

Review Article

Antimicrobial treatments for textiles

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This review presents a critical analysis of the various aspects of producing antimicrobial textiles. The microbes involved, their mechanism of adherence on natural and synthetic fibres, effect of microbial growth on textiles, principle and mechanism of antimicrobial activity and the compounds being used for this purpose have been covered.

Keywords: Antimicrobial treatment, Bioactive textiles, Finishing, Microbes, Protective textiles

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1 Introduction

Microorganisms can be found almost everywhere in the environment. NASA researchers have found microorganisms even at a height of 32 km and to a depth of 11 km in the sea. In the ground, microorganisms have been found during oil drilling to a depth of 400 m. It is estimated that the total mass of all microbes living on earth is approximately 25-fold the mass of all animals. For their growth and multiplication, the minimum nutritional requirements are water, a source of carbon, nitrogen and some inorganic salts.¹ These are normally present in the natural environment. Textiles, by virtue of their characteristics and proximity to human body, provide an excellent medium for the adherence, transfer and propagation of infection - causing microbial species.

In the last few years, the market for antimicrobial textiles has recorded a double digit growth. This growth has been fuelled by the increased need among the consumers for fresh, clean and hygienic clothing. Extensive research is going on to develop new antimicrobial finishes. This paper reports, in detail, the role of textiles in microbial propagation, the mechanism of antimicrobial activity and principles of antimicrobial finishing of textiles.

2 Textiles as Carriers of Microorganisms

Bacteria, both pathogenic and odour causing, interact with fibres in several phases including the

initial adherence, subsequent growth and damage to the fibres and dissemination from them. The attachment of bacteria to fabrics is dependent upon the type of bacteria and the physico-chemical characteristics of the fabric substrate. Microbial adherence is also affected by the substrate and bacterial cell wall hydrophobicity while the retention has been shown to depend on the time of contact between the fabric and microbe.² In general, the rougher is the surface, the more is the retention.

Natural and synthetic fibres vary greatly in their response to microbial growth. Both may act as willing substrates but the mechanism in the two cases is very different. Natural fibres are easy targets for microbial attack because they retain water readily and microbial enzymes can readily hydrolyze their polymer linkages.³ Cotton, wool, jute and flax are reported to be most susceptible to microbial attack. If 10^5 colonies in 1 ml water are applied to approximately 0.5 g cotton, after a few hours, a logarithmic growth is observed and the population increases from 10^5 to 10^9 colonies. The damage caused by the fungus *Aspergillus niger* on cotton has been extensively investigated by Ucarci and Seventekin.⁴ They found that there were differences in strength of cotton as the time, temperature, pH and medium conditions changed. Within the natural fibres too, the persistence period varied greatly.

Growth of microbes is slower on synthetic fibres as compared to their natural counterparts because their polymer backbone does not retain much water.

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However, these fibres encourage the holding of stale perspiration in the interstices, wherein the microbes multiply rapidly.^{5,6} Foot infection, for example, has been found to be more pronounced for synthetic fibre socks than natural fibre socks. You and Merry² found that the adherence of bacteria to the fabrics increased as the content of polyester in the fabrics increased.

Synthetic fibres also become susceptible to microbial degradation, if there are finishing agents, such as polyethylene and polysiloxane emulsions, on these fibres. These additives allow the microorganisms to degrade the polymer into 'chewable bites' by utilizing the acidic or basic by-products of their metabolism, thus initiating the cycle of hydrolysis. In this way, even the tough polyurethanes can be broken down. Polypropylene, nylon and polyester fibres have all been seen to be subject to microbial attack under conducive conditions.³

A matter of greater concern, however, is that the textiles not only act as substrates for microbial growth but they may act as active agents in propagation of microbes. At least two viruses of public health importance, namely *Polio* and *Vaccinia*, have been shown to persist on cotton and wool fabrics for sufficient periods of time.^{7,8} Viruses can persist on fabrics like cotton sheeting, terry towel, washable wool suit, polyester / cotton shirting and nylon jersey for up to 16 h. Synthetic fibres allow greater degree of viral persistence and transfer than cotton. When subjected to laundering, the virus gets physically removed from the fabric but is not inactivated, as it was found to be present in extracted water. Detergents that reduce the surface tension assist this physical removal. Thus, virus transfer can occur easily during normal cold laundering process. Also, some bacteria continue to actually survive on laundered fabric as well.^{9,10}

3 Effect of Microbial Growth on Textiles

3.1 Generation of Body Odour

Textile products can provide all such requirements for bacterial growth, which result in a range of undesirable side effects.^{11,12} The presence and growth of these microorganisms can cause health problems, odours and finally fabric deterioration. As microbes often attack the additives applied to textiles, discolouration and loss of textile's functional properties such as elasticity (brittleness) or tensile strength can also occur.

