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Antibacterial Agents in Textile Industry

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1. Introduction

With the growing public health awareness of the pathogenic effects, malodors and stain formations caused by microorganisms, there is an increasing need for antibacterial materials in many application areas like medical devices, health care, hygienic application, water purification systems, hospital, dental surgery equipment, textiles, food packaging, and storage. (Shahidi et al, 2007)

The spread of HIV and hepatitis viruses by contact of contaminated materials has created increased pressure for protection of personnel with functional clothing; also, all articles of apparel and home textiles are susceptible to problems of hygiene in normal daily use, for example, socks, sport wear and working clothes as well as mattresses, floor coverings, and shoe linings. Textiles for outdoor use are constantly exposed to the influence of microbes and bacteria. Application of natural antimicrobial agents on textiles dates back to antiquity, when the ancient Egyptians used spices and herbs to preserve mummy warps. Textile goods, especially those made from natural fibers, provide an excellent environment for microorganisms to grow, because of their large surface area and ability to retain moisture. Most textile materials currently used in hospitals and hotels are conducive to cross infection or transmission of diseases caused by microorganisms. Practically every class of chemical compound has been utilized to impart antibacterial activity to textiles. Two different aspects of antimicrobial protection provided by chemical finishes can be distinguished. The first is the protection of the textile user against pathogenic or odour causing microorganisms (hygiene finishes). The second aspect is the protection of the textile itself from damage caused by mould, mildew or rot producing microorganisms. Bacteria are not as damaging to fibres, but can produce some fibre damage, unpleasant odours and a slick, slimy feel. Often, fungi and bacteria are both present on the fabric in a symbiotic relationship. (Heywood, 2003; Bellini, 2001)

Substances added to fibres, such as lubricants, antistatics, natural-based auxiliaries (for example size, thickener and hand modifiers) and dirt provide a food source for

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microorganisms. Synthetic fibres are not totally immune to microorganisms, for example polyurethane fibres and coatings can be damaged. Of course, because of evolution, natural fibres are more easily attacked. Wool is more likely to suffer bacterial attack than cotton, and cotton is more likely than wool to be attacked by fungi.

2. Antimicrobial treatments of textile

There are various chemical and physical possibilities that can be considered in the production of antimicrobial fabrics. In practice, the antimicrobial effect is obtained through the application of specific chemical products during the finishing stage, or through the incorporation of these substances into chemical fibres during the spinning process.

These possibilities are:

- The addition of bactericidal substances to the spinning solution, prior to the extrusion stage. substances like Triclosan (2,4,4-hydrophenyl trichloro (II) ether), a member of the antiseptic and disinfectant family.
- A different method for the production of antimicrobial and fungicidal fibres has been adopted by an English company. Its "Stayfresh" fibres exploit the properties of silver and silica, both of which, on coming into contact with water or humidity, arrest the growth of bacterial populations in carpets, fabrics, furniture, mattresses and bed linen, by cutting off a source of their nutrition. As well as having antimicrobial and fungicidal properties, these fibres are safe, non toxic and inorganic because, they guarantee total mildew and fungus control, preventing the propagation of bacteria such as *Escherichia coli* and *Staphylococcus aureus*.
- Modification through grafting or other chemical reactions. It is in this sector, that the Institut Textile de France in Ecully has developed the so-called bio textiles. In these products, the chains of molecules containing antiseptic substances are grafted onto the base polymers of the raw fabric. The base polymers are activated by electronic rays and, in the course of the process, they are refracted in given positions, into which is inserted the first graft molecule. The chains of polymers, which grow laterally from the first molecule, confer on the fabric its bactericidal properties. In the event of direct contact, these fabrics act very rapidly against bacteria and their bactericidal property remains intact even after washing.
- Fibre blends.
- Textile finishing treatments with specific active principles. Following heat treatment (drying, condensation), these substances, being incorporated into polymeric and resinogenic finishing products, become fixed to the structure of the textile.
- Plasma coating (sputtering)(Schindler and Houser, 2004; Heywood, 2003)

3. Antimicrobial finishing agents

Man has adopted antimicrobial substances since ancient times, a fact that is demonstrated by their use in Egyptian mummies and in similar applications in other cultures. In this regard, the protection and preservation of fabrics, too, have long fulfilled a role of the utmost importance. The need to protect and preserve is still fundamental in many textile applications today .Antimicrobials are protective agents that, being bacteriostatic, bactericidal, fungistatic and fungicidal, also offer special protection against the various

forms of textile rotting. Here it is focused on some of important antibacterial agents that are used in textile finishing.

3.1 Quaternary ammonium

There are numerous antimicrobials suitable for immobilization on polymer surfaces. Quaternary ammonium compounds seem attractive because their target is primarily the microbial membrane and they accumulate in the cell driven by the membrane potential. To maximize efficiency, quaternary ammonium compound is used as monomeric link in the polymeric leash and poly(4-vinylpyridine) (PVP) is usually selected as the carrying polymer. Tiller et al. showed that the surfaces of commercial polymers treated with *N*-alkylated PVP groups were lethal on contact to both Gram-positive and Gram-negative bacteria, and it was also shown that *N*-alkyl chain of six carbon units in length was the most effective. In recent years, trialkyl ammonium chlorides have been reported to possess germicidal effect in dilute aqueous solutions. (Yao et al, 2008)

Kumar et al showed that mutual radiation grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton cellulose is an effective method to incorporate anti-bacterial property onto the cotton cellulose matrix. (Kumar et al, 2005) Shao et al showed that, a novel quaternary ammonium salt, which contains both perfluoroalkyl group and diallyl groups, should be suitable a finishing agent for providing the fabrics with barriers against microorganisms, water, oil, soil and blood. Moreover, the introduction of diallyl groups into the quaternary ammonium salt not only can enhance the antimicrobial activity, but also extend its application fields. It can be applied in two categories of antimicrobial finishes: one category is part of the fiber-forming process and the other category is the one incorporated in the finishing process. It can also be used as a perfluoroalkyl-containing monomer in the polymer field, which is a convenient method incorporating perfluoroalkyl chain in the polymer. (Shao et al, 2003)

3.2 Triclosan

Triclosan (2,4,4-hydrophenyl trichloro (II) ether), a member of the antiseptic and disinfectant family. Triclosan is a halogen containing derivative of phenol, and is used in cosmetics and toothpastes. It has a wide range of action against gram-negative and gram positive bacteria. This compound, thanks to the presence of the acaricide benzyl benzoate, also offers protection against mites and is used in acaricide (spray or powder) formulas, as well as in a solution (25% concentration) for the treatment of scabies. This compound is non toxic. Benzyl benzoate is an acaricide that acts, chemically, directly on the mites.

