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REVIEW ARTICLE

Finishing of Textiles With Fluorocarbons

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ABSTRACT: Fluorochemicals have its applications in many fields, as in firefighting, electroplating and electronics industries. A number of novel approaches using fluorochemicals in textile processing are a portent area for better marketing of textile goods. Value added finishing of textiles is a new development in textiles processing and these fluorochemical finishes impart water repellency, oil repellency, soil repellency giving value addition to the textile substrate. Application of the fluorochemical finish has been found to be versatile in nature and can also be used to make fluoropolymer coatings and products that resist heat, oil, stains, grease, etc. In the recent times, C_8 carbon atoms which was found to be carcinogenic in nature has been replaced by C_6 and C_4. C_6 chemistry produces a byproduct called PFHA (perfluorohexanoic acid), which is supposed to be 40 times less bio accumulative than PFOA and found to be environment friendly.

Keywords: : Fluorochemicals, water repellency, oil repellency, PFHA

INTRODUCTION

Value addition is achieved by introducing some novel finishing. Finishing is the heart of the textile and by applying some novel finishes on apparel many desired properties like the fabric absorbency, stains to be easily removed from fabric and apparel faster, rise in the wicking action for better comfort in wear, fabric are easily dry-cleanable, good laundry durability, and maintains brightness after respective repeated laundering can be easily achieved. Hydrophobicity is one of the most widely spread textile finishes today. Finishes that repel water, oil and dry dirt are important in all parts of the textile market – for clothing, home and technical textiles [1]. The oldest water repellant finishes for fabrics were simply coatings of paraffin or wax – and they are generally washed out eventually[2-5]. Perfluorochemicals (PFC's) are the only chemicals capable of repelling water, oil and other liquids that cause stains. Fabrics finished with PFCs have nonstick properties; this family of chemicals is used in almost all the stain repellant finishes in the market today [2-5]. Other materials can be made to perform some of these functions but when subjected to oil and other liquids are considerably less durable [6,7].

The purpose of this finish is self-evident. Drops of water should not spread on the surface of the textile and should not wet the fabric. The drops should stay on the surface and easily drip off. Similarly, oil repellent finishes should prevent oily fluids from wetting treated textiles[8]. In a similar manner, soil-repellent finishes should protect textiles from both dry and wet soils. In all cases, the air permeability of the finished fabric should not be significantly reduced. In addition to the desired repellency effects, other undesirable fabric properties are often found with repellent finishes [8]. These include problems with static electricity, poor soil removal in aqueous laundering, stiffer fabric hand, greying (soil re-deposition) during aqueous laundering and increased flammability [6,7]. Some fabric properties that are often improved by repellent finishes include better durable press properties, more rapid drying more rapid drying and and increased resistance to acids, bases and other chemicals [8].

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FLUOROCHEMICAL FINISHES

Fluorochemical finishes (also termed fluorocarbon finishes) were first applied to textiles in the 1960s and their growth, particularly during the 1990s, has been greatly stimulated bythe consumer demands for easy-care properties such as water and oil-repellency, stain repellency, and soil and stain-release properties. Fluorochemicals (fluorocarbons) are a class of synthetically produced organic chemicals that contain a perfluoroalkyl residue in which all the hydrogen atoms have been replaced by fluorine [9,10,12-16]. Fluorochemicals exhibit outstanding chemical and thermal stability, low reactivity through their incompatibility with water and oil, and considerable reduction in surface tension [12-17]. It is this latter property which is of particular importance in the context of water- and oil-repellency, while their chemical and thermal stability contribute towards the durability of the surface finish to fabric care treatments such as laundering, dry-cleaning and tumble-drying.