Among the side effects, the formation of malodour is of particular importance.¹³⁻¹⁵ When microorganisms grow, they metabolize nutrients, such as sweat and soiling present in it and produce odour causing molecules, e.g. the metabolism of Gram-positive bacteria *S. aureus* is believed to generate 3-methyl-2-hexanoic acid, which causes the characteristic body odour. The unpleasant odour develops when among other things, bacteria convert human perspiration into foul-smelling substances, such as carboxylic acid, aldehydes and amines. Gram-negative bacteria *P. vulgaris* is known to be able to metabolise urea to form ammonia and is the cause for generation of odour in baby diapers.¹⁶

Several products can be used to tackle the odour problem in textiles. The first two approaches involve either trapping the odour causing molecules by incorporating adsorbent materials into textiles or using perfumes to mask the malodour. Such measures, however, only tackle the odour problem that is already there. Another approach is to use antimicrobials to prevent the formation of odour causing compounds by inhibiting the growth of bacteria. In many personal care products around the world, such as underarm deodorants, antimicrobial agents such as triclosan have already been widely used with satisfactory results.

3.2 Effect on Human Health

Kloos and Musselwhite¹¹ Observed the occurrence of various bacteria on human skin and their persistence after one year in the same person. They found that the normal skin supports resident microorganisms, and different microorganisms are predominant on different parts of the body and on the people of different age groups. Bacteria isolated from clothing were similar to those isolated from normal skin flora such as:

- Under shirts contained *Staphylococcus epidermis* and *Coryneform* bacteria, which are responsible for body odour.
- Trouser legs and pockets contained *Bacillus* and lesser amounts of *Staphylococcus epidermis* and *Micrococcus*.
- Skin of groin, perineum and feet contain *Staphylococcus aureus*, Gram-negative bacteria, yeast and fungi *Candida albicans*, which produce skin infections, as those areas are normally moist and dark.¹⁰

The wearing of clothing coupled with factors such as contamination of skin with feces and urine and

other body effluents and the provision by garments of moisture and darkness can enhance the probable infections. Clothing in the inguinal and perineal areas soiled by urine and feces have been found to promote the growth of the *Brevibacterium ammoniagenes*, *E. coli* and *Proteus mirabilis*, thus enhancing diaper rash and associated infections. Over 75% of foot infections is attributed to the dermatophytic fungi—*Trichophyton interdigitale* and *Trichophyton rubrum* isolated from socks. It was seen that the simple laundering failed to eliminate these pathogens. Some microorganisms can also directly cause diseases, e.g. mould fungus of the *Aspergillus* type, which can produce lung disease.¹⁷ Some disease causing microorganisms and insects are listed in Table 1.

3.3 Degradation or Staining of Textiles

Microbial growth increases with increasing moisture and repeated laundering of textiles, and is maximal at neutral pH (7-8).¹⁸ Bacteria, except the phototropic species grow well in dark. They are sensitive to UV light and other radiations. Exposure to light can bring about pigment production, which may cause coloured stains on fabric.

Some proposed mechanisms for microbial degradation of cotton are as follows^{8,11}:

- The secondary wall of cellulosic fabric may be directly damaged by fungal hypha (thread like element of fungus), and then fungus starts growing inside the lumen.
- In some fibres, hypha penetrates in the lumen without breaking the outside surface. Fungal hypha is coarser (5 µm) than the cotton pore (16 Å) or even NaOH swollen pores (40-50 Å).
- Bacterial decomposition of cellulose takes place from outside to inside, but it cannot digest cellulose directly. Cellulolytic microorganisms secrete enzymes, which make cellulose soluble followed by the diffusion of microbes inside the cell.
- Carbon heterotopy type of bacteria degrade polysaccharide chains into shorter ones and these are eventually hydrolyzed to shorter oligomers and then finally to cellobiose and D-Glucose.

As a result of enzymatic degradation, the strength of cotton reduces by about 34% in 3-5 days at 40°C.

