Kirk-Othmer Encyclopedia of Chemical Technology.

WATER, WATERPROOFING AND WATER/OIL REPELLENCY

1. Principles of Repellency

A thorough discussion of water repellency was published in 1963 (1).

When a drop of liquid is placed on a solid surface, the shape of the drop depends on the equilibrium among three forces, as shown in Figure 1.

On an ideal surface, the contact angle θ depends on three surface tensions: the liquid–air interfacial tension, γ_{LA}; the solid–air interfacial tension, γ_{SA}; and the solid–liquid interfacial tension, γ_{SL}. Wetting of the solid by the liquid results from the reduction of the contact angle of the advancing liquid so that the liquid spreads easily. A surface is made repellent by raising the advancing contact angle, so that spreading and migration into capillaries do not occur.

The nonequilibrium spreading coefficient S_{SL} for a liquid on a solid is defined by the equation (2):

$$S_{SL} = \gamma_{SA} - (\gamma_{LA} + \gamma_{SL})$$

The term γ_{SA} is the same as the free energy of the solid surface in air, and γ_{SL} is the free energy per unit area of the solid–liquid interface. If the spreading coefficient is positive, spreading can occur spontaneously and the liquid should spread to form a thin film on the solid. A liquid spreads on a surface because spreading causes a decrease in free surface energy. Conversely, spreading does not occur if the spreading coefficient is negative. This is because γ_{SA} is low, ie, the surface is a low energy solid or has been treated with a chemical that converts it to a low energy solid. Surfaces that contain nonpolar hydrocarbon, siloxane, or fluorocarbon groups are low energy surfaces. These repel a liquid unless the surface tension of the liquid, γ_{LA}, and the interfacial tension of the solid–liquid interface, γ_{SL}, are sufficiently low to make the spreading coefficient positive.

The measurement of contact angles is a convenient means for judging the degree of wetting or repellency for a liquid on a planar solid surface. Measurements of advancing or receding contact angles, which form when the liquid moves outward or contracts on the surface, are generally more reproducible than measurements of static contact angles (2) because of the existence of a large number of metastable states at the three-phase boundary (3). Methods for measuring advancing and receding angles are available (2). The advancing contact angle most nearly represents the low surface energy or repellent component of the surface, whereas the receding angle is representative of the high surface energy or more wettable component of the surface. Most real surfaces are made up of a complex mixture of low and high energy surface components and exhibit significant differences between advancing and receding contact angles. This phenomenon is termed contact angle hysteresis. Whereas receding angles can be important, the advancing contact angle is appropriate for investigating whether a liquid will advance or "wet" over a substrate, and the bulk of this discussion will focus on advancing contact angle.

A number of methods have been developed for estimating advancing contact angles of liquids on surfaces. These methods can be used to estimate wettability of a given liquid–solid system.

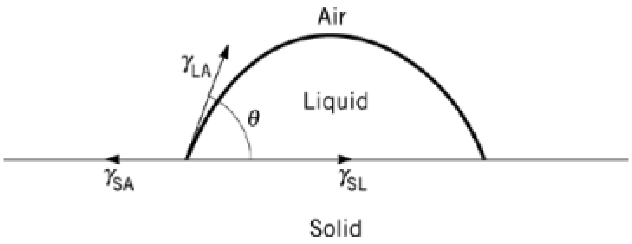

Fig. 1. Diagram of forces determining shape of a drop of liquid placed on a solid surface. See text.

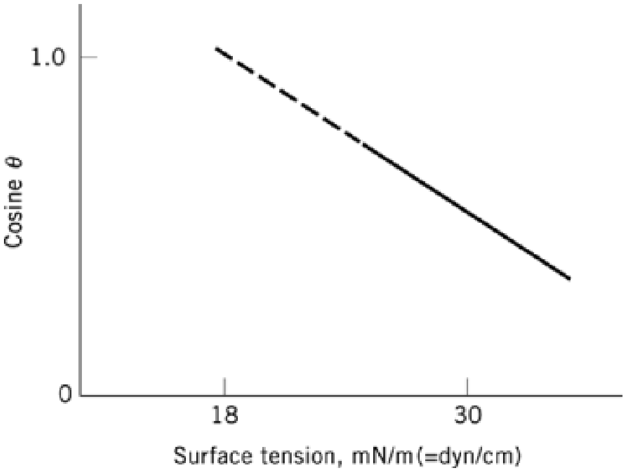

Fig. 2. Determination of a critical surface tension.

The critical surface tension (CST) of a surface is the maximum surface tension for a liquid that has an advancing contact angle θa equal to 0°. Advancing contact angles on low energy solids depend approximately on only the surface tensions of the wetting liquids (4). The CST for a planar surface can be estimated by measuring the advancing contact angles of a series of liquids, eg, alkanes, on the surface. A plot of cosines of advancing contact angles against surface tensions of the liquids gives approximately a straight line, as shown in Figure 2.

Extrapolating this line to $\cos\theta a = 1$ (contact angle = 0°) gives the surface tension required for a liquid to wet the solid. Given a surface of known CST and a liquid of known surface tension, an estimate of advancing contact angles can be made.

There are several other methods for estimating the contact angles that specific liquids will make on surfaces. These methods depend upon breaking the free surface energy into different components (5). A surface can be characterized as having a polar and nonpolar surface energy component which together equal the total surface energy. A specific liquid also has a polar component and a dispersive (nonpolar) component of the surface tension, which interact with the surface. Several theories allow the advancing contact angle to be predicted based upon this approach. In many cases the advancing contact angles are quite accurate and can be predicted, given the polar and dispersive parameters (5–9). Another approach is to use the acid–base interaction to predict advancing contact angles based upon the inherent acid and base character determined for a surface and its contacting liquids (10).