Fluorine, first isolated by Moissan in 1886, is the most strongly electronegative element in nature and is extremely chemically reactive [15]. In the fluorine atom the electrons are held close to the atomic nucleus. The interaction of fluorine atoms with carbon atoms to form strong carbon–fluorine bonds leads to the carbon atoms in fluorocarbons being closely surrounded by fluorine atoms [14,15]. Thus the basis for the low reactivity of fluorochemical finishes is the high degree of protection provided by the fluorine atoms to the shielded carbon scaffold. In addition, the extremely low critical surface tension and high surface activity associated with fluorochemicals are also a consequence of this unique molecular topography [9, 12,14-16,18]. Fluorochemicals are used in many fields, for example, as durable lubricants, corrosion protection coatings for metals, flame-retardant polymers, fluorine elastomers used in the rubber industry and heat transfer fluids in refrigeration technology [15]. They are widely used as protective agents against water and oil, stains and soiling in the textile, paper and leather industries. Some fluorochemicals are used for specialist wetting applications in the textile field; others are used in firefighting, and in the electroplating and electronics industries [14].

TECHNIQUES FOR THE FORMATION OF FLUOROCHEMICALS

The current techniques available for the formation of fluorochemicals depend upon [9, 13-16]:

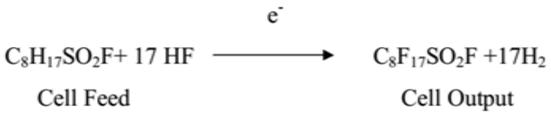
Telomerisation
Electrochemical fluorination
Oligomerization

However, the first two techniques have been the most widely used to manufacture fluorochemicals for repellent finishes [9], but finishes based on electrochemical fluorination were discontinued by 3M (Minnesota Mining and Manufacturing Company) in 2001 on eco-toxicological grounds concerning the type of fluorochemicals produced [19-20]. In telomerization, a fluorinated ethylene derivative (taxogen) is reacted with an initiator for chain growth polymerization (telogen), producing the desired FC. Telomerisation was used by Du Point. This process involves a free radical polymerisation process of tetra fluoroethylene as described in Fig 1 [21].

$$F_3C–CF_2–CF_2–CF_2–CF_2–CF_2–CF_2–CF_2–CH_2–CH_2–OH$$

Figure 1 Perfluorooctance Telomere alcohol

In electro fluorination, a hydrocarbon product is dissolved in hydrogen fluoride. Under an applied electrical current, the hydrogen atoms on the hydrocarbon are replaced by fluorine atoms[21]. The oligomerization process is similar to telomerization, but results in high molecular weight fluoropolymers, and thus is not generally used for production of FC finishes.



$$\underset{\text{Cell Feed}}{C_8H_{17}SO_2F + 17\ HF} \xrightarrow{e^-} \underset{\text{Cell Output}}{C_8F_{17}SO_2F + 17H_2}$$

Figure 2 Electrochemical Fluorination

Fluorochemical finish formulations

Fluorochemical finishes are based upon fluorocarbon dispersions and are mainly acrylate polymers containing a perfluorinated acrylate as the major component [9,13-16]. However, practically none of the commercial fluorochemicals consist of pure perfluoroacrylate homopolymer and normally there are various comonomers present. The main components that may be present in typical fluorochemical dispersion are illustrated in Figure 2 [16]. Oil-repellency and water-repellency depend crucially upon the perfluoroacrylate component but the presence of long-chain fatty alcohol acrylates, such as lauryl and stearyl acrylate, has been shown to produce synergistic improvement in water repellency with the perfluoroacrylate without adverse impairment of the oil-repellency[16]. Vinyl chloride, vinylidene chloride, methyl methacrylate and acrylonitrile are also frequently incorporated as co-monomers where special performance characteristics are required, such as soil-repellency or resistance to organic solvents and white spirit.