4 Mechanism of Antimicrobial Activity

Different terms are used in practice, viz. bactericide- bacteriostatic, fungicide - fungistatic,

Table 1—Microorganisms and the disease caused by them

Microorganism	Disease or conditions caused
Gram-positive bacteria	
<i>Staphylococcus aureus</i>	Pyrogenic infections
<i>Staphylococcus epidermis</i>	Body odour
<i>Corynebacterium ditheroides</i>	Body odour
<i>Brevibacterium ammoniagenes</i>	Diaper rash
<i>Streptococcus pneumoniae</i>	Bacterial pneumonia
<i>Myobacterium tuberculosis</i>	Tuberculosis
Gram-negative bacteria	
<i>Escherichia coli</i>	Infections of urinogenital tract
<i>Pseudomonas aeruginosa</i>	Infections of wounds and burns
<i>Proteus mirabilis</i>	Urinary infections
Fungi	
<i>Candida albicans</i>	Diaper rash
<i>Epidermophyton floccosu</i>	Infections of skin and nails
<i>Trichophyton interdigitale</i>	Athletes' foot
<i>Trichophyton rubrum</i>	Chronic infection of skin and nails
<i>Aspergillus niger</i>	Damage cotton
Viruses	
<i>Poliomyelitis visum</i>	Poliomyelitis
<i>Vaccinia virus</i>	Local disease induced by vaccination against smallpox
Protozoa	
<i>Trichomonas vaginalis</i>	Vaginal infections

biocide and biostatic. When a product has a negative influence on the validity of a microorganism, it is generally termed as an antimicrobial. When the bacteria are killed, the suffix cide and when only the growth is stopped the suffix static is used.

Antimicrobial agents act in various ways. The main modes of action are¹:

- protein coagulation;
- disruption of cell membrane resulting in exposure, damage or loss of the contents;
- removal of free sulphhydryl groups essential for the functioning of enzymes; and
- substrate competition. A compound resembling the essential substrate of the enzyme diverts or misleads the enzymes necessary for the metabolism of the cell and causes cell death.

Microorganisms contain a semi-permeable cell wall, which maintains the integrity of cellular contents. Bactericidal agents cause the rupture of this cell membrane and damage the cells. Bacteriostatic agents only prevent the multiplication of bacteria, which may however remain alive, by inhibiting the synthesis of cell wall, alteration of cytoplasmic

membrane permeability, alteration of the physical and chemical state of proteins and nucleic acids, inhibition of enzyme action and inhibition of protein and nucleic acid synthesis. A chemical that is bactericidal at a particular concentration may only be bacteriostatic at a higher dilution.

Leaching type Antimicrobial Agents

The vast majority of antimicrobial products work by leaching, i.e. moving from the surface on which they are applied and entering the microorganism, poisoning it, and disrupting a life process or causing a lethal mutation. The dosage of antimicrobial agent used is critical for efficiency. If too little of the compound is used, then the microbe is not controlled and can adapt. However, if too much of it is used then it can harm other living things too. This type of product also has a limited durability and has the potential to cause a variety of other problems when used in garments. The chemical may affect the normal skin bacteria, cross the skin barrier, and / or cause rashes and other skin irritations in users.

Bound type Antimicrobial Agents

Another set of antimicrobials with a completely different mode of action is one that molecularly bonds to the textile. This product makes the substrate surface antimicrobially active and works by rupturing the cell membrane of the microorganism when it comes into direct contact.¹ These give durable antimicrobial property on textiles.

4.1 Antimicrobial Finishing Agents

Antimicrobial finishes add value to textiles and garments by providing protection in different ways, such as (i) prevent the growth of bacteria and fungi, thus protecting textiles against unpleasant odours, mildew spots and the premature loss of functional properties; (ii) protect the wearer or user of a textile against bacteria, yeast, dermatophytic fungi and other related microorganisms for aesthetic, hygienic or medical purposes; (iii) protect the textile itself against bio-deterioration caused by mould, mildew and rot producing fungi; and (iv) protect the textile from insects and other pests for preservation of the fibre and/or protection of persons wearing clothing from insects and pests.

Though many antimicrobial products are available commercially, the ones that satisfy the needs of the textile industry are few. An ideal antimicrobial for textiles would have to fulfill the following basic requirements:

Safety—Low toxicity to the consumers; for example, it should not cause allergy or irritation to skin.

Compatibility—No negative influence on textile properties or appearance and compatible with common textile processing methods such as dyeing, finishing and laundering.

Durability—The antimicrobial agent should be durable to repeated laundering.

