplets.

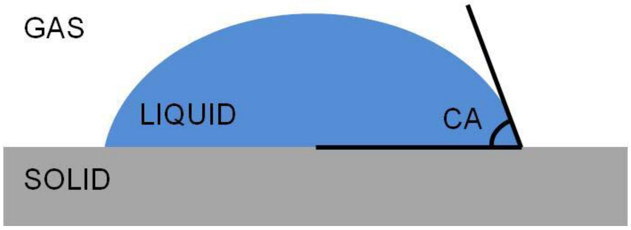

Figure 2: Contact angle measurement.

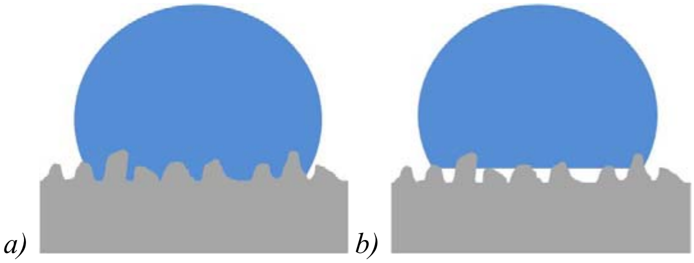

Figure 3: Effect of surface roughness on liquid droplets a) Wenzel state, and b) Cassie-Baxter state.

The terminology developed to define the various degrees of liquid wetting of a surface is summarized in Table 1. The liquid repellency of a surface is categorized according to its CA with the selected probe liquid [2]. Probe liquids are classified into two categories, water and non-water (which are typically oils).The material is in a complete wetting state when the contact angle is 0°, while the material is in a complete non-wetting state when the contact angle is 180°. Surfaces classified in the "super" state in addition to having very large CAs, are also typically self-cleaning and droplets can easily roll off their surface when the surface is tilted. These low angles at which the surface must be tilted in order for the droplet to slide of the surface are usually <10°. Surfaces in other regimes such as the omniphobic state can also have these low sliding angles. Ideally, a coating used for PPE should be in the highest regimes and have both water and oil liquid repellency. In Table 1, these most desirable properties can be seen in green, while acceptable properties can be seen in yellow. Properties that should be avoided are portrayed in red.

Table 1: Liquid repellency terminology.

Contact Angle (CA)	**Test Liquid**		
	Water	**Oil**	**Water and Oil**
CA = 0°	Complete wetting		
CA < 90°	Hydrophilic	Oleophilic	Amphiphilic or Omniphilic
90° ≤ CA ≤ 150°	Hydrophobic	Oleophobic	Amphiphobic or Omniphobic
CA> 150°	Superhydrophobic	Superoleophobic	Superamphiphobic or Superomniphobic
CA = 180°	Complete non-wetting		

2.2 Liquid repellent coating design factors

According to the wettability theories discussed previously, there are two major parameters which influence the degree of a material's liquid repellency: the chemical composition of the surface, and the roughness of the surface. These two parameters can be manipulated to transform an inherently liquid absorbent material such as a textile into a highly liquid repellent surface. These textiles can then be used in PPE to protect individuals against many liquid hazards.

2.2.1 Hazards

Liquid repellent surfaces used for PPE must be able to protect against any number of hazardous liquids such as toxic chemical substances, or biologically contaminated aqueous fluids. These liquids can come in any drop size and contamination density. The duration of the spill, the amount of liquid, and degree and length of the contact with the liquid will greatly influence the severity of the incident.

Chemical warfare agents (CWAs) include nonliving substances that will cause damage to the body through chemical reactions [1]. These consist of chemical warfare agents, toxic industrial chemicals, and even toxins.

Chemical warfare agents are very effective, toxic and come in many forms, and are a particular concern for the military. They can also pose a high threat to civilians. One way to classify them is according to the targeted physiological system as follows:

- Choking agents which attack the lungs, such as phosgene gas (CG, Carbonyl chloride),
- Blood agents which interfere with oxygen movement from the blood to the tissues, such as hydrogen cyanide (AC), or cyanogen chloride (CK),
- Blister agents which attack the skin, such as distilled sulfur mustard (HD, Bis (2-chloroethyl) sulfide), or lewisite (L, Dichloro(2-chlorovinyl)arsine),
- Nerve agents which affect the nerve pathways between the brain and the voluntary muscles, such as Sarin (GB, Isopropyl methylphosphonofluoridate), Soman (GD, Pinacolyl methyl phosphonofluoridate), Cyclosarin (GF, Cyclohexylmethylphosphonofluoridate), or VX (O-Ethyl-S-(2-diisopropylaminoethyl) methyl phosphono-thiolate),
- Riot control agents which temporary incapacitate, such as CS tear gas ([(2-Chlorophenyl)methylidene]propanedinitrile), and
- Psychochemical agents which disorient the mind, such as LSD (Lysergic acid diethylamide).

Blister and nerve agents are the two main classes of classical chemical warfare agents that require high levels of dermal protection due to their significant dermal toxicity. Table 2 shows the toxicity estimates for selected chemical warfare agents such as the median lethal (LD_{50}) and the effective (ED_{50}) doses [12]. In this case, LD_{50} is the amount of liquid expected to kill 50 % of a group of exposed and unprotected individuals, while ED_{50} is the amount of liquid expected to cause a severe effect in 50 % of a group of exposed and unprotected individuals. The dosages are given as milligrams per 70 kilogram body weight man. In addition, the relative persistency of the chemicals is also noted (where a persistent agent will be able remain in place to cause casualties for more than 24 hours, while a non-persistent agent will dissipate and lose its ability to cause casualties after perhaps 10-15 minutes). As can be seen from the table, VX is a chemical of very high concern.

Table 2: Toxicity of selected chemical warfare agents.

Chemical warfare agent	Lethal (LD_{50}) in mg/70 kg man	Severe effect (ED_{50}) in mg/70 kg man	Persistent?
VX	5	2	Yes
GD	350	200	No
GF	350	200	No
HD	1400	600	Yes
GB	1700	1000	No

Toxic industrial chemicals (TICs) are any chemical that is toxic and is produced for industrial and civilian purposes. They are typically available in bulk quantities and more readily than CWAs, since they are not as restricted as chemical warfare agents. These chemicals were not designed to be used as warfare agents but as useful chemicals in many applications. One of the best known TICs is chlorine gas which was used as an agent in World War I. Compiling a list of standard chemicals for testing is difficult since there are thousands of TICs. Standard test lists have been developed by a number of organizations, found in documents such as the CAN/CGSB/CSA-Z1610-11 by the Canadian Standards Association [13], NFPA 1994-12 by the National Fire Protection Association [14], and ASTM F1186-03 by the American Society for Testing and Materials [15].

On the other hand, toxins are poisonous products which are chemical in nature, but originate from biological sources. They are nonliving large molecules which have been isolated from biological sources such as microorganisms, animals, or plants. Thus, they can also be classified under biological warfare agents. They display traits of either CB agents with a toxicity level in between these two agents. They are dry powders and can be dissolved in water to yield a contaminated liquid.

Biological warfare agents are living organisms that can be used intentionally to cause disease [1]. These consist of microorganisms such as fungi and bacteria, vectors, which are disease carrying animals, and the above mentioned toxins. They could be encountered in many forms, in particular in liquids such as water or body fluids. They are usually much easier to decontaminate than chemical agents since harsh conditions can kill them such as acids, high temperatures, and ultraviolet light.

2.2.2 Surface chemistry

One of the factors determining the liquid repellency of a material is the surface chemistry, in particular the surface free energy. Surface free energy is the net energy from the intermolecular forces of the surface molecules of a solid [2], and it is the work expended to increase the size of the surface. A similar parameter for liquids can be derived from the liquid surface tension. Surface tension is the net intermolecular force of the surface molecules of a liquid as shown in

Figure 4. Due to these unbalanced forces present at the surface, an internal pressure is created. Liquids will contract to minimize their surface area and contact with air. A solid surface would be able to repel liquids with surface tensions higher than its surface free energy (both are expressed in units of energy per unit area); therefore a low surface energy solid is most effective at repelling a large variety of liquids.

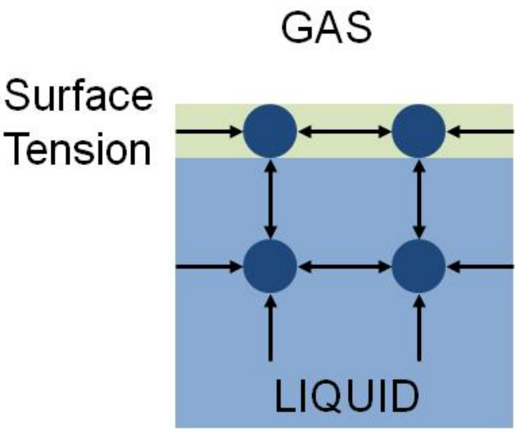

Figure 4: Forces giving rise to surface tension in liquids.

Low surface free energy substances such as fluorochemicals and silicones are commonly used to treat surfaces to convey liquid repellency, due to their ability to repel a wide range of liquids. According to Zisman, the surface free energy of chemical groups decreases as follows $–CH_2–$ (molecular backbone) > $–CH_3$ (side group) > $–CF_2–$ (molecular backbone) > $–CF_3$ (side group) [16]. The surface free energy also decreases from ~21 mN/m to ~11 mN/m as the chain length, n, increases from 0 to 8 for $–(CF_2)_n–CF_3$ side groups [17]. For example, fibres treated with acrylic polymers where n is 7, had an oil rating in the AATCC 118 standard test method [18] of 7 – 8, while in the case of polymers where n is 8, the oil rating was 8 (where 8 is the highest possible oil repellency rating, see Section 2.3.1). Nishino reported a surface free energy for $–CF_3$ groups on a flat surface as low as ~6.7 mN/m with a water contact angle of 119° [19]. Fluorochemical-based coatings would easily be able to repel liquids with high surface tensions such as water (72.8mN/m) [20] and also low surface tensions liquids such as hexadecane (27.5 mN/m) [21]. However, environmentally friendly silicone-based coatings have a higher surface free energy (for example, 19.8 mN/m for polydimethylsiloxane [22]), which results in a narrower range of repelled liquids. Table 3 summarizes the surface tension of a number of chemicals used as testing liquids in the characterization of repellency (no colour), common industrial chemicals (in yellow), chemical warfare agents (in red), and some chemical warfare agents simulants (in orange), in decreasing order.

Table 3: Surface tension of select liquids.

Liquid	Surface Tension in mN/m at 20°C
Water	72.8 [20]
Sulfuric acid– concentrated	54 [23]
Diiodomethane	50.9 [21]
Nitrobenzene	43.9 [24]
Dimethyl sulfoxide (L simulant)	43.5 [25]
Distilled Sulfur Mustard (HD) (Blister Agent)	43.2 [26]
Methyl salicylate (HD simulant)	41.8 [25]
N,N-Dimethylformamide	37.1 [24]
Dimethyl methyl phosphonate (GB simulant)	36.7 [25]
Cooking oil	33.8 [27]
2-Chloroethyl ethyl sulfide(HD simulant)	32.2 [25]
Cyclosarin (GF) (Nerve Agent)	32.3 [28]
VX (Nerve Agent)	32.0 [26]
Triethyl phosphate(GD simulant)	30.6 [25]
Toluene	28.4 [24]
Tributyl phosphate (GD simulant)	27.8 [25]
n-Hexadecane	27.5 [21]
Sarin (GB) (Nerve Agent)	26.5 [26]
Tetrahydrofuran	26.4 [24]

Liquid	Surface Tension in mN/m at 20°C
Acetone	25.2 [24]
Soman (GD) (Nerve Agent)	24.5 [28]
Ethyl acetate	23.8 [20]
Methanol	22.7 [24]
n-Octane	21.6 [24]
Potassium cyanide	18.9 [20]
n-Hexane	18.4 [24]
Hydrogen cyanide (AC) (Blood Agent)	17.1 [29]

2.2.3 Surface roughness

Surface roughness is another factor that influences the liquid repellency of a material. Micro- and/or nanometer scale roughness can lead to air pockets getting trapped underneath a liquid droplet resulting in a highly liquid repellent surface, such as the lotus leaf discussed earlier [11]. Textiles are already rougher than hard surfaces such as glass, due to their micrometer sized fibres; thus, they can be turned highly liquid repellent more easily than flat surfaces. Decreasing the fibre sizes and fibre bundle sizes also leads to better liquid repellency in textiles [30]. The distance between the fibre bundles or weave opening influences their repellency too. Decreasing the distance between the fibre bundles and creating a tighter weave leads to an increase in liquid repellency [25]. Introducing additional roughness into the textiles such as smaller micrometer and/or nanometer sized particles would also increase a fabric’s liquid repellency [31]. By optimizing these parameters to maximize the number and durability of air pockets which will be trapped underneath a liquid, highly repellent textiles can be obtained [32].

More recently, another design parameter was reported for textiles, the shape of the fibre [33]. The spherical shape of a 30 micrometer fibre was modified by engineering channels into the fibre itself to create trapezoidal-shaped features along the fiber length. This helped with trapping air pockets underneath a liquid droplet. Thus, this change in fibre design increased its repellent properties.

2.3 Characterization methods

Over the years, a wide range of characterization methods has been developed to measure a surface’s degree of liquid repellency. The standardization of these methods is still a challenge. Researchers sometimes use similar methods but modify the type, amount, or number of liquids used in their tests. Some researchers might only report results from only one or two methods. However, some standard tests have been developed such as those from the Canadian General Standards Board (CGSB), the American Society for Testing and Materials (ASTM), the American Association of Textile Chemists and Colorists (AATCC), or the International Organization for Standardization (ISO) [1][34]. Results from these methods are rarely reported in articles on novel laboratory coatings, while commercial products only claim repellency properties without providing any technical information. Thus, it is difficult to compare amongst various technologies. A summary of some of these methods can be found in Table 5 at the end of this section.

2.3.1 Liquid repellency characterization methods

The most common measurement for liquid repellency reported in the literature is the apparent CA. The CA can be measured using the sessile drop method [35]. A drop of the test liquid (5, 10, or 20 μL) is placed on the coated surface and an image of the drop's profile is acquired using an optical system. The image is then processed to obtain the CA of the surface as seen in Figure 2. Common test liquids in the literature include water, diiodomethane, cooking oil, and n-hexadecane. The higher the measured CA is, the higher the liquid repellency of the material. The wettability of a material as classified by CA can be seen in Table 1. For example, a hazardous liquid droplet contacts the arm of military personnel wearing liquid repellent coated textiles. The droplet will not be able to penetrate into the fabric if the textile has a high contact angle for this particular liquid. However, it is noteworthy that if there are outside stimuli such as pressure, then the droplet still might be able to penetrate into the fabric.

Other laboratory methods have been developed to determine repellency which do not need an accurate determination of the CA, in particular, the sliding angle and the shedding angle. These measurements can also help to differentiate the degree of wettability between surfaces that have the same CA values. The sliding angle is the minimum angle of inclination at which a liquid droplet starts to roll off the surface [2]. A liquid droplet is placed on the surface of a material and the material is tilted from the horizontal position until the droplet starts to roll off the surface. This tilting angle is then taken as the droplet's sliding angle. A schematic of this measurement can be seen in Figure 5. Surfaces that have very low sliding angles are typically in the Cassie-Baxter wetting state and have self-cleaning properties. In the case of textiles, sometimes protruding fibre ends might prevent a droplet from rolling off the surface. Associated with this angle is the contact angle hysteresis, which is the difference between the advancing angle – the angle formed at the front side of the sliding droplet, and the receding angle – the angle formed at the back side of the sliding droplet (as shown in Figure 5). Low sliding angles and contact angle hysteresis are associated with highly repellent surfaces. Going back to the previous example of a hazardous liquid droplet on the arm of a person wearing liquid repellent textiles, if the sliding angle for this liquid is low, the liquid will be able to come off the fabric easily, such as when the person moves his arm.

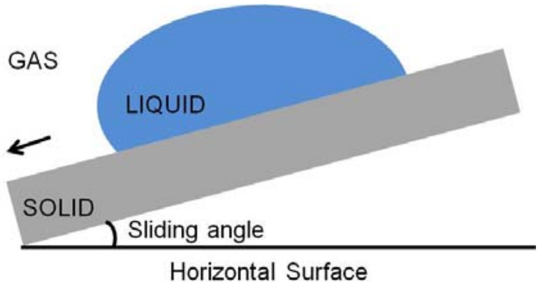

Figure 5: Schematic representation of sliding angle measurement.

On the other hand, the shedding angle is the minimum angle at which a droplet dispensed from a distance onto a tilted surface rolls off the surface [36]. A schematic of this measurement can be seen in Figure 6. The material is mounted at a tilt angle of 85° and the angle is subsequently reduced until a dispensed droplet no longer rolls off the surface. The shedding angle is then taken as the last angle at which the droplet rolled off the surface. The lower the value of the tilt angle of the surface, the higher is the ability of the coated surface to repel liquid droplets upon impact. The shedding angle is affected by the size of the droplet, the distance between the material and the liquid dispensing syringe, or the porosity of the material. If the material has large pores, there is a greater chance the droplet will get pinned to the surface and will not roll off the material. Going back to the previous example of a person wearing liquid repellent textiles, if a hazardous liquid droplet falls onto the arm of the person, if the shedding angle for this liquid is low, the droplet will roll off the arm immediately upon contact.

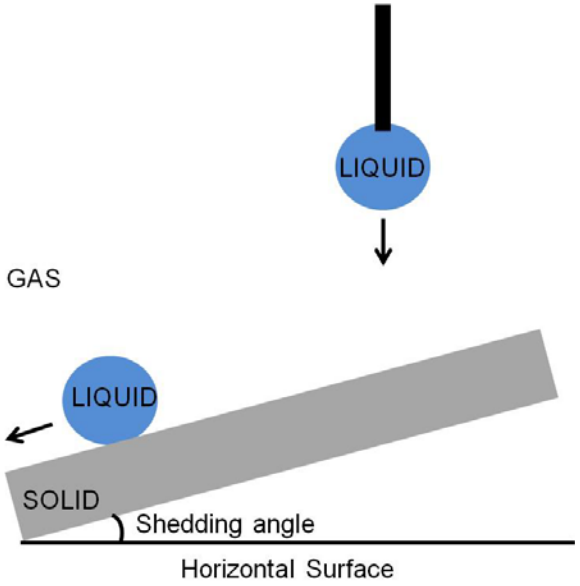

Figure 6: Schematic representation of shedding angle measurement.

Standard tests developed to measure aqueous liquid repellency include method ASTM D5946 [37], and AATCC 193 [38]. ASTM D5946 describes how to measure the water contact angle on a polymer surface. This is very similar to the laboratory contact angle measurement described above. AATCC 193 is a ‘pass or fail’ type of method and is used to determine repellency to aqueous liquids of various surface tensions. Eight drops of water/alcohol solutions with decreasing surface tensions are placed on the coating and visually observed for wetting. If the droplet spreads across the material or penetrates into the material, the material fails the test for that particular droplet. The number assigned to the solution that does not wet the sample is taken as the repellency grade.

AATCC 118 is also a ‘pass or fail’ type of method that tests for oil liquid repellency instead of for aqueous liquids [18]. It is very similar in its methodology to AATCC 193 [38]. AATCC 118 uses eight liquid hydrocarbons with decreasing surface tensions to determine oil repellency. The scale for the oils ranges from 0 (fail) using Kaydol, a mineral oil with a surface tension of 31.5 mN/m at 25 °C, to 8 (highest oil repellency) using n-heptane, which has a surface tension of 19.8 mN/m at 25 °C and 20.1 mN/m at 20 °C, as shown in Table 4 (which also shows some chemical warfare agents and their surface tension at 20 °C for comparison). The drops of liquid are placed on the coating and also visually observed for wetting. The number assigned to the oil that does not wet the sample is taken as the repellency oil grade. There are two types of passes for this test, a level A pass where the droplet has a clear well rounded appearance with a high contact angle, and a level B borderline pass where the droplet is not as rounded and some partial darkening is observed. The droplet can be in the oleophobic range of Table 1 to pass. A schematic of this scale can be seen in Figure 7. From a practical military perspective, as illustrated in Table 4, the coating that has an oil grade number corresponding to a surface tension equal to or lower than the surface tension of a given chemical warfare agent would be able to repel that agent. However, in reality the surface tension is not the only factor influencing repellency.

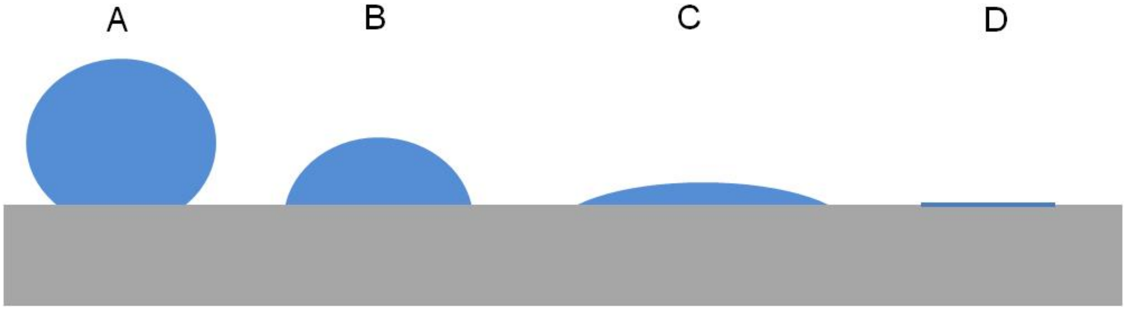

Figure 7: Schematic of oil repellency rating scale where A is a pass, B is a borderline pass, and C and D are fails.

