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Innovative technologies for high performance textiles

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Review article

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Increasing global competition in textiles has created many challenges for European dyers and finishers. The rapid growth in technical textiles and in their end-uses has generated many opportunities for the application of innovative chemical finishes. Novel finishes of high added value for apparel fabrics are also greatly appreciated by a more discerning and demanding consumer market. This review will concentrate on some of the new approaches to producing high added value textiles that provide consumers with greater levels of comfort, safety, aesthetics and functional performance. Some of the technologies to be described are developed to the commercial exploitation stage, while others are still in development but offer potential for the future. Textile finishing personnel and companies must be active in keeping abreast of the developments in chemical finishing that are emerging globally, in order to survive and prosper in this very competitive and cost-conscious sector of the textile industry. The future of textile finishing within Europe depends upon rapid adoption of high performance, high added value finishes that provide innovation and novelty to the consumer, and in seeking out new end-uses and markets for such finishes.

Introduction

An analysis of the global textile and apparel industries carried out in 2005 by the United Nations Conference on Trade and Development (UNCTAD) demonstrated the growth in world trade during the period 1990–2003 [1]. In 2003, the 20 largest textile exporters exported US$172 604 million of textiles out of a world total of US$185 596 million, some 93% of the total. The 13 countries in the European Union (EU) in 2003 supplied US$59 906 million of this total (32.3%). However, after the ending of the Multi Fibre Arrangement there has been a dramatic rise in exports of apparel from countries such as China, India, Pakistan and Turkey into North America and the European Union.

The global market for fibres totalled 64 million tonnes in 2004 according to the PCI Consulting Group [2]. It was estimated that the main end-uses were apparel (65%), household textiles (18%) and technical textiles (17%). It is generally recognised that commodity textile and apparel manufacture has shifted away from North America and Western Europe into Asia and in parallel with this change dye manufacturing has also moved into Asia, principally into China. Some 64 million tonnes of fibres were estimated to have been consumed worldwide in 2004, with synthetic fibres (40 million tonnes) exceeding the consumption of natural fibres (24 million tonnes). The breakdown was considered to be polyester (40%), cotton (36%), polypropylene/other olefins (7%), polyamide (6%), acrylic (4%), regenerated cellulosic fibres (4%) and wool (2%) [2].

As the world population increases there will be an increase in global fibre consumption, but in the developed countries fabrics for apparel have become lighter in weight and the use of heavy fabrics for apparel has declined. North America and EU countries cannot compete with low wage cost countries producing commodity textile and apparel items. Instead, the way forward for the highly developed textile industries of North America and Europe is considered to be the high performance, high value-added route to textile manufacture. This utilises the high technical skills currently available in these industries in order to produce textile materials of high quality, high technical performance and perceived high value added to satisfy the growing consumer markets.

It is widely perceived that the end-uses for technical textiles will continue to increase each year and the modification of commodity fibre and fabric properties by innovative finishes can be a cheaper route to high performance than by using a high cost fibre with inherent built-in performance properties. The use of novel finishes and innovative technologies therefore can be applied to apparel fabrics, household textiles and technical textiles to increase their appeal to the consumer and stimulate the growth in niche markets.

Innovation is the lifeblood of the retailers who are always seeking products that are better, cheaper and faster delivered [3]. Consumers worldwide are more discerning and demanding, but many will pay a higher premium for products with a perceived higher value added, providing the consumer with greater individuality and status, as well as with higher standards of comfort, aesthetics, appearance, handle and functional performance.

The major sector of technical textiles continues to grow worldwide and many textile companies that have seen their traditional markets eroding through low labour cost countries that dominate the commodity textile and apparel markets have switched production to technical textiles, developing innovative products with high value-added functional performance levels [4]. In this way, niche markets have been opened up using lower volume, higher added value technical textiles that can be marketed and expanded into major sectors of industry, e.g. automotive fabrics, filtration, chemical protection, etc. Innovation in technical textiles is bounded only by the imagination of research, development and marketing teams and as a result the end-uses for textile fibres are continuing to expand, year-on-year.

This study will provide a brief review of some of the innovative technologies that are emerging in the textile field. The worldwide interest and investment in nanoscience and nanotechnology, in particular, could open up many opportunities in the technical textile and apparel markets [5].

Easy care, durable press and wrinkle-free finishes

For fabrics containing cotton or other cellulosic fibres the attainment of easy care, durable press and wrinkle-free finishes is essential to maintain the image of cotton in high performance apparel textiles. Traditionally such treatments utilise a chemical crosslinking agent together with a catalyst and fibre lubricant/softener. Many chemical types of finishes have been used [6,7] such as:
- 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU);
- 1,3-dimethyl-4,5-dihydroxyethylene urea;
- glyoxal urea;
- 1,2,3,4-butane tetracarboxylic acid;
- citric and malic acids;
- polymaleic acid derivatives and
- phosphonocarboxylic acids.

In addition to these approaches research has been conducted into novel chemical finishes based upon [7]:
- 1,3,5-triacryloylaminohexahydro-s-triazine-amino derivatives;
- DMDHEU/α-amino acids, e.g. aspartic acid/glutamic acid and
- ionic crosslinking using cationised chitosan.

The advantages and limitations of chemical crosslinking systems have been comprehensively reviewed in respect of the type of chemical finish applied [6,7]. However, new approaches to the application of chemical crosslinking agents could prove fruitful.

High-grade easy-care finishing of cellulosic fabrics is conventionally carried out using dry crosslinking (*ca.* 95%), moist crosslinking (*ca.* 5%) or wet crosslinking (0.1%) [8]. The highest functional performance is, however, achieved through moist crosslinking but this has entailed the highest processing costs because of the long fabric dwell time of 24 h at 30–35 °C. In the novel continuous moist crosslinking treatment jointly developed by Huntsman Textile Effects (Basel, Switzerland) and Monforts, the Monforts MXL Process, continuous moist crosslinking is completed on the Monforts Thermex hotflue [8]. Cotton fabric is padded with a crosslinking agent, dried at 110 °C for 3 min using 30% v/v steam on the Thermex hotflue to give a residual moisture content in the fabric of 5–6%, cooling to 20 °C. There is thus no dwell time.

The benefits of this novel approach to continuous moist crosslinking of cellulosic-based fabrics are [8]:
- continuous process;
- no separate dwell process necessary;
- low space requirement;
- lower investment costs;
- simpler residual moisture control with constant dwell time;
- no overdrying because of the use of controlled steam/air mixtures;
- reliable process management and process control and
- combinable with other finishing processes.

Total easy-care wool knitwear

The use of wool in knitwear is principally confined to fully fashioned and flat knitting, together with some circular knits [9]. However, wool is seldom used in warp-knitted fabrics. High quality knitwear has traditionally been manufactured on fine gauge fully fashioned machines and coarser gauge flat-knitting machines. More limited quantities of knitwear and tailored garments are produced using circular weft-knitted fabric. Because the wool fabric is produced in tubular form there are some limitations in the knitting, dyeing and finishing steps while the fact that garments must be produced by the cut and sew route creates waste. The cut and sew route is used for relatively fine gauge wool circular jersey products, but because the cutting waste can reach as high as 25% of the total fabric this processing route is economically unattractive.

Consumers now demand wool knitwear that is machine-washable and modern requirements for total easy-care wool include the need for tumble-dryability as well [10,11].

The increasing use of domestic washing machines after the Second World War and of tumble-dryers since the 1990s has intensified many research efforts to produce improved shrink-resist methods for wool. This ultimately led to treatments based upon a two-stage process [10]. The first stage involved an oxidative pretreatment using either chlorination or permonosulphuric acid. This was followed in a second stage by the application of a polymer.

The major method subsequently developed was the chlorination–Hercosett process applied as a continuous top treatment [10,11]. The chlorination pretreatment modifies the scale edges of wool and increases the critical surface tension of the fibre. This is an essential pretreatment, because this allows the Hercosett polymer (a polyamide–epichlorohydrin-based product) to wet and spread over the surface of the wool. This ensures that the scales are coated with a highly hydrophilic polymer that swells greatly when placed into water. Thus, the scales are sheathed or masked and the directional frictional effect (DFE) caused by the difference in friction between μ_a (friction coefficient when rubbing in the against-scale direction) and μ_w (friction coefficient when rubbing in the with-scale direction). As the DFE is the principal factor causing wool felting, treatments that eliminate the DFE give rise to a shrink-resist effect on wool.