In addition to the effective control of bacteria, molds and fungi, such finishes must also fulfill following other requirements:

- Have a wide spectrum of activity and must be effective against all microorganisms, that is bacteria including spores, viruses, protozoa and fungi;
- Be active in the presence of organic matter;
- Be effective in acid as well as alkaline media;
- Have speedy action;
- Have high penetrating power;
- Be stable;
- Be compatible with other antiseptic and disinfectants;
- Not corrode metals;
- Not cause local irritation or sensitization;
- Not interfere with healing;
- Not be toxic if absorbed into circulation;
- Be cheap and easily available; and
- Be safe and easy to use.

4.2 Technology of Antimicrobial Finishing

There are many different types of fungicides or bactericides such as metal salts and organometallics, iodine and iodophores, quaternary ammonium salts, formaldehyde and formaldehyde containing derivatives, amines, urea and guanidines, phenols and thiophenols, antibiotics, etc. which have the ability to interrupt the usual metabolism of the microorganism and inhibit their growth, thereby imparting antibacterial and antifungal activity to cellulosic fibres. The conventional practices used to bind antimicrobial agents to textiles are:

- Fibre reaction and formation of metastable bonds.
- Interaction with thermosetting agents.
- Formation of co-ordination compounds.
- Ion-exchange methods.

Washing durability of the finish depends on the affinity of antimicrobials or, in the case where polymeric coating products are used, on how strongly

the polymers can bind with the textile surface. The mechanisms used to impart durable treatments are categorized as (i) surface application, (ii) chemical bonding, and (iii) internal entrapment that undergoes release slowly.

Chemical bonding is theoretically the best way to achieve durability and it works well on cellulose, wool and polyamide. However, this method requires suitable reactive groups on the fibres to work effectively. Ionic charge is another factor to consider for fibres such as acrylics.

Internal antimicrobial release is a viable option for synthetic fibres for which antimicrobials can be incorporated into the fibres when they are spun. The same incorporation can be achieved by using antimicrobials as "disperse dyes." Durability of antimicrobials cannot be achieved by self-crosslinking materials because of regulatory implications and possible changes of antimicrobial activity profiles.¹⁹ Microencapsulation modified with multifunctional reactive groups is now an established technique for durable application.

4.3 Principle of Antimicrobial Activity

Controlled release (e.g. microencapsulation), durable & and re-generable principle, and blocking action are the three currently used techniques.

4.3.1 Controlled Release Technique

The majority of antibacterial finishes function by the controlled release mechanism.²⁰ It is based on the principle of applying a chemical finish that would produce an active germicidal species continually regenerated by, say the addition of a bleaching agent during laundering, or the exposure to UV light, which would break some strategic covalent bond in the chemically modified fibre during regeneration. Thus, the model has theoretically an unlimited reservoir of antibacterial agent. The microencapsulation technique comes closest to this model, though its reservoir of antibacterial compound is not unlimited.

Microencapsulation, although not a chemical finishing process, is a physicochemical technique where the antimicrobial compound is held in a micro or nano capsule; as the capsules burst under agitation or mechanical pressure, they release the active compound. Encapsulation technology is proven to be the best for achieving good antimicrobial durability for synthetic fibres. Substrates like polyester, cellulose, vinyl acetate and polyethylene can also be treated. Mattress covers, for example, can be

protected against mites and other microbes for over 6 years this way. However, this kind of technology does not work well on cotton due to the properties of the fibre. For treating cotton, the microcapsules themselves are modified with multifunctional reactive groups that are capable of forming covalent bonds with the fibre.¹⁹ One such system comprises a combination of carboxy methyl starch (CMS), trimethylolated melamine (TMM) and Cu⁺ ions in presence of an acid catalyst.²¹

4.3.2 Durable and Re-generable Principle

Multifunctional property fabrics are often produced by grafting polymers & photopolymers, by copolymerization onto the fibre or by chemical modification of the fibre by formation of covalent bonds. Graft, homo, and/or copolymers are usually affixed to fabrics to create a positively or negatively charged functional group in the fibre, which is then immersed in counter ions.