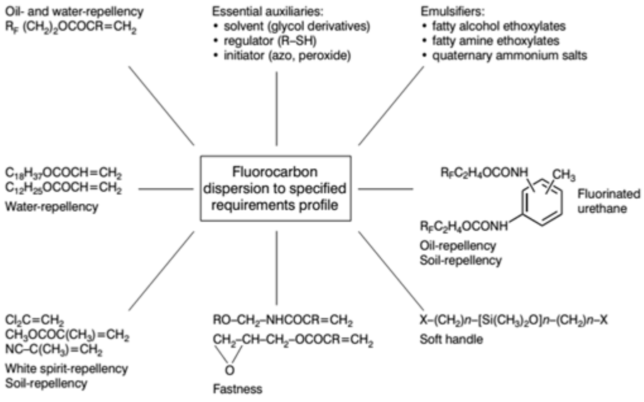


Figure 3 Major components of fluorocarbon dispersion

Mechanisms of repellency

Repellent finishes achieve their properties by reducing the free energy at fiber surfaces. If the adhesive interactions between a fiber and a drop of liquid placed on the fiber are greater than the internal cohesive interactions within the liquid, internal cohesive interactions within the liquid, the drop will spread [22]. If the adhesive interactions between the fiber and the liquid are less than the internal cohesive interactions within the liquid, the drop will not spread. Surfaces that exhibit low interactions with liquids are referred to as low energy surfaces [23]. Their critical surface energy or surface tension γ_C must be lower than the surface tension of the liquid γ_L(the internal cohesive interaction) that is repelled. γ_L of water, at 73 mN m^{-1}, is two to three times greater than γ_L of oils (20–35 mN m^{-1}). Therefore, oil repellency finishes with fluorocarbons (γ_C= 10–20mN m^{-1}) always achieve water repellency, but fluorine-free products, for example silicones (γ_C= 24–30 mN m^{-1}) will not repel oil. Low energy surfaces also provides measure of dry soil repellency by preventing soil particles from strongly adhering to fiber surfaces [2, 16-17, 24]. This low interaction allows the soil particles to be easily dislodged and removed by mechanical action.

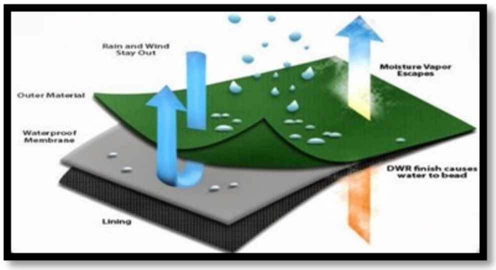


Figure 4 Mechanism of Repellency

Application methods for fluorochemical finishes

The method of application of the fluorochemical finish to the textile depends upon the form of the material – for example, flat woven, weft knitted fabric, velvet or pile fabric or carpet – and whether the fluorochemical finish is required to penetrate the structure and provide a film covering all the fibres uniformly, or whether a topical (or surface) application is all that is required [9, 13-16, 25-26]. Light and medium weight fabrics (linings, apparel, and home furnishing fabrics) may be saturated by immersion in a pad bath containing the fluorochemical and any appropriate auxiliaries followed by squeezing in a two-bowl or three-bowl nip [13, 25-26]. The fiber content and fabric construction normally dictate the wet pick-up range that is possible, and the wet pick-up is controlled by the nip bowl pressure. The chemical add-on of fluorochemical deposited on the fabric is typically around 0.15–0.3% on the weight of the fabric. The chemical add-on is controlled principally by regulating the fluorochemical finish concentration in the pad bath, rather than by regulation of the wet pick-up. As an alternative to padding, other methods of minimum application may be used such as lick-roll or nip padding or vacuum extraction. In the latter case, excess removal may be recycled back to the pad bath.

The vast majority of the fluorochemical finishes used in the treatment of textiles are cationic in nature and the recommended pH of the finishing bath should therefore preferably be around pH 5, which can be attained usually by addition of a small amount of acetic or formic acid [9,13-16, 27]. This ensures that any residual alkalinity in the fabric is neutralized and also that the finish bath is stabilized because the cationic emulsifiers used are much more effective at this pH level.