Table 4: AATCC 118 oil repellency test standard [18] test liquids.

Composition	Oil grade number	Surface tension in mN/m at 25°C (20°C)	CWA expected to pass at the same Grade	Surface tension in mN/m at 20°C
None (fails Kaydol)	0	-	-	-
Kaydol	1	31.5	HD GF VX	43.2 32.3 32.0
65:35 Kaydol: n-hexadecane (volume)	2	29.6		
n-Hexadecane	3	27.3 (27.5)		
n-Tetradecane	4	26.4 (26.6)	GB	26.5
n-Dodecane	5	24.7 (25.4)		
n-Decane	6	23.5 (23.8)	GD	24.5
n-Octane	7	21.4 (21.6)		
n-Heptane	8	19.8 (20.1)	AC	17.1

A dynamic standard test method to determine the resistance of a fabric to water on its surface is the spray test, AATCC 22 [39] and ISO 4920 [40] (an equivalent to these methods is also the CAN/CGSB-4.2 No.26.2 [41] which is currently withdrawn but expected to be replaced). In the spray test method, the taut surface of a fabric is sprayed with water and a wetted pattern is produced. The pattern on the fabric is compared to a photographic standard chart and a rating is assigned to the coated fabric. The ratings are 0 (fail), 50, 70, 80, 90, and 100 (no wetting from water) in the AATCC 22 scale, and ISO 0 to 5 for ISO 4920. An abbreviated illustration of the rating scale is shown in Figure 8.

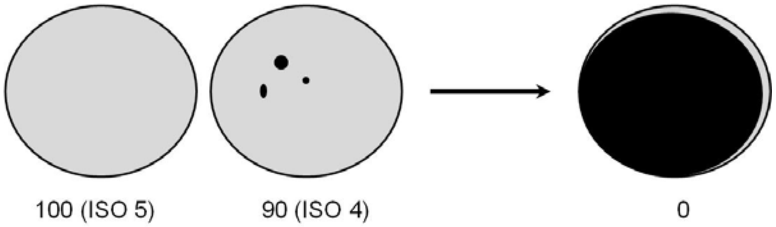

Figure 8: Spray test rating chart from 100 (No wetting) to 0 (Fail).

2.3.2 Durability characterization methods

Liquid repellent fabrics must be able to withstand laundering, since at least in the absence of hazard exposure, it is preferable to use most garments more than once. Standard test methods include ISO 6330 [42], CAN/CGSB-4.2 No. 24 [43], AATCC Monograph M6 [44], AATCC 135 [45], and CAN/CGSB-4.2 No. 58 [46] (which is currently withdrawn and expected to be replaced). These methods provide specific instructions for washing such as washing temperature and detergent, drying such as tumble drying, and sometimes restoration such as hand ironing for textile fabrics. There are also a number of in-house non-standardized laboratory procedures, for example using a flask instead of a laundering machine [47], or modifying a standard method such as AATCC 61 [48][49]. The fabric is repeatedly washed and dried for a number of times with or without detergent. The liquid repellency of the fabric can be assessed throughout and at the end of the test.

The repellent coating also needs to be able to withstand abrasion such as from wear, transportation, or even storage. Standard test methods include ASTM D3884 [50], ISO 12947(1-4) [51], and AATCC 93 [52]. In ASTM D3884, the fabric is abraded by the rotary rubbing action of two abrading wheels for a specific number of times with or without a load. Afterwards, the liquid repellency of the fabric can be reassessed. In-house non-standardized laboratory procedures have also been developed using sandpaper to rub the coating [53].

Other measurements of textile durability include the tensile strength and the tear strength of the fabric [54]. Standard tests to measure the tensile strength include CAN/CGSB-4.2 No. 9.1 [55] and ISO 13934-1 [56]. The fabric is placed between two clamps and tension is applied to stretch the fabric until it breaks within a specified time interval. Standard tests to measure tear strength include CAN/CGSB-4.2 No. 12.1 [57] and ISO 13937-2 [58]. In this case, the force required to propagate a single-rip tear through the fabric is measured.

2.3.3 Other characterization methods

The comfort of the person wearing the coated fabric should not be neglected, especially if the garment needs to be worn for prolonged periods of time. If air and moisture vapour are not allowed through the fabric, the wearer could become very uncomfortable and even become a heat casualty. Hence where some form of permeability is possible, the air and moisture vapour permeability should be high to boost sweat evaporation and cooling, but not so high as to interfere with the liquid repellency properties. A standard test method to measure air permeability is ASTM D737 [59], or CAN/CGSB-4.2 36 [60], or ISO 9237 [61], while ASTM E96, Proc B [62] or ISO 11092 [63] can be used to measure the moisture vapour transmission rate.

There also standard tests for physical comfort. These include ASTM D3776 [64], CAN/CGSB-4.2 5.1 [65], or ISO 3801 [66] which measure the mass, ASTM D1777 [67], ISO 5084 [68] or CAN/CGSB-4.2 37 [69], which measure the thickness, and ASTM D747 [70], which measures the stiffness of the coated fabric.

Table 5: Characterization methods.

Property	Characterization Method
Liquid Repellency	Contact Angle [2] ASTM D5946 (Corona-Treated Polymer Films Using Water Contact Angle Measurements) [37] Sliding Angle [2] Contact Angle Hysteresis [2] Shedding Angle [2][36] AATCC 193 (Aqueous Liquid Repellency: Water/Alcohol Solution Resistance Test) [38] AATCC 118 (Oil Repellency: Hydrocarbon Resistance Test) [18] AATCC 22 (Water Repellency-Spray Test) [39] ISO 4920 (Textile fabrics – Determination of resistance to surface wetting (spray test)) [40] CAN/CGSB-4.2 No.26.2 (Textile Test Methods: Textile Fabrics – Determination of Resistance of Surface Wetting (Spray Test)) – Withdrawn [41]
Laundering	ISO 6330 (Textiles – Domestic washing and drying procedures for textile testing) [42] CAN/CGSB-4.2 No. 24 (Textile test methods: Colourfastness and dimensional change in commercial laundering) [43] AATCC Monograph M6 (Home Laundry Test Conditions) [44] AATCC 135 (Dimensional Changes in Automatic Home Laundering) [45] CAN/CGSB-4.2 No. 58 (Textile Test Methods: Dimensional Change in Domestic Laundering of Textiles) – Withdrawn [46] In-house laboratory flask method [47] AATCC 61 (Colorfastness to Laundering: Accelerated) [48] Laboratory modified AATCC 61 method [49]

Property	Characterization Method
Abrasion	ASTM D3884 (Abrasion Resistance of Textile Fabrics (Rotary Platform, Double-Head Method)) [50] ISO 12947(1-4) (Textiles – Determination of the abrasion resistance of fabrics by the Martindale method) [51] AATCC 93 (Abrasion Resistance of Fabrics: Accelerotor Method) [52] In-house laboratory sandpaper method [53]
Tensile strength	CAN/CGSB-4.2 No. 9.1 (Textile test methods: Breaking strength of fabrics— Strip method — Constant time-to-break principle) [55] ISO 13934-1 (Textiles – Tensile properties of fabrics –Part 1: Determination of maximum force and elongation at maximum force using the strip method) [56]
Tear strength	CAN/CGSB-4.2 No. 12.1 (Textile test methods: Tearing strength – Single-rip method) [57] ISO 13937-2 (Textiles – Tear properties of fabrics – Part 2: Determination of tear force of trouser-shaped test specimens (Single tear method)) [58]
Air permeability	ASTM D737 (Air Permeability of Textile Fabrics) [59] CAN/CGSB-4.2 36 (Textile test methods: Air Permeability) [60] ISO 9237 (Textiles — Determination of the permeability of fabrics to air) [61]
Moisture vapour transmission rate	ASTM E96, Proc B (Water Vapor Transmission of Materials) [62] ISO 11092 (Textiles – Physiological Effects – Measurement of thermal and water vapour resistance under steady-state conditions (Sweating Guarded Hotplate test)) [63]
Weight	ASTM D3776 (Mass Per Unit Area (Weight) of Fabric) [64] CAN/CGSB-4.2 5.1 (Textile test methods: Unit Mass of Fabrics) [65] ISO 3801 (Textiles -- Woven fabrics -- Determination of mass per unit length and mass per unit area) [66]

Property	Characterization Method
Thickness	ASTM D1777 (Thickness of Textile Materials) [67] ISO 5084 (Textiles – Determination of thickness of textiles and textile products) [68] CAN/CGSB-4.2 37 (Textile test methods: Fabric Thickness) [69]
Stiffness	ASTM D747 (Apparent Bending Modulus of Plastics by Means of a Cantilever Beam) [70]

3. Liquid repellent coatings

Liquid repellent fabric finishes, as the name implies, have the ability to repel liquids from the surface of the fabric by preventing the liquids from spreading and allowing for easy removal of the liquids. Fabrics are typically fabricated by either coating a repellent layer onto the fabric itself or by laminating the repellent layer at the surface of other layers [71]. Coating the repellent layer onto the fabric can produce a highly durable material, although the coated substance might not have all the desired properties such as broad-spectrum protection. On the other hand, laminating the repellent layer to other protective layers allows for the combination of materials with different properties to yield a layered material that has high broad-spectrum protection, comfort, and strength, though, since the components are clearly separated, there is a risk that they might detach.

The liquid repellent finish should result in a garment that not only has liquid repellency, but other desirable characteristics such as physiological comfort. Desirable properties include [1][34]:

- protection from multiple hazards
- durability
- thermal comfort
- physical comfort
- no physical impairment
- aesthetics
- flame retardancy
- multifunctional abilities
- low maintenance
- quick drying
- ultraviolet resistance
- decontamination capacity
- no noise increase

Nevertheless, it might not always be possible to procure a garment constructed from fabric that has all the required properties. The circumstances of the situation must be taken into account, such as the environment where the garment will be worn, to produce a ranked list of properties by their importance in order to select the appropriate material by eliminating low ranked items. Another problem may arise if the wanted fabric has only been tested in the laboratory. The fabric should be further tested in an operational environment and even in an actual mission in order to demonstrate a high technology readiness level.

3.1 Properties desired of liquid repellent coatings

The most important property for these coatings, as the name implies, is liquid repellency. The coating must be able to protect the user against any hazards they might encounter. In particular, military personnel have a high chance of coming into contact with a wide range of dangerous substances such as chemical and biological warfare agents, or TICs. If the personnel are not protected, they can be injured or even killed by these substances; thus, the protective coating must be able to provide a broad spectrum of protection and preferably shed off the hazardous liquids. These liquids can have surface tensions varying from high values such as 72.8 mN/m for water [20], to low values such as 24.5 mN/m for GD [28]. Fabricating coatings that can repel low surface tension liquids is challenging due to the narrow choice of suitable finishes that have the low surface energies required.

Next in importance is the durability of the coating. If the coating fails to perform when needed, for example by detaching from the fabric, it does not matter if the coating is the best liquid repellent available. In general, multiple use garments need to be more sophisticated and better constructed than single-use garments. The coating must be abrasion resistant in order to withstand wear by the user. The user must be able to perform regular functions such as flexing fingers, bending elbows, or walking, without detaching. The coating must also be durable to laundering since fabrics are typically washed after wear. The durability of the coating can be increased by chemically bonding the repellent to the fabric or by using an adhesive as an intermediate to create a bond between the repellent layer and fabric. Another solution to increasing usage durability would be to renew the coating by reapplying it, either by the user or by the manufacturer. However, this is not typically encouraged by the manufactures due to potential problems such as uneven pickup of treatment by the different parts of the finished garment, or shrinkage and even melting of the finished garment if a high curing temperature is needed for the coating, or damaging other layers in a multi-system ensemble such as an inner layer of activated carbon.

Connected to the durability of the coating is the overall durability of the garment. The coating should not affect the integrity of the fibres. The coating should not decrease the tensile or tearing strength of the material. If it does, it will lead to earlier failure in the field.

PPE, especially air permeable garments geared toward CB protection for the military, are typically composed of multiple layers. For example, the outer shell layer could be made of a liquid repellent coated textile, while the inner layer can be made of a filter material such as activated carbon that acts as a barrier layer in case any toxic vapours break through the first layer. Other protective layers may be included in addition or instead. These layers are sometimes combined to form a protective garment through lamination. The liquid repellent coating should not interfere with the lamination process. Nonetheless, it is possible that the coating would affect this process due to its repellent properties. In this situation, the solution might be to laminate a pristine textile layer to all the other desirable layers, and then apply the repellency treatment to the outer pristine layer. If this is the case, the liquid repellent finish should not negatively interfere with the other layers.

In addition, due to the complex issues associated with modern warfare, a variety of specialized treatments have been developed to address them. These treatments include camouflage, infrared reflectance, flame retardant properties, insect repellency, antimicrobial control, or antistatic capabilities. For camouflage, the coating should be compatible with the Canadian Disruptive Pattern (CADPAT) treatment which is a digital produced camouflage pattern that protects soldiers against detection by the naked eye as well as by night vision devices [72], or other camouflage patterns used by the CAF. Like all camouflage patterns, CADPAT uses combinations of colours such as green, brown, and black, and the repellent finish should not interact with the dyes/pigments and affect the colours; similarly the different colours must be able to take the finish. In summary, the repellent coating should be compatible with all operationally necessary additional finishes. However, this might be difficult to achieve due to the limited number of bonding sites on the fabric.

Another requirement is thermal comfort. Thermal strain can occur in a user if heat is not dissipated from the body and the temperature of the body increases. Heat strain can result in impaired abilities, or even death. This is a particular problem in hot and/or humid conditions such as jungles, deserts, and tropical environments, as well as during vigorous activities such as exercise, all of which generate heat stress. Excess heat can be removed from the body by cooling mechanisms such as convection, where a cooling medium such as air picks up the extra heat and removes it, or evaporation, where water loss occurs through sweating or respiration. Ideally, the coating and the fabric system should be breathable so as to minimally affect the normal function of these mechanisms. Where the fabric system is not air permeable, the repellent treatment combined with the fabric should have a high moisture vapour transmission rate to allow the passage of water vapour molecules.

In order to improve heat dissipation from the body and improve comfort, wicking properties can be fabricated into garments; moisture produced by the body such as sweat and water vapour is drawn away from the body [2], spreads across the surface, and may more easily evaporate. Even where evaporation is prevented, wicking can improve comfort by minimizing bulk water collection in extremities (fingers and feet). A wicking layer can be added as the innermost layer to a typical CB protective liquid repellent laminate system. Research such as that of Zeng et al. [73] has gone into developing a dual purpose fabric where one face of the fabric has liquid repellency properties, while the other face of the fabric has wicking properties. The material would be able to perform both functions without the need of multiple layers, which can save cost and improve air permeability.

Physical comfort of the user should also be maintained. The coating should not add significant weight to the fabric. Military personal usually carry an array of garments and equipment, and adding an extra burden could impact their health. Additionally, the coating should not irritate the user such as through surface roughness or irritating compounds, especially substances that could cause some allergic reaction or more adverse health effects. The original fabric softness and feel should be maintained and maybe even improved. The coating should not affect any stretch properties of the garment, if stretch is added to provide improved comfort, fitting, and donning/doffing.

The coating should not cause any physical impairment. The user should be able to perform normal body functions such as walking or running and any necessary tasks such as picking up an object, writing, or typing on a computer. The fabric stiffness should not increase and affect movement and dexterity.

Decontamination of the coated fabric might be required during its lifetime. Ideally, any hazards should be easily removed by decontamination. However, for porous materials such as air permeable fabrics, the decontamination solvent might boost penetration of the hazardous agent into the material resulting in incomplete decontamination and the presence of a residual hazard. The coating should also not react with the decontamination solutions and lose its properties. This is especially necessary for multi-use garments and garments worn by the people performing the decontamination.

The coating itself should not have adverse effects to humans and the environment. The coating fabrication process should not release dangerous chemicals into the environment. The coating should not degrade into toxic substances. However, this is not always possible if a coating posing an environmental risk is the only protection available to personnel in very high hazardous situations.

Another parameter to consider is the type of fabric and garment system the coating can be applied to. The coating should not have limitations and be able to be used on the desired fabric, typical examples being cotton, 50 % cotton – 50 % nylon blend, or Nomex blends. In high hazard environments, air impermeable PPE may be used, and the coating could be of benefit on these types of materials as well.

Other issues that need to be taken into account include the complexity of applying the coating to the material. The coating should be able to be applied through standard industrial practices such as dip-pad-dry treatment processes. If only very specialized procedures can be used, a cost within the budget, and availability in large quantities, might not be achievable. Also, connected to this is the feasibility of proof-of-concept coatings to be scaled up from laboratory swatches to mass produced full garments.

3.2 Classification scale

One system for measuring the maturity level of a technology that can help in comparing between different fabric finishes is the Technology Readiness Level (TRL) scale. This scale first originated with the US National Aeronautics and Space Administration and it was later adopted by other agencies such as the US Department of Defense [74] and the Public Services and Procurement Canada–Build in Canada Innovation Program [75]. A compressed version of this scale can be seen in Table 6. The coatings in this report have been classified following into three categories: proof-of-concept coating (TRL 1-4), tested coating (TRL 5-7), and commercially available coating (TRL 8-9). In terms of procurement, technology that is fully developed and tested, TRL 8-9, would be the most facile to acquire in the short term. Technology that has only been tested and not fully developed, TRL 5-7, would be good to acquire in the medium term if it has better properties than current market products. In the long term, technology at TRL 1-4, might be a good avenue for research if it has the potential for superior properties; however, this type of technology does not always make it past the laboratory stage due to manufacturability issues such as scale up and cost.

Table 6: Compressed Technology Readiness Level (TRL) scale.

TRL	Definition	Description
1–4	Basic principles observed and reported –Concept validated in the laboratory	Scientific research begins – The integration of basic technological components to see that they will work together
5–7	Concept validated in simulated environment – Prototype ready for demonstration in an operational environment	The integration of basic technological components for testing in simulated environment –Prototype near or at planned operational level
8–9	Technology completed and qualified through tests– Technology proven in successful mission operations	Technology has been proven to work in its final form under expected conditions – Actual application of the technology in its final form under mission conditions

3.3 Historical coatings

Early attempts at achieving liquid repellency were driven by the need to make fabrics resistant to water to protect people from adverse weather and water splash [2]. These coatings were based on oils such as linseed oil, waxes such as paraffin wax, metal emulsions of waxes, natural rubber derivatives, and vulcanized rubber. However, these coatings made the fabric not only repellent to water, but also not breathable and prevented the passage of air and sweat vapours. The wearer became uncomfortable with time and overheated. They were also not very durable and repeated laundering would remove the treatment. Breathability was introduced into fabrics during World War II when a fabric called Ventile was developed for the British military. This fabric is a densely woven cotton material with no other coatings on it. The water protection comes only from the weaving type.

Since the 1950s, long chain fluorochemical coatings usually based on C8 chemistry have been used to impart water repellency to textiles. These coatings represented 90 % of the durable water repellency finishes during the 1990s [2]. Fluorochemicals have a very low surface free energy and thus impart superior water repellency to fabrics. In addition, they also have very good oil repellency. For example, Ruco-Guard AFB CONC from Rudolf GmBH is a C8 fluorochemical-based coating which has water, oil and soil repellency [4]. It has a water spray rating of 100 out of 100 in the AATCC 22 test [39] and an oil rating of 8 out of 8 in the AATCC 118 [18] test before and after laundering. Nonetheless, as previously discussed, coatings based on C8 fluorochemicals are a health and environmental problem due to their association with PFOA and PFOS compounds. Emission of these compounds can occur during the coating's manufacturing process and later during the application of the coating to the fabric and loss of the coating from the fabric during its lifetime usage. Recent restrictions and bans throughout the world have decreased their popularity. Companies have eliminated these finishes from their products or have pledged to do so, in particular in the US and Europe. For example, 3M used to be the largest manufacturer of these compounds in the world and it used C8 fluorochemicals for its water and oil liquid repellent line, Scotchgard Protector [4]. By 2008, 3M stopped its production and usage of these compounds under the US Environmental Protection Agency 2010/2015 PFOA stewardship program [3]. Other companies have also partnered with voluntary environmental textile associations such as the Zero Discharge of Hazardous Chemicals program [76], Bluesign [77], or OEKO-TEX [78], to help them make this transition. Nevertheless, not all countries have strict regulation in place to control these chemicals and they are still produced in large quantities in countries such as China [4]. After 3M stopped production and use of these chemicals, China greatly increased its chemical production and usage in particular for PFOS and became the global leader in this market.