A repellent material functions by lowering the surface energy to a value such that the liquid now has a high advancing contact angle on the surface. For example, a fluorochemical finish on a nylon fabric can lower the surface energy from ca 43 mN/m (=dyne/cm) for the untreated fabric to <10 mN/m for the treated fabric. Such a treated fabric would repel water with a surface tension of 72 mN/m and oils or solvents with surface tensions down to ca 20 mN/m. Unfortunately, advancing contact angles cannot be measured directly on textile yarns that are complex bundles of twisted fibers. Other methods must be employed to predict the wettability behavior.

Most of the surfaces that require repellent treatments are not smooth but contain capillaries into which a liquid can migrate, even though the advancing contact angle of the liquid on the surface is $>0°$. The law for the movement of liquids into an idealized capillary is given by the equation:

$$\Delta P = \frac{2\gamma_{\mathrm{LA}}\cos\theta \mathrm{a}}{r} = \frac{2\left(\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}}\right)}{r}$$

where ΔP is the pressurerequired to force the liquid back out of the capillary, and r is the diameter of the capillary. ΔP is positive, ie, the liquid rises in the capillary, if the liquid wets the capillary with an advancing contact angle $\theta\mathrm{a} < 90°$ $(\cos\theta\mathrm{a} > 0)$. If $\theta\mathrm{a} > 90°$, cos θa is negative, making ΔP negative. In the latter case, the solid repels the liquid, and pressure is necessary to force the liquid into the capillary. The second equation for ΔP shows that, for a negative value of ΔP, γ_{SA} (the free energy or surface tension of the solid in air) must be less than γ_{SL} (the interfacial tension of the solid in the liquid).

The limiting contact angle for repellency of a solid surface for a liquid depends on the physical form of the solid. The capillaries in textiles, paper, leather, or masonry are not ideal, smooth, and round. In a textile or in paper, the wicking of liquids can be lateral, ie, through the sides of fibers, or longitudinal, ie, along the length of fibers (11–13). In masonry, liquids can migrate through an array of irregular capillaries.

In a bundle of fibers, as in a textile yarn, fabric, or paper, the fibers may repel a liquid even though the advancing contact angle is $<90°$ (9). Pressure on the liquid that contacts the fibers, however, can force the liquid into capillaries or interstices between fibers, thereby effecting wicking. The pressure required for wicking into repellent treated fibers depends upon the surface energy of the treated fibers and the geometry of the system. Wicking occurs even without pressure on the liquid if the advancing contact angle is approximately 70°; wicking occurs because the liquid surface can contact fibers beneath the surface. The combination of lateral and longitudinal wicking into a fiber assembly illustrates the gradual wicking of aqueous fluids, solvents, or oils into fabrics, paper, or nonwoven products (see Nonwoven fabrics). The gradual advance of a moving liquid front along capillaries can also explain the migration of liquids through masonry and concrete.

2. Textiles

Early waterproofing of textiles was generally accomplished by the use of impermeable coatings, such as natural fats, oils, waxes, pitch, and asphalt. Later, vulcanized natural rubber became an important waterproofing material. By the 1930s, repellent finishes durable to washing and dry cleaning were introduced. The following definitions apply to fabrics with water-repellent properties (14).

Water-repellent fabrics resist wetting or repel waterborne stains; they pass AATCC Test Method 22 (Spray Test).

Water-resistant fabrics protect against water penetration during a light or brief shower and pass AATCC Test Methods 22 and 42 (Impact Penetration Test).

Rain-resistant fabrics protect against water penetration during a rain of moderate intensity and pass AATCC Test Methods 22 and 35 (Rain Test).

Waterproof is normally used to describe plastic, plastic-coated, or nonbreathable fabrics. However, the term has been used for some chemically coated fabrics that allow the penetration of air.

Durable finishes maintain a high level of performance after laundering, dry cleaning, or both. Durable has also been used to describe resistance to abrasion.

The levels of water repellency required to pass the preceding tests depend upon the specifications for particular fabrics.

Oil-repellent fabrics resist wetting by oily liquids and repel oilborne stains. The level of performance of such fabrics is judged by AATCC Test Method 118.

2.1. Waterproof Finishes

Waterproofing results from coating a fabric and filling the pores with film-forming material such as varnish, rubber, nitrocellulose, wax, tar, or plastic. The materials may be applied as hot melts, eg, waxes or some polymers, as solvent solutions, or as aqueous latexes. The continuity of the film provides the water resistance. Except for tents, tarpaulins, and covers, coated fabrics have been largely replaced by plastics, and by fabrics treated with water and oil repellents that do not reduce permeability to air and water vapor. Fabrics are also commonly laminated to films, such that the total structure is waterproof (15), or in some cases water-resistant but breathable (16).

2.2. Repellent Finishes

The following are six classes of repellent textile finishes.

2.2.1. Fluorochemicals

Fluorochemicals are the most important class of repellents for textiles. They are the only repellents that provide repellency to water, waterborne stains, oil, oilborne stains, and oily particulates. The various products have a variety of repellency and durability properties for certain fabrics, and the specific compositions are proprietary. The first company to market fluorochemical repellents was 3M in the 1950s (Scotchgard Fabric Protector), followed by DuPont (Zepel and Teflon Fabric Protectors). Several other companies such as Auralux Corporation, Ciba Specialties, Eastern Color & Chemical, Glo-Tex Chemicals, IVAX Industries, Lindley Laboratories, NICCA U.S.A., Piedmont Chemical, Sedgefield Specialties, Sequa Chemicals, and Yorkshire Pat-Chem also market such finishes (17). Fluorochemical finish application areas include rainwear, upholstery, drapery, and automotive fabrics, roofing materials, and carpeting. Both natural and synthetic textile fibers can be treated.

The performance of fluorochemical repellents depends on the presence of perfluorocarbon chains, $CF_3(CF_2)_{-N}$. The length of the perfluoroalkyl group is at least four carbon atoms. For many products, it is eight carbon atoms, or a mixture of chain lengths averaging about eight. The products are primarily copolymers of perfluoroalkyl acrylates or methacrylates with other comonomers. The comonomers in the polymeric products are esters of acrylic or methacrylic acid containing alkyl groups of several carbon atoms, alkylamide groups, or polyether groups. The comonomers modify the physical properties of the polymers (eg, control the hand of the finished fabric) or improve the performance of the polymer (eg, provide soil release) and reduce the manufacturing cost of the product.