After impregnation, the fabric is dried at temperatures of about 110–130 °C followed by heat curing at a temperature normally in the range 150–170 °C. This may be carried out in separate stages in circulating hot air ovens or more usually in a single-pass treatment on a stenter. The higher the curing temperature, the shorter is the curing time to avoid yellowing of the textile material. Thus, heat-curing treatments at 150 °C for 3–4 min, or 160–180°C for 30–45 S, are typical of the conditions to be encountered in practice [27]. However, carpet products may be heat-cured at a minimum temperature of 110 °C while other products may be treated for 2 min at 170 °C, or for as little as 30 S at 190 °C. The heat-curing conditions used must provide optimal film formation and are dependent upon the chemical nature of the fluorochemical, the presence of extenders used to boost the fluorochemical performance and the durability performance required. Fibers that are heat-sensitive, such as wool or polypropylene, are cured at lower temperatures[25]. Where multifunctional finishes are used for example, fluorochemical combined with an easy-care finish– the heat-curing conditions selected must ensure that both the fluorochemical and the easy-care finish are satisfactorily cross linked to achieve the optimum fabric performance.

Other products

Chemical additives, such as wetting agent, thermosetting resin, extenders, softeners, antistatic agents, builders, flame-retardants, or fungicidal or anti-bacterial agents, may also be incorporated into the pad bath to obtain multifunctional finishes [9, 12-13, 25, 28]. Their effects upon the pad bath stability, or problems due to chemical incompatibility that may impair the final finished fabric performance, must be evaluated to optimize the process and product performance [9, 12-13, 25, 28].

The final polymer, when applied to a fibre, should form a structure that presents a dense -CF_3 outer surface for maximum repellency. The length of the perfluorinated side chains should be about 8–10 carbons [9, 12-13, 25, 28]. The small spacer group, mostly ethylene, can be modified to improve emulsification and solubility of the polymer. Co- monomers (X, Y, for example stearyl- or lauryl methacrylate, butyl acrylate, methylol- or epoxy functional acrylates and block copolymers from α, ω-dihydroxy dimethylpolysiloxane) affect fabric hand, film formation and durability [9, 12-13, 25, 28].

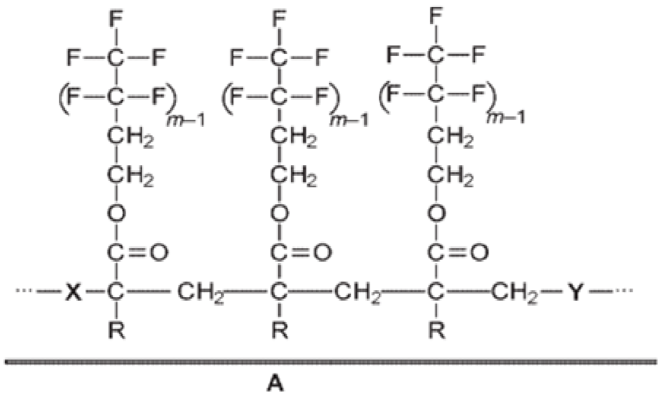


Figure 5 Fluorocarbon repellent on fiber surface. m= 8–10. X and Y are comonomers, mainly stearylacrylates. R = H or CH_3 (polyacrylic or polymethacrylic acid esters). A is the fiber surface.