Due to its antibacterial properties, triclosan has found widespread use in a variety of consumer products including toothpastes, deodorants, soaps, polymers and fibers. (Allmyr et al, 2006)

3.3 Metallic salts

Numerous chemicals have been used to improve the antimicrobial activity of cotton textiles. Many heavy metals are toxic to microbes at very low concentrations either in the free state or in compounds. They kill microbes by binding to intracellular proteins and inactivating

them. (Shahidi et al, 2010) Although some other metals, such as copper, zinc and cobalt, have attracted attention as effective antimicrobial agents for textiles, silver is by far the most widely used in general textiles as well as in wound dressings. It has a MIC value of 0.05– 0.1 mg/l against *E. coli*.

Some concerns have been expressed about the development of bacterial resistance to silver.

For synthetic fibers, silver particles can be incorporated into the polymer before extrusion or before nanofiber formation using electro spinning.

The treatment of natural fibers with metals can only be undertaken at the finishing stage and various strategies have been devised to enhance the uptake and durability. Cotton has been pretreated with succinic acid anhydride, which acted as ligand for metal ions to enhance the subsequent adsorption of metallic salts (Ag^+ and Cu^{2+}) and to provide very effective antibacterial activity.

Preparation of nano-sized metals and metal oxides, mainly silver (Ag), titanium dioxide (TiO_2), zinc oxide (ZnO) and copper II oxide (CuO) has enabled the development of a new generation of biocides.

Among these antimicrobial agents, silver has been widely used in many fields because it shows strong biocidal effects on many pathogenic bacteria. In addition, nanosized inorganic particles possess high surface area/volume ratio and display unique physical and chemical properties. Accordingly, the immobilization of silver nanoparticles on various fibers has recently attracted a great deal of attention. Concerning the studies of fiber/silver nanocomposites, most researches have been interested in preparations of ultrafine fiber containing silver nanoparticles. These developments are important and contribute greatly to the textile industry. However, the conventional cotton microfibers are still highly popular in textile markets. Surface modification of cotton microfibers with silver nanoparticles can increase both the price and purpose of the fibers. (Chen & Li Chiang, 2008)

The antimicrobial properties of the silver ion Ag^+ have been exploited for a long time in the biomedical field. The significant feature of the silver ion is its broad-spectrum antimicrobial property, which is particularly significant for the polymicrobial colonization associated with biomaterial related infections. The general finding is that bacteria show a low propensity to develop resistance to silver-based products, and therefore both metallic and ionic silver have been incorporated into several biomaterials such as polyurethane, hydroxyapatite (HA) and bioactive glasses.

Silver containing products are also interesting materials for wound repair applications. When metallic silver reacts with moisture on the skin surface or with wound fluids, silver ions are released, damaging bacterial RNA and DNA, thus inhibiting replication. Sustained silver release products have a bactericidal action and manage wound exudates and odour. In particular, Lansdown et al. have shown that silver aids healing in the sterile skin wound in rat models: silver treatment appeared to reduce the inflammatory and granulation tissue phases of healing and induce epidermal repair. (Blaker et al, 2004; Potiyaraj et al, 2007; Bingshe et al, 2007; Chen & Schluesener et al, 2008; Montazer et al, 2012; Ibrahim et al, 2012)

The results of the counting test showed more reduction of survival of bacteria in the case of loading samples with metal salts.

The result of counting test is shown in Figure 1. As it can be seen, no colony of bacteria was found in agar culture for Ag and Cu loaded samples. It means that the bacteria were killed by silver and copper loading of cotton fabric and causes 100 % reduction of bacterial growth. The interaction between silver and copper ions with bacteria can change the metabolic activity of bacteria and eventually causes the death. Also the results related to Nickel and Cobalt loaded samples shown a few amounts of bacteria spread over the agar plate. However, in case of Ti, Sn and Sb loading, it is seen that, more survival bacteria remain and growth in agar culture. The counting test results related to Sb-loaded samples as compared with Sn and Ti, showed better result, and caused fewer bacteria to growth. Although the amount of survival bacteria for Sn-loaded sample as compared with Ti-loaded one are less. In this research work no ultraviolet light were used before bacteria counting test for Ti-loaded sample and all the samples were analyzed in same condition without UV light. So the results related to bacterial counting test for Ti loaded sample shows moderate reduction percentage of bacteria however by using proper UV light, more reduction of bacterial colonies can be maintained.

It can be concluded that, silver and copper salts causes killing of bacteria and percentage reduction of bacteria reach to 100%. It means that, no bacteria can spread over the agar plate. Also the results of antibacterial efficiency for Cu, Ni and Co loaded samples are very good. And the antibacterial activity for Sn and Ti is moderate as compared with the mentioned elements, However better antibacterial efficiency were achieved for Sb treated sample as compared with Ti and Sn. Scanning Electron Microscope (SEM) is the best known and most widely used tool for morphological analyses. SEM micrographs of untreated cotton fabric and metal salt loaded samples are shown in Figure 2. As shown, some new particles were created on the surface of treated cotton fabrics that did not exist on the surface of untreated one. As it is seen, the particles size appears on the surface of Sb and Sn loaded samples are larger than the others but it does not mean that large size of these particles made our samples with more antibacterial efficiency. (Ghoranneviss et al, 2012)

