

HYBRID ORGANIC-INORGANIC COATINGS FOR WOOL TEXTILES

S J McNeil^{1,2}, O C Standard², M T Pailthorpe^{2,3}

¹*Canesis Network Ltd, PO Box 4749, Christchurch, New Zealand*

²*School of Materials Science and Engineering, University of New South Wales,
Sydney, 2052, Australia*

³*Canesis Pty Ltd, PO Box 3084, Willoughby North 2068, Australia*

Advanced textiles based on smart and nano technologies are attracting considerable interest because they give textile producers an opportunity to add high value and to differentiate their products. The greatest impact of advanced textiles to date has been in active sportswear and military apparel, but this is likely to spread into other sectors.

Hybrid organic-inorganic materials prepared by the sol-gel process offer a practical way of preparing many types of advanced textiles. These hybrid materials combine some of the useful properties of ceramics and polymers, and can be prepared on wool as either continuous films or discrete particles. These materials can be produced under mild conditions and their structures can be controlled at the nanometre scale.

This paper describes the development of hybrid coatings with physical and chemical properties compatible with wool, with the objective to provide a platform for a range of solutions to some of wool's existing limitations, and take it into a whole new range of end-products.

At the last International Wool Textile Research Conference, the paper by Textor, Bahners and Schollmeyer described the possibilities of hybrid organic-inorganic coatings for textiles (1). These polymeric materials can be prepared by the sol-gel process from alkoxysilanes, titanates and the like. Since the last conference, the potential of these materials has been discussed in reviews of advanced textile finishing (2-5) and scientific papers examining applications as diverse as binders for dyes, water repellency, photocatalysis, and stab-resistant fabrics have been published (6-17). These coatings are particularly attractive for industrial textiles for which increased resistance to abrasion, heat, tearing, microbes, sunlight and water are desirable properties.

The majority of the research and development of hybrid organic-inorganic materials is directed towards non-textile areas. Applications include protective coatings for steel, glass and masonry; scratch resistant coatings for polymers; contact lenses and nanoparticles. Such coatings offer potential to modify the properties of textiles. The underlying sol-gel technology and its application to textiles are examined below. Preliminary development of a silane-based coating for the modification of wool is then described.

The Sol-Gel Route to Hybrid Organic-Inorganic Materials

The sol-gel process is a colloidal route to prepare inorganic and organic-inorganic materials in which precursor molecules are hydrolysed through a solution state (colloidal suspension/nanosol) then a gel state, before being dried. An example of a typical reaction sequence is shown in Figure 1.

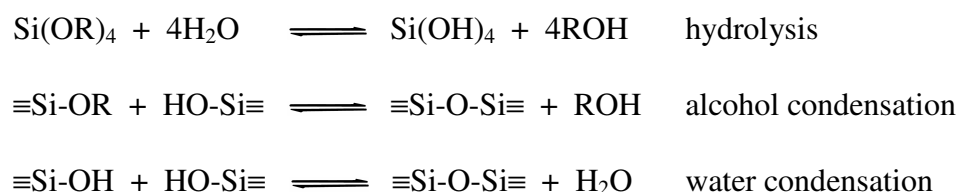


Figure 1 Mechanism of the sol-gel process

This process can form coatings, thin films, fibres, fine powders and monoliths and is attractive for many reasons. It can form different types of hybrid organic-inorganic materials which combine the properties of polymers (flexibility) and ceramics (chemical stability, high abrasion resistance). The rate of the various reactions, such as nucleation and growth of the primary colloidal particles, can be readily modified, giving a high degree of control over the properties of the final material and many different monomers can be used. Monomers may contain 4 hydrolysable groups, e.g., tetraethoxysilane, titanium(IV) isopropoxide, zirconium(V) butoxide, 3, e.g., octyltriethoxysilane, 3-(glycidoxypropyl) trimethoxysilane, perfluorooctyltriethoxysilane, 2, e.g., diethoxydiphenylsilane or 1, methoxy(dimethyl) octylsilane. Conventional ceramics require 1000-1200°C for sintering, whereas sol-gel coatings can be thermally cured at less than 200°C or by UV radiation. This means that the coatings can be applied to a wide range of substrates, including heat sensitive ones. It is a low-cost process which is easy to scale-up. The main drawbacks are that raw materials such as silanes are expensive, alcohol solvents are needed, and the process can be sensitive to humidity.