Fluorochemicals repel both water and oil because they produce an extremely low energy surface (18–26). The effectiveness of the fluorochemicals depends upon uniform surface coverage and orientation of the molecules on the fiber surface so that the perfluoroalkyl chains are directed away from the surface. The result is a CST as low as 5–10 mN/m (dyne/cm). Fluorochemical finishes are often formulated with nonfluorinated resin-based water-repellent extenders. These water repellents not only reduce the cost of the finish but may also improve durability (27, 28).

Quarpel is an important combination of fluorochemical finish and resin-based extender developed by the U.S. Army Natick Laboratories for military use. This finish typically contains 4–6 wt % commercial fluorochemical emulsion, 4–6 wt % resin-based repellent emulsion, 0.1 wt % acetic acid, and 5 wt % isopropyl alcohol. If necessary, the formulation includes a catalyst to cross-link the resin-based component. Quarpel specifications demand excellent initial water and oil repellency and excellent durability to washing and dry cleaning.

Fluorochemical repellents are commercially available as emulsions or solvent solutions. The most widely used emulsions for fabrics and carpet are cationic, but nonionic emulsions are becoming more prevalent. The emulsifier in the formulation can affect the repellency and durability of the product (28). Surfactants used in the fluorochemical emulsions or added to finish baths should be nonrewetting and have a minimum adverse effect on oil repellency. Solvent solutions of fluorochemicals are becoming less common as a result of toxicity and environmental concerns.

The choice of application conditions for fluorochemical repellents depends on the textile, the repellent formulation, and level of repellency required. Suppliers provide detailed recommendations in their product bulletins. Where a high level of repellency is required or the generally somewhat higher cost is tolerable, pad application is the most effective method. For lower levels of repellency, spraying or foam finishing may suffice. The usual application level of repellent solids on any textile is 0.2–0.5% of the fiber weight, although higher levels may be needed. There should be no silicones on fabrics prior to treatment with fluorochemicals, because trace levels of silicone lubricants can diminish the oil repellency of the fluorochemical. The effect may result from poor wettability of the silicone-treated fiber with the fluorochemical repellent. Also, silicones can attract oils and oily soil.

Many fluorochemical finishes for fabrics require curing at up to about 175°C. Curing allows melt-spreading of the fluorochemical to ensure maximum leveling of the finish on the fibers and to promote optimum orientation of the pendant fluorinated portion of the molecules on the fibers.

Nonwoven textile products often require fluorochemical finishes (29). Medical nonwovens (operating room gowns, central supply wraps) represent the largest market. Although they require oil and alcohol holdout, aqueous-based fluid repellency is the most important property. Because these products are mostly disposable, the treatments are designed for nondurable, high water repellency. This is best achieved on nylon, polyester/cellulose and adhesively bonded cellulose nonwovens with a low level of fluorochemical, and a high level of a combination wax/resin emulsion or water-repellent extender. The polypropylene nonwovens, fluorochemical treatments must cure at low temperature conditions, and sometimes require special wetting agents.

2.2.2. Silicones

Silicones are exceeded only by fluorochemicals in the volume used as repellents for textiles. They are widely used on cellulosic and synthetic fiber fabrics. Silicones provide water-based stain resistance; good durability to washing; improved tear strength; a soft, slick hand; and improved fabric sewability.

The most widely used silicones are polymers of methyl(hydrogen)siloxane and of dimethylsiloxane. Polydimethylsiloxane is the basic polymer used in silicone repellents. If the polymer is terminated with methyl groups it is inert; however, if it is terminated with hydroxyl groups, it can be cross-linked. Continuous, durable coatings result from the use of curable blends of polydimethylsiloxane and polymethyl(hydrogen)siloxane. The silicone finish encapsulates individual fibers.

Silicones are supplied as aqueous emulsions or as solvent solutions. Dow-Corning and OSi Specialties are primary manufacturers and suppliers. Emulsions are usually applied to fabrics by padding or exhaustion. Solvent solutions can be applied by spraying. With either type of product, coapplication of a catalyst is necessary. The level of silicone solids on the weight of fabric should be 0.5–1.5%. Most of the silicone emulsions can be coapplied with durable-press resins. Curing occurs at about 150°C.

The water repellency of silicone finishes results from the low CST (ca 22 mN/m or dyne/cm) produced by the methyl groups in the silicone that are oriented away from the fiber surface. The CST is lower than that produced by any class of compounds except for fluorochemicals.

2.2.3. Resin-Based Finishes

Resin-based water repellents are durable finishes that are modified melamine resins, blended with waxes. In some cases, the resin helps disperse the wax in the repellent formulation. The resin provides water repellency and binds the wax onto the fabric.

Resin-based repellents may be used alone or in combination with durable-press resins. They are widely used as extenders for fluorochemical repellents. When used alone, several of the resin-based finishes require an acid catalyst and curing at temperatures above 150°C for maximum repellency and durability. When coapplied with durable-press finishes, which themselves require a magnesium chloride catalyst, the catalyst and curing conditions for the durable-press finish provide the necessary conditions for the repellent.

Resin-based finishes are applied to fabrics by padding. A concentration of 1.5% resin solids on the weight of the fabric is a common application level. The concentration of repellent solids required for good initial repellency and good durability is about 0.3–0.5%, based on the weight of the fabric. The compositions of commercial products are proprietary.

2.2.4. Waxes and Wax–Metal Emulsions

Waxes and wax–metal emulsions are the lowest priced, widely used water repellents and fluorochemical extenders. They can be applied by padding or exhaustion with no cure commonly required. However, waxes have only poor-to-fair durability to washing and dry cleaning, and tend to show streaks from abrasion.