EFFECT OF FLUOROCHEMICAL CHAIN LENGTH

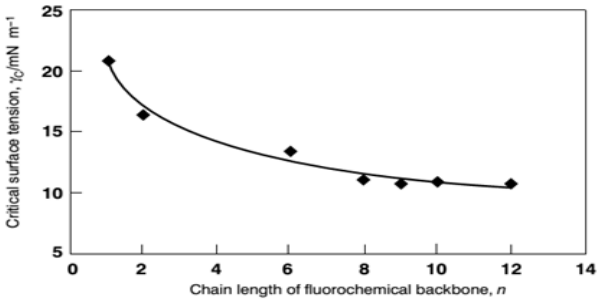


Figure 6 Effect of the fluorochemical chain length on surface tension

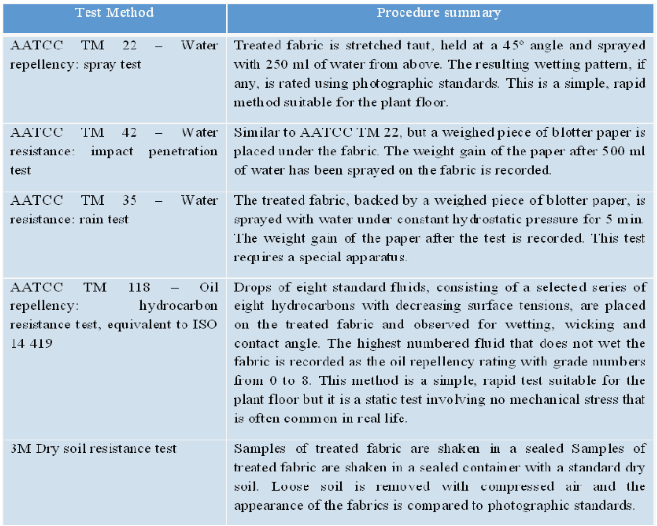
The effect of the fluorochemical chain length upon the critical surface tension (γ_c) is illustrated in Figure-6 [9]. It can be clearly seen that the critical surface tension decreases fairly rapidly as the chain length (n) increases from 1 to 8, after which little further decrease in critical surface tension is noted [9, 13]. As the critical surface tension of the fluorochemical film on the fiber surface is decreased, the water- and oil-repellency rise, reaching their maximum protective value around a chain length of n= 9. This dramatic improvement in repellency performance is illustrated in below table in which the oil-repellency (as measured according to AATCC Test Method 118) rises from 0 with a $-CF_3$terminal group to 8 with a $-(CF_2)_8-CF_3$ side chain. In addition, the water-repellency (as determined by the spray test ISO 4920) also rises from 50 up to 80. Thus an increase in the perfluorinated chain length from $CF_3$to C_9F_{19} (that is, $-(CF_2)_8-CF_3$) gradually enhances the oil repellency and, to a lesser extent, the water-repellency.

Perfluorinated groups	Measurement of oil-repellency (AATCC 118)	Spray test (ISO 4920)
$-CF_3$	0	50
$-CF_2-CF_3$	3-4	70
$-(CF_2)_2-CF_3$	6-7	70
$-(CF_2)_4-CF_3$	7-8	70
$-(CF_2)_6-CF_3$	7-8	70
$-(CF_2)_8-CF_3$	8	80

Oil- and water-repellency of fabrics treated with acrylic polymers

EVALUATION

Test methods for fabric with repellent finish [8]



Test Method	Procedure summary
AATCC TM 22 – Water repellency: spray test	Treated fabric is stretched taut, held at a 45° angle and sprayed with 250 ml of water from above. The resulting wetting pattern, if any, is rated using photographic standards. This is a simple, rapid method suitable for the plant floor.
AATCC TM 42 – Water resistance: impact penetration test	Similar to AATCC TM 22, but a weighed piece of blotter paper is placed under the fabric. The weight gain of the paper after 500 ml of water has been sprayed on the fabric is recorded.
AATCC TM 35 – Water resistance: rain test	The treated fabric, backed by a weighed piece of blotter paper, is sprayed with water under constant hydrostatic pressure for 5 min. The weight gain of the paper after the test is recorded. This test requires a special apparatus.
AATCC TM 118 – Oil repellency: hydrocarbon resistance test, equivalent to ISO 14 419	Drops of eight standard fluids, consisting of a selected series of eight hydrocarbons with decreasing surface tensions, are placed on the treated fabric and observed for wetting, wicking and contact angle. The highest numbered fluid that does not wet the fabric is recorded as the oil repellency rating with grade numbers from 0 to 8. This method is a simple, rapid test suitable for the plant floor but it is a static test involving no mechanical stress that is often common in real life.
3M Dry soil resistance test	Samples of treated fabric are shaken in a sealed Samples of treated fabric are shaken in a sealed container with a standard dry soil. Loose soil is removed with compressed air and the appearance of the fabrics is compared to photographic standards.