One of the major issues in the field of wool shrink-resist finishing is the continual search for alternatives to chlorination pretreatments and chlorine-containing shrink-resist polymers [11]. New approaches are highly desirable to remove the problem of AOX (absorbable organohalogen compounds) which is created by the reaction of chlorine on wool. In Germany, a limit has been set for AOX at 1 ppm in drinking water. A similar limit applies for AOX in effluent in many European countries.

Oxidative pretreatment of wool followed by enzymatic treatment to produce shrink-resist wool yarns and fabrics was a feature of the Perzyme Process developed by WIRA Leeds, UK which was used during the Second World War. The wool was first given a short treatment with hydrogen peroxide at pH 10.5, followed by treatment with a mixture of papain and sodium bisulphite [12,13]. One of the most novel treatments for batch processing is the ARS-patented process, which was developed at the USA Army's request for itch-free, washable wool underwear made from American wool [14]. The ARS process consists of a pretreatment with a stable activated peroxide followed by proteolytic treatment with an enzyme, either serine or cysteine protease.

In the ARS process wool fabric is whitened, biopolished and imparted with machine-washable properties [14]. The wool fabric is first pretreated for 30 min at 30 °C with a powerful, stable peroxide (percarboximide) formed from dicyandiamide and alkaline hydrogen peroxide with gluconic acid stabiliser for sustained whitening. In a subsequent treatment at 45 °C for 40 min with serinase assisted by sodium sulphite, or unassisted cysteinase applied at 50 °C for 60 min, biopolishing and machine-washable performance is obtained without appreciable loss in strength or elastic recovery.

Another recent development is a shrink-resist process for machine washability in which the wool is first pretreated with hydrogen peroxide in a salt solution to restrict reaction to the fibre surface followed by treatment with proteolytic enzyme linked to a polymer to decrease the enzyme diffusion into the wool fibre interior [15]. In this way, the reaction is restricted to the surface and wool fibre damage is minimised.

A novel continuous shrink-resist treatment for wool tops and loose stock is the Perachem process, developed at the University of Leeds, UK [16]. This consists of a preliminary step in which the surface energy of the wool fibres is increased by the removal of much of the hydrophobic covalently bound surface lipids through treatment with a nucleophilic agent. This treatment also oxidises the cystine in the A-layer of the cuticle and is followed by sulphitolysis with sulphites to generate Bunte Salt groups ($-SSO_3^-$). These groups create a negatively charged wool fibre surface and give cuticle swelling which also contributes to the overall shrink-resist effect of the treatment. Exhaustion of a cationic low–AOX Hercosett resin then follows, the whole process being carried out in a continuous six-bowl treatment. It is claimed that this patented process results in a wool that is whiter and softer than that achieved in conventional chlorine/Hercosett treatments while the dyeing properties are the same.

The German Wool Research Institute (DWI, Aachen, Germany) has examined the application of a continuous atmospheric plasma treatment for wool tops at 5–7 m/min over a width of 150 cm [17]. Using five electrodes the energy output was raised to 3.5 kW in order to decrease the wetting time of the wool. The effect of the plasma treatment is adversely affected by a higher moisture content in the wool. Plasma treatments can generate a rather harsh handle because they remove a large proportion of the covalently bound lipids from the fibre surface which necessitates the need for a softener. Arristan 64 (CHT R. Beitlich GmbH, Tübingen, Germany) is a special reactive polysiloxane-based softener which not only imparts a soft handle, but also enhances the shrink-resist and colour fastness performance.

At present the major continuous top treatments for Superwash wool are conducted using ranges manufactured by Andar (Timaru, New Zealand), Fleissner (Egelsbach, Germany) and Kroy (Schia, Italy). Andar has also introduced a novel loose wool shrink-resist applicator for small lot processing which could open up new opportunities for wool knitwear end-uses, especially for lambs' wool.

Additive treatments alone using polymeric finishes to mask the scales when applied by padding can give rise to a relatively hard handle because of interfibre bonding. Ciba have introduced a highly crosslinked silicone rubber (Dicrylan 7702) which further reacts on the wool fibre when a special metal-free catalyst (Phobotone Catalyst 7639) is used [18]. A combination of crosslinkable silicone rubber with silicone-modified polyurethane allows tumble-drying after washing, but this performance is not achievable using silicone rubber alone.

A novel polymer termed DP5570 has been recently developed by Devan-PPT Chemicals (Ambergate, UK) that fully meets total easy care standards and is claimed to compete economically with the Hercosett polymer as well as offering some additional benefits [19]. This is a low solids add-on polymer process (0.3% at pH 5–6) compared with Hercosett (2% at pH 7–8). The DP5570 polymer can be cured at a lower temperature providing energy savings while the treatment imparts control over the hairiness/facing/pilling that occurs during washing which remains a problem with the standard shrink-resist treatments. The use of DP5570 polymer is claimed to impart a natural softness as well as yielding a whiter wool with improved dyeability.

Ultrahydrophobic surface treatments and self-cleaning finishes

The whole area of water repellency and waterproofing including oil-repellent and stain-repellent finishes has recently been reviewed in depth [20–24].

In fluorochemicals based upon fluoroacrylates the perfluorinated side-chains are oriented away from the fibre surface, with the $-CF_3$ terminal groups creating a low-energy surface [21,22]. The optimum orientation takes place only if the length of the perfluorinated side-chain is at least seven carbon atoms and wash fastness on cotton is improved through the use of methylol groups. During washing the orientation of the side-chains changes and has to be restored generally by heating at 70–80 °C, typically by tumble-drying or hot ironing. Modern versions of fluorocarbons can be reorientated to restore the repellency at *ca*. 60 °C, but research is continuing to lower the reorientation temperature [21–24].

It is clear that the demands for fluorocarbon finishes will increase as many forms of textile garments, traditionally never given a water-repellent or stain-repellent finish, will be given such treatment in the future to provide a higher added value through the improved easy-care performance. Research and development to optimise the effects, decrease curing times and temperatures, promote reorientation at lower temperatures, and maintain high effectiveness through multiple wash cycles will continue throughout the next decade. The ability of fluorocarbon finishes to provide durable repellency properties without impairment of garment breathability (i.e. high water vapour transmission rates) is an important marketing advantage [20].

Biomimetic finishes are an interesting area for future development. The self-cleaning action of the surface of the lotus leaf has given rise to the so-called 'lotus effect' which is being utilised to produce ultrahydrophobic finishes [21,25,26]. The surface of the lotus leaf is covered with characteristic wax microstructures, which can generate contact angles of up to 170°, significantly higher than with smooth fluorochemical-based surface coatings. This ultrahydrophobic (or superhydrophobic) effect also ensures the rapid and effective removal by water of any soils on the surface of the lotus leaves, providing a self-cleaning effect.

Nature is now being copied by bio-engineering textile materials using nanocoatings and other approaches that generate a low surface energy finish with a surface roughness that creates an ultrahydrophobic and self-cleaning effect. One approach is that marketed by Nano-Tex LLC, (Greensboro, NC, USA) which produces a self-cleaning cotton or cotton-blended fabric finish termed Nano-Care [26]. The Nano-Care finish utilises whisker-shaped 10 nm molecules of a fluorinated monomer copolymerised with a carboxylic acid oligomer and converted to the anhydride to react with the fibre. 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 fibres in the fabric. Nano-Tex technology is then licensed to other companies [27,28] and such fabrics are used in workwear, casualwear and sportswear [28].