Textile Applications of Sol-Gel Technology

Modification of Surface Energy. Coatings which impart water, oil and soil repellency are used on carpets, upholsteries, work-wear and out-door textiles. Coatings of poly(methacrylic acid), tetraethoxysilane and perfluoroalkyltriethoxysilane have been investigated on carpets (6). The poly(methacrylic acid) gave the coating flexibility and imparted stain-resistance, and high water and soil repellency was achieved with a very low level of fluorine. The fluorine component is thought to be concentrated at the coating-air interface (6).

High water repellency was imparted to polyamide and polyester/cotton fabrics without fluorine compounds, by coatings of tetraethoxysilane, 3-(glycidoxypropyl)trimethoxysilane and hexadecyltrimethoxysilane (7). The coatings were fast to washing, which suggests that there was good adhesion between the coatings and the substrate.

The resistance of polyester fabrics to electrostatic charging has been improved by applying a silicate coating with high moisture absorption, without affecting the whiteness, strength or handle of the fabric (8).

Coloration. One way of achieving the high lightfastness required of the dyes used in lasers is to encapsulate them in transparent inorganic solids. The dyes are combined with the silanes and the silicate network forms around them, with groups orientated to give the maximum hydrogen bonding and hydrophobic interactions between the dyes and the network (see the left-hand side of Figure 2).

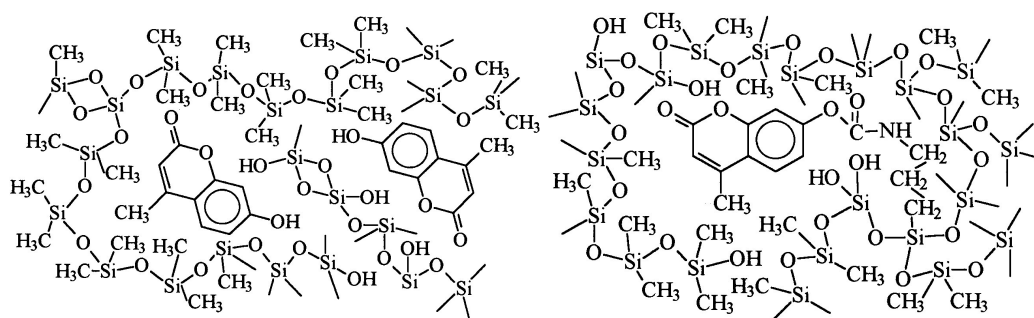


Figure 2 Dye molecules in nanosol matrices (Adapted from reference 9)

Photostability is high because the dye is physically constrained, which hinders the formation of decomposition transition states with different shapes to the original molecule and radical propagation is hindered because the matrix is largely inorganic. Photostability is also assisted by the dye molecules being isolated from each other (enabling high loadings without aggregation), as well as from impurities and photodegradation products. The matrices themselves typically have good photostability and good transparency down to UV wavelengths (10). The greater rigidity and isolation of dyes in inorganic matrices (compared to organic ones) also enhances their fluorescence.

Encapsulation of dyes in silicate matrices can give better resistance to leaching than is achieved in organic polymer matrices (11). Reactive silanol groups can be introduced to some dyes so that they become covalently bound into the silicate network, which gives high resistance to leaching (see the right-hand side of Figure 2). For good resistance to leaching, the dye needs to have good compatibility with the matrix. Pigments can also be encapsulated, but the dispersant required by the pigment reduces the strength of the coating.

Other Textile Applications. A 3-(glycidoxypropyl)trimethoxysilane coating prevented felting of a wool fabric during laundering at 60°C; conditions which strongly felted the untreated fabric (1). The amount of UV light blocked by cotton fabric has been increased by a visibly transparent coating of titanium dioxide (12). The coating was around 100 nm thick, non-porous, with some cracking and it increased the bursting strength of the fabric by 10%. Titanium dioxide coatings have also shown photocatalytic antibacterial (13) and stain removing (14) activity.