Toxicology and ecological considerations concerning PFCS

Traditional commercial FC products consist of 15–30 % fluorocarbon polymer, 1–3 % emulsifier,8–25 % organic solvents and water. The exhaust air of the drying and curing processes of fluorocarbon finishes therefore often contains high amounts of volatile organic compounds (VOC), like glycols and other organic solvents and a lower content of residual monomers [29-30]. Cellulosic fibers retain most of the glycols [29-30]. The exhaust air problem is greater with FC finishes on synthetic fibers. VOCs can be reduced by more than 90 % by the addition of corresponding boosters, providing equal effects with lower quantities of finish products. Perfluorochemicals (PFCs) are a group of chemicals used to make fluoropolymer coatings and products that resist heat, oil, stains, grease and water . During Electrofluorination and Telomerisation a small amount of **PFOS** (perfluorooctane sulphonate) and **PFOA** (perfluorooctanoic acid) is produced [31-32].

PFOA persists in the environment and does not breakdown. Scientists noticed that PFOS (the C8 fluorocarbon) began showing up everywhere: in polar bears, dolphins, baby eagles, tap water and human blood. They kill laboratory rats at higher doses, and there are potential links to tissue problems, developmental delays and some forms of cancer. Below are results which the U.S. Environmental Protection Agency released from data collected by 3M and DuPont; some humans have more PFOA in their blood than the estimated levels in animals in this study [31-32].

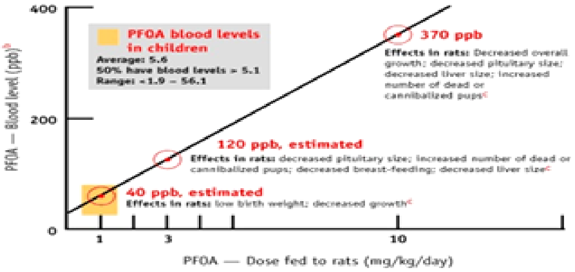


Figure 7 PFOA levels in human blood overlap with level in laboratory studies that cause harmful effect

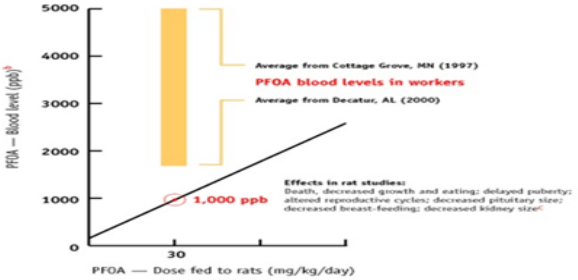


Figure 8 PFOA levels in human blood overlap with level in laboratory studies that cause harmful effect

PFOA and PFOS, according to the U.S. EPA:

- Are very persistent in the environment.
- Are found at very low levels both in the environment and in the blood of the U.S. population.
- Remain in people for a very long time.

PFOA and PFOS cause developmental and other adverse effects in laboratory animals [33-34].

C_6 and C_4 Chemistry

C_6 – this chemistry produces a by-product called PFHA (perfluorohexanoic acid), which is supposed to be 40 times less bio accumulative than PFOA. But it's also less effective, so more of the chemical has to be used to achieve the same result [33-34].

Manufacturers are trying to find smaller and smaller perfluorocarbon segments in their products, and even C_4 has been used. The smaller the fluorocarbon, the more rapidly it breaks down in the environment. Unfortunately, the desired textile performance goes down as the size of the perfluorcarbon goes down. "C_6 is closest chemically to C_8, but it contains no PFOA. It breaks down in the environment – a positive trait – but it doesn't stick as well to outerwear and it doesn't repel water and oil as well as C_8, which means it falls short of meeting a vague industry standard, as well as individual company standards for durability and repellency" [33,34].

3M settled on perfluorobutane sulfonate, or **PFBS,** a four-carbon cousin of the old chemicals. This new C4-based chemistry is completely safe. According to 3M, the results show that under federal EPA guidelines, **PFBS** isn't toxic and doesn't accumulate the way the old chemical did. It does persist in the environment, but 3M concluded that isn't a problem if it isn't accumulating or toxic. **PFBS** can enter the bloodstream of people and animals but "it's eliminated very quickly" and does no harm at typical very low levels.