Schoeller Textiles AG (Sevelen, Switzerland) has introduced its NanoSphere technology which imparts water repellency, soil-repellent, anti-adhesive and self-cleaning properties [29]. Their technology leads to the formation of micro-rough three-dimensional surface structures from which water, dirt and oil simply roll off. Using their NanoSphere 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. NanoSphere technology is said to use a so-called guest–host system of substances that allow spatial self-organisation 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 fibre surface topography in combination with chemical finishes. Research by the German Textile Research Centre North West, Krefeld, Germany has described the application of a photonic surface treatment using a pulsed UV-laser (excimer laser) to yield a regular micron-scaled structure over a wide range of pulse energies [30]. 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 ultra-hydrophobic effects which can be used not only for water-, oil- and stain-repellency [31], but can also be used for chemical protection, e.g. in nuclear, biological, chemical protection suits, for protection against nerve agents [21,31–35].

Glow-discharge plasma treatments can be used for activation, grafting, deposition or etching. Using an RF capacitive system at 13.56 kHz wool and cotton fabric samples have been treated with a trichloroethylene solution of Zonyl fluoromonomer (DuPont, Wilmington, DE, USA) in argon plasma to obtain high levels of water and oil repellency [36,37].

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 sterilising. 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 around 140 °C [38].

A recent development has been the introduction of a special fluorocarbon product Anthydrin NK (Zschimmer & Schwarz Mohsdorf GmbH & Co., Burgstädt, Germany) which is a low temperature cure product [39]. Use of a special crosslinking system allows curing at around 110 °C compared with conventional crosslinking at around 160 °C. A booster product Polappret VIB is co-applied if the finish must be fast to washing.

In two important recent publications [40,41] Gao and McCarthy [41] have criticised some previous publications on ultrahydrophobic surfaces for not adequately reporting contact angles and for ignoring older significant literature on this subject [42]. It was emphasised that contact angle hysteresis (i.e. the difference between the advancing and receding contact angles) and not high contact angle actually controls water droplet movement (water-repellency) [40]. A number of authors have defined superhydrophobic surfaces as those exhibiting water contact angles >150°, while contact angle hysteresis often is not mentioned [40,41]. The earlier publications by Fogg [43] and by Cassie and Baxter [44] predate the 'lotus effect' literature by five decades, demonstrating that leaves exhibited advancing water contact angles >150°.

Gao and McCarthy established that lotus leaves in their laboratory exhibited advancing water contact angles (θ_A) of 156.1° and receding water contact angles (θ_R) of 151.1° [40]. The value of the contact angle hysteresis ($\cos\theta_R - \cos\theta_A$) was 0.039. Application of a water-repellent treatment according to a patented method originally applied to cotton [45] was then applied to conventional polyester and to microfibre polyester fabrics. Both fabrics were extracted with dry toluene and dried in air before being dipped in a toluene solution of 4 wt% methylsilicone followed by drying at 100 °C for 1 h. On conventional polyester the advancing and receding water contact angles were $\theta_A = 151.2°$ and $\theta_R = 140.1°$, but on microfibre polyester $\theta_A = 170.2°$ and $\theta_R = 165.1°$ [40].

It was observed that water droplets rolled easily on both fabrics, but much more readily on the microfibre polyester. The force (*F*) required to move the droplets is given by:

$$F \sim \gamma_{LV}(\cos\theta_R - \cos\theta_A)$$

where γ_{LV} is the surface tension of the liquid (i.e. water) [40]. For conventional polyester the value of ($\cos\theta_R - \cos\theta_A$) was 0.109, but for the microfibre polyester the contact angle hysteresis was considerably lower at 0.019. Thus, Gao and McCarthy pointed out that it took six times as much force (7.85 dyn/cm *vs* 1.3 dyn/cm) to move a droplet on conventional polyester compared with microfibre polyester [40]. It was considered that this resulted from the nature of the contact line structure and the barriers to its advancement and recession, it being easier for a water droplet to recede from a 2 μm diameter polyester microfibre than from the 40 μm diameter conventional polyester fibres. It was observed that the binary length scale topography (*ca*. 2 μm/50 μm) for the microfibre polyester diameter/microfabric weave fineness was dimensionally similar to that of the lotus leaf, but it has been asserted that the 'right' single length topography is more effective at water-repellency [40].

An exciting development is the recent production of a perfectly hydrophobic surface on silicon wafers by Gao and McCarthy that has been termed 'Lichao's surface' and which exhibits $\theta_A/\theta_R = 180/180°$ [41]. The silicon wafers were submerged in toluene solutions of $MeSiCl_3$ at room temperature, rinsed with toluene, ethanol and water and dried. Vessels were closed to the air during reaction, but exposed (relative humidity *ca*. 40–65%) during solution and sample introduction. Water droplets, it is claimed, do not come to rest on horizontal surfaces treated with this procedure, and some 70% of samples treated by this method exhibited a perfectly hydrophobic surface [41].

A method for measuring extreme hydrophobicity was devised to distinguish between surfaces with a slight affinity for water ($\theta_A/\theta_R = 175–179/175–179°$) and those with no affinity ($\theta_A/\theta_R = 180/180°$) [41]. The surface to be examined was lowered onto a supported droplet, and repetitive contact, compression and release of the droplet were recorded by video. Surfaces with contact angles <180° exhibited affinity for the droplet during attachment and release, whereas droplets on a perfectly hydrophobic sample with a Lichao's surface show no affinity for this surface during contact or release after compression. The work of adhesion is apparently zero.

Stereoscanning electron microscopy of $MeSiCl_3$-derived silicon wafer surfaces demonstrated a network of cylindrical fibres with diameters of *ca*. 40 nm [41]. Gao and McCarthy consider that the conditions used for this modification promote 'vertical polymerisation' of $MeSiCl_3$ into a covalently attached toluene-swollen 3-D methylsiloxane network [41]. Rapid extraction of toluene by ethanol then induces phase separation. The siloxane is not swollen by ethanol. If the humidity is not sufficiently high or the reaction time is too short, smoother surfaces with lower contact angles are generated. If the humidity is too high, phase separation creates spherical-shaped particles which generate surfaces with lower contact angles. A vessel with a perfectly hydrophobic inner surface would thus hold, but not touch water [41].

It is clear that the application of such approaches to textile fabrics could produce a new generation of perfectly hydrophobic fabrics with outstanding water-, oil- and stain-repellency. There are many potential end-uses for such surfaces in technical, industrial, medical and military end-uses, for protection from a wide variety of liquids.

Hydrophilic softeners and moisture management systems

Three very detailed reviews of chemical softeners and their effects on textile materials have been recently published [46–48] which should stimulate developments for softening textile fabrics.

Clariant (Basel, Switzerland) has introduced a novel cationic silicone softener, Sandoperm SE1 oil liq which is described as a new development in the area of silicone chemistry [49]. The novelty lies in the fact that for the first time the emulsifiers are linked through a covalent bond to the silicone chain to produce a self-emulsifying amino-functional silicone fluid. By this special chemical engineering of the molecule Sandoperm SE1 oil liq is emulsified for its applications simply by stirring it in water. This process creates nanoemulsions wherein the particle size is extremely small and the silicone fluid is hydrophilic.

Compared with typical macroemulsions (>150 nm particles) and microemulsions (50–150 nm) Sandoperm SE1 oil liq produces nanoemulsions (10 nm) which impart an inner softness with a unique cool, natural and dry handle to woven and knitted fabrics [49]. Applicable to all types of cellulosic fibres, e.g. cotton, viscose, modal, lyocell, and to polyamide, polyester and their blends, the hydrophilicity imparted is classed as permanent to washing. When applied to blends like polyester/viscose or polyester/modal fibres the handle obtained can simulate a wool-like handle, while on synthetic fabrics a so-called 'silky-touch' which is still a very soft and dry handle, can be obtained.

Sandoperm SE1 oil liq is a flexible softener which is applicable by padding or by exhaustion and is designed to be stable in combination with resin finishing baths in the presence of crosslinking agents and catalysts [49]. It is claimed that Sandoperm SE1 oil liq does not yellow on white fabrics which have been given a fluorescent brightening treatment. Used along with Cassapret SRHA liq, Clariant has achieved finishes on polyester and polyester blend fabrics that combine soil-release properties that are wash-permanent, extremely hydrophilic and allow moisture transport, the so-called 'silky touch' finish.