In late 1959, a water and oil repellent durable coating called Quartermaster repellent (Quarpel) was developed at the (currently named) Natick Soldier Research, Development and Engineering Center (NSRDEC) and later adopted by the US military for CB purposes [79]. Quarpel is a combination of a quaternary ammonium compound and a C8 fluorocarbon. This coating was more breathable and comfortable than the previous rubber based materials. This coating has been very successful and according to Gibson in a report from 2008, was still the standard water and oil repellent fluorochemical fabric finish for the US military [80]. He also went on to show that this coating still performs better than some experimental nanotechnology-based coatings. For example, Quarpel treated 50 % cotton – 50 % nylon blends had a water spray rating of 100 out of 100 in the AATCC 22 test and an oil rating of 7 out of 8 in the AATCC 118 test before laundering [81]. After 10 laundry cycles, the liquid repellency decreased and the new water spray test rating was >70, while the oil test rating was >5. However, for the reasons already mentioned, the US Army has been working on replacing the Quarpel coating with the newly developed and commercialized C6 fluorochemical-based EverShield coating (see Section 3.4), since this latter coating is more environmentally friendly, over repeated laundering has better properties than the Quarpel finish such as retention of oil repellency properties, and has good air permeability [34]. In the case of CAF, the chemical warfare protective coveralls also use a fluorochemical-based liquid repellent outer layer which is combined with a vapour-protective inner barrier layer [82].

3.4 Commercially available coatings (TRL 8-9)

As companies move away from long chain C8 based fluorochemical coatings, they have brought to market more environmentally friendly finishes based on shorter chain fluorochemicals such as C6, or even completely replaced fluorochemicals with more benign alternatives such as silicon and hydrocarbons. A selection of various coatings available on the market will be discussed in this section and a summary can be found in Table 7. In Table 7, the most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red. Additional coatings available on the market can be found in Annex A, Table 15 with similar colour coding; these additional coatings include alternate, less highly performing, coatings made by the same company (for example, a fluorine-free coating, where a fluorinated coating or coating with similar type of chemistry is already presented in this section). To compare between the different technologies, values from measurements for two standard test methods, AATCC 22 – Water Repellency – Spray Test [39] and AATCC 118 – Oil Repellency: Hydrocarbon Resistance Test [18], are presented as the spray test value and oil value (as the results from these two methods are the most common test values reported by companies in the US, Europe, and Asia). Furthermore, where known, the compatibility of these coatings with military requirements such as the preservation of colours after coating to inhibit damage to camouflage patterns, the ability to use the coating in laminated ensembles, and the preservation of fibre properties such as stretch and strength, are discussed as well. This information is then summarized in Table 8. In Table 8, the most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow. In the following discussions, for the most part it is assumed that the application under discussion is to air permeable fabrics, whose generic properties after application are described.

3.4.1 Commercial fluorine-based coatings

Fluorine-based finishes are the best performing coatings on the market in terms of liquid repellency. They have superior water and oil repellency in the omniphobic regime and some might even be in the superomniphobic range. However, CA or sliding angle measurement values are usually not reported by companies. It is thus difficult to predict if a coating is superomniphobic. Some of these commercially available coatings include:

- StainSmart® by Miliken & Company [83]: is a fluorochemical-based coating. It is water and oil repellent. After 30 washes it still maintains its repellent properties. In addition, it also wicks moisture on the inside and releases stains in the wash. Over time, the fabric stays soft, the color does not fade, and it is wrinkle resistant. The coating is used in the US Coast Guard Operational Dress Uniform and in the US Marine Corps optional dress white cover.
- NUVA® N1811 by Archroma (formerly Clariant) [84]: is a C6 based fluorochemical microencapsulated coating. It is water, oil, alcohol, soil, and stain repellent. It has a spray rating of 100 and an oil rating of 6 [4]. After 20 washings, it has a spray rating of >80 and an oil rating >4. It protects from acid and caustic substances. The fabric is permeable to air, stays soft with no negative impact on abrasion resistance and tear strength. Archroma is in the military uniform market.
- Lurotex® Duo by BASF [85]: is C6 based fluorochemical combined with a booster coating. Coating has a low curing temperature. It is water, oil, and dirt repellent with stain release properties. It has a spray rating of 100 and an oil rating of 7. After 20 washings, it has a spray rating of 90 and an oil rating 6. The booster imparts high level wash durability and the laundry can be air dried. The fabric is soft, permeable to air with no color change. It can be combined with a wrinkle-free system.
- Asahi Guard E-series^{TM} by AGC Chemicals Americas [86]: is an aqueous C6 based fluorochemical coating. It is water, oil, and dry soil repellent, for example, a spray rating of 100 and an oil rating of 5. After 20 washes, it has a spray rating of >80. The coated fabric is permeable to air, the coating is durable, and does not affect the texture or colour of the fabric. It can be used on textiles, paper, non-woven fabrics, and leather. It can be used for working clothes and uniforms. In particular, it is used for durable lightweight fabrics in the emergency response and military sectors.
- Ruco-Guard® AFC6 by Rudolf GmBH. [87]: is an aqueous C6-based fluorochemical coating. It is water, oil, and soil repellent. It has a spray rating of 100 and an oil rating of 5 [4]. After 3 washings, it has a spray rating of 100 and an oil rating of 2. The fabric is permeable to air, stays soft, and the coating is highly durable. It can be used for military clothing.
- NanoSphere® by Schoeller Technology AG. [88]: is a coating made of C6 fluorochemicals in a matrix with nanoparticles. It is water, oil, stain, and dirt repellent. It has a spray rating of 100 and after 40-50 washings, it has a spray rating of >90. It has good laundering durability, at least 50 washes. The fabric is not affected by the coating in terms of look and feel. It is permeable to air and has a high level of abrasion resistance. It can be applied on all types of textiles such as cotton or synthetics. Schoeller is in the military and police market.

- EverShield by UltraTech International Inc. [81][34]: is a coating made of C6 fluorochemicals in a polyurethane matrix with dual micro/nanostructures. It is water, oil, and stain repellent, and it lowers dirt and dust attraction. It has a spray rating of 100 and an oil rating of >7. After 20 washings, it has a spray rating of >80 and an oil rating >6. It has a water CA >160° and sliding angle of 5°, and a hexadecane CA >140°. It repels water and reduces the formation of ice. It still maintains its properties after 50 washes. It has better laundering durability than Quarpel. The fabric stays soft, is permeable to air, has good moisture vapour transport properties, and has better abrasion resistance and tear strength than an uncoated fabric. It can be applied to many types of fabrics such as 50 % - 50 % nylon/cotton or NOMEX. It minimally affects colour. It is compatible with anti-microbial agents. It does not compromise base fabric flame retardancy. It was coated on 20 army combat uniforms (ACU) and underwent military field testing in 2011 for durability, performance, and user acceptance, during which it received the Outstanding Warfighting Transition Award. The US army is working on replacing the current Quarpel coatings with this coating.
- Fluorolink® P56 by Solvay [89]: is an aqueous polyurethane perfluoropolyether structure with a high molecular weight. It is water and oil repellent with stain and soil resistance. It should have some laundry durability and should also not affect the textile’s breathability. It can also be used to treat metal, plastic, and glass surfaces.
- Scotchgard^{TM} Protector from 3M [90]: is a coating made of C4 fluorochemicals with urethane. It is water, oil, and stain repellent. It is a liquid aerosol that needs to be reapplied after every washing. It does not affect the color, breathability, or feel of fabrics. However, users are advised to test for colourfastness. It can be used on most washable fabrics such as cotton, or synthetic fabrics. Other products that use this technology to coat textiles include Ever C4 Water Repellent Treatment Fabrics by Everest Textile Co. [91] and Defender Repellent Systems® by Prime Leather Finishes Inc [92].
- Unidyne TG-5601 by Daikin Industries Ltd. with Dow Corning Corporation [93]: is a coating made of C6 fluorochemicals mixed with silicone. It can be cured at low temperatures. It is water and oil repellent with stain release. It has a spray rating of 100 and an oil rating of 6. After 20 washings, it has a spray rating of >60 and an oil rating <5. It has high wash laundering durability. The fabric has extreme soft hand-feel and it is permeable to air. It can be used on any fabrics. A study by Ryu et al. used this coating as the liquid repellent finish in a laminated system [94]. The liquid repellency treatment was applied before the lamination process was performed.

3.4.2 Commercial fluorine-free based coatings

Alternative fluorine-free based finishes such as silicon and hydrocarbon are increasing on the market due to their environmental friendliness. However, the performance of these coatings in terms of liquid repellency is not as good as the fluorine-based finishes. They also have superior water repellency properties, but no oil repellency to date. They are typically in the hydrophobic range and maybe even in the superhydrophobic range, but once again lack of measurements makes it difficult to place them in the superhydrophobic state. Some of these commercially available coatings include:

- Epic by Nextec® (Nextec Applications Inc.) [95]: is a silicone-based polymer technology. It encapsulates the individual fibres of the fabrics with an ultrathin silicon layer. It is water repellent and has good laundering durability. The fabric is fast drying, permeable to air, has better abrasion resistance and tear strength, and wind resistant. It is used by the US military such as in the Special Operations Forces' Protective Combat Uniform, Army's Gen III Extended Cold Weather Clothing System, and the Marine Corps "Happy" Jacket.

- Texfin RS-WR by Texchem UK Ltd. [96]: is a silicone emulsion based technology. It is water repellent and durable. It has a spray rating of 100 and after 10 washings it has a spray rating of 70. The fabric is soft, permeable to air, and exhibits minimal colour change. It is compatible with other finishing agents and can be used on various fabric types. It can be used in many applications such as work uniforms.
- POLON-MK-206 by Shin-Etsu Chemical Co. Ltd. [97]: is a silicone emulsion based technology. It is water repellent and has excellent durability to repeated washings. The fabric is soft, has excellent rebound resiliency, and is permeable to air. It also has excellent weather and heat resistance.
- Zelan^{TM} R3 by Huntsman International LLC. [98]: is a non-fluorinated coating made from 63% renewable non-GMO plant-based sources. It is water repellent with a spray rating of 100 and after 30 washings it has a spray rating of 90. No oil repellency was observed. It has excellent laundering durability (up to three times more durable than existing non-fluorinated repellents). The fabric is permeable to air. It works well on a variety of fabrics. It is also compatible with finishing auxiliaries such as resins and cross-linking agents.
- Altopel F^3 by Bolger &O' Hearn Inc. [99]: is an aqueous non-fluorinated coating made from bio-based chemical ingredients. It is water repellent with a spray rating of 100 and after 20 washings it has a spray rating of 90. No oil repellency was observed. It has superior laundering durability. The fabric is permeable to air. It can be used on a variety of fiber types and constructions.
- ChemStik by Green Theme Technologies LLC. [100]: is a coating based on hydrocarbon hydrophobic polymers. It is fabricated through a dry finishing technique such as thermal curing which uses no liquids. It is water repellent with a spray rating of 100 and after 100 washings it has a spray rating of ~100. It has stain release properties. No oil repellency was observed. It has excellent laundering durability for more than 100 washes. The fabric is abrasive resistant and permeable to air. No change to fabric hand or appearance. The treatment can be applied to many types of fibers, finished garments, and laminates. The fabric can also be treated on only one side resulting in a fabric having one side water repellent, while the other side maintains its hydrophilic properties.
- Arkophob® FFR by Archroma [101]: is a fluorine-free encapsulated wax based coating. It is water repellent with a spray rating of 100 and after 20 washings it has a spray rating of 70. It fails the oil repellency test. It has good laundering durability. The fabric is permeable to air, stays soft and has better abrasion resistance and tear strength. Archroma is in the military uniform market.
- Ecorepel® by Schoeller Technology AG. [102]: is a coating made of long paraffin wax chains wrapped in a spiral around the individual fibers. It is water and mud repellent. It has good laundering durability for minimum 30 washing cycles. It is also highly resistant to abrasion and chafing, breathable, and biodegradable. Schoeller is in the military and police market.
- Eco Dry by HeiQ Materials AG. [103]: is a coating made of hyper-branched hydrocarbons that attach to the fibres by a strong polyurethane backbone to form a 3D-structure. It imitates the water repellent feathers of ducks. It is water repellent with a spray rating of 100. After 10

washings and ironing, the spray rating is 100. It fails the oil repellency test. It has good laundering durability. The fabric is permeable to air, stays soft and has high abrasion resistance.

- Aquapel™ by Nanotex Inc. [104]: is a coating made of permanently attached hydrocarbon 'whiskers'. It is water repellent. No oil repellency was observed. It has good laundering durability. The fabric is permeable to air, stays soft and dries fast.
- OrganoTex® by OrganoClick AB. [105]: is a coating made of 3D-structure of organic "fatty" polymers attached to the fibres using plant-based catalysts. It is water repellent with a spray rating of 100. After 10 washings, the spray rating is 90. No oil repellency test. It has good laundering durability. The fabric is soft and is permeable to air.
- H_2O Repel® by Devan Chemicals [106]: is a fluorine-free coating made of a hydrophobic polymer, which does not require high curing temperatures. It is water repellent with a spray rating of 95 and after 20 washings it has a spray rating of 80. It has a water CA between 140 – 150° and a sliding angle of 11°. No oil repellency was observed. It has good laundering durability. The fabric is permeable to air, soft, UV resistant and with its mechanical properties unchanged.

Table 7: Comparison of commercially available coatings.

Coating	Chemistry	Water Repellency	Oil Repellency	Laundering Durability	Breathability
StainSmart [83] (Miliken& Company)	Fluorochemical	Yes	Yes	Yes 30+ washes	Yes
NUVA N1811 [84] (Archroma)	C6 fluorochemical micro-encapsulated	Yes– 100 spray test (20 washes >80)	Yes – 6 oil (20 washes >4)	Yes 20+ washes	Yes
Lurotex Duo [85] (BASF)	C6 fluorochemical with booster	Yes – 100 spray test (20 washes 90)	Yes – 7 oil (20 washes 6)	Yes 20+ washes	Yes
Asahi Guard E-series [86] (AGC Chemicals Americas)	Aqueous C6 fluorochemical	Yes – 100 spray test (20 washes >80)	Yes – 5 oil	Yes 20+ washes	Yes
Ruco-Guard AFC6 [87] (Rudolf GmBH.)	Aqueous C6 fluorochemical	Yes – 100 spray test (3 washes 100)	Yes – 5 oil (3 washes 2)	Yes	Yes
NanoSphere [88] (Schoeller Technology AG.)	C6 fluorochemical in a matrix with nanoparticles	Yes – 100 spray test (40-50 washes >90)	Yes	Yes 50+ washes	Yes
EverShield [81] (UltraTech International Inc.)	C6 fluorochemical in a polyurethane matrix with dual micro and nanoparticles	Yes – 100 spray test (20 washes >80)	Yes – >7 oil (20 washes >6)	Yes 50+ washes	Yes
Fluorolink P56 [89] (Solvay)	Aqueous polyurethane perfluoropolyether structure with a high molecular weight	Yes – 100 spray test	Yes	Maybe yes	Maybe yes

Coating	Chemistry	Water Repellency	Oil Repellency	Laundering Durability	Breathability
Scotchgard Protector [90] (3M)	C4 fluorochemical	Yes	Yes– some	No	Yes
Unidyne TG-5601 [93] (Daikin Industries Ltd.)	C6 fluorochemical mixed with silicone polymer	Yes – 100 spray test (20 washes >60)	Yes – 6 oil (20 washes <5)	Yes 20+ washes	Yes
Epic [95] (Nextec Applications Inc.)	Fibres encapsulated by an ultrathin silicone polymer	Yes	No	Yes	Yes
Texfin RS-WR [96] (Texchem UK Ltd.)	Silicone polymer	Yes – 100 spray test (10 washes 70)	No	Yes 10+ washes	Yes
POLON-MK-206 [97] (Shin-Etsu Chemical Co. Ltd.)	Silicone polymer	Yes	No	Yes	Yes
Zelan R3 [98] (Huntsman International LLC.)	63% renewable non-GMO plant-based sources	Yes – 100 spray test (30 washes 90)	No	Yes 30+ washes	Yes
Altopel F^3 [99] (Bolger &O' Hearn Inc.)	Aqueous bio-based chemical ingredients	Yes – 100 spray test (20 washes 90)	No	Yes 20+ washes	Yes
ChemStik [100] (Green Theme Technologies LLC.)	Hydrocarbon based hydrophobic polymer	Yes – 100 spray test (100 washes ~100)	No	Yes	Yes
Arkophob [101] (Archroma)	Encapsulated wax	Yes – 100 spray test (20 washes 70)	No	Yes 20+ washes	Yes

Coating	Chemistry	Water Repellency	Oil Repellency	Laundering Durability	Breathability
Ecorepel [102] (Schoeller Technology AG.)	Long paraffin wax chains wrapped in a spiral around the individual fibers	Yes	No	Yes 30+ washes	Yes
Eco Dry [103] (HeiQ Materials AG.)	3D structure hyper-branched hydrocarbon with a polyurethane backbone	Yes – 100 spray test (10 washes and ironing 100)	No	Yes 50+ washes	Yes
Aquapel [104] (Nanotex)	Hydrocarbon polymer ‘whiskers’	Yes	No	Yes	Yes
OrganoTex [105] (OrganoClick AB.)	3D-structureof organic “fatty” polymers	Yes – 100 spray test (10 washes 90)	No	Yes 10+ washes	Yes
H_2O Repel [106] (Devan Chemicals)	Fluorine-free hydrophobic polymer	Yes – 95 spray test (20 washes 80)	No	Yes 20+ washes	Yes

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red.

Table 8: Comparison of additional properties of commercially available coatings.

Coating	Company	Colour Preservation	Lamination Capability	Fiber Properties Preservation (i.e., Strength, Stretch ...)
StainSmart [83]	Miliken& Company	Yes	Maybe yes	Yes
NUVA N1811 [84]	Archroma	Yes	Maybe yes	Yes
Lurotex Duo [85]	BASF	Yes	Probably	Yes
Asahi Guard E-series [86]	AGC Chemicals Americas	Yes	Maybe yes	Yes
Ruco-Guard AFC6 [87]	Rudolf GmBH	Yes	Maybe yes	Yes
NanoSphere [88]	Schoeller Technology AG.	Yes	Maybe yes	Yes
EverShield [81]	UltraTech International Inc.	Yes	Maybe yes	Yes
Fluorolink P56 [89]	Solvay	Yes	Probably	Yes
Scotchgard Protector [90]	3M	Maybe yes	Probably	Yes
Unidyne TG-5601 [93]	Daikin Industries Ltd.	Yes	Yes	Yes
Epic [95]	Nextec Applications Inc.	Yes	Probably	Yes
Texfin RS-WR [96]	Texchem UK Ltd.	Yes	Probably	Yes
POLON-MK-206 [97]	Shin-Etsu Chemical Co. Ltd.	Yes	Probably	Yes
Zelan R3 [98]	Huntsman International LLC.	Yes	Probably	Yes
Altopel F^3 [99]	Bolger &O' Hearn Inc.	Yes	Probably	Yes

Coating	**Company**	**Colour Preservation**	**Lamination Capability**	**Fiber Properties Preservation (i.e., Strength, Stretch ...)**
ChemStik [100]	Green Theme Technologies LLC.	Yes	Yes	Yes
Arkophob FFR [101]	Archroma	Yes	Maybe yes	Yes
Ecorepel [102]	Schoeller Technology AG.	Yes	Maybe yes	Yes
Eco Dry [103]	HeiQ Materials AG.	Yes	Probably	Yes
Aquapel [104]	Nanotex	Yes	Probably	Yes
OrganoTex [105]	OrganoClick AB.	Yes	Probably	Yes
H_2O Repel [106]	Devan Chemicals	Yes	Probably	Yes

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow.

3.4.3 Discussion of commercial coatings

Long chain C8-based fluorochemical coatings have been very successful commercial liquid repellent coatings owing to their superior properties. They can repel a broad range of liquids ranging from high surface tension liquids such as water to low surface tension liquids such as oils due to the very low surface free energy imparted to the coated substrate by the fluorine atoms. These coatings can score 100 out of 100 on the AATCC 22 water repellency spray test and 8 out of 8 on the AATCC 118 oil repellency hydrocarbon resistance test. However, as mentioned earlier, restrictions and bans associated with these coatings have prompted some manufacturers such as 3M [90] to completely shift to more environmental friendly solutions, while others such as the Rudolf group [107] or the CHT group [108] have introduced alternative environmentally friendlier coatings while still offering a C8 fluorochemical option.

Fluorine-based chemicals produce the lowest surface free energy coatings. Thus, the shift in coatings has been to replace long chain C8 fluorochemicals with shorter chain C6 fluorochemicals. C6 fluorochemicals are not associated with the environmentally harmful PFOA and PFOS substances. Nevertheless, since C6 chemicals are still in the fluorochemical family, they might not be entirely environmentally benign and could still pose some risk to the environment. These chemicals are known to be persistent in the environment, although they have low bioaccumulation and toxicity [2]. More comprehensive long-term assessment studies are necessary to completely determine their safety.