Halamine Compounds

Qian and Sun^{22, 23} have worked extensively on grafting of cotton with halamine precursor compounds for developing durable regenerable finishes. They combined 3-methylol-2,2,5,5-tetramethylimidazolidinone and dimethylol-5,5-dimethyl hydantoin in different ratios for chemical modification of cellulose fabrics. The mixtures of TMIO and hydantoin rings on the grafted cellulose provided a hybrid of imide, amide, and amine halamine structures in different ratios after chlorination, and led to varied efficacy and durability of biocidal properties on the finished fabrics. 1, 3 dimethylol-5, 5 dimethyl hydantoin (DMDMH) has also been used to finish cotton and polyester/cotton blend fabrics. In another study²⁴, a cyclic amine monomer, 3-allyl-5, 5-dimethyl hydantoin (ADMH) was grafted onto various textile materials. After exposure to chlorine, the grafted hydantoin structures in the samples could be transformed onto N-halamine, which provided powerful, durable, and re-generable antibacterial activities.

Durable and re-generable antibacterial properties have been achieved by using monomethylol-5,5-dimethyl hydantoin (MDMH) a bi-functional compound possessing one side reactive to cellulose and other side active chlorine to form halamine bond.^{25,4} After over 50 machine washes and 11 regenerations with diluted bleach, the biocidal cotton fabrics possessed enough mechanical strength

together with the antimicrobial function. It was found that the finished cotton/polyester blends exhibited better durable biocidal properties than pure cotton fabrics.²⁶

An intermolecular chlorine transfer reaction was considered as a possible cause for improved durability and power of biocidal functions on cotton fabrics containing a mixture of amine, amide, and imide halamine structures.²³

PHMB

Poly(hexamethylene)biguanide hydrochloride^{8,18,27,28} (PHMB) has also been used widely as an antiiodour finish for cotton and other cellulosic materials. PHMB is a relatively safe molecule having low mammalian toxicity. It shows good antimicrobial activity against a broad spectrum of bacteria, yeast and fungi and has low environmental effect since it contains no heavy metal, formaldehyde, organic halogen or phenolic compounds. PHMB has been successfully applied to blends of cotton with polyester or nylon. It has good thermal stability and may be applied in solid form to nylon and polyester at melt spinning stage. *Avecia* protection and hygiene marketed the *Purista*TM branded products which are treated with Reputex 20 which is based on PHMB. This is particularly suitable for cellulosic textiles and blends of cotton with nylon and polyester. Non-leaching type salts, such as 3-trimethoxy silyl propyl dimethyl octadecyl ammonium chloride, have also been used to treat surfaces to impart durable antimicrobial effects.²⁹

4.3.3 Blocking Action

It is mainly used for protecting fabric from mildew and rot producing fungi.²⁰ Cellulose is chemically modified by cyanoethylation or acetylation, or treated with organo silicone polymer containing pendant quaternary ammonium groups to form a bio-barrier on the fabric. The other chemical methods involve insolubilisation of chemical reagents in or on the fibre. Insolubilisation is achieved by the incorporation of agents into spinning baths for synthetic or regenerated fibres, or by padding natural or synthetic fabrics with solutions that on evaporation by curing or other methods deposit a water-insoluble or slightly water-soluble agent onto the fibre.

Broad spectrum antimicrobial activity has been imparted to acrylics, nylon, polyvinyl chloride, cellulose acetate, polypropylene and polyethylene fibres by chemically modifying the fibres using insolubilisation of 0.5-2% of various nitro compounds into wet or dry

spinning baths. Compounds like 5-nitrofurfural and 5-nitro 2-furfurylidene 3-amino 2-oxazolidone have been used for this purpose. Graft polymerization of cellulosic textiles with poly (2-methyl-5-vinylpyridine) or polyvinylpyrrolidone followed by treatment with potassium iodide solution imparts antibacterial and antifungal activity. Physical entrapment (4% owf) of chlorinated phenoxy compound (CPC) on polyester shows durable bactericidal response against *S. aureus* but no effect against *E.coli*.³⁰

5 Agents used for Antimicrobial Finishing

The following classes of compounds have been investigated and found to have antimicrobial properties: gentamicin³¹, antibiotics, trialkyl tin salts and esters, alcohols (ethyl, isopropyl, trichlorobutanol), aldehydes (formaldehyde, glutaraldehyde), thiophenols, alkylphenols, soaps of heavy metals, thiocarbamates, heavy metal inorganic salts, selected amines, imines and imides, selected organic structures, sulfonilamides, mercaptobenzotriazole, chlorinated phenols, alkyl and aryl mercury salts, dyes, surface active agents (quaternary ammonium compounds), halogen complexes, salicylanilides, inorganic salts organic complexes, zeolites³² and gases (ethylene oxide, formaldehyde, beta propiolactone).^{1,8,33} Textile softeners like octadecyl ethylene urea, amine condensate, and some cationic softeners also show varying antimicrobial action.³⁴