Hybrid organic-inorganic coatings have been shown to significantly increase the stab resistance of p-aramid bullet-proof vests (15). Adding tetraethoxysilane and 3-

(glycidoxypropyl)trimethoxysilane to butanetetracarboxylic acid/sodium hypophosphite crease-resist treatments improved the fabric's abrasion resistance but not its crease resistance (16).

A different type of textile application to those described above may be envisioned that makes use of the fact that transparent coatings can be produced with high porosities, as in Figure 3, for example. Because they are formed under mild conditions, they may be able to apply sensitive, active materials to textiles, such as enzymes for self-cleaning fabrics, slow release fragrances or biocides. Additives which change colour or electrical conductivity in response to stimuli such as air pollutants, sunlight or microbes would find many applications. For example, it has been shown that Heme proteins encapsulated in silica matrices retain the ability to change colour when binding different gases such as oxygen, carbon monoxide and nitrogen oxides (17).

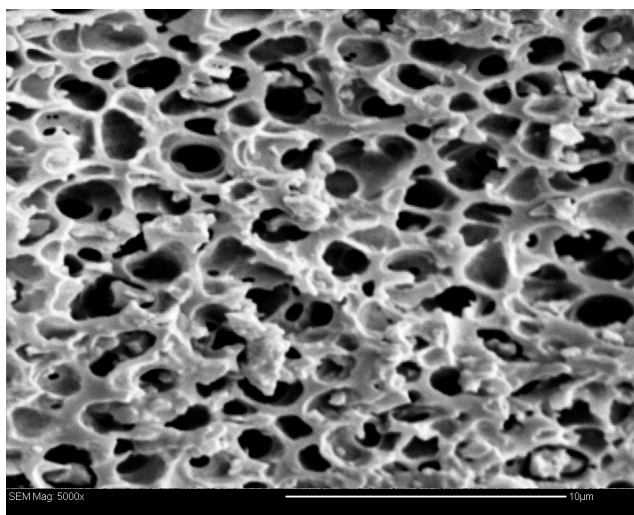


Figure 3 Fracture surface of a hybrid organic-inorganic monolith

Experimental Procedure

The work described below is part of a programme to develop a coating system for wool, based on hybrid organic-inorganic materials, the first stage of which was to investigate some representative coatings and their effect on key textile properties of wool. The following monomer precursors were used to prepare sol-gel coatings: methyltriethoxysilane (MTES), tetraethoxysilane, and 3-(glycidoxypropyl)trimethoxysilane. MTES was selected because its hydrophobicity can cause phase separation during gelation which leads to porous coatings. Tetraethoxysilane was used because it is one of the simplest and least expensive building-blocks for preparing silicate networks by the sol-gel process. 3-(glycidoxypropyl)trimethoxysilane was used because it offers strong potential to react with the surface of wool, thus giving good binding.

Methyltriethoxysilane Coatings. Sols were prepared from MTES, dimethylformamide, water and nitric acid with a solids content equivalent to 29.2 weight percent of $\text{CH}_3\text{SiO}_{1.5}$ (18). The sol-gel reaction sequence is shown in Figure 4. After ageing for 5% of the gel time, the

sols were diluted with ethanol and padded onto 100% wool, plain woven fabric weighing 300 g/m². The padded fabrics were air dried for 15 minutes then dried for 10 minutes at 80°C in a suction drum dryer. Single wool fibres were also dipped in the diluted sol and air dried while suspended under tension.