The number of fluorine groups is lower in C6 fluorochemicals as opposed to C8 fluorochemicals; thus, the performance of these coatings should be reduced with a narrower range of repelled liquids. As can be seen in Table 7, C6 fluorochemical-based coatings have very good water repellency, as good as C8 based coatings, and can also score 100 out of 100 on the AATCC 22 water repellency spray test. Water is the easiest liquid to repel due to its very high surface tension (72.8 mN/m) [20]. The AATCC 118 oil repellency test grade is lower for C6 fluorochemical-based coatings, values ranging between 5 and 7 out of 8. Some of these coatings will have problems repelling low surface tension liquids such as the chemical warfare agent GD (see Table 4). Nevertheless, all these coatings are at least in the omniphobic region of repellency. The best performing coatings had complex formulations such as inclusion of nanoparticles. These additions help to increase surface roughness and in turn repellency properties as discussed previously. In particular, the EverShield [81] coating by UltraTech International Inc. showed superior properties. It combines C6 fluorochemicals with micro- and nano-sized particles. When compared with a Quarpel treated fabric, the EverShield coating freshly applied had worse repellency towards n-octane (21.6 mN/m [24]), however, the EverShield coating resisted wetting by n-octane after five washes, while the Quarpel coating wetted out with n-octane after one wash [34].

A fluorine-free, environmentally friendly alternative coating type is based on silicone (polymerized siloxanes). Silicone is not known to be persistent or be highly hazardous to the environment and human health [2]. Siloxane polymers typically consist of a backbone of alternating silicon and oxygen bonds with organic substituent groups attached to the silicon atom. These polymers are considered low surface free energy substances as well, although they are not as low as fluorine. These coatings easily repel water with very good water repellency similar to the fluorine-based coatings, 100 out of 100 on the AATCC 22 water repellency spray test. Since the surface free energy of silicon is not as low as fluorine, these coatings will not be able to repel low surface tension liquids; however, in theory they should be able to repel some oils which are of higher surface tension such as cooking oils. Nonetheless, no oil repellency is reported for the commercial products. Thus, all these coatings are at least in the hydrophobic regime of liquid repellency. In order to improve their performance, Daikin Industries Ltd. mixed C6 fluorochemicals with silicones for its Unidyne TG-5601[93] coating, in order to increase its repellency level to the omniphobic state. The fluorochemical content of this coating should be lower than traditional fluorine-based coatings and in turn be more environmentally friendly, but the coating still contains some fluorine so the potential risk of hazard is still present. Silicone-based coatings have the potential of replacing fluorinated alternatives if their oil repellency properties can be improved through innovative strategies, such as introducing appropriate surface roughness by mixing in nanoparticles of various sizes.

Other fluorine-free alternative coating solutions are based on hydrocarbons such as waxes and even plant extracts. Hydrocarbons are considered very environmentally safe given that they are mostly low hazard, they are readily biodegradable, and they do not bioaccumulate [2]. These coatings show good water repellency, scoring 100 out of 100 on the AATCC 22 water repellency spray test. However, due to their hydrocarbon nature, none of them show any oil repellency, not even the more complex rougher surface coatings. Thus, all these coatings are also at least in the hydrophobic regime of liquid repellency. Once again, this technology has the potential to replace fluorinated alternatives if the oil repellency properties can be improved. However, if only water repellency is necessary such as for a rain coat, then these solutions are the most environmentally benign choices.

In terms of durability, all coatings showed good laundering durability. In particular, the omniphobic EverShield coating from UltraTech International Inc. is rated to 50+ washes, as well as the water repellent Eco Dry coating from HeiQ Materials AG. The water repellent ChemStik coating from Green Theme Technologies LLC is rated even higher at 100+ washes. Also, after 30 washes, the water repellent Zelan R3 coating from Huntsman International LLC has excellent water repellency with a score of 90 out of 100 on the AATCC 22 water repellency spray test. Typically, the coatings do not negatively affect the abrasion resistance, the tensile strength or tear strength of the fabric. Some coatings even improve these properties, for example EverShield, Epic from Nextec Applications Inc., or Arkophob FFR from Archroma. The effect of the coatings on the fabric stretching abilities is usually not mentioned by manufacturers.

Most coatings can be used on many types of fibres such as natural cotton fibres, or synthetic polyester fibres, or blends. Nevertheless, the compatibility of the coating with lamination processes is another property not typically mentioned by companies. Military CB protection often relies on multi-layer material systems with a liquid repellent coating on the outer layer followed by an activated carbon layer. If the outer layer is constructed from a laminate, the ability of the coating to be part of this system without affecting the success of the lamination is important (whether by treating after lamination, or applying pre-lamination such that it does not interfere with the process). It has been shown that laminating already liquid repellent-coated fabric layers can lessen the adhesion and durability of the laminate [34]. The GreenStik technology from Green Theme Technologies LLC presented earlier was used in a laminated fabric, although no other details were given.

An additional important characteristic of these coatings is to not affect a fabric's colour. This does not seem to be a problem, since most companies claim no or minimal colour change when using their treatment on fabrics. However, more critically, the coating should not affect camouflage colours which are paramount in protecting personnel from visual detection. Modern camouflage can be complex and incorporate infrared reflectance to prevent detection using visual aids in particular by night. This might not be a problem for some coatings, given that some of the companies listed above are involved in the military garment market such as Archroma and Schoeller Technology AG, and they should be familiar with these requirements. UltraTech's International Inc. EverShield coating was field tested on army combat uniforms; thus, it should not affect modern camouflage colours.

These coating systems do not negatively affect the thermal comfort of the wearer in a significant way. All of the coatings are permeable to air and do not completely block the pores of the fabric like impermeable rubber based coatings. Thus, the human body's natural cooling mechanisms should not be greatly affected.

In terms of physical comfort, all these new coatings do not add significant weight to the fabric. The fabric is generally soft after treatment with the silicone-based coatings, having very good performance. In particular, the silicone-based coating Unidyne TG-5601 from Daikin Industries Ltd. is reported to have extremely soft hand feel.

The best replacement for C8 based fluorochemical coatings available at the present time is C6 based fluorochemical coatings such as Lurotex Duo from BASF or EverShield from UltraTech International Inc. However, there is still a potential environmental risk associated with them; thus, research should be focused on improving the knowledge of potential long-term hazard, as well as improving properties of more environmentally benign alternative coatings such as silicone or hydrocarbon based coatings.

3.5 Tested coatings (TRL 5-7)

Tested coatings as defined here are TRL 5-7 coatings not yet available commercially that have not been proven to work in their final form. The coatings have been validated to work in a simulated environment and the prototypes are ready for demonstration in an operational environment such as field testing of the prototype. Reports of technology at this level are hard to find. Usually, most proof-of-concept coatings have not been tested beyond laboratory conditions due to numerous factors such as cost, or difficulty to scale up. If a coating has potential and efforts are made to bring it to market, the results are not typically published in the open literature and only in internal reports. Similarly if a company is developing a new product, the reports at this stage would not be available for the general public. A summary of the few coatings in this category with available information can be found in Table 9.

Table 9: Comparison of tested coatings.

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Truong et al. [25]	C8fluorochemical – silicone: Heptadecafluorodecyl polyhedral oligomeric silsesquioxane (Fluoro-POSS) cage-like molecule and Tecnoflon BR 9151	Yes CA 138° to 147°	Yes CA n-hexadecane 94° to 104° (oil 3)	Yes
Artus et al. [109]	Silicone nanofilaments	Yes CA >150°	No	Maybe yes

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow. Properties that should be avoided are portrayed in red.

3.5.1 Tested fluorine-based coatings

Truong et al. published a report on a pilot-scale coating of fabrics with a fluorochemical silicone blended coating developed by the Massachusetts Institute of Technology and NSRDEC [25]. In particular, a blend of heptadecafluorodecyl polyhedral oligomeric silsesquioxane (Fluoro-POSS) cage-like molecule and Tecnoflon BR 9151, a fluorinated elastomer, was used to coat nylon fabrics. In previous laboratory studies, an army combat uniform made of 50 % cotton –50 % nylon blend and a polyester fabric were also coated. The pilot scale fabrics were coated in a continuous pad-dry-cure textile finishing process. The best fabrics had a spray rating of 100 out of 100 on the AATCC 22 water repellency spray test. Liquid CAs were measured with 10 µL droplets, yielding a water CA between 138° and 147°, and n-hexadecane CA between 94° and 104°. N-Hexadecane is rated as oil grade 3 on the AATCC 118 oil repellency test grade, thus, this coating has at least an oil score of 3. The coating could be classified at the low end of the omniphobic regime, although the oil repellency is not very high. CAs were also measured for chemical warfare agent simulants. The coatings had dimethyl sulfoxide (Lewisite blister agent simulant) CA between 126° and 132°, and dimethyl methyl phosphonate (GB nerve agent simulant) CA between 87° and 93°. The coated fabric was also able to induce roll off and shed dimethyl methyl phosphonate droplets better than Quarpel treated fabrics. The fabric's air permeability was not affected by the coating. Also, the weight, thickness and stiffness of the fabric were not affected.

3.5.2 Tested fluorine-free based coatings

Artus et al. published a report on a pilot-scale coating of fabrics with silicone nanofilaments [109]. The filaments provide additional roughness to the fibers, while the silicone imparts a low surface tension to the fibers. The coating was applied using a simple a one-step chemical vapour deposition process in the gas phase at room temperature and normal pressure. A polyester fabric of size 1.4 m x 1.55 m, a coat of a polyester suit, and glass panes were coated. Liquid CAs were measured with 10 µL droplets. The coatings had high water repellency, CA >150°. A water puddle on the fabric was able to slide easily and collect dust particles, while artificial rain drops were able to bounce off and not wet the suit coat. No oil repellency is expected for this type of chemistry. Thus, the coating can only be classified in the superhydrophobic regime.

3.5.3 Discussion of tested coatings

As mentioned earlier there are not a lot of reports of coatings at this level in the open literature. Similar to the commercial coatings, only the coating containing fluorine shows some oil repellency properties. Truong et al. [25] fabricated a coating based on fluorine and silicone. The fluorine content of the coating poses a risk to the environment; however, since the coating also contains the much safer silicone chemical and is not made of C8 based fluorochemicals, the coating is not as hazardous as the traditional C8 based coatings. The coating is water repellent and also has some oil repellency. The oil repellency is due to the fluorine component, but it is not very high due to the silicone component. However, some preliminary tests with chemical warfare simulants show promising repellency performance. The thermal and physical comfort properties of the fabric were not affected by the coating. The coating shows potential, but more testing and work is required to improve properties, or environmental safety.

On the other hand, Artus et al. [109] only used silicone nanofilaments, a more environmentally safe substance. Nonetheless, once again similar to commercial based coatings, this silicone coating only has water repellency and no repellency towards oils.

3.6 Proof-of-concept coatings (TRL 1-4)

Proof-of-concept coatings are coatings at the earliest technology development levels. Research on these coatings ranges from basic principles observed to tests performed in the laboratory. This is a very active field of research and numerous coating systems have been developed and reported in the literature. Many review articles have tried to summarize work done in this field such as Zhou et al. [47], or Li et al. [110], or Cortese et al. [111]. This section will focus and compare only some of these coatings. Nevertheless, due to a lack of standard test methods, it is sometimes difficult to compare amongst different coatings, and to commercially available coatings, since laboratory research reports usually do not use standardized test methods. In addition, some reports only present data from a small set of experiments; thus, it is hard to determine the full potential of the coating. For example, most reports only present results from oil repellency tests with n-hexadecane, which has only a score of 3 on the AATCC 118 oil repellency test grade, and they do not test with other oils with lower surface tension in order to determine the lowest surface tension liquid their coating can repel. A brief selection of proof-of-concept coatings will be discussed in this section and a summary of those discussed can be found in Table 10. In this table, the most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while less desirable properties are in darker yellow. Properties that should be avoided are portrayed in red. Additional proof-of-concept coatings can be found in Annex A, Table 16 with similar colour coding (these additional coatings have similar chemistries as the coatings discussed in this section, and some are alternative coatings reported by the same group).

3.6.1 Proof-of-concept fluorine-based coatings

Reports on fluorine-based coatings are very abundant in the literature. In particular, C8 fluorochemical-based coatings are still being developed due to their excellent water and oil repellency. Nonetheless, alternative coatings based on C6 and C4 fluorochemicals are also starting to appear. The fluorine-based coatings discussed in this section show the diversity of proof-of-concept coatings, and have liquid repellency properties ranging from superhydrophobic to superomniphobic. These coatings include those developed by:

- Deng et al. [49] who used radiation-induced graft polymerization to covalently attach a commercially available C4 based fluorinated acrylate monomer, 1H,1H,2H,2H-nonafluorohexyl-1-acrylate, onto cotton. The water CA was 155°. The liquid CAs were greater than 150° in the entire pH range from 0 to 14 and after soaking in 10% sulfuric acid at room temperature overnight. The coating resists liquids with a surface tension higher than 30 mN/m, and is superhydrophobic with a low degree of oleophobicity. The laundering durability was tested using the accelerated laundering test according to the AATCC 61–2006 [48] standard method under conditions 2A and 5A using a 0.15% standard without optical brightener detergent in washing solution and 50 stainless steel balls. The coating had good laundering durability for 10 accelerated laundering cycles, which is equivalent to 50 commercial or domestic launderings. However, if the coating was soaked in water for 72 h and dried after washing, the coating was durable to 50 accelerated laundering cycles, which is equivalent to 250 commercial or domestic launderings. This is due to the detergent sorption onto the coating. The authors also predict it is possible to use their technique for large scale coating fabrication.
- Malshe et al. [112] who used atmospheric pressure glow discharge plasma graft polymerization to covalently attach a C6 fluorocarbon monomer, 2-(perfluorohexyl)ethyl acrylate, onto the front of a 50 % nylon – 50 % cotton fabric. This fabric was already grafted with polydiallyldimethyl ammonium chloride for anti-bacterial properties. In particular, the fabric had high anti-bacterial capability against the bacterial colonies of *K. pneumoniae* and *S. aureus*. Liquid CAs were measured with 10 µL droplets. The water CA was 144°, while the n-dodecane CA was 132°. The coating had a score of 8 out of 8 in the AATCC 193 test method. It also had a score of 5out of 8 on the AATCC 118 oil repellency test, thus, it resists liquids with a surface tension higher than 25mN/m. The coating could be considered to be in the omniphobic regime. Only the front surface of the fabric had the repellent treatment, while the back surface of the fabric was still hydrophilic, thus, the fabric was capable of wicking sweat and minimizing heat stress. The coating is covalently attached to the fabric; as a result some laundering durability is expected. The coating has potential to protect against CB warfare agents.
- Zou et al. [53] who used a C1 based fluorochemical diblock copolymer, poly(glycidyl methacrylate)-block-poly(2,2,2-trifluoroethyl methacrylate), to coat cotton fabrics. The inexpensive poly(2,2,2-trifluoroethyl methacrylate) block imparted a low surface free energy, while the poly(glycidyl methacrylate) block covalently attached the polymer to the cotton fibers as well as increasing durability through its self-cross-linking. The block copolymer formed micellar aggregates with the partially-cross-linked poly(glycidyl methacrylate) blocks forming the core and the poly(2,2,2-trifluoroethyl methacrylate) blocks forming the corona. These aggregates formed nanobumps and created a nanoscale roughness on the cotton fibres. The nanobumps had diameters ranging between 10 and 50 nm. The cotton fabrics were coated by a solution dipping method followed by thermal annealing. Liquid CAs were measured with 5 µL droplets, while sliding angles were measured with 20 µL droplets. The water CA was 163° with a sliding angle of 3°, which leads to classifying the coating as superhydrophobic. The water CA was also >150° and sliding angle <10° after the coated fabric was soaked in ethanol, acetone, tetrahydrofuran, dimethyl formamide, trifluorotoluene, acidic water solution pH 1, and basic water solution pH 14. The coating withstood ultrasonication treatment and refluxing in tetrahydrofuran or trifluorotoluene. The laundry durability was tested with an in-house laboratory flask method. The coating

maintained its water repellency after 50 laundering cycles and after mechanical abrasion with sandpaper, an in-house method. The coating also resisted exposure to ultraviolet irradiation.

- Xiong et al. [113] who used a C8 based fluorochemical and silicone diblock copolymer, poly-[3-(triisopropyloxysilyl)propyl methacrylate]-block-poly-[2-(perfluorooctyl)ethyl methacrylate], to coat cotton fabrics. The fluorinated block imparted a low surface free energy, while the silicone block underwent a sol-gel process to self-cross-link and covalently attach to the cotton fibers. The cotton fabrics were coated by a solution dipping method followed by thermal annealing. Liquid CAs were measured with 5 µL droplets. The water CA was 164° and the sliding angle was 2°. The CAs for diiodomethane, hexadecane, motor oil, cooking oil, pump oil, and used pump oil were 153, 155, 154, 156, 157, and 152°, respectively. The coating can be classified in the superomniphobic regime. The laundry durability was tested with an in-house laboratory flask method. The coating had good laundering durability for 50 laundering cycles. The tensile strength and extension at break of the fabric did not change with the coating treatment.

- Zhou et al. [114] who used a commonly-used and commercially available fluorochemical, poly(vinylidene fluoride-co-hexafluoropropylene), C8 based fluorochemical-silicone, 1H,1H,2H,2H-perfluorodecyltriethoxysilane, and silica nanoparticles, to coat polyester fabrics. The coating can also be used on cotton and wool fabrics. Two sequential dip coating steps were used to coat the fabric. The silica nanoparticles had an average size of 150 nm and provided nanoscale roughness to the coating, while the fluorochemicals provided a low surface free energy as well as immobilization of the particles and self-healing properties. The final coating had a thickness of about 250 nm. Liquid CAs were measured with 10 µL droplets. The water CA was 172° and the contact angle hysteresis was 2°. The CAs for soybean cooking oil and n-hexadecane were respectively 165 and 160°, while the corresponding CA hysteresis was 5 and 7°. The coating can be classified in the superomniphobic regime. The CA was maintained after the coated fabric was soaked in boiling coffee, acidic water solution pH 1, and basic water solution pH 14. The washing durability was evaluated using AATCC 61-2006 [48] test No. 2A. The coating had excellent laundering durability for 600 home laundering cycles. The coating maintained its repellency after 8000 cycles of mechanical abrasion using the Martindale method according to ASTM D4966 [115]. After chemical damage by plasma treatment, the coating can self-heal and restore its properties after a short thermal curing step. The coating had almost no influence on the air permeability of the fabric.

- Zahid et al. [116] who used a commercially available inexpensive C6 perfluorinated acrylic copolymer, DuPont’s Capstone ST-100, silica nanoparticles and a polydimethylsiloxane resin to coat cotton fabrics. First, the cotton fabrics were coated with the polymer and nanoparticles by dip coating and thermal curing. Then, the resin was applied using a rod coater followed by room temperature curing. The top resin layer decreased the roughness of the coating, which affected the repellency properties. Liquid CAs were measured with 5µL droplets, while the sliding angle and shedding angle measurements used 20µL and 8 µL droplets, respectively. The water CA was 147°, the sliding angle was <20°, and the shedding angle was 17°. The coating can be classified in the hydrophobic regime. The CA was maintained after the coated fabric underwent ultrasonication washing for three cycles. The coating maintained its repellency after 30 cycles of mechanical abrasion.

- Leng et al. [117] who used a C8 based fluorochemical-silicone, 1H,1H,2H,2H-perfluorodecyltrichlorosilane, and two different sizes silica micro- and nanoparticles to coat cotton fabrics. The covalently attached microparticles had an average size of 800 nm, while the subsequent electrostatically adsorbed nanoparticles had an average size of 100, 160, or 220 nm. The system was immobilized by the cross-linker silicon tetrachloride. This multi-scale roughness provided enhanced liquid repellency. Liquid CAs were measured with 5μL droplets, while the shedding angle measurement used 20 μL droplets. The water CA was 160° and the shedding angle was 5°. The CA for n-hexadecane was 151°, while the corresponding shedding angle was 10°. The coating can be classified in the superomniphobic regime. The CA was maintained after the coated fabric underwent ultrasonication / ethanol washing.

- Shillingford et al.[118] who fabricated slippery lubricant-infused porous surfaces (SLIPS) by infusing a perfluoropolyether lubricant, DuPont's Krytox 102, in functionalized silica microparticles with C6 fluorochemical-silicone, 1H,1H,2H,2H-perfluorooctyltriethoxysilane, or C10 based fluorochemical-silicone, perfluorododecyl-1H,1H,2H,2H-triethoxysilane, that were coated onto cotton and polyester fabrics. The SLIPS design does not use the traditional air trapping method to improve repellency, instead it uses a lubricating liquid which is anchored in a chemically similar, texturized solid surface. The lubricating liquid should provide a stable interface and be hard to displace. First, the cotton was functionalized with silica microparticles, followed by fluorosilanization, and finally lubrication with Krytox. The microparticles had an average size of 150 to 500 nm. Liquid CAs were measured with 10 μL droplets. The water CAs for muslin cotton or dense polyester were respectively 110 and 145°, while the contact angle hysteresis was 17 and 8°. The AATCC 193 aqueous liquid repellency test grade for muslin cotton or dense polyester was >5 out of 8, and 8 out of 8, respectively. The AATCC 118 oil repellency test grade for muslin cotton or dense polyester was >5 out of 8, and 8 out of 8, respectively. It is hard to classify this coating since its properties do not fit in the typical CA values chart. This could be due to the unique repellency mechanism of this system. The coating can be classified in the omniphobic regime, but its oil repellency properties are much higher than this range. The coatings maintained performance after abrasion tests, twisting and rubbing with a Kimwipe and withstood washing machine cycles. The surface also maintains performance under pressure. The lubricated fabric showed a decrease in breathability, but there are still spaces present through which air and water vapor can flow. SLIPS technology is currently commercialized by Adaptive Surface Technologies Inc. for solid surfaces such as metal, plastics, or glass [119].