Titanium dioxide (TiO₂) photocatalysts, as alternative materials to degrade organic substances for applications, have attracted much attention since the discovery of photo-induced water cleavage on TiO₂ electrodes by Fujishima and Honda in the early 1970s. When TiO₂ is exposed to ultraviolet light ($\lambda < 400$ nm), holes (h_{vb}^+) and excited electrons (e_{cb}^-) are generated. The hole is capable of oxidizing water or hydroxide anions into hydroxyl radicals (UOH). UOH is known to be powerful, indiscriminate oxidizing agents to degrade a wide range of organic pollutants, including aromatics and aliphatics, dyes, pesticides and herbicides. In 1985, Matsunaga et al. reported the antibacterial properties of TiO₂ for the first time, which attributed to the high redox potential of the surface species, affording non-selective oxidation of bacteria. Since then, TiO₂, as the photo-induced antibacterial agent, has attracted increasing interest. With high photo-reactivity, cheapness, non-toxicity and chemical stability, TiO₂ is promising for eliminating microorganisms in self-cleaning and self-sterilizing materials. Photo-excited charge carriers, i.e. electrons and holes, may recombine within nanoseconds. The antibacterial efficiency is determined by the competition between the recombination of charge carriers and the transfer of those to the bacteria. A wide range of transition metal ions has been reported to be used as electron acceptor to decrease the e^-h^+ recombination in the research of photodegradation towards organic substance. Whereas, noble metal, such as Ag, was explored most as antibacterial effect is concerned. (Zhang et al, 2008; Robertson et al, 2005; Matsunaga et al, 1985; Liu et al, 2008 ; Hashemikia et al, 2012)

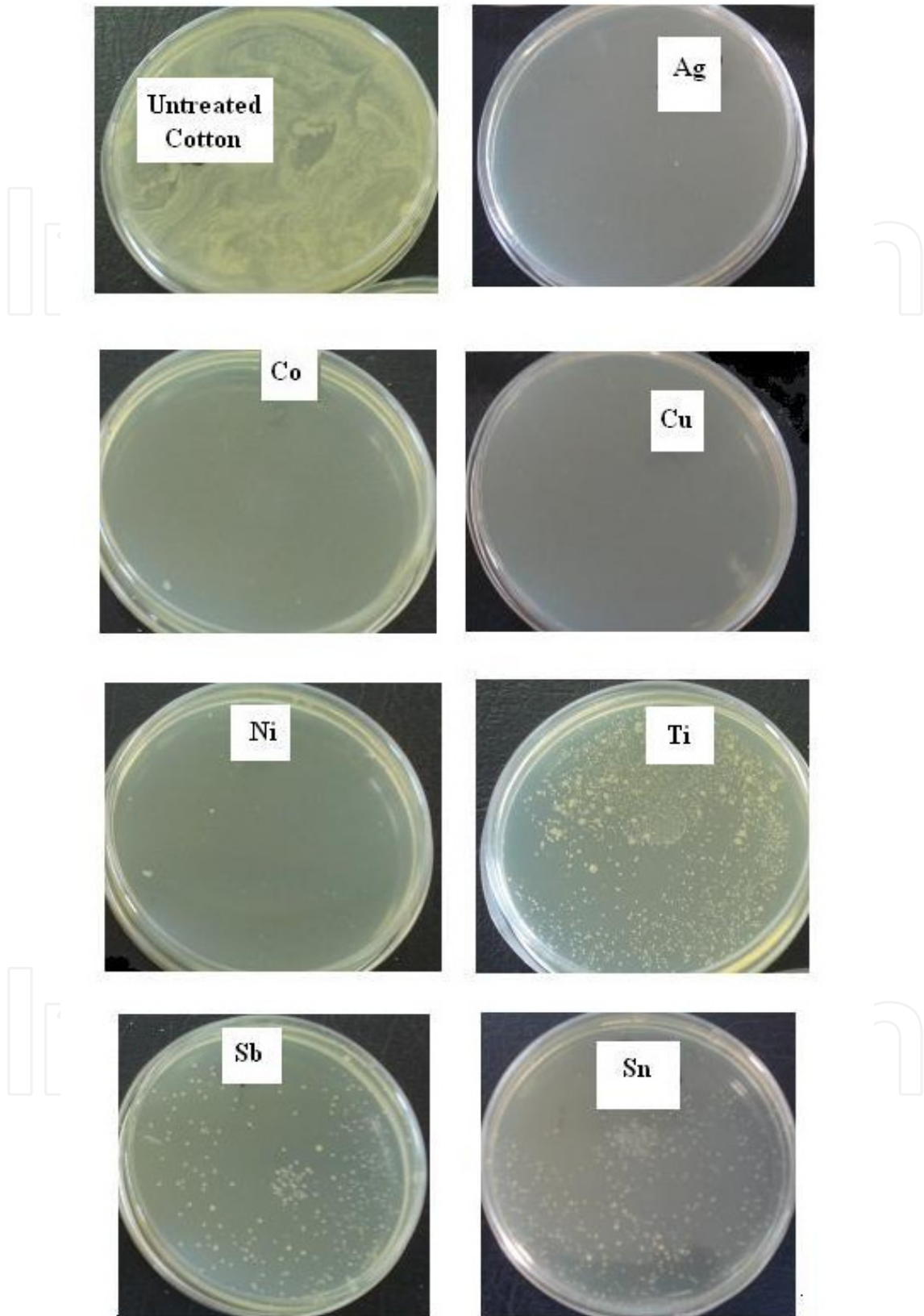


Fig. 1. The bacterial counting test for comparing the antibacterial activity of metallic loaded cotton