Several types of wax and wax–metal emulsions are water repellents (30, 31). Among these are wax dispersions without metal salts and wax dispersions containing aluminum or zirconium salts. The products that do not contain metal salts are anionic emulsions of wax, used alone or in combination with durable-press resins. Specific compositions are proprietary. Their chief use is on nylon, polyester, and acetate fabrics.

Wax–metal emulsions are useful on a variety of fabrics, alone or in combination with resins. Wax–aluminum emulsions, which have largely lost their market share to wax–zirconium emulsions, usually contain paraffin wax, aluminum acetate or formate, and a dispersing agent and protective colloid, eg, glue. They tend to develop amine odors when used with thermosetting resins. Wax–zirconium salt emulsions are useful on a wide variety of natural and synthetic fibers. Some finishes have considerable durability to laundering.

2.2.5. Organometallic Complexes

Werner-type complexes of chromium and long-chain carboxylic acids, eg, stearic acid, are water repellents for fabrics of natural and synthetic fibers. The complexes have a small market in the textile industry.

2.3. Modification of Textile Fibers

The reaction of hydrophobic chemicals with textile fibers offers the possibility of permanent repellency without alteration of the other physical properties of fibers. However, the disadvantages caused by complex processing, and resultant higher costs of carrying out chemical reactions on fiber in commercial textile plant operations, have limited the commercial applications. The etherification and esterification of cellulose have been most effective in terms of achieving durable water repellency (32, 33). Radiation grafting of reactive repellents onto fibers has been studied as a potential commercial process (34, 35), as has modification by plasma polymerization of gas monomers or plasma initiated polymerization of liquid monomers (36).

2.4. Fabric Construction for Water Repellency

Fabric construction, including twist, ply, and coarseness of yarns, affects the performance of water repellents. Waterproof films can more easily be formed on close weaves than on open-weave fabrics. Hydrophobic finishes, which make individual fibers repellent without altering fabric porosity, are generally applied to fabrics whose pores are small (37). The relation of rainwear fabric construction to the performance of repellents has been reviewed (38). Some reports indicate that fabric roughness reduces repellency (28, 37). Mechanical action on fabrics, even after treatment, can reduce repellency if the action increases fiber roughness or exposes fibers that have little repellent treatment.

2.5. Carpet

Carpet, an important textile, may also be treated to provide water and oil repellency; however, the principal functions of the current carpet treatments are to provide soil and stain resistance. High quality carpets, especially those made from nylon, polyester, or wool, have a significant proportion of the surface coated with fluorochemical materials. The treatments can be spray-applied to a finished carpet or applied directly to the fiber during the spinning or dyeing operations. Suitable fluorinated resin materials are readily available from 3M or DuPont.

2.6. Health and Safety Factors

The Material Safety Data Sheets provided by the suppliers should be consulted for each product. In general, products are aqueous emulsions with low levels of toxicity. Products with high solvent content have mostly been eliminated. Personnel handling the chemicals should always avoid contact of the products with skin and eyes, and avoid exposure to vapors if the product contains volatile components.

2.6.1. Test Methods

Many tests are useful for determining water and oil repellency in textiles and for testing the durability of finishes to washing and dry cleaning. The most widely used tests in the United States are described in the *Technical Manual* of the American Association of Textile Chemists and Colorists (14). The selection of tests depends upon the textile being tested, ie, whether it is a fiber, fabric, or nonwoven product. The selection also depends on the nature of the finish, ie, whether it is waterproof, water-repellent, water- and oil-repellent, or solvent-repellent. Special tests may be necessary for fabrics or garments that must meet specific requirements, such as repellency of shell and lining for lined garments (39). Several supplementary tests are important, depending on the textile. These include air and water-vapor permeability, repellency to specific chemicals or vapors, fabric stiffness or softness, color, effects on dyes, and durability of physical properties and color to exposure to light or atmospheric gases.

In the following descriptions of some widely used repellency tests, the term fabric designates any woven, knitted, or nonwoven textile.

The spray test is one of the most commonly used tests for fabrics and nonwoven products. The test material is held tightly on an embroidery hoop and mounted at a 45° angle to the horizontal and 15 cm below a spray nozzle. The fabric is sprayed with 250 mL of water. The degree of repellency is rated by comparing the sprayed fabric or nonwoven with pictures on a standard chart (AATCC Test Method 22 (7); INDA Standard Test 80.1-92 (40)). Durability of the finish to dry cleaning can be evaluated by first cleaning the fabric according to AATCC Method 86 (14).

The rain test simulates the effects of rainfall; the hydrostatic head on the spray controls the intensity of spraying. The repellency is rated by the weight of water that penetrates the fabric and is absorbed by a blotter mounted behind the fabric at a specific intensity of spraying (AATCC Test Methods 35 and 42; INDA Standard Test 80.2-92).

Oil repellency is measured by observing a fabric's resistance to wetting by a selected series of numbered test liquid hydrocarbons with a range of surface tensions. The fabric rating is based on the liquid that does not wet the fabric surface in a specified time (AATCC Test Method 118 and INDA Standard Test 80.7-92). Suppliers of fluorochemical repellents may recommend different times or a different series of hydrocarbons in the evaluation of treated fabrics.

Alcohol holdout tests, which are also used to measure aqueous fluid repellency, involve placing drops of aqueous isopropyl alcohol solutions of concentrations 10, 20, ... 100 wt % on a fabric surface. The rating for the fabric is based on the most concentrated solution that does not penetrate the fabric in the specified time frame (3M Water Repellency Test II, Water/Alcohol Drop Test (41); INDA Standard Test 80.6).

The nonwovens industry also uses a saline repellency test, especially for medical fabrics. Fabrics are evaluated for the lapsed time before wetting when a 115-mm column of water in a mason jar is applied to the surface (INDA Standard Test 80.5-92).