3.6.2 Proof-of-concept fluorine-free coatings

Research into alternative fluorine-free based coatings, in particular silicone-based finishes, is also increasing in the literature due to the need to find a benign alternative to fluorine-based systems. Nonetheless, the performance of these coatings in terms of liquid repellency is similar to commercial finishes, having very good water repellency properties, but no oil repellency. The coatings are typically in the superhydrophobic range, while some systems are in the hydrophobic regime. Their interest here is primarily as a potential basis for future developments with more omniphobic characteristics. A summary comparison is given in Table 10. Some of these coatings were developed by:

- Zhang et al. [120] who used air low temperature plasma with glow discharge at a pressure of 10 Pa induced grafting polymerization to attach 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane onto cotton fabrics. A dense and uniform thin film was produced on the surface of the cotton fabric. Liquid CAs were measured with 5 μL droplets. The water CA was 157°.

The coating can be classified in the superhydrophobic regime. The laundering durability was evaluated using the AATCC 22-1997 standard test. The coating had good laundering durability for 30 laundering cycles.

- Grozea et al. [121] used an aqueous solution containing a silicone-based graft copolymer, poly[(oligo(ethylene glycol) methacrylate)-co-(2-hydroxyethyl methacrylate)-co-(n-butyl methacrylate)-co-(methyl methacrylate)]-graft-poly(dimethylsiloxane), to coat cotton fabrics. The poly(dimethylsiloxane) block imparted a low surface free energy, the oligo(ethylene glycol) methacrylate component imparted water dispersibility, the 2-hydroxyethyl methacrylate component self-cross-linked around the cotton, while the remaining components helped in the cross-linking process. The block copolymer formed micellar aggregates with the poly(dimethylsiloxane) block forming the corona, while the other block formed the core. These aggregates formed nanobumps and created a nanoscale roughness on the cotton fibres. The cotton fabrics were coated by an aqueous solution dipping method followed by thermal annealing. Liquid CAs were measured with 5 μL droplets, while shedding angles were measured with 10 μL droplets. The water CA was 152° and the shedding angle was 32°. No hexadecane repellency was observed. The coating can be classified in the hydrophobic regime. The laundry durability was tested with an in-house laboratory flask method. The coating had good laundering durability for 50 laundering cycles.
- Hou et al. [122] covalently grafted methacryl-heptaisobutylpolyhedral oligomeric silsesquioxane (POSS) cage-like molecule onto coat cotton fabrics. The fibers were first modified with mercaptosilanes followed by photoinduced thiol-ene click coupling with methacryl-heptaisobutyl POSS. This system formed nanoscale protrusions and created a nanoscale roughness on the cotton fibres. The coating was also applied to polyester fabrics, filter papers and melamine sponges. Liquid CAs were measured with 5 μL droplets, while the sliding angle measurement used 8 μL droplets. The water CA was 159° and the sliding angle was 7°. No oil repellency was observed. The coating can be classified in the superhydrophobic regime. The repellency was maintained for water droplets with pH values ranging from 1 to 14, and after the coated fabric was immersed in acidic water solution pH 2, and basic water solution pH 12. The coating withstood ultraviolet irradiation. The coating had good washing durability assessed by ultrasonication in tap water. The coating maintained its repellency after mechanical abrasion with sandpaper. The tensile strength and air permeability of the coated fabric decreased, while the elongation at break increased.
- Wang et al. [123] used hexadecyltrimethoxysilane with 3-glycidoxypropyltrimethoxysilane attached to silica nanoparticles to coat cotton fabrics. The fabric was coated by dip coating and thermal curing. The particles had an average size of 250 nm. The coating was also used on polyester and wool fabrics. The water CA was 170° and the sliding angle was 10°. No oil repellency was observed. The coating can be classified in the superhydrophobic regime. The laundering durability was evaluated using the Australian Standard AS 2001.1.4 (withdrawn) standard test. The coating had good laundering durability for 50 home laundering cycles. When the silicone was replaced with a C8 fluorochemical-silicone, tridecafluorooctyltriethoxysilane, the water CA and laundering durability were similar.
- Liu et al. [124] used hexadecyltrimethoxysilane with 3-azidopropyltriethoxysilane attached to silica nanoparticles to coat cotton fabrics. The coated fabric was prepared by solution dipping using the double-nip-double-dip type dye padder followed by ultraviolet curing. The particles had an average size of 100 nm, while the coating had a thickness of 190 nm. Liquid CAs were measured with 5 μL droplets. The water CA was 152°. No oil repellency was

observed. The coating can be classified in the superhydrophobic regime based on the CA, but could be in the hydrophobic regime since the sliding angle is not reported. The laundering durability was evaluated using the AATCC 61-2007 [48] standard test. The coating had good laundering durability for 30 home laundering cycles.

- Hoefnagels et al. [125] used a silicone-based polymer, polydimethylsiloxane, attached to silica nanoparticles that bonded covalently to cotton fabrics. The particles range in size from 500 nm to 2 µm. Both liquid CAs and shedding angles were measured with 10 µL droplets. The water CA was 155° and the shedding angle was 15°. No repellency towards n-hexadecane and sunflower oil. The coating can be classified in the superhydrophobic regime. The CA was maintained after the coated fabric underwent ultrasonication ethanol washing. When polydimethylsiloxane was replaced with a C8 fluorochemical-silicone, 1H,1H,2H,2H-perfluorodecyltrichlorosilane, the water CA is similar, but the coating has some oil repellency. The CA for sunflower oil or n-hexadecane was 140 and 135°, respectively. The oil repellency is in the oleophobic regime.
- Gao et al. [126] used hexadecyltrimethoxysilane and two different sizes of silica micro- and nanoparticles to coat cotton fabrics. The fabric was coated by a two-step dip-pad-dry-cure method, first attaching microparticles with an average size of 990 nm, followed by a layer of nanoparticles with average size of 110 nm, and finally a dip in a hexadecyltrimethoxysilane solution followed by air drying. This multi-scale roughness led to enhanced liquid repellency. Liquid CAs were measured with 3 µL droplets. The water CA was 160°. The coating can be classified in the superhydrophobic regime based on the CA. No oils were tested. The coating did not affect the tensile strength of the fabric, although it did cause a decrease in the air permeability.
- Zhu et al. [127] used zinc oxide nanoparticles sandwiched between two polydimethylsiloxane layers to coat cotton fabrics. The fabric was coated by repeated dip coating steps and thermal curing. The water CA was 166° and a sliding angle of 8°. No oil repellency was observed. The coating can be classified in the superhydrophobic regime. The repellency was not affected after the coated fabric was soaked in water solutions with a pH ranging from 1 to 14. The coating provided ultraviolet protection and resisted ultraviolet irradiation. The laundering durability was evaluated using the AATCC 61-2006 [48] standard test under condition 2A. The coating had good laundering durability for 20 laundering cycles or 100 home laundering cycles. The coating had good mechanical abrasion resistance as assessed by GB/T 3920-2008 standard [128]. The coating caused a decrease in the tensile strength and air permeability of the fabric.
- Zhong et al. [129] grafted aliphatic fatty chains using acetic anhydride onto cotton fabrics. Fatty acids are biocompatible, biodegradable, and renewable; however, they do not have very low surface free energy. The coated fabric was prepared by solution dipping followed by microwave curing. Liquid CAs were measured with 5 µL droplets. The highest water CA was 139°. No oil repellency was observed. The coating can be classified in the hydrophobic regime. The laundering durability was evaluated using a modified version of AATCC 61-2003 [48] standard test in a laboratory flask. The coating had good washing durability. The repellency was maintained after the coated fabric underwent 37 laundering cycles equivalent to 185 normal home washing; however, this sample had a lower tensile strength than pristine cotton.
- Li et al. [130] used helium low temperature plasma with glow discharge at a pressure of 40 Pa induced grafting polymerization to attach stearyl methacrylate onto cotton fabrics. The coated fabric was prepared by solution dipping. Liquid CAs were measured with 5 µL

droplets. The highest water CA was 149°. No oil repellency was observed. The coating can be classified in the hydrophobic regime. The laundering durability was evaluated using AATCC 22-1997 standard test in a bath pot. The coating had good washing durability. The repellency was maintained after the coated fabric underwent 30 laundering cycles. Fabric objective hand evaluation was done according to AATCC 202-2013 [131]. The relative hand value of the coated fabric was slightly poorer than pristine cotton. Also, the mechanical breaking strength slightly declined.

- Gu et al. [132] used the plant-sourced polyphenol tannic acid, and iron (III) chloride, with 1-octadecylamine, to coat cotton fabrics. The coated fabric was prepared by aqueous solution dipping. Liquid CAs were measured with 5 μL droplets. The highest water CA was 145°. No oil repellency was observed. The coating can be classified in the hydrophobic regime. The repellency was maintained for water droplets after the coated fabric was immersed in hydrochloric acid (pH 1), saturated sodium chloride solution (pH 7), sodium hydroxide solution (pH 12), and acetone. The laundering durability was evaluated using AATCC 61-2006 [48] standard test. The coating had good washing durability. The repellency was maintained after the coated fabric underwent 25 laundering cycles equivalent to 125 normal home washing. The handling properties were measured according to GB/T 18318.1-2009 standard [133]. The bending length and rigidity values were slightly higher than pristine cotton. The air permeability was evaluated according to ISO 9237:1995 standard [61]. The air permeability slightly decreased after the coating process.
- Cai et al. [134] used reduced graphene oxide nanosheets to coat cotton fabrics. The fabric was coated by dip coating and drying followed by a thermal reduction step to reduce the graphene oxide. The cotton fabric changed colour from white to black. The water CA was 125°. No oil repellency was observed. The coating can be classified in the hydrophobic regime. The coating provided ultraviolet protection. The coated cotton was flexible and was also electrical conductive. The laundering durability was evaluated using the AATCC 61-2006 [48] standard test. The coating had good laundering durability for 8 laundering cycles or 40 home laundering cycles.

Table 10: Comparison of proof-of-concept coatings.

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Deng et al. [49]	C4 fluorochemical: 1H,1H,2H,2H-nonafluorohexyl-1-acrylate	Yes CA 155°	Some – oils higher than 30 mN/m (close to oil 1)	Yes 50 washes
Malshe et al. [112]	C6 fluorochemical: 2-(perfluorohexyl)ethyl acrylate	Yes CA 144°	Yes CA n-dodecane132°(oil 5)	Maybe yes
Zou et al. [53]	C1 based fluorochemical: poly(glycidyl methacrylate)-block-poly(2,2,2-trifluoroethyl methacrylate) that forms nanobumps	Yes CA 163°	No	Yes 50 washes
Xiong et al.[113]	C8 fluorochemical – silicone: poly-[3-(triisopropyloxysilyl)propyl methacrylate]-block-poly-[2-(perfluorooctyl)ethyl methacrylate]	Yes CA 164°	Yes CA n-hexadecane 155° (oil 3)	Yes 50 washes
Zhou et al. [114]	Fluorochemical: poly(vinylidene fluoride-co-hexafluoropropylene), C8 based fluorochemical-silicone: 1H,1H,2H,2H-perfluorodecyltriethoxysilane, and Silica nanoparticles	Yes CA 172°	Yes CA n-hexadecane 160° (oil 3)	Yes 600 washes
Zahid et al. [116]	C6 perfluorinated acrylic copolymer: DuPont's Capstone ST-100, and Silica nanoparticles in a polydimethylsiloxane resin	Yes CA 147°	Maybe yes	Yes 3 washes
Leng et al. [117]	C8 based fluorochemical-silicone: 1H,1H,2H,2H-perfluorodecyltrichlorosilane, and two different sizes Silica micro- and nanoparticles	Yes CA 160°	Yes CA n-hexadecane 151° (oil 3)	Maybe yes

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Shillingford et al. [118]	SLIPS: Perfluoropolyether lubricant, DuPont's Krytox 102, infused in a C6 or C10 fluorochemical-silicone: 1H,1H,2H,2H-perfluorooctyltriethoxysilane or per-fluorododecyl-1H,1H,2H,2H-triethoxysilane, functionalized Silica microparticles coating	Yes Cotton – CA 110° Polyester– CA 145°	Yes Cotton – oil >5 Polyester – oil 8	Yes
Zhang et al. [120]	Silicone: 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclo-tetrasiloxane	Yes CA 157°	No	Yes 30 washes
Grozea et al. [121]	Aqueous silicone: poly[(oligo(ethylene glycol) methacrylate)-co-(2-hydroxyethyl methacrylate)-co-(n-butyl methacrylate)-co-(methyl methacrylate)]-graft-poly(dimethylsiloxane) that forms Nanobumps	Yes CA 152°	No	Yes 50 washes
Hou et al. [122]	Silicone: methacryl-heptaisobutyl polyhedral oligomeric silsesquioxane (POSS) cage-like molecule that forms nanoscale protrusions	Yes CA 159°	No	Yes
Wang et al. [123]	Silicone: hexadecyltrimethoxysilane with 3-glycidoxypropyltrimethoxysilane attached to Silica nanoparticles	Yes CA 170°	No	Yes 50 washes
Liu et al. [124]	Silicone: hexadecyltrimethoxysilane with 3-azidopropyltriethoxysilaneattached to Silica nanoparticles	Yes CA 152°	No	Yes 30 washes
Hoefnagels et al. [125]	Silicone: Polydimethylsiloxane attached to Silica nanoparticles	Yes CA 155°	No	Maybe yes
Gao et al. [126]	Silicone: hexadecyltrimethoxysilane, and two different sizes Silica micro- and nanoparticles	Yes CA 162°	Not tested but maybe not	Maybe yes
Zhu et al. [127]	Silicone: Polydimethylsiloxane–Zinc oxide nanoparticles–polydimethylsiloxane	Yes CA 165°	No	Yes 100 washes

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Zhong et al. [129]	Aliphatic fatty chains	Yes CA 139°	No	Yes 185 washes
Li et al. [130]	Stearyl methacrylate	Yes CA 149°	No	Yes 30 washes
Gu et al. [132]	Plant sourced polyphenol tannic acid and iron (III) chloride with 1-octadecylamine	Yes CA 145°	No	Yes 125 washes
Cai et al. [134]	Reduced graphene oxide nanosheets	Yes CA 125°	No	Yes 40 washes

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while less desirable properties are in darker yellow. Properties that should be avoided are portrayed in red.

3.6.3 Discussion of proof-of-concept coatings

There are numerous reports in the literature on proof-of-concept liquid repellent coatings at low TRLs. Diverse chemistries, fabrication, and curing methods have been reported; nevertheless, there is still a strong research focus on fluorochemical-based textile finishes. Long chain fluorinated chemicals such as chemicals based on C8 chemistry are still being developed. Laboratories typically synthesize their own polymers for their coatings, thus, they can make the chemical they desire. These C8 fluorochemical-based coatings have the best performance in terms of water and oil repellency. The high amount of fluorine decreases the surface free energy of the textile and helps to provide broad range repellency. However, to minimize environmental issues, researchers have tried to strongly bind the polymer to the textile and to add another low surface tension component to the coating system, silicone, to reduce the amount of fluorine. Also, nanoparticles were added to many coatings to increase roughness and in turn repellency properties. The contact angles for water and n-hexadecane were greater than 150° with low sliding angles classifying these coatings as superomniphobic, such as the coating by Zhou et al. [114]. The AATCC 22 water repellency spray test and the AATCC 118 oil repellency hydrocarbon resistance test were not performed on these coatings. Since the coatings have such high repellency towards water, they would probably score 100 out of 100 on the AATCC 22 test. In terms of the AATCC 118 test, n-hexadecane is also used in this test and is classified as oil grade 3 out of 8. Thus, the coating would score at least 3 on this scale. The contact angle for n-hexadecane is high, thus, there is a strong probability the coatings would be able to score even better on this test if tested; one coating by Shillingford et al. [118] was tested using the AATCC 118 test and the oil repellency was >5 of 8 for coated cotton and 8 of 8 for coated polyester, but no contact angle values for these liquids were given for comparison.

Short chain fluorochemicals were also used in coating (such as C6 or C4 fluorochemicals as opposed to C8). The water repellency was good, but not as high as C8 fluorochemical coatings. The oil repellency was also not as good due to lower fluorine content. However, a C6 fluorochemical only based coating by Malshe et al. [112] had an oil repellency score of 5 out of 8 on the AATCC 118 test classifying this coating in the omniphobic regime. This value compares well with some aqueous C6 fluorochemical commercial coatings such as the Asahi Guard E-series by AGC Chemicals Americas, or the Ruco-Guard AFC6 by Rudolf GmBH.

The most common fluorochemical alternative finishes are based on silicone. They can also impart a low surface free energy to materials, and additionally, these chemicals can form covalent bonds with textiles such as cotton which improves durability. The water repellency was high, similar to fluorochemical finishes. The contact angles for water were greater than 150°, placing these coatings in the superhydrophobic range. Once again, no standard tests were performed on these coatings, but they would probably score 100 out of 100 on the AATCC 22 test. Similar to commercial silicone-based coatings, none of these coatings had any oil repellency. No oil repellency was reported for complex coatings either where nanoparticles were added to increase coating roughness. One coating by Gao et al. [126] used two different size nanoparticles to create a very rough hierarchical structure (a surface with two scales of surface roughness). The water contact angle was very high at 160° for 3 μL droplets. There is a chance this coating might have some oil repellency, albeit not very high, but the authors did not perform any test to confirm or deny this property.

Not as many reports have focused on other fluorine-free alternative finishes besides silicone. Other alternative coatings developed included substances such as aliphatic fatty chains, stearyl methacrylate, or plant phenols. They have good water repellency, with contact angles close to 150°. However, they are in the hydrophobic range, not the superhydrophobic range similar to the silicone-based coatings. Once again these alternative coatings also have no oil repellency.

In terms of durability, the coatings that were tested showed good laundering durability. This was typically due to the chemical bonding of the coating to the textile. In particular, the coating by Zhou et al. [114] was listed to 600 home machine laundering cycles. Most of the coatings were not tested for abrasion resistance or tear strength of the fabric. The ones that were tested had good resistance to abrasion. Once again, the coating by Zhou et al. was listed as capable of resisting 8000 cycles of mechanical abrasion using the Martindale method according to ASTM D4966 [115].

In general, these coatings did not negatively affect the thermal comfort of the wearer. All of the coatings are permeable to air and did not completely block the pores of the fabric, although some coatings showed a slight decrease in their air permeability as opposed to pristine cotton such as the coatings by Shillingford et al. [118], and Hou et al. [122].

These studies were typically performed on coatings applied to pristine textiles such as white cotton fabric swatches. The coatings did not considerably affect the colour of the swatches. It is uncertain how the coatings will affect dyes and pigments used to colour garments, and in particular camouflage fabrics. Malshe et al. [112] coated a 50 % nylon – 50 % cotton fabric with military camouflage print, and it did not appear the treatment affected the colours; however, they did not specifically test for this. Nevertheless, the coating by Cai et al. [134] used reduced graphene oxide nanosheets, and these changed the white colour of the cotton to black.

It is also uncertain if these coatings can be used in laminate systems. The coatings might be fine in such a system if the fabric is coated first with the repellent treatment and then laminated. The properties of the other layers should not be affected by the repellent treatment. However, the lamination durability might be weakened. Ideally, the lamination should be performed first, but it is hard to predict if this will work with these coatings.

Some of these coatings had additional properties. For example, the coating by Malshe et al. [112] was also antimicrobial. The coating by Zhou et al. [114] could self-heal after chemical damage by plasma treatment. The coating by Zhu et al. [127] offered ultraviolet protection and resisted ultraviolet irradiation, while the coating by Cai et al. [134] was electrically conductive.

The coatings were fabricated either with substances which are commercially available and then cured or with in-house custom synthesized chemicals. It will be easier to scale up coatings fabricated with commercially available chemicals such as polydimethylsiloxane or monomers. In the case of monomers, the polymerization was carried out by irradiation or plasma treatment. It would be possible to scale up these techniques, but it would require custom built set-ups. On the other hand, in-house custom synthesized chemicals would be more difficult to scale up depending on the availability of start-up materials and the complexity of the synthetic method. However, these chemicals were typically attached by a simple solution dipping process followed by thermal curing; thus, the application onto the fabric in these cases would not be difficult to scale up.