5.1 Dyes as Antimicrobial Agents

Azo disperse dyes developed by the reaction of sulfanilamidodiazonium chloride derivatives with indan-1, 3-dione can impart good biological activity on wool and nylon 6,6 (ref. 35). Some dyes can also act as biocides due to the presence of metal ions such as Cu or Cr in their molecules. Masuhiro³⁶ produced antimicrobial silk by using dyes with metal ions like Cr, Cu and Co at 20% owf. Similarly, dyes that are amino derivatives of triphenyl methane, for example Brilliant Green are highly active against bacteria and fungi.

Photoactivated radical generation is another technique. FibreMark of Vermont has patented a method where the substrate is impregnated with a light-activated dye. On exposure to light, the dye generates singlet oxygen that kills a wide range of microorganisms and viruses.^{37,38} In another procedure, acid dye molecules have been used as a bridging unit for incorporating quaternary ammonium salts in the development of antimicrobial nylon fabrics.^{39,40}

In a series of recent studies conducted by the author, antimicrobial properties of some commercially available natural dyes have been studied. Minimum inhibitory concentration (MIC) of the tested dye solutions was found to vary between 5 microgram and 40 microgram, indicating a high potency against Gram-positive and Gram-negative bacteria. The textile material impregnated with these natural dyes, however, showed less antimicrobial activity, as uptake of these dyes in textile material was less than the MIC.⁴¹

On cotton fabric, loading concentration of 12% *Q. infectoria* (owf) dye showed high biocidal activity against *E. coli* and *P. vulgaris* reducing the microbial growth by up to 99%. Use of alum and copper sulphate as mordants enhanced the antimicrobial activity and also made the treatment fast to multiple washes. However, when ferrous sulphate was used as a mordant, the activity was lost completely. Antimicrobial property of natural dyes can be attributed to the presence of tannins in these sources. The protein binding ability of tannins is responsible for this special property of dyes.^{42,43}

TEM analysis was conducted to study the mechanism of activity of natural dyes. Figure 1 shows the change in cell structure of *S. aureus* with time on treatment with *Quercus infectoria* dye. It can be seen from the figure that the dye enters the bacterial cell and brings about the precipitation of protein. The process is well advanced after 6h of treatment. After 16h there is evidence of massive cell wall damage, after which the cytoplasm leaks out of the damaged wall. It could thus be established that the selected natural dyes can provide an ecofriendly alternative to the sometimes toxic antimicrobial agents of synthetic origin.

5.2 Metal and Metal Salts

Silver, copper and mercury compounds are the most effective biocides.

5.2.1 Silver

Silver kills bacteria by strangling them in a warm and moist environment.^{44,45} Highly bioactive silver ions bind with proteins inside and outside bacterial cell membranes, thus inhibiting cell respiration and reproduction. Silver is 3-4 times more active at pH 8 than at pH 6. Silver products are effective against bacteria but not as good against other organisms like fungi, mold, and mildew; they can be used with polyester where many other products cannot. Alginate and chitosan have also been used to make novel antimicrobial materials in combination with silver.⁴⁶

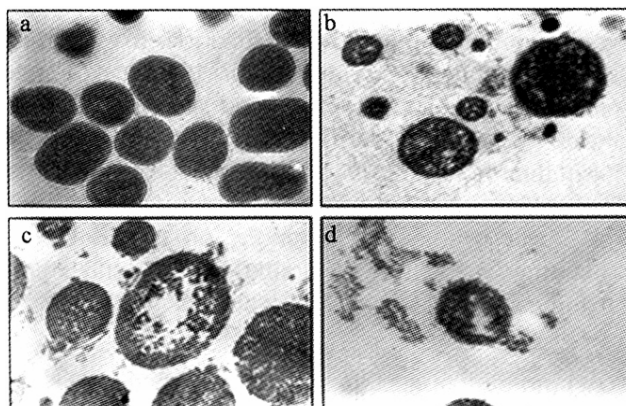


Fig. 1— Action of *Q. infectoria* on *S. aureus* (a) untreated (b) 6 h treatment, (c) 16 h treatment and (d) 24 h treatment