The hydrostatic-pressure test is performed on fabric mounted under the orifice of a conical well. The fabric is subjected to increasing water pressure at a constant rate until leakage occurs at three points on the fabric's undersurface. The rating is the height of the water head in centimeters above the fabric (AATCC Test Method 127; INDA Standard Test 80.4-92).

The dynamic absorption test measures the resistance of fabrics to wetting by water, not the repellency of the total fabric surface. A weighed portion of fiber, yarn, or fabric is tumbled in water for 20 minutes; it is then removed and reweighed to determine the percentage of water absorbed (AATCC Test Method 70).

The specifications for water, oil, solvent, or soil repellency vary with the use of the textile, the nature of the textile, and the nature of the repellent (27–29, 42, 43). Suppliers of repellents may specify a minimum level of repellency for the approved use of a repellent.

3. Leather

For fashionable leather apparel, high quality upholstery such as nubuc or aniline, and for shoes, oil- and water-repellent treatments preserve the leather's original appearance and provide for easy care. The main characteristics required by easy-care leather are the ability to shrug off water- and oil-based stains, and to resist soiling. Water-resistant treatments are useful to reduce the tendency of leather to become stiff and uncomfortable after wetting and drying. Various approaches have been made over the years to meet this need. All have their advantages and disadvantages and none can be said to offer the ultimate solution.

Before the introduction of synthetic water repellents, the best way to protect leather was to apply large concentrations (up to 50% of the leather weight) of oil, tallow, or grease. The treated leather was uncomfortable because the pores of the leather were filled and the water-vapor permeability was low. Water repellents available today are useful at low concentrations and make the leather surface repellent without reducing permeability to water vapor. The theoretical and practical aspects of water repellents for leather have been reviewed (44). Water should bead on the surface of water-repellent leather because of treatment of the individual fibers, both on the surface and in the interior of the leather. The fibers should not become wet even with prolonged soaking, and the leather should be permeable to water vapor for comfort.

Commonly used repellents for leather are silicones, chrome complexes of long chain fatty acids, and fluorochemicals. Fluorochemical repellents also provide repellency to oils and greases so that the treated leather resists staining. A water repellent may also be a hydrophobic chemical insolubilized in the leather. A simple water-repellent treatment consists of forming an aluminum soap in leather by the two-step process of applying a soap, and then an aluminum salt.

The silicones, as supplied by Dow Corning and OSi Specialties, are an important class of repellents (44, 45). Numerous patents describe the use of silicones for leather (46, 47). Silicones are linear polymers, eg, dimethylsiloxane polymers, that bond to the leather. They can be applied as aqueous dispersions in the presence of glutaraldehyde acting as a bridge between the silicone and amide groups of the leather (48). Silicones can also be applied to leather as solvent solutions in a post-tanning operation. The concentration of silicone used is 4.5–15 wt % to provide repellency that resists extended flexing (45, 48).

Organic titanates can be used to cross-link silicones on leather (49). Tetrabutyltitanate and tetrakis(β-aminoethoxy)titanium cross-link silicones, eg, poly(dimethyl siloxane), to increase both water repellency and durability. For example, good repellency results from the impregnation of leather with a solution of 10 wt % tetrabutyltitanate in butyl acetate, followed by impregnation with a 9:1 mixture of silicones and tetrabutyltitanate (50).

Chrome complexes of stearic and myristic acids provide water and aqueous stain resistance, dimensional stability, and lubricity. The products may also enhance the appearance and durability of leather. The chrome complex reacts with the leather molecules to form a permanent bond.

Chrome-complexed fluorochemicals, as well as fluoropolymers, are widely used products. The compositions are proprietary. Fluorochemicals provide a high degree of water repellency as well as repellency to aqueous stains, oils, grease, and oilborne stains. Traditionally, treatments are applied during a drum process in which about 30 min are required for full penetration of the leather to occur. Products are also available for application with spraying equipment and roll coaters.

3.1. Test Methods

Tests for measuring the water and oil repellency of leather include ASTM and AATCC tests, as well as tests developed by suppliers.

In the Spray Test (AATCC Test Method 22), water is sprayed on a taut surface and rating is based on comparison with a standard chart (14).

In Oil Repellency (AATCC Test Method 118), drops of oils of various surface tensions are placed on the leather and monitored to absorption (14).

In the 3M Water/Alcohol Drop Test (41), this test is designed to provide a simple, rapid method to assess the aqueous stain resistance of substrates treated with a protective finish.

The 3M Abrasion Test (51) is used to assess the durability of a protective fluorochemical finish by evaluating its resistance to abrasion and wear. The surface is abraded with an AATCC crockmeter fitted with sandpaper.

For dynamic water resistance, the Bally Penetrometer Test, IUP/10 (52) measures water penetration.

For dynamic water resistance, the Maeser Test, ASTM D2099 (53) measures the number of flexes and water penetration. The flex imparted to the leather is a magnification of the flex given the vamp of a shoe in actual wear.

For static water absorption (ASTM D1815) (53), the weight of water absorbed during 30 min, 2 h, or 24 h, with all surfaces of the leather exposed to the water, is measured.

4. Paper and Paperboard

Paper or paperboard that repels water may be designated waterproof or water-resistant. In this context, waterproof means resistant to the penetration of both water and water vapor. A chemical additive, called a sizing agent, can provide water resistance by lowering the surface energy of the paper without greatly affecting the porosity. A water-vapor barrier or moisture-vapor barrier (MVB) is provided by a film or film-forming coating used in a manner to seal the surface. Acrylic-based overprint varnishes are often used to provide water resistance, as well as abrasion resistance, to a printed surface. Paper or paperboard can also be made resistant to oil-based fluids. Food oil resistance is the most common application for this property. To lower the surface energy enough to provide oil repellency, a fluorochemical additive is required (for pigment or clay-coated paper or paperboard, see Paper; Papermaking additives).