A new era of garment performance has been introduced with the synthesis of novel softening agents that form part of a moisture management system [48,50–52]. With the changing lifestyles of modern consumers, there is now more emphasis upon a more physically active and healthier lifestyle as part of a desire for a more youthful approach to living, thereby providing some degree of anti-ageing effect by keeping the body in good physical condition. However, raising the level of physical activity leads to the production of perspiration exuded in order to maintain a normal body temperature. This perspiration must be rapidly wicked away from the surface of the skin into the overlying garment and evaporated if the wearer is not to feel discomfort through build-up of liquid perspiration on the skin. Modern moisture management systems promote rapid wicking and evaporation and provide high added value to sportswear and casualwear, significantly enhancing the perceived comfort level of the wearer [48,49,51,52].

A novel moisture management agent, Ultraphil HCT from Huntsman Textile Effects is part of their High IQ range which provides 'cool comfort' and is based upon a silicone microemulsion [53]. Engineered for application to cotton by exhaustion, Ultraphil HCT exhibits the highest level of stability to the shearing forces found in high speed jet dyeing machines. Ultraphil HCT imparts hydrophilicity and a very soft handle to cotton, while the quaternary chemical nature of the structure results in a very high durability to washing.

Hydrophilic silicones may be created using a variety of chemical approaches [48,50,51], such as the use of:
– polyether derivatives of silicone softeners with polyglycol functionality;
– silicones with quaternary ammonium groups;
– silicones with tertiary amino groups;
– α,ω-aminosilicones;
– silicones with amino groups modified by acylation or alkylation and
– blends of aminosilicones and hydrophilic polymers, e.g. polyethylene and polypropylene glycols, polyethylene imine, polyvinyl pyrrolidone, polyvinyl alcohol, polytetrahydrofuran, etc.

A new hydrophilic finish from Clariant is Sandoperm RPU Liquid, a new thermoreactive polyurethane for a wash fast, very full and extremely soft handle on cellulosic and polyamide fibres [54]. Applied with silicone softeners Sandoperm RPU Liquid produces a hydrophilic finish, improving the elasticity/shape recovery of knitted goods.

The Nano-Dry finish from Nano-Tex LLC is a durable, hydrophilic finish for nylon and polyester [27]. On the latter fibre polyethylene glycol and amino silicone in nano-form are claimed to be applied to sportswear and underwear requiring perspiration-absorbency.

Novel approaches to flame-retardant finishes

Harsh handle and decreased tensile and tear strength and abrasion resistance are inherent problems associated with the high chemical add-on and the use of flame-retardant formulations that self-crosslink or crosslink or react with the fibre. Thus, the major method used in the upholstery field has been the use of resin-bonded antimony–bromine flame-retardant systems applied via a back-coating technique so as not to impair the aesthetics of the fabric face [55–57]. Decabromodiphenyl oxide (DBDPO) or hexabromocyclododecane (HBCD) have been mainly used in conjunction with antimony trioxide. However, this system still has a marked effect upon the fabric physical properties.

The future of flame retardancy is hindered greatly by environmental and ecotoxicological considerations, both of the flame retardants used and the toxic nature of the products released upon combustion of textile fabrics [55–59]. Ideally, the best flame-retardant system for cotton should char the fibre, releasing no toxic smoke or gases, and prevent afterglow. Novel thin-film encapsulation of all the fibres with an inherently flame-retardant coating system could be one path to progress, but the effects on fabric aesthetics would require optimising. Alternatively, the use of intumescent systems for flame- and heat-protection offer some promise, but at present the chemical add-on levels tend to be high and the activation temperature and speed of response of the system must ensure thermal protection during the initial ignition period [60].

Flame retardancy, as a research area, has progressed only slowly, and some of the current major flame-retardant suppliers and their products have been summarised elsewhere [61].

Thor Specialities (UK) Ltd (Wincham, UK) has introduced two phosphorus-based products for use with a binder in flame-retardant back-coatings to replace antimony/halogen systems [62]. Aflammit BCC is engineered for application to cotton and cotton-rich blends, and Aflammit BCS is claimed to be effective on a range of synthetic fibres.

A novel flame retardant applicable by exhaustion on polyester is Cetaflam DB7 (Avocet Dye & Chemical Co. Ltd, Brighouse, UK) [57]. Cetaflam DB7 can be applied in jet dyeing of polyester at temperatures of 130 °C to provide a durable flame-retardant finish. Cetaflam DB7 is non-foaming and the dyed and flame retarded polyester can be washed off or reduction cleared after dyeing as normal.

Recent research has studied the co-application of crosslinking agents for cellulosic fibres such as trimethylolmelamine or 1,2,3,4-butanetetracarboxylic acid with a hydroxy-functional organophosphorus oligomer (Fyroltex HP from Akzo-Nobel, Arnhem, The Netherlands) [63,64]. Applied by a pad–dry–cure process using a catalyst, the add-on used was relatively high which adversely affected the fabric handle.

Devan Chemicals (Belgium) has focused upon halogen-free flame retardants and has studied intumescent finishes using three different approaches, [64] namely:
– encapsulating microscopic amounts of flame-retardant particles in a thin polymer film, which forms a solid wall. This decreases the aqueous solubility of the flame retardant;
– use of nanoclay technology, in which layered silicates in the form of reticular layers of crystals measuring a few nanometres and based upon a modified montmorillonite, have been used and
– use of expandable graphites whereby the physical expansion of intercalated (layer lattice-structured) graphite is initiated by heat with vaporisation of the intercalates. This creates a volume expansion effect around one hundred times greater than the original.

For flame-retardant back-coating of textile fabrics a new approach has recently been developed [65]. The TexFRon product range (ICL – Industrial Products, Israel) consists of aqueous self-crosslinking dispersions of nano-size brominated acrylic copolymers. The bromine is thus locked into the structure as part of the polymer chain and the TexFRon coatings are designed for use with antimony trioxide and are applicable by padding, dipping, coating, spraying, foam application and screen printing. These brominated acrylic copolymers are resistant to aqueous leaching tests, have a solid content of 40–50% and a bromine content (percentage on dry basis) of 30–46%.

In attempts to produce a halogen-free flame-retardant back-coating system Horrocks *et al.* have reported on phosphorus derivatives which can function, like bromine, in the vapour phase [66]. One system developed was based upon an intumescent phosphorylated pentaerythritol derivative together with relatively volatile tributyl phosphate. A phosphorus-based flame retardant or a component of the flame retardant that can be volatilised either as a decomposition product or by evaporation or by an impinging flame could therefore offer one potential approach to a halogen-free and antimony-free flame-retardant back-coating system.

Research in Russia at the Semenov Institute in Moscow led to the introduction of a novel flame retardant for wool termed Noflan (Firestop Chemicals Ltd, UK) [67]. This is an organophosphorus compound based on the ammonium salt of an amidoalkylphosphonic acid with a phosphorus content of 14%. This patented process involves application by a pad–dry–cure technique, while wool carpets could be treated by a spray–dry–cure or spray–dry–steam method. Noflan promotes solid phase charring of wool, but is principally intended for fabric and carpet applications, especially for transportation fabrics.

A recent extension of Noflan technology is Noflan E [67]. This is an encapsulated form of the flame retardant currently under development, directed towards unsaturated polyesters and polyurethanes.

Noflan currently contains chlorine in the form of ammonium chloride, but research and development to introduce a halogen-free flame-retardant system has resulted in Bizon, a patented halogen-free, antimony-free, phosphorus-based flame retardant [67]. This is said to be produced by a reaction of nitrilotris(methylene) triphosphinic acid with urea to produce an ammonium salt of nitrilotris(methylene)triphosphinic acid amide. This functions via a solid phase charring mechanism and has many potential applications, including polyolefines and high temperature plastics.