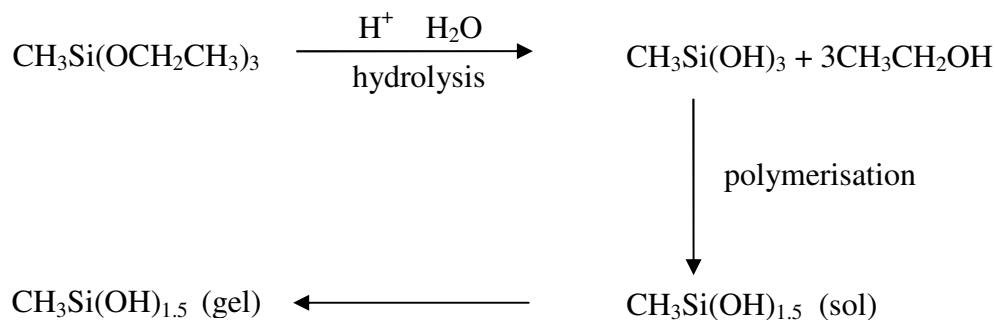


Figure 4 Mechanism of the sol-gel reaction of methyltriethoxysilane

The morphology of the coatings on the wool fibres was examined using transmitted light microscopy and scanning electron microscopy. The bending rigidity of the coated fabrics in the warp direction was measured using a FAST 2 instrument. Of particular interest, was whether the coating would make the fabric unacceptably stiff. For comparison, Hercosett (polyamide-epichlorohydrin, Hercules, USA) coatings were applied to the fabric at different levels. Controls for the MTES and Hercosett coatings were prepared by padding fabrics with ethanol and water, respectively.

To investigate their water repellency, MTES coatings were prepared as described above at 0.3% MTES on mass of wool (omw) with the addition of octyltriethoxysilane (sufficient to give a molar ratio of methyl to octyl groups of 29:1) and Nuva FSN fluorocarbon water repellent (Clariant, Switzerland) (0.6% omw). Water repellency was assessed by the length of time the fabrics could repel water droplets for and the International Wool Secretariat Test Method 258 for Assessing the Oil and Water Repellency of Textile Floor Coverings, which is based on the repulsion of droplets of different ratios of water and propan-2-ol.

Silicate and Acrylic Coatings. To investigate the ability of a silicate matrix to improve the lightfastness of textile dyes, a set of 13 dyes were padded onto wool fabric in acrylic (Viscopol 8800, cross-linking acrylic nitrile, Nuplex, New Zealand) and silicate coatings. The silicate coating was prepared from tetraethoxysilane and 3-(glycidoxypropyl)trimethoxysilane with an acid catalyst. Each dye was applied to several fabrics at different levels with the two types of coatings, and the lightfastness of the two fabrics with the closest colours for a given dye was tested (Wools of New Zealand Test Method TM 5, 1994). In some cases the colour differences between the same dyes in different matrices were significant, because of the colorant's sensitivity to the different polarities of the acrylic and silicate matrices.

Results and Discussion

Methyltriethoxysilane Coatings. Typical morphologies of the MTES coatings are shown in Figures 5 and 6. The coatings occurred in various forms, namely smooth (the predominant form) particulate, sharp projections, porous, and striated. The final form of the coating was largely determined by the amount of sol applied. Thin films of sol could not maintain coverage of the fibres during drying, and retreated to the fibre junctions, leaving behind small particles on the fibre surface. At higher add-ons, the sol coatings were thick enough for phase separation to occur, resulting in porous coatings. Porosity is desirable as it would enable vapour transport between the fibre and the environment, as well as increasing the flexibility of the coating. The porosity arose during drying of the water/ethanol solvent. As the ethanol evaporated, there was a phase separation between the remaining water and the hydrophobic organosilicate gel (18).