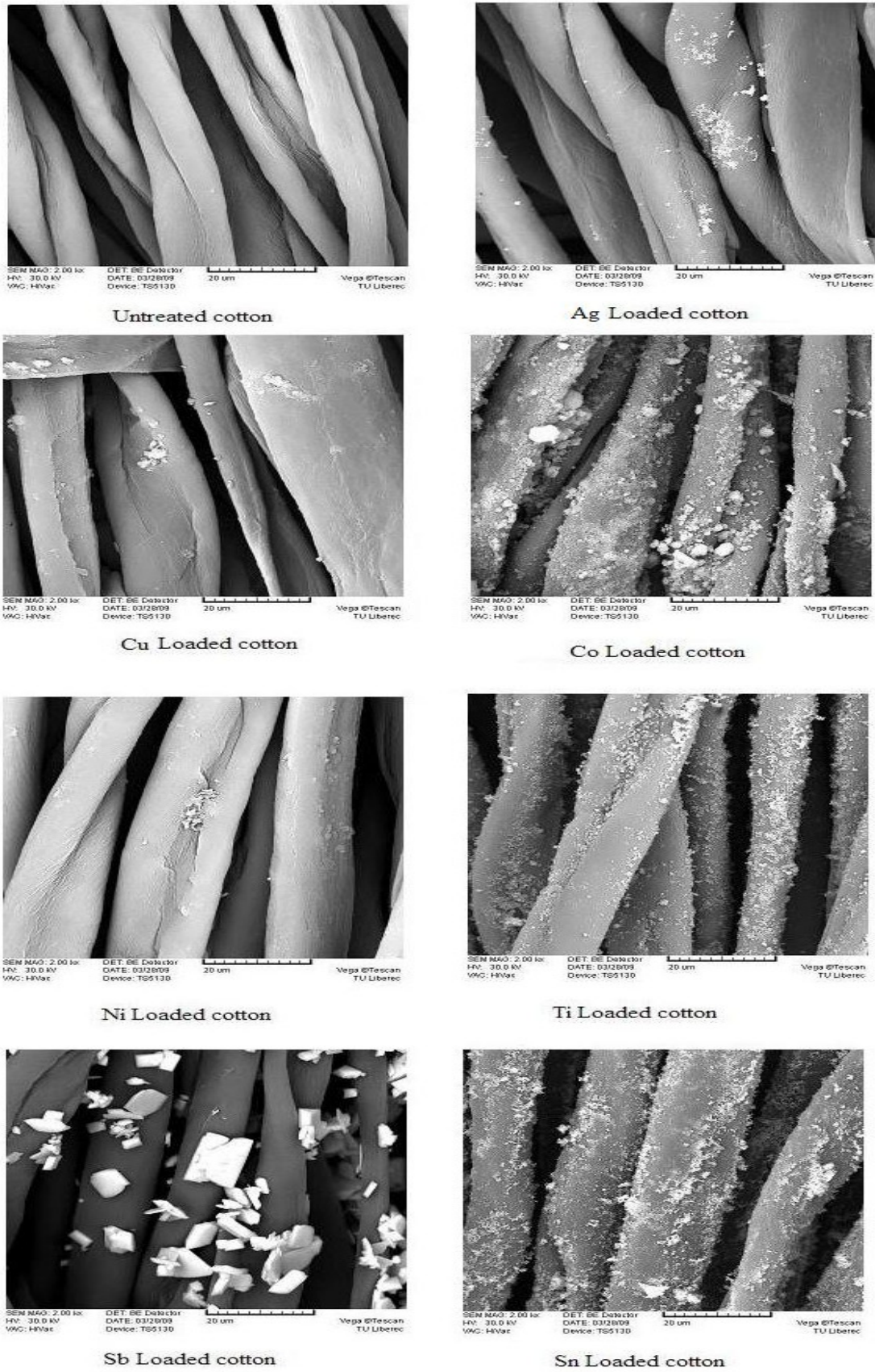


Fig. 2. The SEM images of metallic loaded cotton

The ZnO nanoparticles have been measured to possess probable biological applications as efficient antimicrobial agents, drug carriers, bioimaging probes and possessing cytotoxic behavior for the treatment of cancer. Being a semiconducting material, the band gap between conduction and valence electrons plays a vital role in the generation of reactive oxygen species (ROS), which bring about conformational changes/oxidant injury to the surface of the microorganism membrane. The ZnO nanoparticles, which have positive zeta potential, easily rupture the cell membrane of *Escherichia coli* (gram negative) on contact and release Zn^{2+} ions, which cause lysosomal and mitochondrial damages. Finally, it is leading to the death of bacterial cells.

The surface defects and morphological changes of ZnO nanoparticles do not play a significant role in the antibacterial activity. That the antibacterial activity depends on the particle size, with an increase in antibacterial activity observed for decreasing size of nanoparticles.

Recently the Krishna Raghupathi et al also reported the properties of antibacterial activity against particles size. This report described the antibacterial activity of ZnO nanoparticles in the range from 212 nm to 12 nm particle size. The antibacterial activity of ZnO nanoparticles is inversely proportional to the size of the nanoparticles. (Krishna Raghupathi et al, 2011; Selvam & Sundrarajan et al, 2012)

3.3.1 Plasma sputtering

However, conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments) generally use wet-chemical process steps and produce a lot of wastewater. Plasma treatment, on the other hand, is a dry and eco-friendly technology, which offers an attractive alternative to add new functionalities such as water repellence, long-term hydrophilicity, mechanical, electrical and antibacterial properties as well as biocompatibility due to the nano-scaled modification on textiles and fiber. Moreover, the bulk properties as well as the touch of the textiles remain unaffected. (Shahidi et al, 2010)

In recent years, innovative aspects on the use of coated fabrics have been revealed. Coatings can be applied onto fabrics thus influencing their light reflectivity, electrical conductivity, thermal insulation or for serving decorative purposes. Anti-microbial properties of fabrics are of elevated importance if they are exposed to enhanced biological activity such as in close contact to soil or in a humid environment. In the investigations presented here, the antimicrobial effectiveness of thin films is assessed and the effort of additional finishing for sufficient material protection is determined.

In recent years, physical vapor deposition (PVD) has been applied to modify textile materials due to its inherent merits, such as environmental friendly, various functions and solvent-free process. Sputter coating is one of the most commonly used techniques in PVD, which has been widely used in glass, ceramic and micro-electronic industries.