New approaches using enzymes

The range of enzymes available for application in textile wet processing continues to increase each year and new uses will clearly be found over the next decade. The book by Cavaco-Paulo and Gübitz provides an excellent overview of textile processing with enzymes [68] and a short review of the major types of enzymes and their actions has also been published [69]. The use of various enzymes to carry out surface hydrolysis of polyester fibres to increase fibre hydrophilicity and modify dyeability has been reported [70–72]. The use of nitrile hydratase enzyme to modify the dyeing efficiency of acrylic fibres has been studied and the treatment modifies the surface of acrylic fibres converting the surface nitrile groups into amide groups, thereby increasing the hydrophilicity and the antistatic properties of the fibres [70,71,73,74]. The major types of enzymes used so far are amylases, cellulases, lipases, pectinases, catalases, proteases and laccases [68,69].

Enzymes are biocatalysts and based upon high-molecular weight protein structures. In conventional catalysts, the catalyst nominally takes part in the chemical reaction, but is left unaltered at the end of the process. However, side reactions such as hydrolysis or oxidation of the enzyme may occur in textile wet processing and separation of the enzyme from chemical contaminants/breakdown products from the fibres present will clearly complicate any attempts at enzyme recovery and enzyme recycling, although if methods could be found the cost of enzyme processing could be decreased, and water and energy also recycled. Research into this area could yield some fruitful results.

Microencapsulation of chemical finishes and fragrances

Microencapsulation technologies have now only really begun to be exploited [75–79]. Phase-change materials (PCMs; e.g. Outlast, Frisby) that absorb or release heat according to the conditions are interesting for some end-uses [75,78]. However, a more interesting development is that of the incorporation of fragrance within the microencapsulated polymer spheres, allowing a gradual release of an appropriate fragrance to promote aromatherapy [77–79]. Typical perceived benefits could include:

- uplifting/head clearing, e.g. active sportswear;
- relaxing/encourages sleep, e.g. fragrances for nightwear or bedding;
- muscle easing, e.g. for after-sport activity and
- clear thinking/confidence building, e.g. formal businesswear suits.

In addition, there are opportunities for health and well-being by using cosmeto-textiles in which substances that enhance skin appearance, or vitamins can be absorbed by the skin [76–81]. Skin moisturisers and skin-cooling products, or even appropriate drug therapy could become important markets with an ageing population. Another important area could be the application of microencapsulated insect-repellents for protection against mosquitoes and other insects [78,82].

Potential areas for growth in microencapsulated finishes

The following areas are considered to offer potential for the use of microencapsulated finishes [75,82].

- Phase-change materials for thermoregulation;
- Fragrance release;
- Aromatherapy agents;
- Antimicrobial finishes;
- Deodorising finishes;
- Biocides;
- Insect-repellent finishes;
- Insect-resist treatments;
- Skin-moisturising agents;
- Skin-cooling agents;
- Controlled release of vitamins and pro-vitamins;
- Controlled release of other agents absorbed through the skin.

– Depilatory agents;
– UV-absorbers;
– Antistatic agents;
– Flame retardants;
– Water repellents;
– Antisoiling agents;
– Chemical protection;
– Softeners;
– Cross-linking agents;
– Pleating agents;
– Colorants;
– Enzymes.

In addition, there are opportunities for microencapsulation in other fields such as biosensors and anti-counterfeiting agents [80].

Phase-change materials for thermoregulation

A new concept for the thermoregulation of skin temperature was developed in the 1980s for the US National Aeronautics and Space Administration (NASA) which was originally designed with the aim of controlling the thermal barrier properties of garments for use in space suits [80]. Although microencapsulated PCMs were developed these were never utilised for space suits. The inventor, the Triangle Research and Development Co., (Raleigh, NC, USA) subsequently licensed the technology to Outlast Technologies, Inc. (Boulder, CO, USA) and phase-change technology has been exploited in textile fibres and fabric coatings.

Phase-change materials utilise microencapsulated chemicals such as nonadecane ($C_{19}H_{40}$) and other medium-chain length alkanes [76,78,80]. When the ambient temperature increases above 32.1 °C (the melting point of nonadecane) the nonadecane melts and latent heat is absorbed thereby interrupting the increase in temperature of a garment. Once the ambient temperature falls the PCMs solidify and the latent heat is released providing a heating effect. The crystallisation temperature of nonadecane is 26.4 °C. Thus, PCMs can be used to provide a cooling effect, or a heating effect, upon the garment microclimate depending upon the ambient temperature.

The use of PCMs has been widespread with as many as 150 companies using microencapsulated PCMs under licence from Outlast Technologies, Inc. which has consolidated its position as the world leader through the acquisition of substantially all of the remaining assets of Frisby Technologies, Inc., (Winston-Salem, NC, USA) including various technology licences, the Thermasorb trademark, logo, website and intellectual property rights in the field of PCM technology. Phase-change material microcapsules have walls <1 μm thick and typically may be 20–40 μm in diameter with a PCM loading of 80–85%. The relatively high surface area for heat transfer afforded by the small microcapsule size ensures that the response of the PCM to external temperature changes is very rapid [80].

Outlast Technologies Inc. (Boulder, CO, USA) Adaptive Comfort technology uses their patented microencapsulated PCMs (termed Thermocules) in a wide variety of textile applications especially on garments for those parts of the body where extremes of temperature are most keenly felt. Outlast Technologies' Thermocules have been used in gloves, socks, hats, outdoor wear, e.g. vests, thermals, parkas, snowsuits and trousers and in household textiles such as blankets, duvets, mattresses and pillowcases. Other applications include microclimate control in medical textiles.

Ciba Specialty Chemicals has introduced Encapsulence PC140 using their in-house microencapsulation systems and their microencapsulated PCM is utilised for Outlast thermal regulation [83]. Ciba Encapsulence PC140 microcapsules have been incorporated into acrylic fibres using late injection technology by Acordis UK for Outlast. Some 5–10% of microcapsules are permanently locked into the acrylic fibres with no change in fibre properties or changes necessary to the fibre processing.

Aromatherapy/fragrance release

Aromatherapy has entered into the lifestyle of many consumers in the stressful ambience of the modern global village in which we all live. Aromatherapy utilises the controlled release of an aroma or fragrance to promote feelings of comfort and well-being amongst consumers [76,79,80]. Amongst the many applications for aromatherapy, a number of fragrances such as camomile, lavender, lemon, peppermint, jasmine and rose can provide a broad spectrum of advantages when applied to performance apparel. These are summarised in Table 1 [79].

Table 1 Aromatherapy benefits from fragrances [79]

Benefit	Fragrance
Uplifting	Lemon, peppermint
Relaxing	Camomile, lavender, jasmine
Aphrodisiac	Jasmine, rose
Balancing	Lavender, jasmine, rose
Clear thinking	Peppermint
Confidence building	Jasmine, rose
Head clearing	Peppermint
Muscle easing	Peppermint
Encourage sleep	Camomile, lavender

LJ Specialities (Holmewood, UK) has pointed out that an uplifting/head clearing fragrance-like microencapsulated peppermint could be used for active sportswear, while lavender on bedding has been shown in customer wearer trials to relax customers and encourage sleep [79]. Peppermint is also claimed to have muscle-easing properties, another advantage for active sportswear end-uses. Microencapsulated fragrances that encourage clear thinking/confidence building could be applied to suitings for formal wear. There are clearly a myriad of essential oils with many potential applications.

A major advance in this field especially for wool fabrics has been the introduction of Sensory Perception Technology (SPT) microcapsules manufactured by International Flavors and Fragrances (IFF) based in New York, USA the largest flavour ingredients house in the world [84].

SPT microcapsules are distributed and sold globally by Woolmark Development International Ltd (WDI) part of the Woolmark Company (Ilkley, UK) which helps in the technology transfer to mills and wet finishing plants. SPT microcapsules are based on a chemical similar to melanin together with certain binders that create strong chemical links with the fibres to impart high durability. SPT microcapsules will withstand repeated domestic washing, and even ironing treatments [84].

SPT microencapsulation technology is highly versatile; for aromatherapy end-uses thousands of different types of fragrances may be provided or bespoke fragrances created for specific textile applications. Because the SPT microcapsules provide a reservoir of fresh perfume this reduces the need to use quantities of the less volatile 'bottom' notes and use far more of the volatile 'top' notes instead without the associated fragrance fade problem.