Various techniques have been explored to attach silver to textile materials. For preparation of antimicrobial fabrics suitable for sterilization of air, cellulose was grafted with acrylic acid and treated with silver nitrate to bind the silver ions to the –COOH group of graft copolymer.⁴⁷ For developing a durable finish on wool, it was treated with a complexing agent such as tannic acid or ethylene diamine tetra acetic dianhydride (EDTAD). Wool thus treated can react easily with copper and silver and inhibit the propagation of *S. aureus* and intestinal bacteria effectively. Deposition or interstitial precipitation of tetrasilver tetroxide crystals within the interstices of fibres, yarns and / or fabrics has also been reported in a US patent.⁴⁸

Some commercial wound healing products based on silver include :

- (i) Acticoat—A nano crystalline silver based resin.
- (ii) AlphaSan—A non-toxic antimicrobial based on the use of silver sodium hydrogen zirconium phosphate. It slowly releases silver ions and provides long lasting effectiveness.
- (iii) Actisorb Silver 220—It is beneficial in the treatment of infected wounds, particularly when colonized by Gram-negative bacteria.
- (iv) Aquacel Agr—It is sodium carboxymethyl-cellulose with 1-2% silver in ionic form. It is the first antimicrobial dressing that provides immediate and sustained antimicrobial activity.
- (v) Novaron (zirconium silver phosphate)—It is another antimicrobial product prepared by bonding silver to anion exchanger.

5.2.2 Copper

Broad spectrum antimicrobial and antimite activities have been introduced in copper-impregnated

fibres and polyester products for production of antiviral gloves and filters (which deactivate HIV-1 and other viruses), antibacterial self-sterilizing fabrics (which kill antibiotic-resistant bacteria), antifungal socks (which alleviate symptoms of athlete's foot), and antidust mite mattress covers.⁴⁹

Copper compounds are extensively used for the preservation of tents, canvas, bags and geotextiles. A familiar compound copper naphthanate is available under trade names, such as Cuprimol and Nuodex. Mixtures of copper and zinc naphthanate with mercuric or phenylmercuric naphthanate are even better. Treatment of cellulosic fabrics with succinic anhydride followed by metallic salts such as copper sulfate and zinc sulfate also imparts activity durable up to 10 laundering cycles.⁵⁰⁻⁵¹ Copper-carboxymethyl starch and trimethylolated melamine with cotton fabric also give excellent antimicrobial properties.⁵²

5.2.3 Other Metals

Among other metals, zirconium salts have been found to be effective against algae. Use of zirconium compounds along with copper, mercury and some phenol on cotton increases the solubility of insoluble mold.^{53,54} Cadmium selenide and cadmium sulfoselenide are good mildew- and algae-inhibiting agents. Water soluble selenium is slowly lost from fabric and is activated when exposed, even intermittently, to solar energy, but not in the dark. The colour of these compounds and the toxicity issues associated with them make them less useful as antimicrobial agents.⁵⁵

Reaction products of magnesium acetate tetrahydrate and hydrogen peroxide, magnesium hydroperoxyacetate (MHPA) and magnesium dihydroperoxide (MDHP), have also been applied as antimicrobial agents for woven cotton and cotton/polyester blended fabrics.⁵⁶

5.3 Chitosan—A Multifunctional Natural Antimicrobial

Another compound which has gained tremendous popularity in recent years is chitosan. Chitosan, a deacetylated derivative of chitin, is a natural, nontoxic, microbe resistant and biodegradable polymer. The antimicrobial property of cotton treated with chitosan is attributed to chitosan's amino group, which converts to ammonium salts in dilute acid solution particularly with citric acid. This salt can then attach to the negatively charged protoplasm of the microorganisms and destroy the cell wall and prevent the growth of cells by inhibiting RNA

transcription. Chitosan binds with proteins and results in selective antimicrobial activities towards fungi or bacteria. Lim and Hudson⁵⁷ have reviewed extensively the applications of chitosan and its derivatives as antimicrobial agents. The molecular weight, degree of deacetylation, pH of medium and temperature can all affect the antimicrobial activity of these compounds.