Sputter coating produces very thin metallic or ceramic coatings on to a wide range of substrates, which can be either metallic or non-metallic in different forms. Sputter coating has also been used to coat textile materials for technical applications. The sputtered atoms have a high energy and when they impinge on any surface, they form a surface coating. The adhesion between the coated layer and the substrate plays a very important role in various

applications of the sputter coated materials. (Scholz et al, 2005; Wei et al, 2008; Hegemann et al, 2007; Yuranova et al, 2003 ; Brunon et al, 2011 ; Yuranova et al, 2003)

The advantages of sputtering are the following: simple process, time saving, environmental friendly, and a resulting coating with superior adhesion to substrates.

Deposition of copper on the surface of cotton samples was performed in DC magnetron sputtering, made by Plasma Physics Research Center (Tehran, Iran), by using the setup schematically presented in Figure 3. Copper post cathode was used; also as it can be seen that samples were placed on the anode, and exposed to argon plasma in a cylindrical glass tube. The chamber was evacuated to a pressure of 10^{-5} Torr, using rotary and diffusion pumps, and then argon gas was introduced into the chamber up to a pressure of 0.05 Torr. Voltage was kept at 950 V and the discharge current was about 220 mA.

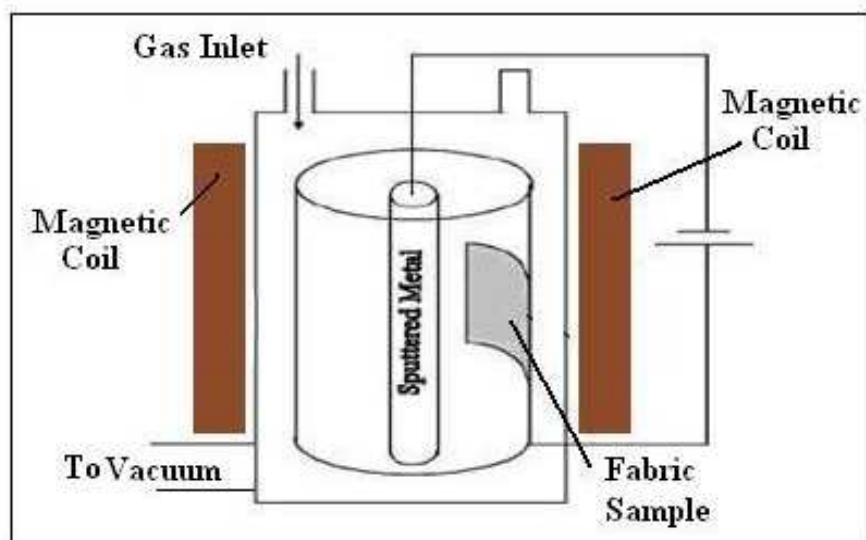


Fig. 3. The schematic view of Plasma sputtering system

Copper particles were deposited on the surface of cotton samples, and the antibacterial has been developed, through incorporation of copper particles on fabric surfaces. The antibacterial properties of the fabrics were connected with the presence of copper on their surface. After plasma treatment, the physical and chemical properties of the fabrics have been examined by surface analysis methods and textile technology tests. Also the antibacterial efficiency was determined by the Halo method.

The agar culture medium is transparent, when the bacterium is inhibited from growth, a transparent area in the form of a halo around the fabric will be observed.

There is no halo observed for untreated cotton fabric. This control test shows that the original cotton fabric does not have any antibacterial properties. Figure 4 illustrate the test results for the untreated and cotton-coated fabric for 30 seconds with *S. aureus*. (Shahidi et al, 2007; Ghoranneviss et al, 2011)

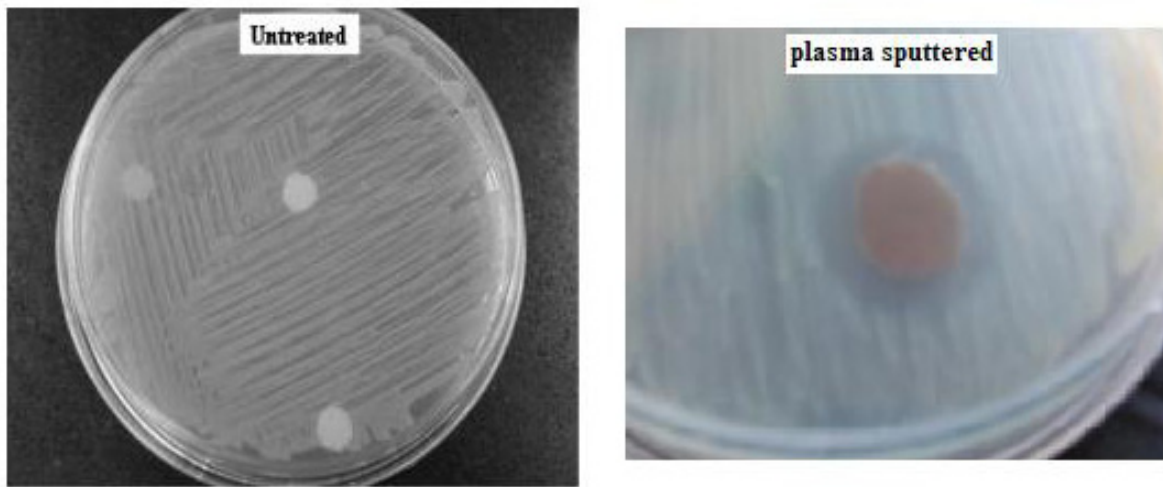


Fig. 4. The inhibition zone of *S.aureus* around untreated and copper coated cotton.