Another innovative approach could be, for example, clothes that could actually repel or negate odours. Quest International UK Ltd (Ashford, UK) has developed a unique set of ingredients that is the equivalent to 'white noise' to tobacco smoke, which can be added to clothes via SPT. Such treatments could be applicable to fibres and fabrics used for seats or carpeting, creating 'smart environments' which always smell fresh, e.g. in public transport systems [78].

Table 2 Cognis: Skintex products and their benefits [85]

Products	Active ingredients	Benefits
Moisturising	Squalane Vitamin E Manoï de Tahiti Passion fruit oil	Moisturiser from clothes
Cooling	Myritol Menthol	Cooling skin care in the fabric
Energising	Menthol Orange Ginger Rosemary	Revitalising aroma in the fabric
Relaxing	Valerian Amber tree resin oil Lavender	Relaxing aromatherapy from fabric
Anti-heavy legs	Grapefruit Menthol Lemon Thyme	Revitalising care for tired legs
Mosquito repellent[a]	Various	Effective mosquito repellent in the fabric

a Active ingredients being used in mosquito repellent include *N,N*-dimethyl-*m*-toluamide (DEET), permethrin, pyrethrum and essential oils
Source: Cognis

Cosmeto-textiles and skin care benefits

There is now an increasing vogue for so-called cosmeto-textiles which are essentially garments that are designed to come into contact with the skin which then transfer some active substance that may be used for cosmetic purposes, in particular to combat ageing effects. Because people in the developed nations are living longer and acting younger (the so-called 'youthful ageing' effect) there is now a demand for products which are designed to beautify and to combat ageing. Microencapsulation of active ingredients, e.g. Aloe vera gels that can be released gradually and be absorbed through the skin are typical of this type of finish [76,77,80].

The problem of cellulite, thought to occur in some 85% of women, is considered to be caused by poor micro-circulation. Sensory Perception Technology utilises kelp bladderwrack as an iodine source which is easily absorbed into the epidermis [84]. This speeds up the micro-circulation, stimulating glands and the connective tissues. This is claimed to fight the root causes of cellulite. Worn for long periods of time next to the skin in hosiery and underwear, kelp can also be applied with Aloe vera to promote an anti-cellulite effect.

Vitamin E has been widely used in skin creams for medicinal and cosmetic purposes. Its action is basically considered to be that of a powerful anti-oxidant, protecting skin cells against the damaging effects of free radicals which age the skin. Vitamin E has been used on walking socks using SPT microcapsules for its blister healing effects and also applied along with Aloe vera and kelp to underwear/hosiery to help fight the effects of stretch marks (i.e. for maternity wear).

Cognis Deutschland (Düsseldorf, Germany) has introduced their Skintex Care System, termed 'Wellness to Wear'. In the Cognis-patented Skintex System, active ingredients are microencapsulated using chitosan, a substance made from the shells of shrimps in order to turn a simple garment into one termed an 'active-wellness' garment [78]. Cognis has introduced a variety of active agents which have been microencapsulated and can be applied by exhaustion onto the fabric during wet processing. The properties of the Cognis Skintex System are claimed to be retained over several domestic washing cycles.

Cognis recently launched its latest innovation, Skintex Reloading, to meet the consumer demand for long-lasting effects by making it possible to recharge textiles with new microcapsules. Skintex Reloading is available for the slimming effect, using care ingredients such as Shea butter, apricot kernel oil, rose hip oil and red algae extract. The Reloading technology can also be used to refresh the cooling/moisturising properties of Skintex-treated clothing [78].

The active ingredients of the Cognis Skintex System are delivered by three separate means [78]. The most important method is by friction between the microcapsules in the fabric and the skin. Secondly, the natural biopolymer membrane of the microcapsules can be biodegraded by enzymes naturally present in the skin. Thirdly, when the microcapsule biopolymer membrane (which is insoluble at pH 6–7) comes into contact with human skin (at pH 4–5) this causes the membrane to dissolve, thereby delivering the actives. The Cognis Skintex System has been designed for use on hosiery, underwear and sportswear made from cellulosic fibres and all other fibres and blends. Cognis Skintex ingredients have been produced for skin moisturising and relaxing, for combating the effects of cellulite (anti-cellulite) on the skin, while other areas include hair retardant and tanning purposes. A list of Cognis Skintex products and their benefits is given in Table 2 [85].

Speciality Textile Products Limited (Loughborough, UK) market their Biocap series of functional biocapsules which incorporate vitamins such as vitamin A, D and E and Aloe vera for application to underwear, T shirts, stockings, socks and bedding [81].

Antimicrobial and deodorising finishes

A major growth concept over the last 5 years has been the introduction of the concept of durable freshness applied to all kinds of textile apparel, especially those which are worn under conditions of strenuous physical exertion, or in hot climates. The growth of bacteria on the perspiration entrapped into a garment can rapidly lead to the build-up of undesirable odours which then necessitates the garment being washed or dry cleaned to restore the freshness [86,87].

Garments such as intimate apparel, socks, gloves and especially textile products used in footwear clearly offer a large potential market for retention of freshness during wear. In addition, there are many other areas with potential for exploitation of the durable freshness concept, including household textiles, e.g. carpets, curtains, cushions, etc., as well as opportunities in textiles used in automotive textiles such as car seating and floor coverings, and textiles for other forms of transportation, e.g. trucks, buses, trains and aeroplanes [86–89]. Another important area is that of performance sportswear for all manner of physical activities. The many approaches to antimicrobial finishes are reviewed in the section on antimicrobial finishes.

Microencapsulation of antimicrobial agents could provide a long-term controlled release effect that could be utilised to prevent the growth of bacteria in textiles that can give rise to undesirable odours, or to combat the growth of more harmful bacteria.

The AB Cap (antibacterial microcapsule) marketed by Speciality Textile Products Limited (Loughbrough, UK) contains a nonionic product with a pH of 7 ± 0.5 (1% solution) [81]. This provides an excellent dispersion in liquids and is effective at the 1–2% level on a wide range of bacteria. More revolutionary still is the patented Silver Cap, in which an innovative manufacturing technique places silver nanoparticles on the outer wall of the microcapsules [81]. Silver ions are claimed to sterilise some 650 different viruses and can provide a highly effective antibacterial effect when applied to textiles. The wall material may be of natural or synthetic polymer and may incorporate other materials, e.g. perfume, Aloe vera, colour-changing dyes or other antimicrobial agents.

Microencapsulation of antimicrobial agents is an area which is now receiving attention in the fight against methicillin-resistant *Staphylococcus aureus* (MRSA) infections. Micap plc of Newton-le-Willows (UK) has developed a mixture of three essential oils, combined in a specific ratio, which are microencapsulated and applied in a gelatine base to the wound dressing [90]. Ultimately the microencapsulated essential oils will be incorporated into the wound dressing and there is interest in this technique from companies that manufacture wound dressings [78].

With the increasing resistance of microbes to antibiotics, considerably more interest is now being shown in the antimicrobial properties of essential oils such as tea tree oil, eucalyptus and clove. Essential oils are generally volatile and will rapidly evaporate from surfaces so that microencapsulation within Micap yeast microcapsules can be used to minimise evaporation and greatly extend the shelf life. Tests have demonstrated that the selective release of Micap essential oil combinations upon contact with MRSA results in a superior rate of kill [78,90].

Tea tree oil has been used in SPT microcapsules because it possesses natural antibacterial and antifungal properties. A member of the Eucalyptus family it contains over one hundred different compounds. It has been shown to be effective against a wide variety of bacteria [78]. Tea tree oil is said to be antiseptic and has a stronger action against bacteria than many usual household disinfectants.

Medical textile applications

The microencapsulation of antimicrobial agents within textile fibres, yarns and fabrics clearly has potential for many forms of medical textiles for preventing bacterial and fungal infections. The controlled release of antibiotics from textiles in contact with the skin offers up the prospect of a marked decrease in post-operative infections after surgery [91]. Surgical sutures containing microencapsulated antibiotics could give a controlled release of antibiotic around the site of the surgical incision speeding patient recovery and preventing post-operative infection in the first few important days after surgery.