The problem associated with chitosan, however, is that it has no affinity for cotton and is soluble only at pH <6. This makes it difficult to apply on cotton as a durable finish. Either a crosslinker such as DMDHEU⁵⁸ or citric acid⁵⁹ has to be used, or either the cotton or the chitosan has to be functionalized to create affinity. Recently, a water soluble carboxymethyl derivative of chitosan has been prepared⁶⁰ for application on cotton. Treated samples showed good antimicrobial activity against *E. coli* and *S. aureus* at 0.1% concentration as well as improved wrinkle recovery. Having acquired multifunctional properties, the treated cotton also showed better dyeability with direct and reactive dyes, and at the same time it became cationic dyeable due to the creation of amino groups on the surface. Another approach has been the preparation of chito-oligosaccharides for textile applications⁶¹⁻⁶³. It has also been possible to impart effective antimicrobial activity to polypropylene using chitosan compounds.^{64,65}

5.4 Polyethylene Glycols

Crosslinked polyethylene glycols (PEGs) can offer substantial resistance to most microorganisms. The property has been attributed to a physico-chemical phenomenon. The first factor responsible for the activity of PEG is the thermal adaptivity of the modified fibres and the second is the property of PEG to crosslink on the fibre and absorb appreciable amounts of water. Since most microorganisms need moisture to proliferate, competition with the PEG for moisture leads to microbial desiccation. PEGs, whether in solid state (on fibre surface) or diffused on the fibre, are known to disrupt cell membrane equilibrium by causing dual hydrophobic – hydrophilic behaviour.⁶⁶

6 Novel Fibres and Fabrics with Antimicrobial Properties

Various fibres having antimicrobial properties are available in the market. Trevira bioactive is a multifunctional polyester fibre with bioactive

Table 2—Some commercial antimicrobial products and their composition

Trade name	Chemical composition	Company	Application
Sanitized-AG	Halogenated phenoxy-compound and isothiazolinone derivates.	Sanitized AG, Switserland	Socks, apparel
Reputex 20	PHMB	Zeneca Biocides	Durable for cotton
Sensil 555	Not disclosed	Senka Corp., Japan	Antimicrobial and deodorant finish for cellulosics
Ultrafresh Range	5-chloro-2-(2,4-dichlorophenoxy)phenol	Thomson Research Associates, Canada	Non ionic odour protection and anti staining
Steri-Septic Range	Triclosan	Thomson Research Associates, Canada	Cationic, anionic and nonionic; are available for cotton and polyvinyl fibres
Bioden/Amolden Range	Cationics /Phenylamides	Daiwa, Japan	Bedding, garments, nonwovens for deodorising
Biosil	Quarternary ammonium compounds	Toyobo, Japan Dow Corning Asia	Bedding, towels, socks, undergarments
Peach Fresh	Tertiary ammonium compounds	Nisshinbo, Japan	For PET fibres and fabrics
Aegis Microbe shield	3-(trimethoxysilyl) propyl dimethyl octadecyl ammonium chloride.	PPT, UK	Combat growth of candida and yeast that cause thrush
Sanitan	Tertiary ammonium compounds	Kuray, Japan	For PET fibres and fabrics
Tinosan Range	Triclosan based on 2,4,4'-trichloro-2'-hydroxy - diphenyl ether	Ciba Specialist Chemicals, Switzerland	Durable treatment for cotton, polyester, polyamide, acrylic and their blends with cotton

properties.^{38,67} Brennet of Germany is offering three antimicrobial materials suitable for work wear shirts and blouses for use in the hospital sector based on blends of Trevira and cotton. As the antimicrobial affect is embedded in the fibre, the effect cannot be washed out, and the risk of allergies is reduced.

Kimberly-Clark have developed antimicrobial fibres by extruding a composition of thermoplastic polyurethane and antimicrobial siloxane quaternary ammonium salts. Agion Technologies have developed a medical or vascular graft into which they incorporate an inorganic antimicrobial agent such as zeolite. The coating comprises biocompatible materials such as acrylic, polyurethane, silicone or latex.

Malden Mills have developed a composite textile fabric, which includes a layer incorporating antimicrobial synthetic fibre. The first layer is made from a hydrophobic synthetic yarn. The second layer incorporates a moisture absorbent material. This layer is blended with synthetic fibres treated with silver or copper sulphide to inhibit bacterial proliferation on the outer surface of the fabric. Another approach has

been to introduce a pyridine based antimicrobial agent in the dye bath itself.⁶⁸

Some commercial antimicrobial products available in the market are summarized in Table 2 (refs 9, 27, 28, 69-73).

7 Conclusions

With the increasing demand for fresh and hygienic textiles, the consumption of antimicrobials is increasing day by day. Research and development activity is trying to keep pace by developing more and more effective and safe solutions. There is increased interest in natural materials as probable sources, including those from animal (chitosan) and metal sources (copper and silver). The field continues to be one of the most dynamic and one that needs to be kept a watch on for newer and innovative technologies.

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