In the other research work, wool samples have been sputtered by silver particles. The antibacterial counting test was used and the results are shown in Figure 5-8. Both *E.coli* and *S.aureus* were used as a bacterial medium. As it is seen, in case of untreated samples, the bacterial colonies cover the completely the agar plate. But after Ag sputtering less amount of bacteria growth in agar plate. However this effect is more significant in case of using *s.aureus* as bacteria. (Shahidi et al, 2007; Ghoranneviss et al, 2011)



Fig. 5. The bacterial counting test for untreated wool with *E. coli*



Fig. 6. The bacterial counting test for untreated wool with S.aureus



Fig. 7. The bacterial counting test for silver coated wool with E.Coli



Fig. 8. The bacteria counting test for silver coated wool with *S.aureus*

3.3.2 Chitosan

Chitosan [poly-(1-4)-d-glucosamine], a cationic polysaccharide, is obtained by alkaline deacetylation of chitin, the principal exoskeletal component in crustaceans. As the combination of properties of chitosan such as water binding capacity, fat binding capacity, bioactivity, biodegradability, nontoxicity, biocompatibility, acceleration of wound healing and antifungal activity, chitosan and its modified analogs have shown many applications in medicine, cosmetics, agriculture, biochemical separation systems, biomaterials and drug controlled release systems. There are also many studies showing that chitin and chitosan accelerated wound healing in many clinical cases and some types of chitin remedies have already been marketed in Japan. Chitin and chitosan was used in the forms of filament, powder, granule, sponge, and composite with cotton or polyester in most studies. (Yang & Lin, 2004)

Chitosan obtained from the shells of crabs, shrimps and other crustaceans, chitosan is a non-toxic, biodegradable and biocompatible natural polymer, and has long been used as a biopolymer and natural material in the pharmaceutical, medical, papermaking and food processing industries. Because of its polycationic nature, chitosan possesses a good antibacterial property against various bacteria and fungi through ionic interaction at a cell surface, which eventually kills the cell. Previous studies have shown that its antimicrobial activity is influenced by molecular weight (Mw), degree of deacetylation, temperature, pH and cations in solution. Because chitosan is one of the safest and most effective antibacterial agents, it has been widely applied for cotton and other textile antibacterial finishes. (Ye et al, 2005)

It comprises copolymers of glucosamine and N-acetyl glucosamine and has a combination of many unique properties, such as non-toxicity, biocompatibility and biodegradability. Chitosan has got wide application in textile dyeing and finishing as a substitute for the various chemicals used in textile processing. It has been used as a pretreatment agent in dyeing of cotton, in textile printing, wool dyeing and shrink proofing and in durable press finish. (Gupta & Haile, 2007; Knill et al, 2004; Fan et al, 2006)

It is known that chitosan derivatives with quaternary ammonium groups possess high efficacy against bacteria and fungi. It is now widely accepted that the target site of these cationic polymers is the cytoplasmic membrane of bacterial cells. (Ignatova et al, 2007; Ignatova et al, 2006)

Chitosan-based core-shell particle, with chitosan as the shell and a soft polymer as the core, has been designed as a novel antibacterial coating for textiles by Ye et al. The core-shell particles were synthesized via a graft copolymerization of n-butyl acrylate from chitosan in aqueous solution. Properties of the particles, including composition, particle size and distribution, surface charge as well as morphology, were characterized. The treatment of cotton with poly(n-butyl acrylate) (PBA)-chitosan particles confers the fabric with excellent antibacterial property. It is well recognized that chitosan has good antimicrobial activity, especially against the growth of *Staphylococcus aureus* (*S. aureus*). Figure 9 shows the result of treated and untreated specimens. As expected, the untreated fabric gave a negligible antibacterial activity of less than 5% while all finished cotton showed over 99% bacterial reduction.

Thus chemical modification of the chitosan through the graft copolymerization does not affect its antimicrobial property. (Ye et al, 2005) Also the TEM images of core-shell particles are shown in Figure 10.

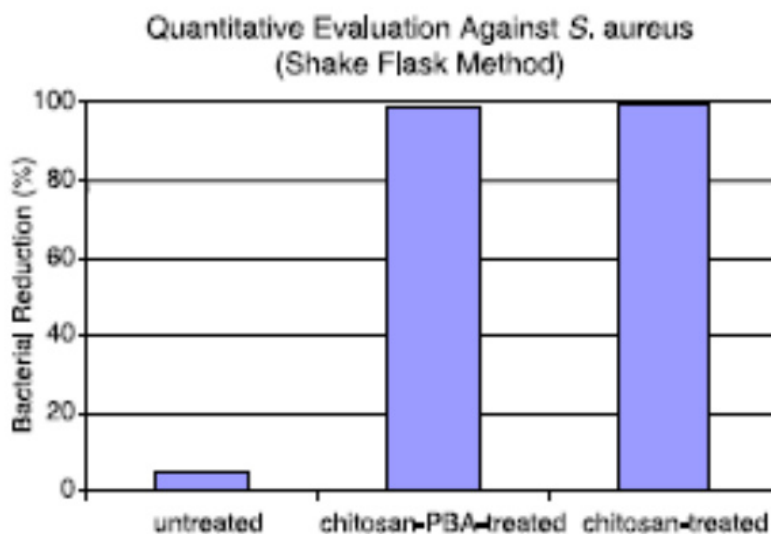


Fig. 9. Comparison of bacterial reduction before and after coating cotton fabrics with chitosan-PBA particles or chitosan solution (after 1 h shaking).