There is also the prospect of the development of the microencapsulation of drugs to give a controlled slow release of the active ingredient to be absorbed through the skin. This may be one area where nanocapsules or small microcapsules may be developed for specific applications, for use in medical dressings, etc. [80].

Insect-repellent and insect-resist treatments

For apparel designed to be worn in tropical climates where mosquitoes abound there is clearly a market for insect-repellent treatments that have a long-lasting effect. Microencapsulation of insect-repellent agents can be employed to provide a longer lasting controlled release effect. Thor SARL (Salaise sur Sanne, France) have developed a method of microencapsulating a synthetic pyrethroid, permethrin, which is a known insecticide [78,82]. A particular area of use is in clothing for the military serving in tropical climates.

Textiles treated with tea tree oil SPT microcapsules have been tested by the Carrol Loye Biological Research Institute (CA, USA) and shown to demonstrate significant mosquito repellence properties [78,84]. The natural organic ester plant oils act effectively as a nerve agent on insects but more importantly recent research has shown that these have an unusual effect on mosquitoes which is termed ‘jamming’. This effect results in the ‘black box’ which helps the mosquito search for victims being turned off. As a result microencapsulated release of these plant oils has been shown to significantly decrease the bites per minute in test boxes from 50 to virtually none.

Another area is that of microencapsulated insect-resist treatments for textiles containing natural protein fibres-like wool and silk. Such finishes could provide long-term protection against the ravages wrought by the larvae of moths and particularly many types of beetles [88,89].

Flame-retardant textiles

Conventional flame-retardant treatments often suffer from a lack of durability to soaking in water or to domestic washing procedures because of the aqueous solubility of the flame retardant used. Microencapsulation could help to protect the active flame retardants from the action of wet treatments, prolonging the durability of the effect and enabling treated textiles to pass flammability tests which involve a presoak in water prior to testing. Moreover, the adhesion of the microencapsulated flame retardant to the textile could be engineered by a suitable choice of polymer coating to maintain the durability to leaching tests or multiple wash cycles containing bleach-activated detergents [77,80].

By careful selection of the polymer coating used for microencapsulation it may be possible to provide a polymer coating that not only functions as a protective coating for the intumescent flame retardant combination, but also may additionally provide satisfactory adhesion and contribute to the carbonific component of the finish.

Chemical protection

This is a vast subject and for recent developments the authoritative book by Scott should be consulted [92]. There is now much greater interest in developing effective methods of protection against chemicals, either from the hazards created by accidents and spillages, as well as from chemical attacks. The global upsurge in terrorist activity and the needs of the military to protect their personnel against chemical attacks have stimulated developments in a difficult field in which to conduct research.

Chemical decontamination clothing is clearly a high priority and interfacial polymerisation and phase separation techniques have been utilised in order to generate microcapsules of ethylcellulose (1–10 μm diameter) containing a chemical decontamination agent [80].

Against the highly potent nerve gas Sarin (isopropyl methylphosphofluoridate) almost total deactivation was claimed for monoethanolamine and a small proportion of 4-(*N*,*N*-dimethylamino) pyrimidine microencapsulated in methyl cellulose-based microcapsules. Laundering for 1 h at 45 °C, or irradiation in a Weather-Ometer at 40 °C to simulate 1800 hours of sunlight exposure did not lead to any loss of detoxification power [80].

Clearly this area of performance apparel will attract a very high added value, and durability of the effect to prolonged storage prior to use will be important. In most cases such garments will probably only be used once and then discarded, so that the highest performance criteria are required for a single exposure to highly toxic chemicals. Undoubtedly microencapsulated decontamination agents will form only one element of a multifunctional chemical protection suit, which will also incorporate low-energy surface finishes to prevent wetting and wicking of chemicals into the garment and hence onto the skin [92].

Antimicrobial finishes

As some lifestyles have become more active, sportswear, activewear and casualwear may become more easily contaminated by perspiration leading to bacterial growth and body odours [86–89]. A number of antimicrobial treatments are now on the market that can kill bacteria and enable garments to remain smelling fresh for longer [86–89]. An alternative approach is that of β-cyclodextrin which, with a suitable reactive group, could be covalently bound to cotton [93]. It has been shown that body odours become trapped within the hydrophobic internal surfaces of this torus-shaped molecule eliminating the building up of body odours. This area is set for growth as the environment warms up through global warming and if garments are required to be washed less frequently then this decreases environmental pollution. The use of antimicrobials for preventing infections has already been discussed in detail.

No one antimicrobial finish, as yet, fulfils all the necessary criteria for all textile end-uses but some very effective and durable antimicrobial finishes have been developed and their utilisation in textiles, clothing and footwear is increasing, as their undoubted benefits take hold in the conscious minds of consumers worldwide.

Antimicrobial finishes inhibit or preferably kill microorganisms by a number of different mechanisms that act around the cell wall of the microorganism [86–89,92]. Thus cell wall damage, alteration of cytoplasmic membrane permeability, alteration of the physical or chemical state of proteins and nucleic acids, inhibition of enzyme action, or inhibition of protein or nucleic acid synthesis are all chemical approaches that can be utilised by antimicrobial finishes to inhibit or kill the microorganism.

It is well known that certain other chemical finishes can also help in promoting antimicrobial action. Thus, the application of easy care/durable press finishes based upon *N*-methylol compounds is known to help prevent rotting of cellulosic textiles [88]. In a similar way the application of hydrophobic finishing agents such as silicones and fluorochemicals that provide a water-repellent effect can help to prevent microbial attack of textile fibres and fabrics. In some applications the durability of the antimicrobial finish to washing may be improved by the use of a binder or resin system [88,89].

For apparel fabrics it is important that the antimicrobial finish leaves the garment comfortable to wear. A very important consideration for antimicrobial finishes applied to apparel fabrics is that such treated fabrics and garments are safe to handle and use. Antimicrobial finishes for apparel should be non-toxic, non-irritating and where handled regularly, the finish must also be non-sensitising.

Antimicrobial finishes have been developed that rely upon the following approaches for their effectiveness [88]:

– provide controlled release of the antimicrobial agent (the major method currently used);
– provide a barrier/blocking action using inert films or coatings to physically block bacteria, or films/coatings with direct surface activity against bacterial growth and

– regenerable active microbial agents, which can be regenerated by treatment with a bleaching agent during laundering or with ultraviolet radiation.

In order to increase the durability of the antimicrobial action to washing treatments a number of approaches can be utilised, according to the chemical nature and mode of action of the antimicrobial agent, [88] e.g.

– insolubilisation of the antimicrobial agent either in or on the fibre;
– fibre treatment with resins, condensates or fibre crosslinking agents;
– microencapsulation of the antimicrobial agent and durable binding of the microcapsules to the fibre;
– coating of the fibre surface;
– chemical modification of the fibre by covalent bond formation and
– use of graft polymers, homopolymers and/or copolymerisation onto the fibre.

The modern approaches to antimicrobial finishing have been summarised in detail elsewhere [86–88,92–96].

Nanocoating technology and smart coatings

A comprehensive review of coating and lamination has been given by Woodruff [97]. This is a very interesting area with many potential end-use applications and possible markets for all types of textile fabrics. Coating technologies based upon aqueous coating systems, foam coating, hot melt or even warm melt systems are becoming more important than the older solvent coating processes on the grounds of lower environmental pollution [97–99].

Microporous and hydrophilic polyurethane coatings and also lamination techniques have been developed to provide waterproof 'breathable' fabrics with a suitable level of water vapour permeability [19,90]. These provide higher levels of moisture comfort in clothing designed for outdoors, under foul weather or survival conditions or for sports activities involving strenuous physical exercise. The mechanisms of action of microporous and also hydrophilic polyurethane coatings have been reviewed by Lomax [100–102].