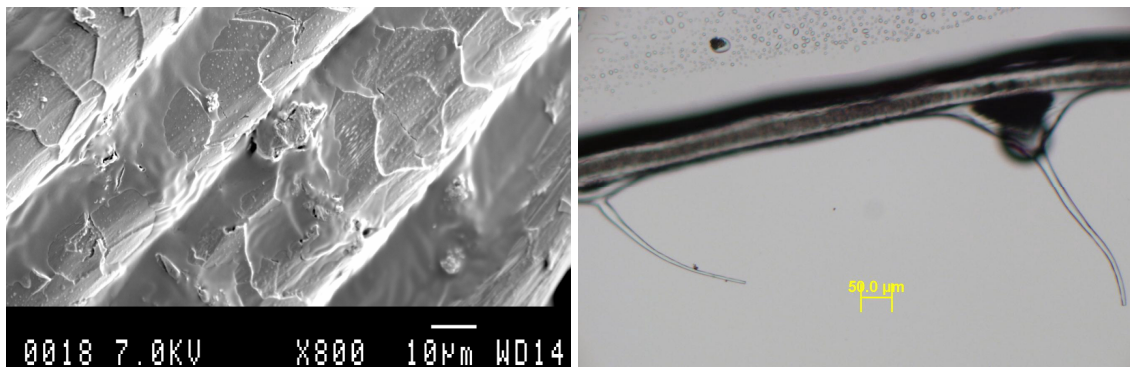


Figure 5 Scanning electron micrograph of wool fabric padded with MTES sol (left) and optical micrograph of a single wool fibre dipped in MTES sol (right)

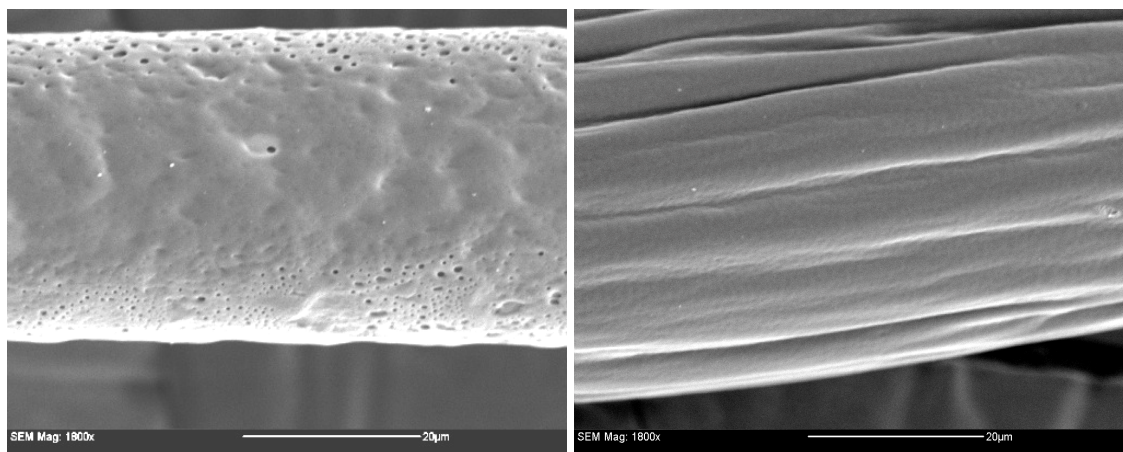


Figure 6 Scanning electron micrographs of single wool fibres dipped in MTES sol

The bending rigidity of the fabrics in the warp direction is plotted as a function of add-on in Figure 7. Treatment with ethanol slightly reduced the weight of the fabric, possibly by removing some of the residual processing aids and extracting some lipids from the wool.

Padding with ethanol also slightly reduced the bending rigidity of the fabric. At 1% solids add-on, the organosilicate and Hercosett coatings gave similar fabric rigidities. These results suggest that the organosilicate coating was not imparting an unacceptably stiff handle to the fabric.