4.1. Waterproof

Waterproof paper or paperboard is commonly made by lamination of a polyethylene film or wax that is applied by extrusion coating. The MVB properties derived from wax emulsions are generally inferior to those derived from extrusion coatings, but both forms provide excellent waterproof properties. Polyester film is used in food board and other applications where the composite material must withstand temperatures such as those encountered when re-heating or cooking foods in an oven. Currently (ca 1997), there are efforts to replace the standard film laminants with aqueous coatings. An important consideration is improvement in the yield and ease of repulping and recycling. Aqueous wax-based coatings are not very useful in this regard because wax residues in the recycling process cause problems in papermaking. Polyvinylidene chloride-based aqueous coatings provide excellent MVB properties, but paper and paperboard with chlorine-containing coatings are becoming less common because of concerns regarding cost, aging characteristics, and residual chlorine-containing products in the environment. Aqueous coatings that provide a good moisture barrier can be applied by air knife, rod, or rotogravure. To provide protection to exposed cut edges or to protect from failure at pinholes, it may be beneficial to use paper or board that is sized or has an oil repellent treatment. As an example, paperboard for milk carton stock is strongly sized with alkyl ketene dimer (AKD) and laminated with a polyethylene to make it waterproof. In these ways, useful paper products can be made for boxes, bags, liners, roofing material, and protective coverings that are waterproof.

4.2. Water-Resistant

Paper or paperboard that is resistant to water can be produced by chemical addition of a sizing agent at several points in the manufacturing process or during subsequent converting operations. If the sizing is added to the aqueous suspension of pulp fibers before sheet formation, it is called internal or beater sizing. This gives chemical modification of the fiber surface throughout the sheet or ply. Surface sizing done on a paper machine can actually be a deep treatment from a pond size press, or a shallow treatment applied by a premetered size press, blade, or rod coater. A surface treatment can also be applied at a printing station in a converting operation. Over 75% of all paper and paperboard produced in North America is sized to some extent, the two largest segments being fine paper and unbleached kraft. Extensive reviews of sizing are available (54–58) as well as listings of available commercial products (59, 60).

4.3. Internal Sizing

The most widely used internal sizes are alkyl ketene dimers (AKD), alkenylsuccinic anhydrides (ASA), and rosin-based sizes that are used with papermaker's alum (aluminum sulfate with 14 waters of hydration), polyaluminum chloride (PAC), or polyaluminum silicosulfate (PAS) (61). The rosin-based sizes are used under acidic conditions. Since the mid 1980's there has been a steady conversion from acid to alkaline paper production, resulting in static to declining demand for the rosin-based sizing systems. Rosin is a complex mixture of compounds and consists primarily of monocarboxylic acids with alkylated hydrophenanthrene structures (62). A main constituent of wood rosin, gum rosin and tall-oil rosin is abietic acid. Rosin is commonly modified with maleic or fumaric acid to improve efficiency. Since the 1970s, dispersions of unsaponified rosin have become more popular as a result of their improved sizing efficiency, lower alum requirements, and reduced pH sensitivity vs saponified rosins. Cationic dispersed rosin size, which can be effective at near-neutral and neutral papermaking conditions, is also available (63–65). Commercially available rosin sizes include Pexol, Neuphor, and Hi-pHase (Hercules Inc.), Plasmine and NeuRos (Plasmine), Stafor (Westvaco), Novaplus, and Novasize (Georgia Pacific), and NeuRos and Roscol (Akzo Nobel).

The AKD and ASA sizes are used in neutral to alkaline papermaking. ASA has the advantages of faster development of water-repellent properties and a lesser tendency to give slip, but it is supplied as a two- component system that must be emulsified shortly before use at the paper mill site, owing to the short active half-life of the ASA. Commercially available ASA sizes include Accosize (Cytec), Nalsize (Nalco), and Bersize (Bercen). AKD is supplied as a one-part system as an aqueous emulsion. It has an active half-life measured in months at room temperature, but this can be extended with refrigerated storage. AKD-sized paper exhibits excellent resistance to penetration by acidic fluids such as milk and fruit juice, as well as water. Commercially available AKD sizes include Hercon and Aquapel (Hercules Inc.), Rasiofob (Raisio), Keydime (Akzo Nobel), Basoplast (BASF), and Darasize (Grace Dearborn). In 1995, a new alkenyl reactive size, under the name Precis (Hercules Inc.), was introduced. It is best suited for fine paper grades where properties such as improved printability are desired since it does not give the strong sizing of the AKD and ASA.

4.4. Surface Sizing

Surface sizing is generally used for modification of other properties of paper or paperboard such as printability, smoothness, porosity, coefficient of friction, opacity, surface strength, anti-linting or coating holdout. Anionic starch is perhaps the most common additive or co-additive used for surface sizing.

Most of the surface sizes used in North America are modified styrene maleic anhydride (SMA) copolymers. Commercially available materials include Scripset (Monsanto/Hercules Inc.), Cypres (Cytec), Sursize (Akzo Nobel), MSA (Morton), NovaCote (Georgia Pacific), and HTI (Hopton Technologies). Styrene acrylate emulsions that are commonly used include Jetsize and Unibond (Akzo Nobel), Basoplast (BASF), and Cypres (Cytec). Other materials used as surface sizes include acrylonitrile acrylate copolymer (Basoplast, BASF), stearylated melamine resin (Sequapel, Sequa), polyurethane (Graphsize, Vining Chemicals), and diisobutylene maleic anhydride copolymers (Baysynthol, Bayer).

Chromium complexes of long-chain fatty acids are excellent water repellents which are also used for their food-release properties in certain packaging applications. The presence of chromium has raised environmental concerns, despite the fact that the metal is in the trivalent rather than in the highly toxic hexavalent state. This material is available as Quilon (DuPont).

In most cases, some internal size is still required to control the depth or penetration of the surface size, the runnability through a size press, or other properties. Surface sizing reviews and leading references are available (66, 67).