4. CB and liquid repellency requirements and evaluation

Depending on the intended use, the level of protection requirements varies between organizations such as the military and firefighting sectors, and also within an organization depending on the role and situation of the person such as equipment for a combat soldier versus a CB operational specialist. PPE requirements must be set as high as reasonable to protect an individual against any potential hazards. Nevertheless, this is not always possible due to the abundance of potential hazards and conflicting requirements that may demand trade-offs.

Additionally, even if appropriate PPE is selected, if the test methods used to validate the properties of the material are not up to the task, such as failing to evaluate the liquid repellency for one of the chemicals with which the material might come into contact, the protection provided by the PPE might not be adequate. Test methods that are suitable to test a material at the research and development stage might be unsuitable for the finished product. Laboratory test methods might also not be able to capture real world usage. Full scale chambers and even field testing on full ensembles might be required. Hence, test methods should be chosen carefully and reviewed to detect any gaps and issues that might be present, and hopefully these can be dealt with. Time constraints and limited budgets can prevent a material from being fully tested, and users should be aware of the limitations of the test methods.

4.1 Textile requirements

PPE is particularly important for military personnel because of their increased risk of encountering hazardous substances such as chemical warfare agents. CB protective textiles can be used to protect individuals against potential threats. The Horizon 1 chemical warfare coveralls are part of an individual protective ensemble used by members of the CAF [82]. This garment is composed of two layers, a liquid repellent outer layer and a vapour-protective inner barrier layer, and comes with two versions of the CADPAT colour treatment, temperate woodland and arid region. The exact chemical composition of the liquid repellent layer as well as performance test results for various properties is not available for this product. Nevertheless, Public Services and Procurement Canada (PSPC) posted a Request for Information on behalf of the Department of National Defence in 2017 to inform industry of a future intent to post a Request for Proposal for procurement of chemical warfare coveralls to replenish its stock of in-service coveralls [135]. In addition, it also requested feedback on a number of technical documents and questions.

One technical specification document within the PSPC listing, Appendix 2 - DSSPM 2-2-80-227 dated 2016-06-06, gives textile requirements for two fabrics that would be used to form dual layer chemical warfare protective clothing. The outer layer fabric is required to be a cotton - nylon blend with an oil and water repellent finish, while the inner barrier layer is required to be a composite laminated or bonded filter material containing activated carbon. The fabric should have the CADPAT treatment, be able to withstand decontamination, laundering, abrasion, 168 hours of cumulative wear, and have a shelf-life of 10 years. The outer layer fabric must also undergo standard characterization tests such as the ones outlined in Table 5. In particular, the fabric is required to score at least 100 in the water repellency CAN/CGSB-4.2 No. 26.2 [41] spray test and at least 5 in the AATCC 118 oil repellency test. After 10 laundering cycles, the score for these tests can be lower, a minimum of 80 for the water repellency test and a minimum of 4 for the oil repellency test. The finished garment should have good air permeability. The chemical protection is assessed with the chemical warfare agent HD before and after laundering, referencing NATO AEP-38 [137] standard test for protective clothing. Additionally, environmentally friendly materials and fabrication methods are preferred.

On the other hand, in the US, the Department of Defense uses the Joint Service Lightweight Integrated Suit Technology (JSLIST) as a general purpose CB protective garment for its military personnel. The detailed specifications for this garment have been described in the military standard MIL-DTL-32102 [138]. The garment is a multi-layer textile with an outer layer made of a cotton - nylon blend with a Quarpel liquid repellency finish, while the inner filter barrier layer contains activated carbon spheres. As discussed previously, the Quarpel treatment is based on C8 fluorochemicals. The fabric also has the woodland and desert camouflage colours, is able to withstand decontamination, six launderings, battlefield contaminants, abrasion, extreme temperature ranges, and 720 hours of cumulative wear (45 days). The garment should also minimize heat stress and have good air permeability. The chemical protection is assessed using the Defense Technical Information Center test operations procedure (DTC TOP) 8-2-501 [139] with actual warfare agents such as GD, HD, or VX.

Furthermore, the US's Department of Defense also established a Small Business Innovation Research (SBIR) [140] program in which funding is awarded to small business to conduct research and development and potential commercialization in areas such as chemical and biological defense to bridge technology gaps. In 2008, SBIR requested proposals for super-oleophobic/hydrophobic coatings for non-stick, self-cleaning textiles under solicitation 8.3 –A08-184 [141]. They wanted the development of coated textiles that will have a very low surface free energy desirably <5 mN/m and no more than 21.6 mN/m, which is also the surface tension of n-octane. These textiles would have very high water and oil repellency and be able to demonstrate roll off of organic liquids. The finishes were also required to not affect the performance of currently fielded uniforms, such as integrity of camouflage patterns. The coated textiles had to be abrasion resistant, resist 5 laundering cycles using method FTMS191A[1] TM 2724 [142], not influence air permeability measured using method FTMS191A TM5450 [143], and have a score of >100 in the spray test FTMS191A TM 5526 [144] modified to use octane instead of water. This grant was awarded to Quoc Truong from NSRDEC and Luna Innovations Inc. which went on to develop the EverShield coating [34]. As discussed previously, the EverShield omniphobic coating is commercially sold by UltraTech International Inc. and has excellent water and oil repellency. It had a score of 100 in the AATCC 22 water spray test and an oil rating of 7A in the AATCC 118 hydrocarbon oil test.

A more recent SBIR proposal from 2016, requested the development of chemical and biological aerosol and liquid repellent coatings for textiles and solid surfaces under solicitation FY16-CBD161-002 [142]. The surface free energy of the technology should be less than 18.4 mN/m, which is also the surface tension of n-hexane. The coated surface should have the highest scores in the water spray test such as the AATCC 22 test, a rating of 100, and in the hydrocarbon oil repellency test such as AATCC 118 oil test, a rating of 8A which corresponds to having oil repellency towards n-heptane which has a surface tension of 19.8 mN/m. The finish should also maintain fabric tensile strength, abrasion resistance, air permeability, moisture vapor transmission rate, and be dried in less than 30 minutes. Awards were granted to Triton Systems Inc. and HygraTec LLC.

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[1] FTMS191A is a US federal test method standard for textiles.

As can be seen from the previous examples, the exact requirements for air permeable CB protective garments can vary. In all cases, a garment is required that will be abrasion resistant, with a treatment that repels CWAs and water, has laundering durability, does not affect the properties of the fibers such as the tensile strength, and maintains properties after laundering and after decontamination. Having a material with good air permeability is also important. This will minimize the thermal burden placed on the wearer. Depending on their performance levels some textile coatings will be able to meet all the requirements for multiple agencies and applications. Nonetheless, if cost or other factors such as availability are an issue, an agency might have to select a finish that has a lower level of performance but high enough to provide adequate protection for its intended application.

Nevertheless, these are just a few examples of textile performance requirements. Other countries, jurisdictions, industries, or even different roles within the same industries, have their own requirements tailored to their specific needs. Lists of CB protection standards that specify performance levels, how to test performance, and even guidelines to select appropriate clothing for specific situations can be found in [1]. These include not only air permeable materials, but also semi-permeable and impermeable systems. For example, NFPA 1994 [14] is a standard describing protective ensembles for first responders to CBRN (chemical, biological, radiological, and nuclear) terrorism incidents, while NFPA 1992 [146] is a standard describing liquid splash protective ensembles and clothing for hazardous materials emergencies.

4.2 Test methods requirements

Setting suitable textile requirements for PPE to meet an adequate level of personnel protection for a particular situation is a challenging task. However, even if appropriate requirements are selected, if these values are not measured using suitable test methods, then the actual PPE properties might be overestimated. Test methods requirements should be chosen carefully. The capabilities and limitations of the selected test methods should be well understood. If an adequate test method cannot be found to measure the required property, it might be possible to either modify an existing test method or combine test methods. It might also become necessary to develop new methods to deal with specific situations.

In the field of liquid repellent coatings, there are still no universal standard test methods used by all the different people and organizations involved in this area. Test methods have been developed by various groups, and some methods are more routinely used than others. Some groups such as research and development university laboratories prefer to use methods such as the shedding angle method to test for repellency, which were developed by other researchers. Other groups such as companies prefer to use standard methods developed by standards organizations. Textile requirement documents for procurement of CB protective garments for military personnel, as well as government funded research programs, also prefer to use standard test methods from a variety of standard making organizations.

The most common standard test methods called out are the AATCC 118 [18] and AATCC 22 [39] tests. The AATCC 118 test measures the degree of oil repellency against liquids with surface tension ranging from 19.8 mN/m to 31.5 mN/m. The AATCC 22 method is a spray test that measures liquid repellency using only water; for the Horizon 1 coveralls replenishment information proposal [135], the documents require the use of CAN/CGSB-4.2 No. 26.2 [41] test instead of the AATCC 22 test, a similar water spray test. These two methods try to cover a range of possible liquids that could be encountered in real life using surface tension as the selection criteria. The number of liquids used is very limited, and more test liquids would provide a better understanding on the level of liquid protection. These methods could also be made more realistic by mounting the textile at different angles and testing its properties, since garments can be found situated at various angles on a person.

PPE, in particular CB protective garments, is designed not only to protect against various common liquids and chemicals, but most importantly against warfare agents. A more specialized set of standard methods were developed to measure protection against these agents. Military standards describe testing procedures and passing criteria such as liquid droplet placement. It is typically required to test protection against HD, and sometimes as well as for GD and VX. These tests are performed under strict regulations and in a limited number of places due to the nature of the test agents; there could be value in developing a set of correlated, validated tests using non-hazardous simulants, resulting in requirement for only limited validation testing using agents.

Garments are typically worn more than once, especially more complex systems. The liquid repellent finish should be able to withstand laundering. For the Horizon 1 coveralls replenishment information proposal, the documents require the use of CAN/CGSB-4.2 No. 58 test with conditions III, E, and 3 [135]. This test specifies laundering conditions such as temperature, cycle duration, detergent type, drying methods, and post-drying treatments. It is important to take into account real life usage and processes, and test the material accordingly. Laundering cycles can remove the coating, if it is not strongly attached to the textile, resulting in reduced performance or no protection. Other important military pre-treatments include contaminating the material with non-CB agent field contaminants such as oils, lubricants, or solvents, before measuring protective performance. However, these are not required tests in the Horizon 1 coveralls replenishment documents.

Testing the level of liquid protection for PPE should not be the only measurement, even though this is the most important property. The PPE most also be tested for other properties if a durable and comfortable material that could be used for long periods of time is required. A list of standard test methods developed to test for other properties were summarized in Table 5. These additional tests can help make a more informed decision when selecting PPE. These can become especially important when multiple material choices are available with similar liquid repellency capabilities.

5. Discussion and recommendations

Liquid repellent textiles are very useful in many sectors such as military, industrial, healthcare, or home goods. They can prevent liquids from spreading and wetting fabrics which can avert stains and contact with the skin underneath the fabric in case of garments. Stains can be permanent or difficult to remove requiring replacement of the object/garment or specialized laundering. More importantly these coatings can stop liquids or their vapours from contacting bare skin, which is critical if the substance is hazardous to human health. Military personnel are at a higher risk of encountering many types of hazardous liquids, from chemical warfare agents to petroleum products to cleaners, due to the nature of their work. Wearing PPE with liquid repellent finishes can not only protect them from these potential hazards, but can also benefit them in everyday situations by preventing their clothes from getting dirty and reducing the need for laundering since laundering can be particularly challenging in the field.

Liquid repellent finishes based on C8 fluorochemicals have been very successful due to their long unrivalled performance in repelling a broad range of liquids from water to oils. Nevertheless, some countries such as Canada and US have placed restrictions and bans on them because of their negative impact on the environment, and the level of restriction is only expected to increase (and may expand to include related fluorochemical treatments). This will potentially affect current and future procurements. Alternative coatings such as C6 based fluorochemicals, silicones, or hydrocarbon finishes have started to appear on the market and have been reported in the literature from university research centres. Nevertheless, there is still an intense focus on developing repellent coatings in this field by university and company laboratories, as the level of performance of these alternative coatings still needs some improvement.

The test methods used to assess performance could be improved by designing novel methods, or combining existing tests. The improvements should also focus on making the evaluations more realistic and relevant to actual final usage. It may be that by providing more realistic tests, the performance requirements may have to be altered to require more or less liquid repellency.

This section will focus on addressing potential issues that may arise with garment procurement, liquid repellent coatings, and methods used to assess their properties. Recommendations on how to address these problems are explored in the short-, medium- and long-term timeframe. Of particular importance is how these apply to the military sector.

5.1 Procurement

Procuring traditional liquid repellent finishes based on C8 fluorochemistry is becoming an issue in places where regulations have been put in place. The regulations typically target new manufacturing and imports. Items that have already been manufactured, or are currently on the market, or even chemicals that have already been produced before the restrictions were active and will be used later to coat new products, are usually still allowed. Current military procurement, and perhaps short-term procurement, might not be affected by the increasing unavailability of these coatings. Nevertheless, once supplies are depleted, efforts to procure these coatings will become problematic. If these coatings are still necessary for some military applications such as for PPE for personnel that have to go into highly contaminated areas, it might be possible to procure them – for example, the government might issue special dispensations to allow for the production of these chemicals or allow for their importation from countries where production restrictions do not exist. This might be a feasible solution for the medium- and long-term timeframes. However, with time, the cost might become so prohibitive, or restrictions become so tough around the world, that procurement would no longer be an option. Therefore, given the lengthy timescales for procurement and to bring new finishes to market, consideration of alternative procurement solutions is strongly recommended at this time.

New repellent coatings have come onto the market in the last years. The best performing coatings to date are based on similar fluorochemistry to traditional finishes, except the fluorochemicals used are made of shorter polymer chains, in particular, C6 fluorochemicals. They also have superior broad repellency towards various liquids ranging from high surface tension liquids such as water to low surface tension liquids such as oils. Since these chemicals have lower fluorine content, the repellency toward very low surface tension oils is not as high as the C8 fluorochemical case. For most applications, this underperformance might not even be noticeable. For example, the CAF’s textile requests for chemical warfare protective clothing as discussed earlier requires a score of at least 5 on the AATCC 118 test method. There are a number of coatings that meet and exceed this requirement such as Lurotex Duo from BASF or EverShield from UltraTech International Inc. Procuring these finishes should pose no problem in the short- and medium-term timeframes. In the long-term, acquiring these coatings might also become an issue. They are more environmentally friendly than C8 fluorochemical-based coatings with lower bioaccumulation and toxicity; however, they still contain fluorine chains which persist in the environment. Over time, studies might show negative effects from these compounds and regulations might be put in place if they are deemed to be sufficiently hazardous.

Other alternative coatings are based on more benign chemistries which include silicones and hydrocarbons. None of these coatings show liquid repellency towards low surface tension liquids. They do have very good repellency towards high surface tension liquids, in particular towards water. If repellency towards water-based liquids is the only requirement, then these coatings are the best solution due to their performance and environmental safety; this might be the case for some forms of protection against biological hazards (in aqueous solution, blood or body fluids). There are no restrictions on these chemistries foreseeable in the future; thus, short-, medium- and long-term procurement of these finishes should not be a problem.

In terms of coatings under development, similar chemistries to those in commercially available coatings, such as fluorochemicals or silicones, have been reported in the literature by university research laboratories. If these coatings are brought to market, they will offer more choice in about the same cost/performance space. However, these coatings would not be available for purchase in the short- to medium-term timeframe.

5.2 Research and development

The area of developing liquid repellent coatings is a very active research field with many reports being published every year from groups throughout the world. This area became particularly active after the report by Barthlott and Neinhuis [8] in 1997 on the self-cleaning properties of lotus leaves (due to surface morphology/roughness) in which water would bead up and roll off the surface of the leaf taking any contamination with it, now called the “lotus effect” [2]. After this, more examples of this surface morphology-based liquid repellency effect were found in nature such as on wild cabbage leafs, butterfly wings, duck feathers, or springtail cuticles. Researchers have tried to mimic this surface morphology in the laboratory, and artificially fabricated surfaces that can repel different types of liquids were successfully produced. Nevertheless, development is still underway and there are a number of issues that have arisen which need to be addressed and solved. Some problems that face this field include the presence and degree of oil repellency, durability under activities such as abrasion and laundering, scale up from small laboratory swatches to commercial full size products such as garments, and the impact on the environment during and post fabrication. A discussion of the general future of chemicals of this nature is given in [136].

5.2.1 Oil repellency

Highly liquid repellent coatings have been fabricated by manipulating the surface free energy of a material and/or its surface roughness. The most common approach has been to coat the desired material with a very low surface tension chemical such as fluorine. Usually a material would be able to repel a liquid whose surface tension is higher than its surface free energy. Roughness is also typically introduced on flat surfaces such as glass, and sometimes on already rough surfaces such as textile fibers to improve liquid repellency. Surface roughness can be improved by adding small particles such as nanoparticles, or microparticles, to the surface.

Research has shown that it is much easier to fabricate materials that are highly liquid repellent towards water than towards oils. Water has a high surface tension as opposed to oils which have low to very low surface tensions; thus a surface that successfully repels oil will also repel water. Water repellent surfaces can not only be fabricated using the chemical with the lowest surface free energy, fluorine; but, they can also be fabricated using chemicals with higher surface free energies such as silicon and carbon. To date, oil repellent surfaces are all derived from some form of fluorine-based coating. No other type of chemistry has been reported to show this property, not even when the surface is highly modified to have multiple layers of roughness. Nevertheless, when mixing fluorine with other substances such as silicone polymers, an oil repellent surface can still be produced. This leads to using less fluorine, and in the case of textiles, the silicone imparts a very soft feel to the fabric.

More research and development efforts are necessary to improve our understanding of liquid repellency and how to design better surfaces. It might be the case that it is not possible to have oil repellency without the use of fluorine. It might also be possible that the right combination of parameters required to obtain oil repellency without the use of fluorine have not been discovered yet. For example, maybe only a specific size and combination of nanoparticles and microparticles with a particular weave type and fibre dimensions might have this property; perhaps spherical particles are not the correct shape, or they might have to be combined with other objects with different shapes such as rods, or trapezoids, to obtain this property. Finally, a more radical and innovative approach may be required to achieve this such as the SLIPS approach where liquid droplets come into contact with and sit on top of embedded liquids rather than the traditional entrapped air pockets. Development of novel liquid repellent surfaces has come a long way in recent years, but our basic understanding is still relatively poor.

5.2.2 Durability

Durability has been another challenging problem. These coatings due to their nature and purpose are highly repellent, however, they need to be attached and remain on the coated surface after undergoing real life usage. In the case of textiles, coatings can undergo abrasion caused by rubbing against the skin of a person, rubbing against other textile layers, rubbing against each other, rubbing against outside objects such as car seats or door frames, and so forth. Additionally, it is desirable to wear textiles more than once, thus, the textile will most likely have to undergo multiple launderings throughout its lifetime.

Researchers have been able to improve the durability of repellent finishes by creating a chemical bond between the finish and the desired material. One approach was to synthesize an appropriate polymer with multiple functionalities. One part would provide attachment points to the fabric (activated by e.g. thermal curing), while the other part would provide the liquid repellent properties. If the polymer is also able to crosslink with itself during the curing reaction, a much stronger coating is obtained. This method offers a lot of flexibility and many different chemistries can be used, making it a good general approach on which to build. Nevertheless, the synthetic method can be complex, making it costly and time consuming. Another simpler way is to use monomers that once again have dual functionalities, attachment points and repellent properties, and polymerize and graft them to the textile at the same time by methods such as plasma discharge. This method is hindered by the limited number of types of monomers able to undergo this process, and it can become costly due to the cost of the monomers and the specialized curing equipment.

It is not always possible to chemically attach the repellent finish to the textile either due to lack of bonding sites on the textile or the lack of appropriate functional groups that can perform this task. This is also a problem when nanoparticles are introduced into the coating. Polymers that can crosslink can help to solve the problem. First, the polymer chains can wrap themselves around the textile fibre, and subsequent curing could then crosslink them to form a stable polymer layer. If nanoparticles are mixed into the polymer before curing, they could become trapped into the polymer matrix and become harder to detach. Another more robust way is to use a polymer that can form covalent bonds with both the nanoparticle and the textile, as well as have liquid repellent properties. In this manner, the entire system would be covalently attached throughout.

In reality, even if the repellent finish is chemically attached to the textile, over the lifetime of the textile, the finish or part of it might still come off. To solve this, self-healing functions could be built into the coating. After damage, the polymer could restore its properties through some form of trigger such as heat or washing. Another way would be to just reapply the coating, not always possible especially for finished garments (for example, if the polymer requires high curing temperatures, parts of the garment might get damaged).

Many different strategies have been employed to increase the durability of liquid repellent finishes. Ideally, the coating should be chemically attached to the textile and also be crosslinked. Built-in self-healing properties would be a useful bonus. More research should go into discovering simple, time and cost effective ways to achieve this chemical attachment. Additionally, research should focus on discovering a way to chemically attach coatings to surfaces that are non-reactive to currently developed chemistries.