The Nextec EPIC process (Nextec, Vista, CA, USA) which gives rise to fibre encapsulation sheathes each fibre with its own polymer coating, but leaves each fibre distinct from its neighbours [103]. This maintains the water vapour permeability of the fabric, but provides appropriate levels of water repellency together with its own unique handle. If such a method could be developed to apply coatings that would impart total easy-care properties including water repellency properties it could give rise to a very useful fabric finishing technique.

Nanocoatings are now exciting considerable interest because of the current explosion of interest in nanoscience and nanotechnology [5,104–106]. The main thrust in nanocoating applied to textiles and clothing will be to:

– improve the properties and functional performance of existing materials;
– develop smart and intelligent textiles with novel functions;
– greatly increase the use of fibres in technical textiles, biomedical and healthcare end-uses and
– open up opportunities for textile sensors.

Many of the recent developments in the field of nanocoating were recently described at the 3rd European Coating Congress in Kortrijk (Belgium) [103].

Nano is derived from the Greek word nanos, meaning dwarf, and in the basic SI system (Système International d'Unités – the International System of Units) the prefix nano is used as a factor indicating 10^{-9} [104,105]. Thus, 1 nm is one billionth of a metre (10^{-9} m). By comparison the diameter of a single human hair is *ca*. 80 000 nm, a human red blood cell is *ca*. 7000 nm wide and a water molecule is almost 0.3 nm wide [105].

Therefore, nanoscience and nanotechnology are essentially concerned with materials that are very small [104–107]. The term nanoscale has generally been taken to lie in the range of 100 nm down to the size of atoms, i.e. down to *ca*. 0.2 nm. Nanoscience has been defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where the properties of materials differ markedly from those at a larger scale [104]. Nanotechnologies, on the other hand, refer to the design, characterisation, production and application of structures, devices and systems, by controlling shape and size at the nanometre scale [104,107,108].

Nanoscience, the science of materials at the nano-scale, is fundamentally different from the macromolecular scale for two principal reasons. Nanomaterials have a relatively larger surface area compared with the same mass of material produced in a larger form [5,104–106,108]. One consequence of this increase in surface area is that some materials that are normally inert in their larger form become reactive in their nanoscale form. Thus, the strength and the electrical properties of the material may be altered. A second important reason is that as the size of the material approaches the lower end of the nanoscale, i.e. towards the molecular and atomic scale, the behaviour of matter becomes more reliant upon quantum effects [105,106,108]. As a result the optical, electrical and magnetic behaviour of many materials are changed from those at the nanoscale.

Nanocoating the surfaces of textiles, clothing and textiles for footwear is one approach to the production of highly effective antimicrobial treatments that are effective in killing the bacteria that can lead to malodour formation [106,107]. Purista (Arch Biocides, UK) is an antimicrobial nanocoating based upon a cationic polymer [poly(hexamethylenebiguanide hydrochloride)] [109]. This product has a degree of polymerisation of 16 and can be applied by exhaustion, padding or by spraying. The Purista nanocoating is held on the fibre surface by strong electrostatic and hydrogen bonds and punctures the bacterial cell wall, killing bacteria that can accumulate in textiles and clothing through the retention of human perspiration exuded during physical activity and wear. The Purista treatment thus enables garments to be 'fresher for longer' and is currently being used in a wide variety of high-street garments, suit linings, sportswear and bedding as well as for wound healing in the USA.

Nanocoating of textile fabrics, complete finished garments or shoes can be obtained during plasma polymer treatments [110]. Plasma is the fourth state of matter (after solids, liquids and gases) which was first termed 'radiant matter' by Sir William Crookes in 1878 as a result of experiments in the passage of electricity through gases [111]. The word plasma is derived from a Greek term meaning something formed, fabricated and moulded and was first used by Irving Langmuir in 1928 [112,113]. The plasma generated by electrical discharge through a gas consists of a mixture of positive and negative ions, electrons, free radicals, ultraviolet radiation and many different electronically excited molecules. By varying the conditions of the plasma treatment and the nature of the specific gas or gases present, a variety of surface treatments can be produced that change the chemical or physical nature of the fibre surface, thereby radically altering all treatments that depend upon fibre adhesion, e.g. coating, lamination and bonding [114].

Plasma polymer treatments may be considered for the application of a wide range of ultra- or super-hydrophobic, antistatic, insect-repellent, odour control and flame-retardant treatments. Work at the University of Durham and the Ministry of Defence in the UK originally intended to provide anti-chemical warfare agent coatings has now been commercialised and extended to other treatments [114–116]. The nanocoating of silk and cotton in a radiofrequency inductively coupled plasma reactor has been carried out in collaboration with Surface Innovations Ltd, Wolsingham, Co. Durham, UK. Using gases or the atomised spray pressure deposition technique 3–5 nm thick super-repellent coatings had been generated [114–116]. Such coatings exhibited critical surface tensions as low as 6 mN/m, well below chemical warfare agents such as mustard gas (43 mN/m), VX (30.4 mN/m) and GD (25.0 mN/m). Current research is in hand on antimicrobial coatings and smart proteins [116,117]. The P2i Ltd pulsed plasma polymerisation technology is designed for treatment of finished end products, e.g. whole garments, gloves, socks, shoes, etc. and provides an environmentally friendly closed treatment system [116,117].

Another interesting approach is the coating of textiles with nanoparticles of titanium dioxide. Research work in Switzerland has demonstrated that nanoparticles composed of a mixture of 80% anatase and 20% rutile titanium dioxide can effectively decolorise red wine stains in the presence of water, oxygen and a range of radiations from sunlight to neon light [118].

In the USA, research is currently being conducted on body armour consisting of Kevlar bullet-proof vest material which has been dipped in a shear-thickening fluid consisting of colloidal silica particles (average size *ca*. 450 nm) which are supported in a liquid phase [119]. Under the impact of a high-velocity bullet the particles cluster and jam under the applied stress leading to a high strength ceramic materials response, but under normal conditions the colloids do not shear thicken.

Another fertile area for smart coatings is for nanocoatings that when subjected to wear or abrasion become scratched or scuffed, but due to their special physicochemical characteristics will self-heal, thereby maintaining a pristine surface appearance [5,106]. The possibility of producing a super-repellent, anti-soil and anti-stain nanocoated surface that would self-clean and self-heal if scuffed represents the Holy Grail to footwear manufacturers. Combined with an immobilised anti-microbial this should provide undreamt-of performance in sports shoes, boots and normal footwear. The potential for footwear for sports and the military, children's and fashion shoes is bounded only by the limitations of human imagination. Cleaning shoes could be a thing of the past!

Recent work on paints in the Swedish Ministry of Defence is aimed at producing multispectral camouflage coatings to conceal military hardware in the field [119]. Ultimately the goal was to make an object invisible at all three wavelength regions – the visible, infrared and microwave regions (where it would be detected by radar). Deception is currently achieved using micron-sized semiconductor particles in the paint. These absorb infrared radiation and re-emit it at a wavelength outside the working limit of infrared detectors (3–5 and 8–12 μm). By particle size variation the infrared emission can also be matched to the background. Using spray-drying spherical ceramic particles can be produced which contain nanometre-sized pores into which pigments (e.g. green, grey and brown) can be impregnated. These coloured particles are then combined with an organic binder and can be applied by brush or spray coating. Beneath the combined visible/infrared coating there is a second layer to prevent the object being detected by radar [119]. It seems logical to consider such a system for use with camouflage coatings for textiles, although the nature of the organic binder will need to be matched to the fabric end-use.

Conclusions

It has not been possible within this short review to discuss all the innovative technologies that are emerging within the textile industry. Nanotechnology in the form of nanofibres, nanoparticles and nanocoatings holds out much promise for the future. Nanofibres embedded within composites, for example, could open up many opportunities for material reinforcement.

It is clear that all textile scientists and technologists must keep abreast of the latest developments. Textile finishers in particular could harness many of the exciting opportunities now emerging in order to enhance and extend the appeal, the markets and the end-uses for textiles. The frontiers of the art of the possible are continually expanding and imaginative research and development will be needed to convert ideas into reality. In this way, the undoubted aesthetic and functional performance of textiles can be enhanced to excite the imagination of the consumer and extend the markets and end-uses for textile materials.

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