RECENT DEVELOPMENT

A number of novel approaches to repellent finishing, several of which deserve mention, have been examined in recent years [35-36]. Each of the novel approaches has shown significant benefits and could be a potentially important finishing option in the near future.

Nature is now being copied by bio-engineering textile materials using nano coatings and other approaches that generate a low surface energy finish with a surface roughness that creates an ultra hydrophobic and self cleaning effect. One approach is that marketed by Nano Tex LLC, (Greensboro, NC, USA) which produces self cleaning cotton or cotton-blended fabric finish termed Nano-Care [37]. The Nano-Care finish utilizes whisker shaped 10 nm molecules of a fluorinated monomer copolymerized with a carboxylic acid oligomer and converted to the anhydride to react with the fiber. Nano Pel treatments are similar to Nano Care and are designed for use on wool and multiple layer fabrics but Nano-Tex technology has also been said to simulate the surface of a peach which has very fine, short hairs which are durably bonded to the fibers in the fabric. Nano-Tex technology is then licensed to other companies [38-39] and such fabrics are used in work wear, casual wear and sportswear [39].

Schoeller Textiles AG (Sevelen, Switzerland) has introduced its Nano Sphere technology which imparts water repellency, soil-repellent, anti-adhesive and self cleaning properties [40]. Their technology leads to the formation of micro-rough three-dimensional surface structures from which water; dirt and oil simply roll off. Using their Nano Sphere finish dirt particles on the surface of the finished textile cling to water droplets and when the water droplets run off the surface the dirt particles are simply washed away. Nano Sphere technology is said to use a so-called guest–host system of substances that allow spatial self-organization and result in the formation of a micro-rough surface. In parallel with this structure formation, gel-forming additives lead to the development of the porous system of a membrane.

Other approaches rely upon treatments that modify the fiber surface topography in combination with chemical finishes.

photonic surface treatment using a pulsed UV-laser (excimer laser) to yield a regular micron-scaled structure over a wide range of pulse energies [41].

Irradiation in the presence of perfluoro-4-methylpent-2-ene can then lead to radically bound hydrophobic end groups. Pulsed plasma polymerisation of monomers containing long perfluoroalkyl chains linked to a polymerisable carbon–carbon double bond can provide ultrahydrophobic effects which can be used not only for water-, oil- and stain-repellency [42], but can also be used for chemical protection, e.g. in nuclear, biological, chemical protection suits, for protection against nerve agents [43,42-47].
There are very clearly many opportunities for liquid proof and microorganism-impermeable medical textiles, e.g. for reusable surgical gowns made from polyester microfilament fabrics, suitable for repeated washing and sterilizing. Treatment of such fabrics with plasma treated/C_2F_6, plasma treated/H_2 + C_2F_6 (1:2), and plasma treated/C_2H_4 + C_2F_6 (1:2) provides contact angles of around140 °C [48].

A recent development has been the introduction of a special fluorocarbon product Anthydrin NK (Zschimmer & Schwarz Mohsdorf GmbH & Co., Burgsta¨dt, Germany) which is a low temperature cure product [49]. Use of a special cross linking system allows curing at around 110 °C compared with conventional cross linking at around 160 °C. A booster product Polappret VIB is co-applied if the finish must be fast to washing.

CONCLUSION

Flurochemical based chemicals shown in the recent review are viable water repellent, water proofing, durable and high performing finish. Fluorocarbon based water repellent has found wide application in a variety of consumer goods including non-stick cookware, paints and coatings and stain release treatment for carpets. The water repellency is achieved by lowering the surface energy of the fabric, so that water will bead on the surface and doesn't wet out the garments. Although similar finish can be achieved with many types of finishes including waxes, oils and silicones, they are not repellent, oils and lotions and hence fluorocarbon is most effective in repelling both oil and water and hence it is commonly used in water repellence finishes or outwear clothing.

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