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Don't fear the water

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Modifying the way textiles interact with water is a fundamental product differentiator. This report discusses super-hydrophobic surfaces used to create self-cleaning materials, faster-drying textiles, and improved stain resistance.

Water Resistance

This report concerns hydrophobicity in the context of textiles manufacture. It defines the functionality, describes a range current and emerging technologies employed to achieve levels of water resistance and describes how each works. The report also identifies the key providers and owners of the current and potential processing technologies.

Hydrophobicity (Water Resistance)

Hydrophobicity relates to how water interacts with a surface of a material, and whether it is repelled or attracted. Water behaves differently from almost all other materials, resulting in energy differences between hydrophobic (water resistant) and hydrophilic (absorbent) surfaces.

Hydrophobicity is of relevance to most, if not all market sectors, as modifying the way textiles interact with water is a fundamental product differentiator. Hydrophobicity is particularly important in clothing, where clothes that dry quickly or resist wetting are desirable. In addition, demand is rising for carpets or upholstery (including Interiors and Automotive products) that resist wetting, are easy to care for and resist staining.

Hydrophobicity is determined by the fundamental physical properties of Surface Energy and Surface Tension. When a liquid is in a container the bulk liquid molecules, those surrounded solely by other liquid molecules, are subject to different forces from those at the surface, which are partly in contact with air or another medium. The intermolecular forces acting in the bulk liquids are “spherically equivalent”, i.e. the same in all directions. However, at the surface these forces only act in the direction of the bulk liquid, which has the effect of pulling the surface molecules back into the bulk. As a result, the liquid surface contracts to form the smallest possible surface area, for a given volume. This is what creates surface tension and explains the behaviour of hydrophobic materials. When water comes into contact with a hydrophobic surface, such as clean glass, the water forms a spherical shape so as to reduce its surface area to a minimum. This creates a specific contact angle between the water droplet and the surface. It is the contact angle between a water droplet and a surface that is measured to determine hydrophobicity.

There are few regulations that govern hydrophobicity, though there are numerous standard testing methods. The standards BS ISO 23232:2009 and ISO 23232:2009 provide a guide for aqueous stain resistance. The standards BS EN 29865:1993 and ISO 9865:1991 describe the Bundesmann rain test, which measures the repellence of a textile by dropping water on it. A rating between 1 and 5 is given to the textile. In addition, water repellency is defined as “the relative degree of resistance of a fabric to surface wetting, water penetration, water absorption or any combination of these properties”. A water repellent finish is “a state characterised by the non-spreading of a globule of water on a textile material.”

Imparting Hydrophobicity

Hydrophobicity is inherent to some materials, but few untreated textiles are naturally hydrophobic. Hydrophobicity can, however, be quite easily imparted on a textile surface through physical or chemical surface modification.

Repellent finishes (chemical modification) work by imparting a low surface energy quality to a material, lower than the surface tension of the liquid. In the case of water that is lower than 73 mN/m (milliNewtons per metre). Examples of hydrophobic finishes in common industrial use are polysiloxanes, flourocarbons, and waxes.

Waxes were one of the first materials used to impart hydrophobicity and they are still used today in clothing including the famous Barbour jackets. Silicones (-O-Si-O polymers) are also in common use and are applied by “padding” following by curing at high temperature. Fluorochemical finishes repel water readily as they have very low surface energy. They are also durable, but must be applied in an energy-intensive, high temperature, process.

While popular in usage, it is recognised that fluorochemicals have an adverse environmental impact. As they are the highest performance of the conventional chemical finishing methods, their use is widespread, despite their strong "greenhouse effect" and their bio-accumulative nature which is considered to be dangerous.

Another major challenge for hydrophobicity treatments is the durability of the chemical finishes. Even the highest quality fluorochemicals last only for short periods if subjected to continuous abrasion. Once abraded, they are difficult to reapply and are rarely as effective as when new.

Plasma, a relatively new method of imparting hydrophobicity, has been used to prepare very impressive hydrophobic surfaces, though there is concern over how long these coatings will last.

Over the last 15 years there has been widespread research into super-hydrophobicity, creating surfaces with a contact angle greater than 150°, and ultra-phobicity (surfaces with a contact angle greater than 160°. Much of this research has focused on mimicking the effect of natural materials including the lotus leaf, butterfly wings, and the feet of water striders, each of which exhibits super-hydrophobic properties. The lotus leaf is "self-cleaning" as a result of its special surface which has a very low water roll-off angle so that soil particles on the leaf are removed by water droplets rolling off the leaf. The other type of plant leaf is typified by hair-covered leaves, as seen on the Lady's Mantle. In this species, the self-cleaning effect results from the presence of projecting fine surface hairs upon which water droplets lie and then roll off, taking the soil with them. Water droplets form contact angles greater than 150° on this surface with a surface contact area as low as 7% of the total surface area.