5.2.3 Scale-up

New technology typically begins with small scale production in research and development laboratories such as in university or commercial facilities. There is a long process with many stages between ideas to fully functional products. Many products do not make it past the laboratory stage. It is difficult to scale-up a product and bring it to mass production even if the product is highly desirable and has the best properties. The chemicals used to fabricate the product might be difficult to procure in large quantities, might be too expensive, or they might be toxic. The procedure to fabricate the product might be too complex requiring a lot of steps or very specialized equipment which could result in a high cost and a long fabrication time, meaning that investment may be too risky. The procedure might only be possible to perform safely to make small batches of product, which will result once again in long timeframes and high cost. It might be difficult to maintain properties over large application areas. If the product is used in a multi-system assembly, it might not integrate well with the other parts. The properties of the product might degrade over time which could result in a very short shelf life.

A variety of liquid repellent coatings have been reported in the literature lately. Usually they are synthesized in-house using various procedures that are often very complex. Some researchers have tried to use simpler methods. One strategy is to use commercially available monomers and polymerize and graft them to the textile in one step using some outside force such as plasma. This approach has great scale-up potential due to its simplicity, availability of chemicals, and similar curing equipment is already in commercial usage. Nonetheless, the choice of chemicals is limited and initial equipment purchase and set-up will be expensive. Another way is to use once again commercially available chemicals and modify or combine them to obtain the desired properties. Scaling-up should be less challenging since the materials should already be available in quantity, provided the modification procedure is kept simple. The choice of chemicals is also limited in this case. Another way would be to simplify the chemical procedure by using alternate simpler chemicals. For example, a random copolymer would be easier to synthesize than a diblock copolymer, and could have the same functional groups and potentially the same properties as the diblock copolymer.

There is still much work to be done in scaling-up and bringing to mass production new liquid repellent coatings. Research should focus on simple procedures using easily available low cost chemicals, preferably identified to be environmentally friendly (see next section). This will increase the likelihood of future commercialization.

5.2.4 Environmental impact

The most successful and common approach to manufacture liquid repellent finishes is to use fluorochemicals. As we mentioned throughout the report there are major environmental issues associated with these coating, in particular with the traditional long chain based chemicals. They are very persistent, they bioaccumulate, and are toxic to the environment and wildlife. Regulations are making them less desirable and even impossible to use them in products. Shorter chain fluorochemical alternatives are more environmental friendly and are becoming the choice replacement. However, these are not entirely environmentally safe. They are still persistent in the environment and can bioaccumulate but to a lower degree. The exact toxic effects these coatings pose are not well understood. Research efforts need to be focused on understanding the effects on the environment and on human health for these materials. Once the nature of the toxic effects is more clearly understood, it may be possible to design out the relevant toxic properties while retaining the more beneficial characteristics. Unfortunately, more environmental benign and chemically unrelated alternatives such as silicones do not perform as well without any oil repellency documented to date. A summary of the environmental impact of all these coating solutions are summarized in Table 11. In this table, the most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in darker yellow. Properties that should be avoided are portrayed in red. The industry will greatly benefit if a benign alternative can be found.

Table 11: Comparison of environmental impact of liquid repellent coatings.

Coating Chemistry	Human Health	Wildlife/Plant Health	Persistency	Bioaccumulation
C8 fluorochemicals	Maybe Medium to High	High	High	High
C6 fluorochemicals	Maybe Low to Medium	Maybe Low to Medium	High	Low
C4 fluorochemicals	Maybe Low	Maybe Low	Maybe Medium to High	Low
Silicones	Maybe Low	Maybe Low	Maybe Low to Medium	Low
Hydrocarbons	Low	Low	Low	Low

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red.

Nevertheless, the nature of the coating is not the only environmental issue. Most of the chemicals used in these coatings are synthesized using organic solvents. Afterwards, the chemicals are usually dissolved in more organic solvents in order to coat them onto the textiles. These chemicals tend to have some level of toxicity towards the environment and/or towards humans. Some researchers have started to move away from these solvents and incorporate water as a solvent as much as possible. One way to do this is to include a water soluble element into the chemical. The chemical might not be completely soluble in water, but it is possible to make it miscible in water and coat the textile from an aqueous solution. Adding a water soluble element into the coating will decrease the liquid repellency performance; however, for some applications this decrease in performance might not be noticeable. Another way is to use a dry finishing treatment where no solvents are used to cure the repellent finish. Research should focus on using no or less organic solvents. If a solvent is still necessary, the least environmentally toxic solvent option should be chosen.

5.3 Research in test methods

Researching and developing a novel material is a challenging task, however, without appropriate test methods to characterize its properties and performance, it will be difficult to assess its full potential. In fact, one of the more difficult issues in setting requirements is to be able to predict real-world performance using available, usually relatively unrealistic, bench test methods; this can result in unintentional over- or under-specification, which can have an impact on the overall balance of performance of the item. It will also be difficult to compare the performance of the item to other materials in order to discover if this novel material is better than existing technologies and if it has the potential to replace them. Numerous material characterization test methods have been developed over the years by various groups from university laboratories to federal boards to international organizations. Unfortunately, there is still no specific set of standardized methods used by all people involved in this field. However, some methods are used more frequently than others. For example, coatings developed in university laboratories typically report liquid CAs, and sometimes they might report sliding and shedding angles. On the other hand, companies typically report results from water and/or oil repellency tests AATCC 22 [39] and AATCC 118 [18]. Also, companies sometimes have a tendency to only claim their products have liquid repellent properties without providing any technical information. It is challenging to compare products both within and between organizations such as companies and university laboratories.

The discussion that follows outlines how some of the knowledge gaps with respect to how these bench tests characterize repellent materials might be filled, in order to provide a more comprehensive picture of performance, and addresses how tests might be scaled up from flat material swatches to more realistic test item geometries.

Liquid CAs are typically reported in the literature by university laboratory researchers. These values are a good indication of the liquid repellency of a material, in particular how much the liquid will spread onto the material and if the liquid will be able to penetrate into the material. The CA measurement can be affected by drop size, lighting, contrast, camera focus, or the determination of the substrate's baseline, the contact line between the liquid droplet and the solid (see Figure 9 for an example CA photograph). Bias can be very easily introduced when measuring high contact angles. The CA measurement is also a problem for textiles. Textiles are non-reflective, flexible and have macroscopic roughness. This makes it difficult to accurately determine the baseline of the substrate. The exact CA value is important to determine for materials that are close to the transition between various wettability regimes. An error in this value might over- or under-estimate a material's liquid repellency level. This measurement also does not assess the behaviour of the droplet with movement or under outside forces such as pressure. An individual wearing a protective garment will likely perform various tasks such as bending an arm or walking, or they might even sit down or brush against another person or wall. These actions might cause the droplet to roll off the material or penetrate into it. CA values alone should not be taken as the only measurement of liquid repellency. Complementary techniques should be used to obtain a better understanding how a material will perform in real world circumstances.

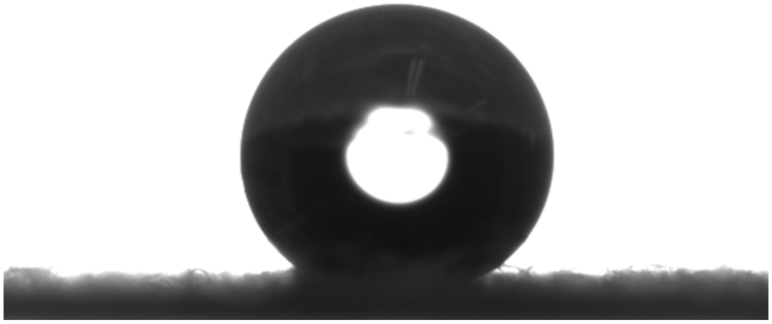

Figure 9: Example of a water droplet on a coated cotton fabric.

AATCC 118 and AATCC 193 [38] tests measure liquid repellency using test droplets placed on the surface of the material as well. The values obtained from these tests will also indicate if a liquid will spread and penetrate into the fabric, or if the liquid will stay on the surface. These methods have two passing grades: a pass when the liquid droplet has a clear well rounded appearance, and a borderline pass when the liquid droplet is not as rounded, and even spreads a bit. A material that has a lower repellency will be able to pass with a borderline grade. These methods also do not take into account real world circumstances such as motion, and complementary tests should be used with them.

Dynamic tests that try to take into account more realistic situations include methods which measure the sliding and shedding angles of droplets. These tests show how a liquid droplet might behave when it contacts a surface for the first time such as falling onto an arm, and when it is already on a moving surface. These tests are affected by the fabric weave (e.g. the size of the pores), the position of the droplet on the textile (on the pore versus on the top of fibres), the number of single fibres sticking out from the fabric, and the size of the droplet. Droplets can contact or be found on a material in various amounts; measurements should be done with a number of droplet sizes. In the case of the shedding angle method, various distances and angles between the droplet and fabric should be used since droplets can fall from different heights and onto differently angled material in the real world.

Another dynamic test method is the AATCC 22 or ISO 4920 [40] water spray test. This method also shows how water liquid droplets will behave when they contact a surface for the first time. However, the textile is mounted only at a 45° angle. In real life, surfaces can be at any angles from horizontal to vertical. The textile should be mounted and its properties tested at multiple angles. The test is affected by the size of the holes in the spray nozzle as well. Nozzles of different dimensions should be used to more realistically test variability in liquid droplets. The distance between the spray nozzle and textile sample would also affect results; thus, different distance parameters should be tested.

The level of liquid repellency protection measured by all these test methods is limited by the number and type of test liquids utilized in the experiments. These tests only use a few chemicals such as water, seven types of hydrocarbon oils, or water and alcohol mixtures. These tests try to measure the repellency for liquids with high to low surface tension. They try to provide a broad understanding of how a material would behave when encountering a liquid. However, not enough liquids are used in these methods and more liquids are necessary to better understand a coating's level of liquid repellency. It is challenging to create a master list of liquids due to the abundance of chemicals produced and used throughout the world that could potentially be very hazardous. These chemicals can be encountered in different concentrations and environmental conditions. In addition, liquid repellent equipment used as CB PPE should not only be tested with traditional liquids, but also with actual warfare agents. Due to the toxicity of these agents and the necessity to measure if these agents can penetrate through the fabric, the typical methods used above are not suitable for these tests. When the whole system is tested, it is recommended to primarily use mannequins for safety reasons, as there may not be enough relevant safe simulants, and agents are preferred for the most realism. The drops can be applied as a laid droplet, or falling droplet, or even as a droplet with pressure application. The pressure applied can be designed to simulate e.g. sitting, 20 kPa pressure, or kneeling, 200 kPa pressure. These methods require specialized equipment and facilities, as well as strict security protocols and safety regulation; they cannot be easily and routinely performed on every product developed due to cost; thus, only high TRL potential products would probably undergo these tests.

A preliminary alternative to testing performance against chemical warfare agents is to use simulants. These are more readily available, less restricted, less expensive, and have much lower or no toxicity. These simulants can be used and should be used as test liquids in the typical procedures described above to better understand coating properties. For example, triethyl phosphate is used as a GD simulant. However, finding simulants that adequately represent warfare agents is challenging. If an appropriate simulant is not available, maybe a series of simulants might be able to cover all the necessary properties. Ultimately, if relevant simulants can be found that are non-toxic, it will be beneficial to test the whole system using humans either in a laboratory setting where they perform typical work tasks, or in an actual field environment. Dyes such as fluorescent dyes added to the simulants can be used to better visualize the performance of the material and determine if or where there are problems.

Adapting standard civilian tests to testing liquid repellency by adding pressure to the liquid droplets to mimic activities such as sitting down and kneeling would be of benefit. Some such tests use coloured paper that permits easy visualization of a dampened area when the liquid penetrates. The use of detection paper that can change colour placed behind the material is also a useful technique to adapt. Another way would be to add dyes straight into the liquid for easier visualization. Once again, if the liquids used in testing are non-toxic, full system testing on human subjects performing realistic activities would be the best course of action.

These test methods should not only be performed on newly fabricated materials/garments. In reality, garments are typically worn multiple times and will likely be washed either in domestic or commercial laundering facilities. Also, during everyday usage textiles will undergo abrasion, stretching, and flexing. Liquid repellency test methods should be combined with pre-treatments that simulate actual utilization, and again possibly during use where for example stretching and flexing could affect performance. There are standard test methods that set guidelines for various preconditioning treatments such as CAN/CGSB-4.2 No. 58 which sets laundering conditions such as temperature, cycle duration, detergent type, or drying methods, and these should become standard practice; full system tests with droplets in flex and stretch areas should be performed during qualification.

Other preconditioning conditions that must be taken into account are environmental effects. The garment could be worn at different temperatures such as an arid environment or a very cold climate. The humidity can also vary significantly from dry such as a desert to very humid such as a rain forest. If the textile is worn against the skin than the temperature of the skin and humidity at the skin's surface need to be used. Storage temperature and humidity should be tested for as well. Precipitation such as rain can affect performance. Wind could also try to push contaminants into the material. These factors can be tested either using special laboratory pre-treatments or actual field experiments.

In real situations, the garment can be exposed to multiple everyday chemicals and other contaminants such as cleaning solvents, detergents, fuels, oils, lubricants, dirt, mud, food products, or even sweat. These are not necessarily toxic hazards; nevertheless, they could interact with the garment for example by forming a layer on top of the liquid repellent treatment, and can potentially negatively affect performance when the garment is actually needed. These should be taken in consideration when designing or choosing test methods. Another important possible contaminant is decontamination solutions. The material should be able to resist these solutions at least over the course of a single decontamination, and this property is particular critical for personnel whose job is to decontaminate people and equipment.

All of these test methods typically measure properties on two to three small swatches such as 1 x 1 cm or 20 x 20 cm in five different locations. Due to time constraints and costs, this is a sufficient approach at the beginning of research and development. However, as materials show promise of potential manufacturing, tests should be done again on larger samples and eventually on the whole system. For example, a larger sub-system sample could be to fabricate only a sleeve or a leg and then use an artificial construct such as a moving "arm" that can mimic the movement of a real person; such a test would incorporate many of the effects of movement and fabric geometry. This will provide a better understanding of the material’s properties and correlation to the real world. Some coatings that showed a lower performance in the swatch tests might do better in these tests or vice versa; effects will be observed such as pooling into material folds that are not seen on flat swatches. Other components can be incorporated to determine how well the coating will perform in conjunction with seams and fasteners and other pieces of equipment such as gloves and respirators. The more realistic test methods are, the better the performance characterization and understanding of a new material.

Test methods that were adequate to measure performance at the beginning of a material’s fabrication during the research and development phase, might not be suitable assessments in latter phases of a material’s life cycle. The material’s performance might have to be re-evaluated using new methods. For example, in the selection and qualification stage, all the test methods outlined above might have to be performed, not just one or two as is usually performed. Also, testing might have to be done in the field and maybe even with human subjects. In the pre-production phase, scaling up to mass production might affect quality, and properties might have to be re-evaluated multiple times until requirements are met. Next, in the production quality control step, perhaps only a few tests would be required to ensure adequate performance of key properties, based on those that were most sensitive to performance during scale-up. Finally, in the storage and deployment phase, some testing would still need to be performed periodically to ensure material stability.

6. Conclusions

Liquid repellent coatings can repel liquids from the surface of a material, can prevent liquids from spreading and wetting the material, and can allow for the facile removal of liquids and any dirt/contaminants in the path of the liquids from a material. They are of particular interest as finishes for garments used as PPE for the military. Military personnel have a higher potential of coming into contact with very hazardous substances such as CB warfare agents and toxic industrial chemicals, in addition to typical everyday substances such as oils, fuel, or even water. These repellent coatings can prevent potential health problems, reduce requirement for laundering, prevent stains and garment damage, and generally save time and money. Such coatings can be used as the outer finish of a single-layer garment, although typically for PPE applications they are used on the outer layer of a multi-layer system, whose outer layer prevents liquid penetration in conjunction with an activated carbon layer to remove penetrated CWA vapours. Other protective functionalities may also be incorporated between those two layers, such as an aerosol removal layer.

A number of liquid repellent coatings for textiles have been developed over the years, and some are available commercially. In this report, a review of coatings at all TRL stages is presented, from current commercially available coatings to coatings still in development. These coatings can be grouped by chemistry type and their performance is summarized in Table 12. In this table, the most desirable property performance can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red. High liquid repellency can be achieved through a combination of low surface free energy and surface roughness. Fluorine has the lowest surface free energy, and thus, fluorochemical-based finishes continue to be the best performing liquid repellent finish to date. They are able to repel both water and a variety of oils. C8-based fluorochemical repellent treatments have the broadest range of liquid repellency; however, their manufacturing components are toxic and pose a high risk to the environment. Legislation has been put in place to ban or restrict their usage in some countries such as Canada and the US, which will make current and future procurement very difficult.

The community has started to shift to other approaches. The shorter chain C6 fluorochemical-based finishes are currently the best performing alternatives. They also provide a broad range of liquid repellency, but due to their lower fluorine content, they perform worse than C8 flurochemicals in the repellency of low surface tension oils. They are also persistent in the environment, but have a much lower bioaccumulation than C8 fluorochemicals, meaning effectively less toxicity. Nevertheless, the exact long-term effect of these coatings on human health and the environment is still being investigated. If very high liquid repellency is not necessary, or the combination of these coatings and activated carbon is more than sufficient to provide adequate protection, procurement efforts should shift towards these coatings in order to save money, time, and have a lower impact on the environment. C4 fluorochemicals have an even lower impact on the environment, although their oil repellency is low to non-existent. Other alternative coatings that have an even lower impact on the environment are based on silicones and hydrocarbons. Their surface free energy is higher than fluorine, and to date no significant oil repellency has been reported for these. Nevertheless, they can also have excellent water repellency. In some cases, nanoparticles have been added to all of these coatings. They have a tendency to increase surface roughness, which leads to improved repellency performance. Research is still very active in this field due to a continuing lack of a high performance coating that is environmentally benign. There are other problems that need to be addressed such as high durability, or compatibility with other finishes such as infrared reflectance or insect repellency, or high stability of laminates.

Table 12: Comparison of liquid repellent coatings.

Coating Chemistry	Water Repellency	Oil Repellency	Environmental Impact
C8 fluorochemicals	Yes	Yes	High
C6 fluorochemicals	Yes	Yes	Potential Medium
C4 fluorochemicals	Yes	Maybe	Potential Low
Silicones	Yes	No	Low
Hydrocarbons	Yes	No	Low

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red.

The existence of adequate test methods that can fully and accurately characterize a material's properties and performance is as important as the material itself. Without appropriate test methods, a material's abilities might be overestimated, which can lead to failure and potential harm to the wearer, or underestimated, in which case the material might be overdesigned for repellency, with other properties potentially negatively affected. A number of test methods have been developed to measure a surface's liquid repellency; however, there is still no consensus on which methods to use, and each organization prefers certain methods over others. A summary of some liquid repellency test methods is given in Table 13. A variety of liquids with different surface tensions have been used for testing ranging from water to chemical warfare agents; warfare agent testing is done only in specialized facilities due to the toxic nature and regulations on these chemicals. Both static and dynamic test methods have been developed such as placing a droplet on the material, or releasing a droplet from a certain height above the material which is tilted at a certain angle. Pre-treatments of the material to simulate realistic usage also exist such as laundering. Nevertheless, these test methods could be improved to better reflect realistic field conditions such as testing whole systems rather than swatches, or testing performance during a variety of activities such as walking or sitting. In addition, efforts should be focused on developing a set of universal standard test methods, which are easy to use, inexpensive, and not take a long time, that can be adopted by all organizations in this field.

Table 13: Comparison of liquid repellency test methods.

Test Method	Typical Testing Liquids	Grading Scale	Organization Commonly Using Method
Contact Angle	Water, Diiodomethane, Cooking oil, n–Hexadecane	0 – 180°	University Laboratories
Sliding Angle	Water, Diiodomethane, Cooking oil, n–Hexadecane	0 – 90°	University Laboratories
Shedding Angle	Water, Diiodomethane, Cooking oil, n–Hexadecane	0 – 90°	University Laboratories
AATCC 22 / ISO 4920 / CAN/CGSB-4.2 No. 26.2	Water	0, 50, 70, 80, 90, 100 (ISO 0 – 5)	Companies
AATCC 118	Hydrocarbon oils	0 – 8 (A – D)	Companies
AATCC 193	Mixtures of Water and Isopropyl alcohol	0 – 8 (A– D)	Companies
Military methods e.g. DTC TOP 8-2-501	Chemical warfare agents such as HD, GD, VX, or simulants	Qualitative (Pass / Fail), Quantitative	Companies Supplying Government

As we have seen throughout the report, there are a number of issues associated with liquid repellent coatings. Resolving these concerns can be challenging due to the difficulty in scaling-up the coatings, or high cost, or a negative impact on the environment. However, the potential payoff might be high, as the risk of losing access to existing technologies is significant. A comparison of these issues and the risks and payoffs is shown in Table 14. In this table, the most desirable properties such as low implementation risk and high payoff and potential value can be seen in green, while less desirable properties are in orange such as medium repellency performance. Properties that should be avoided such as high environmental risk are portrayed in red. When the risks and payoffs are compared, the best solution is to still use the C8 fluorochemical finishes. However, due to the high environmental risk, these finishes should only continue to be used if they are absolutely necessary. A combination of evaluated criteria including low risks associated with acquisition difficulty and lack of knowledge to implement, medium risks associated with environmental impact and repellency performance, combined with high potential payoff results in a high performance value for C6 fluorochemical finishes, all lead to the conclusion that whenever possible, available C6 fluorochemical finishes should replace the traditional C8 fluorochemical finishes. The implementation risks of other possible finishes are higher, mainly due to their lack of repellency performance for low surface tension oils. Mixing alternate finishes with nanoparticles or C6 fluorochemical finishes would boost their performance, but this would increase the difficulty of fabricating these coatings without necessarily greatly increasing the performance payoff. From an environmental perspective, it will be beneficial to try to use a mixture of C6 fluorochemicals with other more benign alternatives such as silicone, in order to decrease the amount of fluorochemical needed for the coating and still maintain oil repellency.