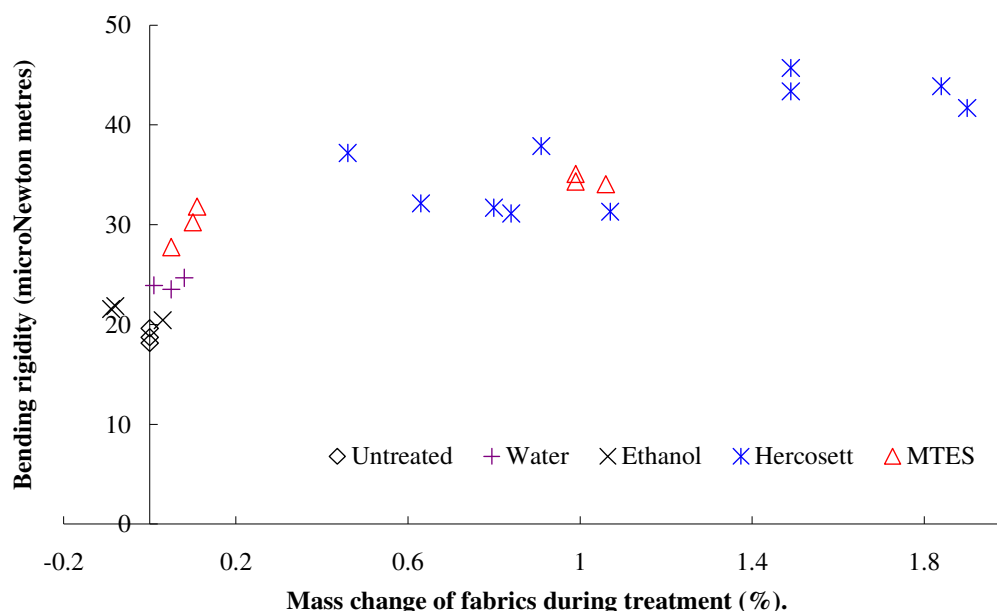


Figure 7 Bending rigidity of treated fabrics in the warp direction

Water repellency data for the coated fabrics are given in Table I. The MTES coating with no additives, increased the length of time the fabric could repel water droplets for, but the effect was not large enough to raise the repellency grade (see Table I). It has been shown that the methyl groups preferentially occur on the surface of these types of coatings (19), and this is the likely cause of the observed water repellency. Both octyltriethoxysilane and Nuva FSN increased the water repellency, as measured by grade and wetting time. The MTES-octyltriethoxysilane coating is an appealing water repellent because it does not use any fluorinated compounds.

Table I Water repellency of untreated and treated fabrics

Additive	Time for repelling water droplets (minutes)	Water repellency grade*
Control, untreated	10	1
MTES	49	1
MTES + octyltriethoxysilane	101	2
MTES + Nuva FSN	135	2

* 1 represents low water repellency and 6 represents very high water repellency

Silicate and Acrylic Coatings. The lightfastness grade of the set of dyes in the silicate and acrylic coatings is given in Figure 8. Of the 13 comparisons, there were four cases where the coating did not significantly affect the lightfastness (i.e., less than half a grade difference). The silicate coating gave the best lightfastness in eight cases, while the acrylic coating gave the best lightfastness only for Reactive Blue 50 (see Figure 8, Colour Index numbers were given for the dyes where known).

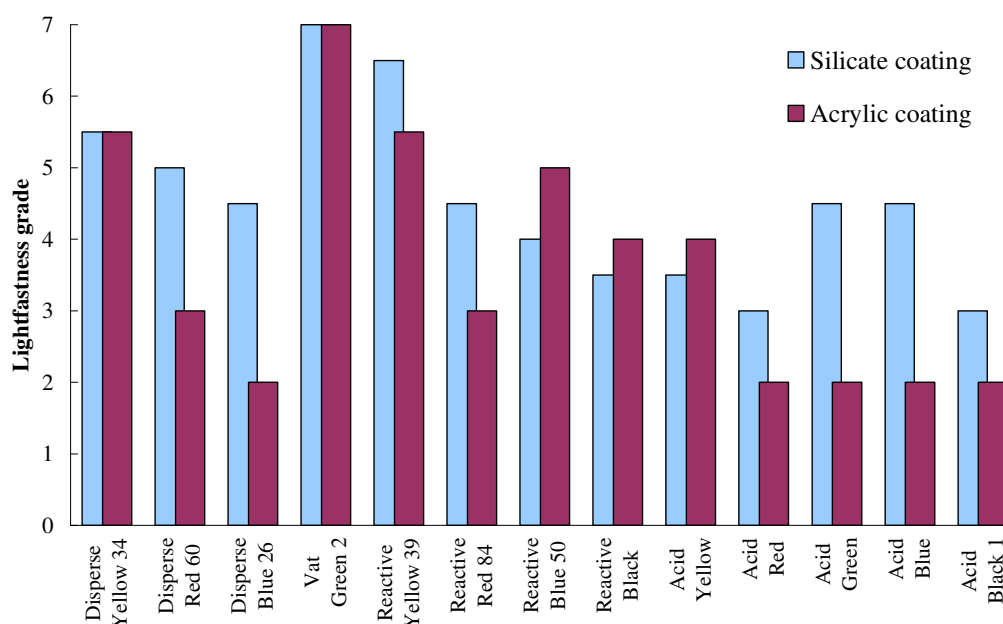


Figure 8 Comparison of the lightfastness of dyes in acrylic and silicate coatings on wool fabric. Grades range from 1, very poor, to 8, very high lightfastness.