4.5. Oil Repellent

Fluorochemicals are the only class of material that can provide oil repellency without altering the porosity of the paper or paperboard. Physical barriers to oil penetration are used primarily for their moisture- or gas-barrier properties, with retarded oil penetration as a secondary benefit. The most common oil-repellent additives are long-chain perfluoroalkyl phosphate salts of ammonia or diethanol amine. Commercial sources include Scotchban (3M), Zonyl (DuPont), and Lodyne (Ciba Specialties). There are also a fluorochemical carboxylate salt, Lodyne (Ciba Specialties), and fluorochemical copolymers, eg, Scotchban (3M). The widest range of oily fluid holdout is provided by the fluorochemical copolymers.

Oily-based fluids become more aggressive in staining packaging papers as they become higher in polar components such as fatty acids, surfactants, and water. Fluorochemicals are primarily used in surface applications made at the size press of a paper machine or the calender stack of a board machine. To a lesser extent they are applied off-machine, in a converting operation. They have also been used in pigment, clay, or MVB coatings. Internal applications (beater addition) of the fluorochemical phosphate salts require the use of cationic retention aids to attach these anionic species to the fibers. The packaging of many items such as snack food, french fries, convenience food, and pet food is facilitated by the oily-stain protection provided by fluorochemicals.

4.6. FDA Regulations

Most of the sizing agents, waterproof coatings, and oil repellents mentioned are regulated by the U.S. Food and Drug Administration (FDA) for use in paper or paperboard that comes in direct contact with food. To avoid raising contamination issues, paper and paperboard mills often require all chemicals to be FDA-regulated if any of their products are used in food contact applications. The regulations often include limitations on the intended use, method, or point of application; upper limits on the amount that can be present on the paper or paperboard; and guidelines related to the filling, storage, and final use of the paper or paperboard (68). For that reason, it is important that every link in the production chain, from the supplier of the chemical additive to the paper mill to the package producer, know the specific limitations governing the materials used to modify the paper or paperboard when they are intended to come in direct contact with food. Suppliers of repellent additives for paper can provide information as to the FDA compliance of their materials and specific limitations surrounding their use.

4.7. Test Methods

The test methods used for water or oil repellency are quite varied, in accordance with paper or paperboard type and end use. Two tests commonly used to measure water repellency, the Hercules Size Test and the COBB Test, as well as others have been summarized (55, 69, 70). The Kit Test (T-559 pm-96) can be used to measure oil repellency when there is no physical barrier to oil penetration such as that provided by a film, foil, or waterproof coating (71). Another measure of oil repellency is the Turpentine Test (T-454 om-89) (71). If a physical barrier is present, tests that measure the weight of oil pick-up or show-through under conditions that simulate the end use are appropriate.

5. Concrete and Masonry

Water resistance is an important factor in concrete and masonry construction for the safety, health, and comfort of building occupants (see Cement). Several texts on concrete construction describe the methods for obtaining water resistance (72–76). The term waterproof describes concrete and masonry that is completely impervious to water and its vapor, whether or not the water is under pressure. Waterproof construction involves the use of some type of barrier that covers all surface pores or capillaries. Water repellent describes concrete or masonry that repels water without significantly reduced permeability to water vapor. In this discussion, concrete and masonry are used synonymously.

Several problems related to excess moisture in concrete are expansion, shrinkage, and cracking; efflorescence, staining, and mildew; spalling due to freeze/thaw cycling; increased thermal and electrical conductivity; chemical attack; damage to contents from leakage; damage to finished walls; and corrosion of reinforcing steel. Care in choosing aggregate and in selecting an appropriate water-cement ratio leads to a watertight concrete that may not require additional waterproofing or water-repellency treatment (77).

5.1. Waterproof

Waterproofing barrier systems may be either hot- or cold-applied. The hot-applied generally involve a bituminous material such as asphalt used in conjunction with a reinforcing fabric such as roofing felt, cotton, or glass cloth. Cold-applied can be bituminous or elastomeric materials either in liquid or sheet form, with or without fabric reinforcement. Liquid elastomeric treatments include neoprene, polyurethanes, and blends of these or epoxies with bituminous materials. Among the commonly used precured elastomeric sheet materials are neoprene, polyisobutylene, EPDM rubber, and plasticized PVC. Polyethylene and PVC films and nonwoven plastic or glass fabric coated with bituminous materials also find use (78). Because these treatments can trap moisture in a wall, the proper selection and application of treatment materials depend on the nature of the concrete structure, such as whether it is made up of exterior or interior walls above or below grade, floors, or roofs (76).

5.2. Water-Repellent

Three techniques used for water repellency are modification of cement by the addition of waterproofers, use of repellent additives to the concrete mix, and surface treatment of concrete structures with repellents. The modification of portland cement by intergrinding with stearate salts or other water-repellent material can reduce the water permeability of mortar. Considerable controversy exists, however, as to whether these cements produce concrete that is superior to carefully mixed concrete without such additives (79).

Admixtures are sometimes used to reduce permeability of concrete (80–82). These include pore-filling materials such as chalk, Fuller's earth, or talc; water repellents such as mineral oil, asphalt, or wax emulsions; organic polymers (acrylic latexes, epoxies); and salts of fatty acids, especially stearates.

The third and perhaps most important class of water repellents consists of materials applied to the surface of concrete for above-grade structures or others where water pressure on the concrete is small. This includes damp-proofing in which treatments cannot be subjected to continuous or even intermittent hydrostatic pressure (83). Repellents that may be used are oils, waxes, soaps, resins, and silicon-based systems (84).

Oils provide short-term benefits on surfaces that are not damaged by the resulting discoloration. For instance, bridge decks may be treated with linseed oil to prevent spalling. Waxes are highly resistant to water, filling pores as well as producing water repellency. Their disadvantages are a tendency to change the appearance of masonry, migration to the surface at high temperatures, and poor abrasion and weathering resistance. Among soaps, the most commonly used are organic solvent solutions of calcium and aluminum stearate.