Unfortunately no ideal solution exists to date. It might not even be possible to completely remove fluorine from a finish and still maintain oil repellency, due to the inherent chemical properties of fluorine that are not reproduced in any other atom. One solution might be, in some cases, to completely remove the oil repellency requirement, use an environmentally benign alternative finish to at least have some protection against high surface tension liquids or use no finish at all, and devise other mechanisms to provide the necessary liquid protection when required.

In the case of test methods used to evaluate the performance of liquid repellency coatings, there are also issues associated with them which are summarized in Table 14. The same colour coding as the chemistry section of the table is used for this. Methods developed in the laboratory tend to give an accurate and reproducible determination of the repellency capabilities of the material. However, they tend to be more tedious and time consuming as shown by the medium implementation risk. The standard test methods are simpler and easier to perform, while some do not require any specialized equipment. Based on the low implementation risk and a high payoff, the AATCC 118 is a particular good method to test oil repellency. Nevertheless, if these coatings are to be used to characterize CB warfare agent PPE, more militarily relevant test methods are required. However such methods require very specialized equipment and facilities, and are quite costly. This leads to a high implementation risk. The potential payoff for these methods is high, but the overall performance value is not high due to the high risk. Equipment does need to be tested with these methods before it is fielded since the whole purpose of the CB PPE is to protect personnel from CB warfare agents.

All of these tests would benefit from some modifications such as using more realistic conditions, but depending on the complexity of the conditions, these tests can become very costly. Static methods where liquid droplets are placed on the surface of the fabric and observed for wetting such as the contact angle method, as well as the AATCC 118 or AATCC 193 methods, could be modified to include a measurement of the droplet’s behaviour with pressure application. The pressure applied would simulate realistic situations such as sitting, 20 kPa pressure, or kneeling, 200 kPa pressure, or even accidental events such as brushing against a wall or other textiles. Additionally, fabric preconditioning to simulate wear and environmental contaminants should also be incorporated into these methods. In particular, laundering and abrasion should be included. Other routinely contaminants found in the field such as dirt or oils can be tested too.

The standard test methods AATCC 22 or ISO 4920 could benefit from some improvements. The measurement is only done at a 45° angle; however, droplets can come into contact with garments while in usage at various angles. Such tests should be done at different angle such as at low and high angles which mimic more realistic positions. Measuring performance at different angles would give a much better idea on the performance and limitation of the repellency finish. Once again, fabrics should also be measured after pre-conditioning to better reflect actual usage.

In the near future, this field would benefit the most from improving and/or developing test methods such as sub-system tests (e.g. static or moving arm, depending on the test) to better characterize the degree and limitations of liquid repellency. Currently comparison of existing treatments is difficult, and research developments should focus on better characterizing these finishes and developing a unified testing protocol. This would not only make it easier to compare between different finishes at all TRLs developed by various organizations, but would also lead to a better understanding of liquid repellency and help to design novel finishes.

In summary, future work in this field that would best address future military requirements lies in the area of:

- Investigation of inclusion of surface roughness to improve performance of existing or novel repellent finishes (Section 5.2.1)

- Investigation of different fabric parameters such as weave type, bundle and fibre size, or fibre shape, to improve performance of existing or novel repellent finishes (Sections 2.2.3 and 5.2.1)

- Investigation of different approaches for covalent attachment of repellent functionalities to improve coating durability (Section 5.2.2)

- Identifying, and funding scale-up for, promising early TRL technologies; identifying common technical barriers to scale-up and addressing through targeted funding (Section 5.2.3)

- Investigation of environmentally friendlier finishes through combinations of existing finishes or developing novel repellent finishes; investigation of environmentally friendlier manufacturing processes (Section 5.2.4)

- Repellency test method improvement, including characterization of material repellency performance using a larger variety of test parameters for commonly used or standardized bench tests; develop a better suite of CWA simulants; develop more realistic sub-system tests (Section 5.3)

- Identifying and developing a unified testing protocol for all organizations involved in the liquid repellency field (Section 5.3)

Table 14: Comparison of issues and risks.

Issue	**Implementation Risk (3 is high)**					**Potential payoff (1 is high)**	**Performance (1 is high)**	**Procurement Ready (P) vs R&D (TRL)**
	Difficulty (Cost/ Time/ Scale-up/ Durability)	**Lack of Knowledge (Cost/ Time for R&D)**	**Environmental Impact**	**Repellency Performance**	**Summary**			
Chemistry								
C8 fluorochemical finishes	Low (1)	Low (1)	High (3)	Low (1)	State-of-the-art (3)	(1)	(3)	P; TRL 9
C6 fluorochemical finishes	Low (1)	Low (1)	Medium (2)	Medium (2)	Good (4)	(1)	(4)	P; TRL 9
C4 fluorochemical finishes	Low (1)	Medium (2)	Low (1)	High (3)	(6)	(1)	(6)	P; TRL 9 R&D
Silicone finishes	Low (1)	Medium (2)	Low (1)	High (3)	(6)	(1)	(6)	P; TRL 9 R&D
Hydrocarbon finishes	Low (1)	Medium (2)	Low (1)	High (3)	(6)	(1)	(6)	P; TRL 9 R&D
Mixing in nanoparticles	Medium (2)	Medium (2)	Low (1)	Medium (2)	(8)	(2)	(16)	P; TRL 9 R&D

Issue	Implementation Risk (3 is high)					Potential payoff (1 is high)	Performance (1 is high)	Procurement Ready (P) vs R&D (TRL)
	Difficulty (Cost/ Time/ Scale-up/ Durability)	Lack of Knowledge (Cost/ Time for R&D)	Environmental Impact	Repellency Performance	Summary			
Mixing different finishes	Medium (2)	Medium (2)	Medium (2)	Medium (2)	(16)	(2)	(32)	P; TRL 9 R&D
Count on activated carbon layer	Low (1)	Medium (2)	Low (1)	High (3)	(6)	(2)	(12)	R&D
Test Methods								
Contact Angle	Medium (2)	Low (1)	Medium (2)	Low (1)	(4)	(1)	(4)	NA
Sliding Angle	Medium (2)	Low (1)	Medium (2)	Low (1)	(4)	(1)	(4)	NA
Shedding Angle	Medium (2)	Low (1)	Medium (2)	Low (1)	(4)	(1)	(4)	NA
AATCC 22 / ISO 4920 / CAN/CGSB-4.2 No. 26.2	Medium (2)	Low (1)	Low (1)	Medium (2)	(4)	(2)	(8)	NA
AATCC 118	Low (1)	Low (1)	Medium (2)	Low (1)	(2)	(1)	(2)	NA
AATCC 193	Low (1)	Low (1)	Medium (2)	Low (1)	(2)	(2)	(4)	NA

Issue	**Implementation Risk (3 is high)**					**Potential payoff (1 is high)**	**Performance (1 is high)**	**Procurement Ready (P) vs R&D (TRL)**
	Difficulty (Cost/ Time/ Scale-up/ Durability)	**Lack of Knowledge (Cost/ Time for R&D)**	**Environmental Impact**	**Repellency Performance**	**Summary**			
Military methods e.g. DTC TOP 8-2-501	High (3)	Low (1)	High (3)	Low (1)	(9)	(1)	(9)	NA
Realistic conditions	High (3)	Medium (2)	Medium (2)	Low (1)	(12)	(1)	(12)	NA

Note: The most desirable properties can be seen in green, while less desirable properties are in orange. Properties that should be avoided are portrayed in red.

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Annex A List of companies/coatings/projectsworking on liquid repellency solutions

A.1 Other commercially available liquid repellent coatings

Table 15: Comparison of other commercially available coatings.

Coating	Chemistry	Water Repellency	Oil Repellency
NK Guard S series[1] (Nicca Chemical Co. Ltd.)	Fluorochemical	Yes	Yes
X-Cape 2014[2] (OMNOVA Solutions Inc.)	Fluorochemical	Yes	Yes
Nano-coating[3] (P2i)	Fluorochemical deposited by pulsed plasma process	Yes	No
Phobol CP-CR[4] (Huntsman International LLC.)	C6 fluorochemical (Capstone by Dupont)	Yes	Yes
Anthydrin NK 6[5] (Zschimmer & Schwarz)	C6 fluorochemical	Yes	Yes
Texfin ND-C6[6] (Texchem UK Ltd.)	C6 fluorochemical	Yes	Yes
CAREGUARD-66[7] (Sarex Chemicals)	C6 fluorochemical	Yes	Yes
TUBIGUARD 90-F[8] (CHT Group)	C6 fluorochemical	Yes	Yes
Unidyne TG-5543[9] (Daikin Industries Ltd.)	C6 fluorochemical mixed with silicon polymer	Yes 100 spray test	Yes 6 oil
FINISH WS 60 E[10] (Wacker Chemie AG.)	Aqueous hydrogen siloxane	Yes	No
Texfin DWR-X New[11] (Texchem UK Ltd.)	Modified wax (hydrocarbon) dispersion	Yes 100 spray test	No

Coating	Chemistry	Water Repellency	Oil Repellency
Phobotex RCO[12] (Huntsman International LLC.)	Non-fluorinated paraffin wax and acrylic copolymer	Yes	No
Ecorepel Bio[13] (Schoeller Technology AG.)	Renewable non-GMO plant-based sources	Yes	No
Smartrepel Hydro[14] (Archroma)	Microencapsulated technology	Yes 100 spray test	No
Bionic Finish ECO[15] (Rudolf GmBH.)	Hyper-branched hydrophobic polymer connected to comb polymers	Yes	No
CAREGUARD-4[16] (Sarex Chemicals)	Non-fluorinated	Yes 100 spray test	No
Aqua Repulse[17] (Allegiance NanoSolutions)	Water based technology: PFOS and PFOA free, solvent free	Yes	No
Curb[18] (Sciessent)	Non-fluorinated	Yes	No
NeverWet Fabric DWR[19] (NeverWet)	Not available	Yes	No

Note: The most desirable properties can be seen in green. Slightly less desirable properties are in yellow, and less desirable properties are in orange. Properties that should be avoided are portrayed in red.

Tiax LLC is also developing commercial non-fluorinated liquid repellent coatings under the US Small Business Innovation Research program.[20]

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3. https://www.p2i.com/
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A.2 Other proof-of-concept liquid repellent coatings

Table 16: Comparison of other proof-of-concept coatings.

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Shi et al.[1]	C6 based fluorochemical: poly[2-(perfluorohexyl) ethyl acrylate]-block-poly(glycidyl methacrylate)	Yes CA 152°	Maybe yes	Maybe 1 wash
Li et al.[2]	Aqueous solution of C3 based fluorochemical: poly(glycidyl methacrylate)-g-[poly(hexafluorobutyl methacrylate)-r-poly(oligo(ethylene glycol) methyl-ether methacrylate)] that forms Nanobumps	Yes CA 152°	Not tested but maybe not	Maybe yes
Zou et al.[3]	Aqueous solution of C8 based fluorochemical: poly(2-perfluorooctylethyl acrylate)-block-poly(glycidylmethacrylate-radom-methoxyoligoethyleneglycolylmethacrylate)	Yes CA 163°	Yes CA n-hexadecane 153° (oil 3)	Yes 50 washes
De Marco et al.[4]	C8 based fluorochemical: 1H,1H,2H,2H-perfluoro-decanethiol with dopamine and silver nitrate	Yes CA 140°	Yes CA Mineral oil 120° (oil 1)	Maybe yes
Chen et al.[5]	Fluorochemical: poly(perfluoropropylene oxide) glycol attached to Silica nanoparticles	Yes CA 155°	Yes CA n-hexadecane 107° (oil 3)	Yes 100 washes
Yoo et al.[6]	C8fluorochemical – silicone: Stacked polymer film composed of a poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) layer and a poly(1H,1H,2H,2H-perfluorodecylacrylate) layer	Yes CA 154°	Maybe yes	Yes 75 washes

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Przybylak et al.[7]	C4 fluorochemical – silicone: Octafluoropentyloxypropyl and trimethoxysilylethylpolyhedral oligomeric silsesquioxane (Fluoro-POSS) cage-like molecule	Yes CA 151°	No	Yes 10 washes
Zhang et al.[8]	C8 based fluorochemical – silicone: poly-[(perfluorooctylethyl acrylate)-co-(tri(isopropyloxy)silylpropyl methacrylate)]attached to Silica nanoparticles	Yes CA 163°	Yes CA peanut cooking oil 153° (close to oil 1)	Maybe yes
Lin et al.[9]	C8 based fluorochemical-silicone: poly-[(styrene)-co-(butyl acrylate)-co-(2-Hydroxyethyl methacrylate)-co-(Vinyltriisopropoxysilane)-co-(Perfluoroalkyl ethylacrylate)]attached to Silica nanoparticles	Yes CA 163°	Yes CA sunflower cooking oil 156° (close to oil 1)	Yes 30 washes
Xu et al.[10]	C6 based fluorochemical-silicone 1H,1H,2H,2H-perfluorooctyltrimethoxysilane, chitosan, and Silica alcogel	Yes CA 164°	Yes CA n-hexadecane 156° (oil 3)	Yes 30 washes
Pereira et al.[11]	C13 based fluorochemical-silicone: tridecafluorooctyltriethoxysilane attached to Mesoporous silica nanoparticles	Yes CA >150°	Yes CA sunflower cooking oil 155° (close to oil 1)	Maybe yes
Zhou et al.[12]	Aqueous C8 based fluorochemical-silicone: 1H,1H,2H,2H-perfluorodecyltriethoxysilane and Teflon nanoparticles with DuPont's Zonyl321 as fluorocarbon surfactant	Yes CA 172°	Yes CA n-hexadecane 161° (oil 3)	Yes 200 washes
Sun et al.[13]	Silicone: vinyl polyhedral oligomeric silsesquioxane (POSS) cage-like molecule	Yes CA 149°	No	Yes 30 washes

Coating	Chemistry	Water Repellency (Water CA)	Oil Repellency	Laundering Durability
Shang et al.[14]	Silicone: Water glass and n-octadecyltriethoxysilane with 3-glycidyloxypropyltrimethoxysilane	Yes CA 152° Spray test 90-100	No	Yes 30 washes
Xu et al.[15]	Silicone: hexadecyltrimethoxysilane attached to Silica nanoparticles	Yes CA 152° Spray test 100	No	Maybe yes
Wu et al.[16]	Silicone: n-hexadecyltriethoxysilane attached to Silica nanoparticles	Yes CA >150°	No	Yes 10 washes
Gao et al.[17]	Aqueous cerium doped zinc oxide nanorods	Yes CA 148°	No	Maybe yes
Yu et al.[18]	Octadecylamine using laccase/2,2,6,6-tetramethyl-piperidine-1-oxyl	Yes CA 117°	No	Yes 10 washes

Note: The most desirable properties can be seen in green. Acceptable properties can be seen in light yellow, while less desirable properties are in darker yellow. Properties that should be avoided are portrayed in red.

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A.3 Projects aimed at liquid repellency solutions

- MIDWOR-LIFE (https://www.midwor-life.eu/): is a consortium which is trying to mitigate the environmental, health and safety impacts of current durable water and oil repellents, based on long-chain fluorocarbons, used in the textile finishing industry by analyzing their non-toxic alternatives. It is co-funded by the European Union under the LIFE+ Financial Instrument under the Grant Agreement LIFE14 ENV/ES/000670.
- TEX-SHIELD (http://www.texshield-project.eu/): is a consortium which is trying to provide a feasible solution to replace C8 fluorochemical coatings that is environmentally friendly and has durable oil and water repellence. It is funded by the European Union Seventh Framework Programme [FP7/2007-2013] under grant agreement 315497.
- FluoroCouncil (https://fluorocouncil.com/): is a global membership organization representing the world's leading fluoro technology companies. It tries to facilitate the global transition away from long chain fluorochemicals and work towards appropriate regulations.

List of abbreviations and acronyms

°	Degree
°C	Degrees Celsius
µL	Microliter
AATCC	American Association of Textile Chemists and Colorists
AC	Hydrogen Cyanide
ACU	Army Combat Uniform
AEP	Allied Engineering Publication
ASTM	American Society for Testing and Materials
C	Carbon
C6	Perfluoroalkyl chains with six fluorinated carbons (C_6F_{13}-)
C8	Perfluoroalkyl chains with eight fluorinated carbons (C_8F_{17}-)
CA	Contact Angle
CADPAT	Canadian Disruptive Pattern
CAF	Canadian Armed Forces
CAN	Canada
CB	Chemical and biological
CBRN	Chemical, biological, radiological and nuclear
CG	Phosgene gas
CGSB	Canadian General Standards Board
CK	Cyanogen Chloride
CSA	Canadian Standards Association
CWA	Chemical warfare agent
DTIC	Defense Technical Information Center
ED_{50}	Median effective dose
et al.	And others
F	Fluorine
FTMS	US federal test method standard
GB	Sarin
GD	Soman
H	Hydrogen
HD	Distilled Mustard

ISO	International Organization for Standardization
JSLIST	Joint Service Lightweight Integrated Suit Technology
kg	Kilogram
kPa	Kilopascal
L	Lewisite
LD_{50}	Median lethal dose
LSD	Lysergic acid diethylamide
m	Meter
mg	Milligrams
mN	Millinewton
NA	Not Applicable
NATO	North Atlantic Treaty Organization
NFPA	National Fire Protection Association
NSRDEC	Natick Soldier Research, Development and Engineering Center
POSS	Polyhedral oligomeric silsesquioxane
PPE	Personal Protective Equipment
PWGSC	Public Works and Government Services Canada
Quarpel	Quartermaster repellent
R & D	Research and Development
RMCC	Royal Military College of Canada
SBIR	Small Business Innovation Research
SLIPS	Slippery lubricant-infused porous surfaces
TIC	Toxic industrial chemical
TOP	Test Operations Procedure
TRL	Technology Readiness Level
US	United States
VX	VX

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Liquid repellent coatings have become frequently used in many sectors due to their ability to repel a broad range of liquids ranging from high surface tension liquids such as water to low surface tension oils. They are used in the military textile field as the outer layer finish of chemical and biological personal protection equipment such as air permeable coveralls. These finishes can help protect personnel not only from warfare agents, but also from everyday substances such as water, oils, fuel, lubricants, cleaning solvents, and other contaminants. Traditionally, long chain C8 fluorochemical-based finishes were used to achieve this protection; however, due to their potential high toxicity, legislation has been put in place to restrict or ban their usage throughout the world. Alternative coatings have been developed and brought to market. Coatings at all technology readiness levels are summarized and compared in this report. In particular, short chain C6 fluorochemical coatings have come close in performance to traditional coatings without the high environmental risk. Other alternative more benign coatings such as silicone and hydrocarbon based finishes have only shown water repellency properties and no oil repellency to date. Additionally, test methods used to evaluate these coatings, ranging from standard test methods to university laboratory developed tests, are discussed and evaluated.

On utilise fréquemment des enduits résistant aux liquides dans de nombreux domaines en raison de leur aptitude à repousser un vaste éventail de liquides, allant de liquides à tension de surface élevée comme l'eau jusqu'aux huiles à faible tension de surface. Ils sont utilisés dans le domaine de textiles militaires et sont appliqués sur la couche extérieure de l'équipement de protection individuelle contre les produits chimiques et biologiques comme des combinaisons perméables à l'air. Ces enduits peuvent aider à protéger le personnel non seulement contre des agents de guerre, mais aussi contre des substances utilisées tous les jours, comme l'eau, l'huile, les lubrifiants, les solvants de nettoyage et autres contaminants. Dans le passé, des enduits à base de substances fluorochimiques en C8 à chaîne longue étaient utilisés pour assurer cette protection. Cependant, en raison de leur toxicité potentiellement élevée, des mesures législatives ont été adoptées pour en restreindre ou en interdire l'usage partout au monde. D'autres enduits ont été mis au point et commercialisés. Des enduits à divers niveaux de maturité technologique sont brièvement décrits et comparés dans ce rapport. Plus précisément, les enduits fluorochimiques en C6 à chaîne courte ont présenté des performances très semblables aux enduits classiques sans poser de risques élevés pour l'environnement. Jusqu'à présent, d'autres enduits moins dommageables comme ceux à base de silicone et d'hydrocarbures ont présenté une résistance à l'eau et non à l'huile. De plus, les méthodes d'essai utilisées pour évaluer ces enduits, soit des méthodes d'essai normalisées ou des essais élaborés par des laboratoires d'université, sont aussi l'objet d'un examen et d'une évaluation.