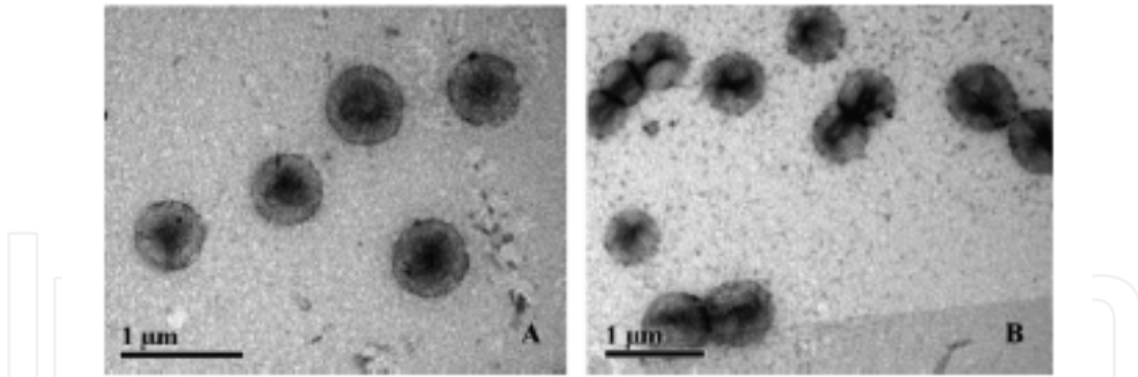


Fig. 10. TEM micrographs of chitosan-PBA particles stained for an appropriate period with 2% PTA solution. (A) Well-defined core-shell particles that consist of PBA cores and chitosan shells; (B) soft PBA-chitosan particles, which deform easily when in contact with each other.

Several mechanisms were proposed for the antimicrobial activity by chitosan:

1. Polycationic structure of chitosan which can be expected to interact with the predominantly anionic components (lipopoly-saccharides and proteins of microorganism surface) resulting in changes in permeability which causes death of the cell by inducing leakage of intracellular components.
2. The chitosan on the surface of the cell can form a polymer membrane which prevents nutrients from entering the cell.
3. The chitosan of lower molecular weight enters the cell, binding to DNA and inhibits RNA and protein synthesis.
4. Since chitosan could adsorb the electronegative substance in the cell and flocculate them, it disturbs the physiological activities of the microorganism leading to death of the cells. (El-tahlawy et al, 2005)

3.3.3 Cyclodextrin

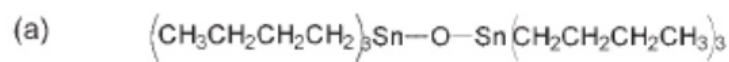
Cyclodextrins are toroidal-shaped cyclic oligosaccharides with a hydrophilic outer surface and an internal hydrophobic hollow interior, which can entrap a vast number of lipophilic compounds into their hydrophobic cavity, depending on their size and molecular structure. The remarkable ability of cyclodextrins to include hydrophobic compounds has been exploited in several fields, spanning from pharmaceuticals to cosmetics, from food manufacturing to commodity

In textile field, a novel functional surface treatment of cotton based on the permanent fixation of cyclodextrin on fabric is receiving increased attention. Some literatures have demonstrated that cyclodextrin fixed to cotton did not affect the hydrophilic properties of cellulose and the immobilized cavities of cyclodextrins did not lose their complexing power to form inclusion complexes with other molecules. (Wang & Cai, 2008)

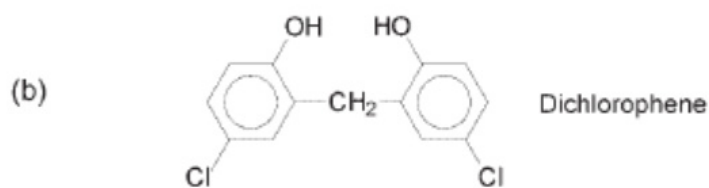
CDs and their derivatives have been used in the textile domain since the early 1980s. The permanent binding of CDs onto textile fibers offers the advantage that the inclusive properties of CDs towards bioactive molecules become intrinsic to the modified fibers. (El Ghoul et al, 2008)

4. Mechanisms of antimicrobial finishes

Despite the long list of requirements, a variety of chemical finishes have been used to produce textiles with demonstrable antimicrobial properties. These products can be divided into two types based on the mode of attack on microbes. One type consists of chemicals that can be considered to operate by a controlled-release mechanism. The antimicrobial is slowly released from a reservoir either on the fabric surface or in the interior of the fibre. This 'leaching' type of antimicrobial can be very effective against microbes on the fibre surface or in the surrounding environment. However, eventually the reservoir will be depleted and the finish will no longer be effective. In addition, the antimicrobial that is released to the environment may interfere with other desirable microbes, such as those present in waste treatment facilities. The second type of antimicrobial finish consists of molecules that are chemically bound to fibre surfaces. These products can control only those microbes that are present on the fibre surface, not in the surrounding environment. 'Bound' antimicrobials, because of their attachment to the fibre, can potentially be abraded away or become deactivated and lose long term durability. Antimicrobial finishes that control the growth and spread of microbes are more properly called biostats, i.e. bacteriostats, fungistats. Products that actually kill microbes are biocides, i.e. bacteriocides, fungicides. This distinction is important when dealing with governmental regulations, since biocides are strongly controlled.

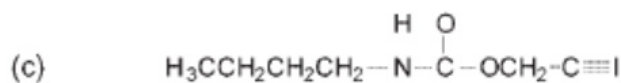


Tributyl tin oxide (TBTO)

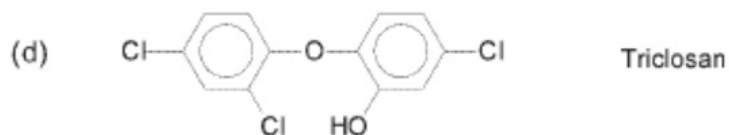


Dichlorophene

2,2'-Dihydroxy-5,5'-dichlorodiphenyl methane



3-Iodopropynylbutyl carbamate



Triclosan

2,4,4'-Trichloro-2'-hydroxydiphenyl ether

Fig. 11. Controlled release antimicrobials

Textiles with biostatic properties, however, are subject to fewer regulations. The actual mechanisms by which antimicrobial finishes control microbial growth are extremely varied, ranging from preventing cell reproduction, blocking of enzymes, reaction with the cell membrane (for example with silver ions) to the destruction of the cell walls and poisoning the cell from within. In Figure 11 and 12 the chemical structures of some of antimicrobial agents are shown.