Conclusions

This paper has outlined some of the many applications of hybrid organic-inorganic materials for textiles that are under investigation by various groups. Our work suggests that these types of coatings can improve the lightfastness of printed fabric and form porous, flexible coatings on wool. The coatings can be readily modified to impart water repellency. Other textile applications of hybrid organic-inorganic materials that we are investigating include photocatalysts for the decomposition of indoor air pollutants and photo-protective coatings.

One author said of organic-inorganic silica-based nanocomposites that “No limitations appear to exist for variations of chemical structure and composition of the materials. New materials and possible technology applications are constantly being explored.” (20). There are many opportunities for these types of materials to improve the properties of textiles.

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References

1. Textor T., Bahnert T., Schollmeyer E. (2000) *Proc. 10th Int. Wool Text. Res. Conf.* Aachen, Germany, Fl-12, 1-5.
2. Knittel D., Schollmeyer E. (2000) *J. Text. Inst.* **3**, 151.
3. Mahltig B., Böttcher H. (2002) *Melliand-Textilberichte*, **83**(4), E50.
4. Holm I. (2002) *Int. Dyer*, July, 11.
5. Amberg-Schwab S., Weber U. (2004) *Int. Text. Bull.* **1**, 14.
6. Satoh K., Nakazumi H., Morita M. (2004) *Text. Res. J.* **74**(12), 1079.
7. Mahltig B., Böttcher H. (2003) *J. Sol-Gel Sci. Tech.* **27**, 43.
8. Xu P., Wang W., Chen S.-L. (2005) *Mell. Int.* **56**(11), 56.
9. Suratwala, T., Gardlund Z., Davidson K., Uhlmann D.R., Bonilla S., Peyghambarian N. (1997) *J. Sol-Gel Sci. Tech.* **8**, 973.
10. Suratwala T., Davidson K., Gardlund Z., Uhlmann D.R. *Proc. SPIE Int. Soc. Opt. Eng.* **2986**, 141 (1997).
11. Trepte J., Böttcher H. (2000) *J. Sol-Gel Sci. Tech.* **19**, 691.
12. Xin J.H., Daoud W.A., Kong Y.Y. (2004) *Text. Res. J.* **74**(2), 97.
13. Daoud W.A., Xin J.H. (2004) *J. Sol-Gel Sci. Tech.* **29**, 25.
14. Lamb R., Zhang H., Jones A., Postle R. (2004) *Proc. Text. Inst. 83rd World Conf.*, Shanghai, China, 682.
15. Textor T., Bahnert T., Schollmeyer E. (2004) *Tech. Text.* **47**, E72.
16. Schramm C., Binder W.H., Tessadri R. (2004) *J. Sol-Gel Sci. Tech.* **29**, 155.
17. Lan E.H., Dave B.C., Fukuto J.M., Dunn B., Zink J.I., Valentine J.S. (1999) *J. Mater. Chem.* **9**, 45.
18. Wongcharee K., Brungs M., Chaplin R., Hong Y.J., Sizgek E. (2004) *J. Sol-Gel Sci. Tech.* **29**, 115.
19. Volpe C.D., Dire S., Pagani E. (1997) *J. Non-cryst. Solids*, **209**, 51.
20. Young S.K. (2002) *Silica-Based Sol-Gel Organic-Inorganic Nanocomposite Materials: A Review of Different Material Technologies*. United States Army Research Laboratory Report, ARL-TR-2734, United States Army Research Laboratory, Aberdeen Proving Ground, Maryland.