Super-hydrophobicity can be imparted by roughening the surface of a low surface energy material, or by lowering the surface energy of a rougher material. These methods leave great room for innovation, and new methods are continually being developed. Super-hydrophobic surfaces are of great interest to the textile industry because of the prospect of self-cleaning materials, faster-drying textiles, and improved stain resistance.

Current and Emerging Technologies

Fluorocarbon finishes are fluoracrylates in which the perfluorinated side-chains are oriented away from the fibre surface and the terminal CF3 groups create a low energy surface, simulating the hairs on leaves. This energy is lower than the surface tension of water, as well as contaminants such as oils and stains. As a result, these contaminants can be removed relatively easily during washing, even at low wash temperatures.

When a garment treated with fluorocarbon is laundered, the orientation of the perfluorinated side-chains can be disrupted and this impairs subsequent repellency properties. However, the preferred orientation and the repellency properties are restored when the garment is heated to a temperature of 70° – 80° C, typically by tumble drying or hot ironing. In recent years, laundry tumble dry (LTD) fluorocarbon finishes and laundry air dry (LAD) fluorocarbon finishes have been developed as a result of advances in chemical modification of the fluorocarbon molecular structure. In the LAD finishes, molecular re-orientation of the perfluorinated side-chains occurs at around ambient temperatures. This avoids the necessity to tumble dry the garment after washing, and thereby saves energy.

Current Producers

Another way of saving energy is to use recently developed fluorocarbon finishes which can be cured at lower temperatures. The Germany-based company Zschimmer & Schwarz Mohsdorf produces a product called Anthydrin NK which can be cured at temperatures of around 110° C, (by comparison, conventional cross-linking temperatures are around 160° C). A booster product called Polappret VIB can be applied simultaneously using a special cross-linking system to enhance the durability of the finish to washing.

Most of the fluorocarbon finishes which were produced commercially a decade ago contained C8 perfluorinated side-chains manufactured using an electrochemical fluorination route. However, there has been growing evidence since the 1990s that the production of such finishes using this route can give rise to a breakdown product, perfluorooctanesulfonic acid (PFOS) which is environmentally persistent, bioaccumulative and exclusively man-made. Accordingly, this method is no longer used for manufacturing C8 fluoropolymers. It is still used, however, to manufacture C4 products because this process does not result in the production of PFOS.

The C8 fluorocarbons used in chemical finishes for textiles are now manufactured by a process called telomerisation. However, when using this route there is a possibility that perfluorooctanic acid (PFOA) may be present in trace amounts as a pollutant. In order to eliminate the presence of PFOA, fluorocarbon resin manufacturers have entered into a voluntary scheme, called the 2010/2015 PFOA Stewardship Program, which is being brokered by the US Environmental Protection Agency (EPA).
To eliminate PFOA contamination, manufacturers have introduced fluorochemicals with shorter fluorinated side-chains based on C4 and C6 fluorocarbons. Although contaminations are possible during manufacture, these involve compounds which have been demonstrated to have a much lower environmental and toxicological impact.

Another product, Oleophobol CP-C, has been developed for use on cotton fibres, synthetic fibres and cotton/synthetic fibre blends by an alliance between Huntsman Textile Effects and DuPont. The product is water repellent, oil repellent and stain repellent finish based on a DuPont Capstone product, based on short side-chain chemistry and is claimed to improve fluorine efficiency beyond the level expected for a typical short chain product. It also provides a step-change reduction in the presence of trace impurities to a level below that which can be detected.

Oleophobol CP-S is a stain repellent product which is similar to Oleophobol CP-C, except that it is formulated for use on synthetic fibres and their blends. Oleophobol CP-R is a stain resistant finish for cotton, synthetic and blends which enables water-based and oil-based stains to be removed more easily during laundering.

The Germany based company RudolfChemie has developed a durable water repellent finish called Bionic-Finish Eco which is biodegradable and free from organic halogens.