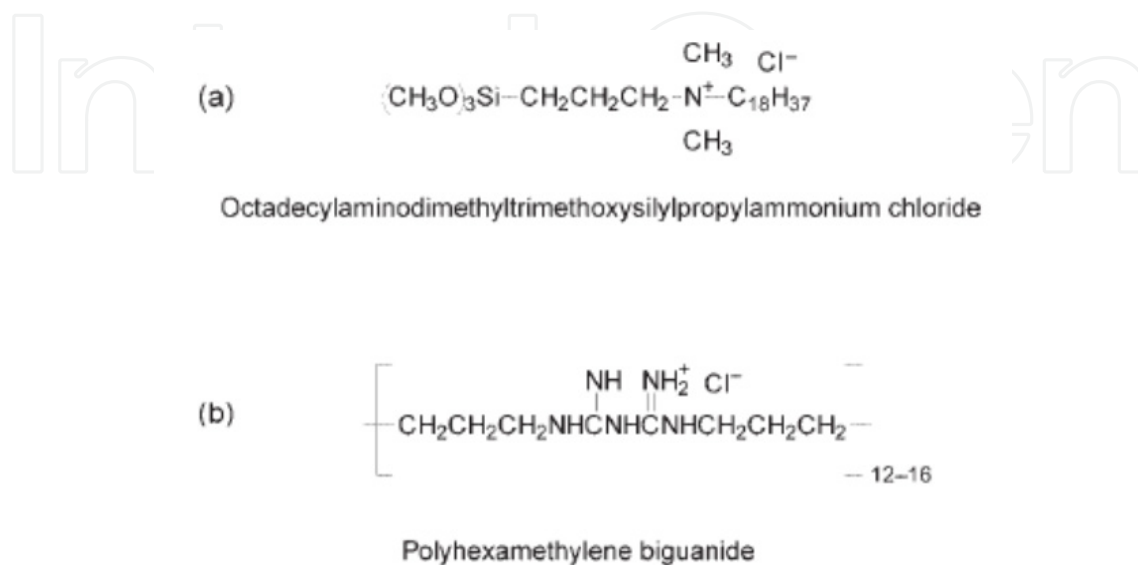


Fig. 12. Bound antimicrobials

5. Practical biocides

It is fairly easy to list the desirable properties of an 'ideal' biocide:

1. wide spectrum of effectiveness against both bacteria and fungi;
2. durable for the life of the product;
3. non-toxic to humans at concentrations used – safe to handle and use;
4. colourless and odourless;
5. reasonable cost, and effective at low concentrations;
6. resistant to leaching, weathering and sunlight;
7. no adverse effect on handle or other physical properties of the fabric;
8. compatible with water-repellent and flame-retardant finishes, dyes and other textile chemicals;
9. does not accelerate or catalyse other degenerative processes;
10. applicable using standard textile machinery;
11. withstands processing conditions and temperatures;
12. no environmental problems.

6. Evaluation of antimicrobial finishes

The AATCC Technical Manual¹² has a number of test methods that are useful for evaluating antimicrobial finishes on textiles. These tests are summarised in Table 1. Two types of antimicrobial tests are dominant, the agar-based zone of inhibition tests and the bacteria counting tests. The relatively new ISO/DIS 20645 and the corresponding EN ISO

20645 are based on the agar diffusion test and ISO 11721 is a burial test (part 1 for the determination of an antimicrobial finish and part 2 for the determination of the long-term resistance). The main difficulties of these tests are mostly poor reproducibility of the test results and often insufficient correlation between laboratory results and actual conditions in the field. Careful attention to detail and trained laboratory personnel are essential for accurate and repeatable results from these methods. (Schindler & Hauser, 2004)

A more rapid test method, developed by the British Textile Technology Group in the late 1980s, is based on adenosine triphosphate (ATP) luminescence. The growth of microorganisms is assessed by firefly bioluminescent detection and ATP analysis.³

AATCC test method	Comments
Antibacterial activity of textile materials: parallel streak method; test method 147(agar plate test)	Rapid qualitative method for determining antibacterial activity of treated textile materials against both Gram-positive and Gram-negative bacteria. Treated material is placed in nutrient agar that is streaked with test bacteria. Bacterial growth is determined visually after incubation. Antibacterial activity is demonstrated by zones of inhibition on and around the textile.
Antibacterial finishes on textile materials, assessment of: test method 100	Quantitative method for determining the degree of antimicrobial activity of treated textiles. The amount of bacterial growth in inoculated and incubated textiles is determined through serial dilutions and subsequent inoculations of sterile agar. Gram positive and Gram-negative bacteria are used.
Antifungal activity, assessment on textile materials: mildew and rot resistance of textiles; test method 30	Four methods for determining the antifungal assessment on textile properties of treated textiles. One method involves testing fabric properties after burial in soil that contains fungi. In a second method, cellulose fabric is exposed to <i>Chaetomium globosum</i> in an agar plate and the subsequent growth visually determined. The third method exposes textiles to <i>Aspergillus niger</i> in an agar plate and visually determines any fungal growth. The fourth method uses a humidity jar to expose textiles to mixture of fungi spores. Any growth on the textile is visually determined.
Antimicrobial activity assessment of carpets; test method 174	Methods are given for the qualitative and quantitative determination of antibacterial activity and the qualitative evaluation of antifungal properties of carpet samples using procedures and materials similar to those in the above test methods.

Table 1. Comparison between different AATCC test methods

7. The future

An anti-microbial finish for textiles involving skin contact will need additional safety data concerning this aspect. For manufacturers with biocides with relatively low volumes the cost of generating the necessary data may make ongoing production uneconomical. Acute toxicity data is relatively cheap to generate but sub-acute and other long-term studies are very expensive. It is therefore likely that the number of biocides being produced in the future will diminish and bringing new products to market will be even more expensive. A possible future development would be the micro-encapsulation of biocides. The potential is considerable if the correct performance and economics can be achieved. Benefits could include better durability and greater safety. The search for more cost-effective testing methods will continue.

Overall the need for anti-microbial and hygiene finishes looks set to continue for the foreseeable future. Improving performance and cost-effectiveness, while meeting environmental and toxicity requirements, will continue to challenge those working in this field. (Heywood, 2003)

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