A wide variety of synthetic polymer resins can be used as water repellents for concrete. These include acrylates, epoxies, chlorinated rubber, polyvinylbutyral, urethanes, elastomeric silicones, and fluoropolymers. They are generally applied from organic solvents or, in some cases, aqueous dispersions or latexes. Some have the disadvantage of inducing gloss and discoloration in the treated masonry.

Concrete can also be made water-repellent by the polymerization of vinyl monomers on the surface (85). Polymerization can be initiated with peroxides, and polyfunctional methacrylates can be used as crosslinking agents. These treatments have a tendency to produce changes in color and gloss.

Siloxanes, alkoxysiloxanes, and alkoxysilanes have in recent years become the most important classes of materials used for water-repellent treatment of masonry, in applications where durability and minimal effect on substrate appearance are important. They achieve these characteristics by penetrating deeply into the masonry (up to 5–10 mm, depending on the substrate and treatment system), hydrophobizing pore surfaces while leaving the surface structure and resultant optical properties largely unaltered. Materials bearing silanol or latent silanol functionality (such as alkoxysilanes, which yield silanols by hydrolysis) can in principle bond covalently to masonry materials through condensation reactions with metal hydroxyl moieties. Silanol self-condensation also leads to cross-linking of the treatment; this combination of reactivity modes, catalyzed by the latent basicity of many masonry types, leads to outstanding durability of water resistance.

Traditionally, materials choice in this area was dominated by solvent-based silanes, siloxane resins or resin–silane combinations (86), and the water-based alkali metal methylsiliconates. The former materials are falling out of favor as a result of a new emphasis on volatile organic compounds (VOC) and solvent reduction, while disadvantages of the latter are their extremely high pH and corrosive nature. In more recent years, aqueous emulsion-based systems have begun to appear which are replacing the older technology.

Two different approaches have been taken toward waterborne alkoxysiloxane and alkoxysilane waterproofing materials. The recent patent literature contains many references to emulsions of alkoxysilanes and silane–resin mixtures (87) that claim stability to hydrolysis until the emulsions are applied and allowed to dry on the masonry, at which point hydrolysis and condensation are underway. Alkoxysilane stability within the emulsion is obtained through judicious choice of emulsifiers and the use of buffering agents to minimize pH drift. Excellent performance in static water holdout tests may be obtained with these systems, although initial water beading by the cured coatings can be somewhat compromised by the presence of surfactant.

A different approach to alkoxysilane or alkoxysiloxane waterproofing agents for masonry is represented by the use of self-emulsifying liquid concentrates (88) intended to be diluted into water and applied within 24–48 h of mixing. These materials owe their ready water-dispersibility to incorporation of low levels of amine functionality protonated by acetic acid; upon drying, the alkoxysilanes hydrolyze and condense, and the acetic acid is lost by volatilization, leaving no residual surfactant behind.

Another class of water-based materials that has recently (ca 1997) begun to see use in masonry water repellency treatments is silicone elastomer latex (89), which can deliver a water-permeable silicone rubber film. These latex elastomers are ideal as water repellents for substrates that contain very large pores, such as concrete block. In addition, the elastomer can bridge minor cracks, and will expand and contract with the substrate.

Oil- and water-resistant treatments have been reported which involve blends of fluoropolymers and alkoxysilane or alkoxysiloxane materials, delivered as 100% actives (90) or from solvent or emulsion (91), fluorinated alkoxysiloxane emulsions (92), and self-emulsifying fluorinated alkoxysilane-based concentrates (93).

5.3. Test Methods

Tests for water repellency of concrete and masonry have been described by several authors (72, 94). The National Bureau of Standards (NBS) evaluated fifty-five clear water repellents for masonry surfaces (95). Performance tests included water absorption, water-vapor transmission, resistance to efflorescence, change in appearance, and durability to accelerated and outdoor weathering. More recently, the National Cooperative Highway Research Program conducted a study of several organic and silicone water-repellent treatments. The results are communicated in Report 244 (96). The testing procedure used in this study is now a popular method for evaluating water-repellent treatments on concrete.

6. Wood

Wood is subject to water infiltration by both liquid and vapor. As the moisture content increases, the wood will swell until it reaches its maximum dimension at its fiber-saturation point (about 30% moisture). Variation in the bound water content between zero and 30% will allow the wood to shrink and swell. Rapid dimensional changes resulting from changes in the level of bound water cause the wood to crack and split. These cracks will then allow moisture to absorb easily and quickly into the wood. At moisture content levels above the fiber-saturation point, moisture will be present as free water, which in turn promotes the rate of wood decay.

After-market water repellents, ie, those applied to wood structures after they are built, are widely sold in the consumer market. Materials used in formulating these water repellents are proprietary, but they can be organic resins, waxes, metal stearates, and acrylics. Three components are generally used for a robust water repellent. These include a water-repellent material that penetrates into the wood pores, a material that remains on the surface to give the visual effect of water beading, and a material that reduces the rate of water-vapor transmission into and out of the wood to improve dimensional stability. To penetrate the wood with a solvent or water-based material, a molecular weight of about 1000 or less is generally needed. Water-based short-chain siloxanes which penetrate and bond with the surface are especially effective. Paraffin waxes are typically used to provide surface-water beading. Because it is very difficult to ensure total moisture vapor impermeability, it can be beneficial to use blends of water vapor-permeable materials and water vapor-occlusive materials in order to allow moisture that has entered the wood to exist. Most manufacturers of paints and caulks sell fully formulated water repellents for wood.

6.1. Test Methods

Few standard text methods are available to test wood water repellents. Two different types of testing are required to test the water repellency and the dimensional stability. A gravimetric water-repellent method is found in ASTM D5401 (53). Dimensional stability can be tested with ASTM D4446 or Federal Specification TT-W-572B, which is termed the swellometer method. Specifications for the swellometer gauges can be found in ASTM D4446 (53).

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