The finish is based on C6 fluorocarbon chemistry and is free of both PFOS and PFOA. The product was used in conjunction with a Sympatex eco-friendly biodegradable membrane in Sympatex's first jacket for the protective workwear market which was made entirely from fibres produced from 100% recycled polyester bottles.

Clariant has developed a product designed to protect against soiling and staining of nylon pile carpets, based on the co-application of the fluorocarbon, Nuva N5151 liq, and a special stain blocker, Nuva SBC liq , marketed as Nuva Stain Blocker Carpet Liquid. Nuva N5151 liq is based on C6 fluorocarbon technology, and also offers high performance in other sectors – including automotive, shoe and filter applications. Nuva SBC liq is an anionic polymer system which claims to offer high compatibility with soil repellents and long lasting performance. Nuva SBC liq offers a number of specific advantages over competitive stain blocking systems based on synthetic tanning agents (syntans) such as condensates of formaldehyde with phenolsulfonic acids, naphthosulfonic acids or sulfonates of dihydroxydiphenylsulfone, or their mixtures. The product does not affect the carpet shade or the handle of a textile and can be applied in pad or foam applications.

The USA based company Alexium has developed a process for rapidly applying a nanoscopic coating to a fabric to enable it to repel liquids such as gasoline, diesel, jet fuel, cooking oils, acids, solvents, oxidisers and water, while still preserving the fabric's breathability, handle and drape. The process, called Reactive Surface Treatment (RST), makes use of microwave technology to apply the coating. The company has also developed a water repellent and oil repellent treatment for synthetic and natural fibre fabrics called Cleanshell.

The USA based company Nano-Tex markets a special finish called Nano-Care. This utilises 10 nm whisker-shaped molecules of a fluorinated monomer which has been copolymerised with a carboxylic acid oligomer and converted to the anhydride form to react with the fibre. Application of Nano-Care results in a self-cleaning finish on cotton or cotton-blend fabrics. The company also produces a treatment called Nano-Pel which is similar to Nano-Care but is designed for application to wool and multiple layer fabrics.

The Nano-Tex technology is said to simulate the surface of a peach. To achieve this effect, the technology essentially generates very fine short hairs which are durably bonded to the fibres from which the fabric is made. Nano-Tex technology is licensed to other companies and has been used in workwear, casualwear and sportswear.

The Switzerland based company Schoeller Technologies has developed a technology called NanoSphere which results in the formation of micro-rough three-dimensional surface structures from which water, dirt and oil simply roll off. NanoSphere technology utilises a so-called "guest host" system of substrates which facilitate spatial self-organisation, thereby resulting in the formation of a micro-rough surface. The technology also uses gel-forming additives which lead to the development of a porous membrane system. NanoSphere

technology imparts water repellency, soil repellency, anti-adhesive and self-cleaning properties.
Alternative approaches to the use of superhydrophobic finishes include the application of compounds such as titanium dioxide to the fibre surface. Under the action of UV light or the ultra-violet radiation present in the sunlight and daylight, the titanium dioxide initiates a series of chemical reactions which can lead to the photocatalytic degradation of stains including red wine, coffee and tea. However, this is a relatively slow process which takes place over a number of hours or days, depending on the nature of the UV radiation applied to the stain, the concentration and type of the stain or other pollutant, and the type and amount of titanium dioxide present. Protective layers are likely to be required beneath the titanium dioxide layer to reduce the effects of fibre photodegradation.

Recent developments for superhydrophobic finishes have included the use of plasma pretreatments and/or plasma polymerisation treatments, or by the use of a pulsed UV laser, known as an excimer laser to modify the fibre surface topography to yield a regular micron-scaled surface structure.

Latest Developments

Development work continues around the linking of multifunctional monomers to form dendrimers, where heating and cooling causes the hydro-carbon side chains to co-crystallise, providing a water repellent finish that gives a similar level of repellency as a fluorocarbon resin finish but with superior abrasion resistance.

Increasing demand for breathability is driving the development of finishes which provide protection from water while allowing water vapour to escape. Some commercial breathable textile products are available, and Mitsubishi is testing a new fabric (Dream Cloth) which has a polymer coating that, reportedly acts like human skin, with a molecular structure that opens when the wearer is hot allowing moisture to escape and which closes when exposed to cold, providing insulation. When combined with shape-memory polymers, many new products become possible.

The chemical company Bolger and O’Hearn has created Altopel F3, a fluorine-free water repellent finish suitable for performance textiles based on hydrophobe-fortified polymers that provides a high level of water repellency alongside improved durability to laundering and with an impressive environmental profile.